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A Review of the Magnetic Relaxation and Its Application to the Study of Atomic Defects in α -Iron and Its Diluted Alloys

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This review presents a *comprehensive survey* on intensive studies performed during the last decades on point defect reactions on α -iron (α -Fe) and its diluted alloys. Our intention is to give an *actual account* of the knowledge accumulated on this subject, as it has been obtained predominantly by means of the *magnetic after-effect* (MAE) spectroscopy. After a concise introduction into the theoretical and experimental fundamentals of this technique, the main concern is focused on the presentation and detailed discussion of the MAE spectra arising – after low-temperature *electron* (e^-)- or *neutron*(n)-irradiation and subsequent annealing – in: (i) *high-purity* α -Fe and α -Fe doped with (ii) *substitutional solutes* (like Ni, V, Al, Cu, Ti, Be, Si, Mn, ...) or (iii) *interstitial solutes* (like O, H, C, N). During the course of systematic annealing treatments, these respective spectra undergo dramatic variations at specific temperatures thereby revealing in great detail the underlying intrinsic reactions of the radiation-induced defects, i.e., reorientation, migration, clustering, dissolution and finally annihilation. In alloyed Fe systems the corresponding reaction sequences are even multiplied due to additional interactions between defects and solute atoms. Most valuable information concerning formation-, dissociation- and binding enthalpies of small, *mixed clusters* (of the type C_iV_k , N_iV_k ; $i, k \geq 1$) has been obtained in high-purity α -Fe base material which, after charging with C or N, had been e^- -irradiated. Concerning the basic *recovery mechanisms* in α -Fe, two complementary results are obtained from the analysis of the various systems: (i) in *high-purity* and *substitutionally alloyed* α -Fe the recovery in Stage-III (200 K) is governed by a three-dimensionally migrating ($H_1^M = 0.56$ eV) *stable interstitial* (dumb-bell); (ii) following the formation and dissociation kinetics of small clusters (C_1V_k , N_1V_k) in *interstitially alloyed* α -Fe the migration enthalpy of the *monovacancy* must hold the following relation $H_N^M (0.76 \text{ eV}) < H_C^M (0.84 \text{ eV}) < H_{V1}^M$. These results are in clear agreement with the so-called *two-interstitial model* (2IM) in α -Fe – a conclusion being further substantiated by a systematic *comparison* with the results obtained from *nonrelaxational techniques*, like i.e. *positron annihilation* (PA), which by their authors are preferentially interpreted in terms of the *one-interstitial model* (1IM).

Die vorliegende Arbeit gibt einen *umfassenden Überblick* über die während der letzten Jahrzehnte durchgeführten, eingehenden Untersuchungen der Punktfehler-Eigenschaften in α -Eisen (α -Fe) und verdünnten Fe-Legierungen. Demgemäß ist diese Zusammenfassung gedacht als ein dem *gegenwärtigen Kenntnisstand* entsprechender Rechenschaftsbericht über die auf diesem Gebiet, hauptsächlich mit Hilfe der *magnetischen Nachwirkungen* (MNW) – Spektroskopie, gewonnenen, tiefreichenden Einsichten in diesen Problemkreis. Nach einer kurzen Einführung in die theoretischen und experimentellen Grundlagen dieser Technik gilt das Augenmerk der Darstellung und eingehenden Erörterung der – nach *Tiefemperatur-Elektronen*(e^-)- oder *-Neutronen*(n)-Bestrahlung und anschließender Erholung – beobachteten MNW-Spektren in (i) *hochreinem* α -Fe und α -Fe, das entweder mit (ii) *substitutionellen* (Ni, V, Al, Cu, Ti, Be, Si, Mn, ...) oder (iii) *interstitiellen* (O, H, C, N) *Fremdatomen* beladen wurde. Während der thermischen Erholung erfahren die Spektren an bestimmten Temperaturen charakteristische Veränderungen, die weitreichende Rückschlüsse über die jeweils zugrundeliegenden Reaktionen der bestrahlungsinduzierten Gitterfehler ermöglichen, wie z. B.: Umorientierung, Wanderung, Bildung und Auflösung von Komplexen und schließliche Annihilation mit Anti-Defekten. In Fremdatom-beladenem α -Fe treten entsprechende Reaktionen

– infolge Wechselwirkung zwischen intrinsischen Gitterfehlern und Fremdatomen – in verstärktem Umfang auf. Wertvolle Kenntnisse über die Enthalpien der Bildung, Auflösung und Bindung kleiner, *gemischter Komplexe* (der Art C_iV_k , N_iV_k ; $i, k \geq 1$) wurden an hochreinem, gezielt mit C und N beladenem α -Fe nach Tieftemperatur-Elektronenbestrahlung gewonnen. Hinsichtlich des *grundlegenden Erholungsverhaltens* in α -Fe wurden zwei entscheidende Ergebnisse erzielt: (i) in *hochreinem*, sowie mit *substitutionellen Fremdatomen* beladenem α -Fe erfolgt die Erholung in Stufe III (200 K) durch dreidimensionale Wanderung eines *stabilen, intrinsischen Zwischengitteratoms* (Hantel); (ii) Die Analyse der Bildungs- und Wieder-Auflösungskinetik kleiner Komplexe (C_iV_k , N_iV_k) in *interstitiell beladenem* α -Fe ergibt, daß die Wanderungsenthalpie der Einfachleerstelle folgender Bedingungen genügen muß: H_N^M (0.76 eV) < H_C^M (0.84 eV) < H_{V1}^M . Diese Ergebnisse stehen in vollkommener Übereinstimmung mit dem sogenannten *Zwei-Zwischengitteratom-Modell* in α -Fe – eine Feststellung, die noch weiter erhärtet wird durch die *Gegenüberstellung* der mit *Nicht-Relaxationsverfahren*, z. B. der *Positronenannihilation*, gewonnenen Ergebnisse, die jedoch von den jeweiligen Autoren vorzugsweise im Rahmen des *Ein-Zwischengitteratom-Modells* gedeutet werden.

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1. Introduction

This report reviews the progress achieved in recent years on the understanding of point-defect reactions in α -Fe. The study of structural defects in α -Fe introduced by fast-particle irradiation, cold-work or quenching from high temperatures is a field which, over the past decades, has attracted an enormous amount of attention from both experimentalists and theorists alike. This is due, on the one hand, to the technological importance of Fe, especially as a structural nuclear material, and also, on the other hand, to a fundamental interest in Fe as being representative of refractory b.c.c. metals generally. Over the years, measurements have been made on material with varying levels of impurities, which have had a pronounced effect on the ensuing defect structure and its annealing behaviour. The effect of impurities is especially important in the case of b.c.c. metals on account of their more open structure and, in the case of α -Fe, this seems to be especially true. *Interstitial* impurities such as carbon (C), nitrogen (N) and hydrogen (H) dissolve as highly anisotropic defects in tetragonal configurations with significant elastic dipole moments giving rise to strong interactions with intrinsic defects produced by either electron (e^-)- or neutron (n)-irradiation. *Substitutional* impurities play an equally important role and one of the problems in the investigation of structural defects in α -Fe has been to distinguish between the influence of intrinsic and extrinsic defects, which were frequently present in comparable concentrations.

However, despite the large amount of information which has been accumulated by many workers using various techniques, as yet, no general agreement has been reached concerning the interpretation of the elementary intrinsic defect reactions giving rise to the so-called recovery Stages I and III in α -Fe and other metals. On the contrary, as highlighted by Seeger [1] in a historical perspective, two opposing models are still under discussion: the so-called one-interstitial model (1IM) and the two-interstitial model (2IM). Both models have a common feature in so far as they attribute the recovery in Stage I, located at 110 K in α -Fe, to an intrinsic interstitial-type defect. In the 1IM, this defect is assumed to be the only self-interstitial type, whereas in the 2IM it is regarded as the one of two possible interstitial types existing, at lower temperatures, as a *meta-stable crowdion* being able to convert, at elevated temperatures, into a second, *stable*, interstitial configuration assumed to be of *dumb-bell* type. Consequently, these two recovery models differ drastically in their predictions concerning the type of defect which migrates in Stage III, i.e. at 200 K, in α -Fe: according to the 1IM, the Stage III defect is associated with the monovacancy, whereas the 2IM identifies it with the stable dumb-

bell configuration. As will be shown in the following, the experimental material presented in this review allows us to discriminate clearly between these two recovery models in favour of the 2IM. This progress in point defect analysis has been achieved by a systematic exploitation of the inherent advantages of the magnetic after-effect (MAE) technique.

(i) The MAE, like Internal Friction (IF), belongs to the group of relaxation techniques which give information not only on the presence of specific lattice defects – to which most other, static, techniques (e.g. Residual Resistivity Ratio (RRR) or Positron Annihilation (PA)) are confined – but also on their motional modes [2 to 6]. Moreover, domain walls – the probes of MAE measurements – due to their three-dimensional nature, are able to interact with large numbers of lattice defects, thus producing the high sensitivity of the MAE to point defect reactions. Further advantages of the MAE are the ease of application and the low temperature range within which the maxima of the defect relaxations occur [7].

(ii) To obtain full information, MAE measurements are performed over wide temperature ranges and, in order to reveal the finest details of reaction kinetics, have been repeated on various systems such as, e.g., high-purity, substitutionally and interstitially alloyed α -Fe under systematically modified experimental conditions, e.g., for varying impurity contents and differing irradiation doses (cf. Sections 5 to 7). Quite obviously, such extended measuring programmes are extremely time-consuming and therefore impracticable to accomplish with conventional MAE methods (cf. Section 3). Fortunately, we were able to apply a highly-sensitive, completely automated MAE technique, based on a modern electronic LC-oscillator system [8], permitting direct digital data acquisition. The combination of this ingenious measuring technique with a refined numerical data analysis, based on efficient approximation algorithms [9 to 11] makes, in our opinion, the MAE the most effective technique presently available for the investigation of point defect reactions in α -Fe [7, 12].

Following this introduction, we shall give, in Section 2, a concise theoretical treatment of the various MAE types. Section 3 will be concerned with a brief description of various MAE techniques. As a typical example of a MAE, we shall consider the so-called Richter MAE of interstitially dissolved C in α -Fe (FeC); this seems appropriate since, in the past C, frequently being present as an unwanted impurity, has played a central role in the relaxation spectra of Fe. Section 4 will be devoted to a discussion of some theoretical predictions made for structural defects in Fe and their interactions with impurities. In Section 5 we shall consider the relaxation spectra of irradiated high-purity α -Fe. This will provide us with the basic information on the *annealing kinetics* of irradiation-induced *intrinsic defects* which is found to be incompatible with vacancy migration in Stage III. In Section 6 we shall report on results obtained on substitutionally alloyed, irradiated α -Fe, which support the view of interstitial rather than vacancy migration in Stage III. Section 7, concerned with defect reactions in C- and N-charged α -Fe, will provide us with further conclusive arguments against vacancy migration in Stage III. The results obtained from these latter systems are most informative since impurity interstitials act not only as traps for intrinsic point defects, as do also substitutionally dissolved impurities, but, in addition, themselves also undergo thermally activated reorientations combined with migration at temperatures above 250 K. The correspondingly richer MAE spectra of these alloys allow us, especially in the case of FeC, to identify defect reactions with higher accuracy than in any other Fe systems investigated so far.

In Section 8 we compare the arguments developed in the past in favour of a 1IM or 2IM defect recovery behaviour. The former, being deduced especially from the analysis of non-relaxation techniques – such as positron annihilation, residual resistivity etc. – are shown to fail when applied to the more detailed information available from the higher resolving relaxation techniques, like the MAE in particular.

Our present report is intended as an up-dating of the currently available knowledge concerning the investigation of point defect reactions in α -Fe by means of the MAE. Previous reviews on these topics have been presented by Seeger et al. [4 to 6] and Kronmüller et al. [13, 14]. A monograph of Kronmüller is devoted to the theoretical aspects of the MAE [15], including a discussion of some of the experimental results available up to 1968. Covering about the same time interval as [15], Dautreppe [16] has published a detailed article on the influence of neutron and electron irradiation on the magnetic properties of ferromagnetic metals and alloys.

2. The Magnetic After-Effect

2.1 General remarks

Although it has long been known that the magnetic properties of a ferromagnet are not static, but depend upon the history of the sample [17, 18], it was not until 1937 that Richter [19] systematically studied the time and temperature dependence of relaxations occurring in carbonyl Fe.

Whereas, from a technical point of view, MAEs are highly undesirable and their elimination can be very costly, from the standpoint of basic research they are very useful. This was first appreciated in 1960 by Seeger et al. [2] and Kronmüller et al. [3] who employed the MAE for an investigation of structural lattice defects in irradiated Ni. Since that time, the MAE technique has been steadily improved and applied extensively to several pure ferromagnetic metals and a great number of alloys in order to obtain detailed information on intrinsic defects, impurity atoms and their interactions. Moreover, this technique has also been applied with considerable success in recent years to the investigation of defect-induced relaxation processes and phase transitions in ferrimagnetic [20 to 22], ferro-electric [23, 24] and superconducting [25, 26] materials.

2.2 Isothermal and isochronal relaxation

If one demagnetizes a ferromagnetic sample, be it pure metal or alloy, one finds in most cases a subsequent time-dependent decrease of the initial susceptibility, χ . This phenomenon, which results from the stabilization of the domain walls in the sample, occurs within a particular temperature range for a given material and is usually referred to as a disaccommodation of the initial susceptibility, χ , or of the initial reluctivity, r , which is defined as $r = 1/\chi$. The observed decrease of the initial susceptibility $\chi(t, T)$ – or increase of $r(t, T)$ – at constant temperature, is known as isothermal relaxation and its strength is found to be strongly temperature-dependent, as is shown in Fig. 1a for $r(t, T)$. Whereas the *isothermal* curves are useful for a study of the *time* dependence of the effect, *isochronal* curves are more appropriate in order to study the *temperature* dependence of a given MAE and to separate it from overlapping relaxation effects and so-called “background” relaxations which vary only slowly with temperature.

Fig. 1. a) Isothermal representation of the thermally activated relaxation of the reluctivity, $r(t, T)$, for various temperatures $T_1 < T_2 < T_3$ within the time interval of measurements $t_1 \leq t \leq t_2$. b) Construction of an isochronal relaxation curve from the isotherms of a); $T_{\max}$: temperature corresponding to the maximum of the relaxation peak; ΔT_H : half-width of the relaxation peak

In order to construct the isochronal relaxation curves, we consider the change of the initial susceptibility, $\Delta\chi$, at temperature T , between two measuring times t_1 and t_2 ($t_2 > t_1$), following a demagnetization of the sample at time $t = 0$,

$$\Delta\chi(t_1, t_2, T) = \chi(t_1, T) - \chi(t_2, T) \quad (2.1)$$

or alternatively, in terms of the reluctivity,

$$\Delta r(t_1, t_2, T) = r(t_2, T) - r(t_1, T). \quad (2.2)$$

These relaxation amplitudes, $\Delta r(t_1, t_2, T)$, are now determined as a function of temperature for fixed measuring times t_1 and t_2 . If a thermally activated relaxation exists within the temperature range investigated, the resulting isochronal relaxation curve exhibits a maximum somewhat similar to that of a Gaussian-shaped error curve. Such a shape can be explained as follows: at low temperature, T_1 , the relaxation occurs so slowly that, within the time interval $(t_2 - t_1)$, almost no relaxation takes place. At a higher temperature, T_3 , the relaxation proceeds so quickly that thermal equilibrium is established before the measurement starts at t_1 . Between the high and low temperature ranges, a maximum exists in the relaxation amplitude at $T_2 = T_{\max}$.

The characteristic parameters of the corresponding isochronal maximum are:

- the temperature at which the maximum occurs, $T_{\max}$.
- the half-width of the relaxation, ΔT_H .
- the amplitude of the relaxation strength, $\Delta r(T_{\max})$.

Whereas the maximum temperature, $T_{\max}$, and half-width, ΔT_H , are independent of the defect concentration, the relaxation strength, $\Delta r(T_{\max})$, is proportional to the number of defects and thus can be used for a quantitative analysis of the defect concentration [27, 28].

2.3 Micromagnetic model of magnetic relaxation

2.3.1 Domain theory

According to the Weiss model of ferromagnetism, a ferromagnet is divided up into many homogeneously magnetized domains inside each of which the spontaneous magnetization is oriented parallel to so-called easy directions of magnetization; in α -Fe, these are coincident with one of the possible $\langle 100 \rangle$ directions. The transition regions between neighbouring domains are the Bloch or domain walls which, in the case of α -Fe at room temperature, have a width in the range 30 to 65 nm [15, 29, 30]. In the demagnetized state, the domain walls lie at the bottom of potential wells and, according to this model, relaxation phenomena may be explained as a deepening of these wells

Fig. 2. Illustration of the reduction in domain wall mobility due to a time-dependent deepening of the potential well

due to a time-dependent component, ϕ_t , in the total potential, Φ_{tot} , i.e.

$$\Phi_{\text{tot}} = \Phi_0 + \Phi_t. \quad (2.3)$$

Whereas Φ_t accounts for the relaxation due to mobile lattice defects, Φ_0 results from the interaction of the domain walls with all defects which are immobile in the observed temperature range.

If χ is measured by means of an ac-technique, where a small alternating magnetic field of constant amplitude is applied so as to oscillate the wall about its equilibrium position, application of the measuring field after a preceding demagnetization of the sample will displace the wall from A to A', Fig. 2. After a finite time, t , the potential well has deepened and, again applying the same field, the wall is displaced a smaller distance than previously, i.e. from B to B'. Thus the domain-wall mobility is found to be reduced, leading to a corresponding decrease in χ .

Following previous treatments [13 to 15], let us consider a domain wall which separates two adjacent domains with magnetization vectors $\mathbf{M}_1$ and $\mathbf{M}_2$. If a field $\mathbf{H}$ is applied, the wall is displaced a small distance u to A' (Fig. 2). Thereby the magnetostatic energy per unit area of wall is increased by an amount

$$\Phi_H = u\mathbf{H} \cdot (\mathbf{M}_1 - \mathbf{M}_2) = uHM_s g,$$

where M_s is the spontaneous magnetization and g a dimensionless factor. In the case of 180° walls, the most mobile domain-wall type, $M_s = |\mathbf{M}_1| = |\mathbf{M}_2|$ holds, thus yielding $g = 2 \cos \phi$, where ϕ denotes the angle between the applied field, $\mathbf{H}$, and the magnetizations $\mathbf{M}_{1,2}$. The magnetostatic force, p_H , necessary to move the wall over the distance u is given by

$$p_H = d\Phi_H/du = HM_s g. \quad (2.5)$$

At the equilibrium position of the wall, A', this magnetostatic force is balanced by the restoring forces due to the potentials Φ_t and Φ_0 , i.e.

$$p_t = -d\Phi_t/du \quad \text{and} \quad p_0 = -d\Phi_0/du. \quad (2.6)$$

For small displacements, $u/L \ll 1$, where L is the linear extension of the domain, Φ_0 and Φ_t may be expanded in a Taylor series,

$$\Phi(u) = \Phi(0) + u\Phi'(0) + \frac{u^2}{2} \Phi''(0) + \dots \quad (2.7)$$

Thus, for small displacements about the equilibrium position ($\Phi'(0) = 0$), we get from eq. (2.6) with

$$d\Phi/du = u\Phi''(0) + \dots : \quad (2.8)$$

$$p_t = -u d^2\Phi_t/du^2 = -R_t u, \quad p_0 = -u d^2\Phi_0/du^2 = -R_0 u. \quad (2.9)$$

Since at equilibrium

$$p_t + p_0 + p_H = 0, \quad (2.10)$$

we have with eqs. (2.5) and (2.9), via

$$HM_s g - R_0 u - R_t u = 0, \quad (2.11)$$

$$u = gM_s H / (R_0 + R_t). \quad (2.12)$$

However, the increase in magnetization parallel to the applied field, H , due to the displacement, u , of the wall is given by

$$\Delta M = gM_s u S, \quad (2.13)$$

where S is the domain-wall surface area per unit volume. With (2.12) this gives:

$$\Delta M = g^2 M_s^2 S H / (R_0 + R_t) \quad (2.14)$$

and we obtain for the reversible susceptibility, $\chi_{\text{rev}}(t) = d\Delta M/dH$,

$$\chi_{\text{rev}}(t) = g^2 M_s^2 S / (R_0 + R_t). \quad (2.15)$$

Hence, the change in the inverse susceptibility between the two times t_1 and t_2 is given by

$$\Delta r(t_1, t_2, T) = r(t_2) - r(t_1) = \frac{R_t(t_2) - R_t(t_1)}{g^2 M_s^2 S} = \frac{1}{g^2 M_s^2 S} \left\{ \frac{d^2 \Phi_t(t_2)}{du^2} - \frac{d^2 \Phi_t(t_1)}{du^2} \right\}, \quad (2.16)$$

i.e., the relaxation of the reluctivity is simply related to the second derivatives of the time-dependent potential with respect to the displacement, evaluated at the well minimum.

2.3.2 The interaction energy

The time-dependent embedding of the domain walls into their potential wells may be attributed to thermally activated rearrangements of mobile defects into energetically more favourable positions (cf. Section 2.4). These rearrangements are governed by interactions of both magnetostrictive and magnetocrystalline type between the defects and the spontaneous magnetization. As can be shown from group theory considerations [15], the energy terms of trigonal, tetragonal or orthorhombic defects in cubic crystals depend on the direction cosines, β_i and γ_i , resulting from the angles formed between the directions of defect anisotropy and spontaneous magnetization with the cube axes of the lattice, respectively. Thus, the total interaction energy, E_i , may be expressed as

$$E_i = E_i(\beta_i, \gamma_i) = E_i^M(\beta_i, \gamma_i) + E_i^K(\beta_i, \gamma_i), \quad (2.17)$$

where E_i^M is the magnetostrictive coupling energy due to long-range interactions between defect-induced lattice distortions and the magnetostrictive stresses of domain walls. E_i^K denotes the magnetocrystalline energy which results from short-range interactions between local lattice distortions and electronic spin-orbit coupling.

2.4 Definition of the various types of relaxation processes

After a demagnetization of the sample, all possible orientations of the defects are occupied with equal probability. On account of the interaction energy, E_i , the number of

defects in energetically favourable positions increases with time. After a time, t , the concentration of the defects in the i -th orientation, c_i , at a position z inside the domain wall will be

$$c_i = c_i(z, t),$$

i.e. a function of position and time.

Let us assume a plane domain wall with its normal parallel to the z axis. If, at a time t after a demagnetization, the wall is displaced a distance, u , from its equilibrium position, then the total interaction energy, or stabilization energy, per unit area of the domain wall is given by

$$\Phi_t(u, t) = \sum_{i=1}^{n_E} \int_{-L/2}^{+L/2} \{c_i(z, t) - c_i(z, 0)\} E_i(z - u, t) dz, \quad (2.18)$$

where n_E and L denote the number of different defect orientations and the extension of the magnetic domain. At time $t = 0$ the stabilization energy, $\Phi_t(u, t)$, is zero; a decrease of this quantity may occur as a result of various types of defect reactions.

2.4.1 Orientation after-effect

The introduction of a lattice defect into a crystal destroys the translational symmetry and will, in general, reduce the point symmetry of the lattice. Such a defect is called “anisotropic” because its symmetry corresponds to a sub-group of the crystal class of the host lattice.

A MAE is said to be of orientation type if thermal equilibrium is approached by a local rearrangement of the symmetry axis of anisotropic defects. This type of relaxation is characterized by a change of the anisotropy axis between two orientations: $i \rightleftharpoons j$, where the process $i \rightarrow j$ occurs more frequently if $E_i > E_j$. The rearrangement is governed by a rate equation of the form

$$\partial c_i / \partial t = - \sum_{i \neq j} \{v_{ij} c_i - v_{ji} c_j\}, \quad (2.19)$$

where v_{ij} corresponds to the atomic jump frequency between neighbouring positions. In general, v_{ij} can be replaced by one unique Arrhenius-type frequency [4, 14], ν , where

$$\nu = \nu_0 \exp(-Q/kT) \quad \text{or} \quad \frac{1}{\nu} = \tau = \tau_0 \exp(Q/kT). \quad (2.20)$$

In eq. (2.20) ν_0 and τ_0 are “pre-exponential factors” of the order of the Debye frequency or its reciprocal, respectively, τ corresponds to the mean time between two jumps of a particle and Q is the activation enthalpy of the process.

The thermodynamic equilibrium distribution of the defects over the various energy levels, established for $t \rightarrow \infty$, is given by

$$c_i^\infty = \frac{c_0 e^{-E_i/kT}}{\sum_{i=1}^{n_E} e^{-E_i/kT}}. \quad (2.21)$$

A theoretical expression for the isochronal relaxation, $\Delta r(t_1, t_2, T)$, is thus obtained by substituting the appropriate expressions for c_i and the corresponding activation energies, E_i , into eq. (2.18) which is then, in turn, combined with eq. (2.16).

In the case of a simple orientation-type MAE this yields [14, 15]

$$\Delta r(t_1, t_2, T) = \Delta r_s(T) (e^{-t_1/\tau} - e^{-t_2/\tau}), \quad (2.22)$$

where $\Delta r_s(T)$ is a temperature-dependent factor, the so-called stabilization reactivity (cf. Section 3.3).

2.4.2 Diffusion after-effect

In addition to a reorientation of its symmetry axis, a defect can also reduce its interaction energy by means of a long-range diffusion within the domain wall, thus giving rise to what was originally described by Dietze [31] as a diffusion MAE. The driving force for this relaxation is the magnetostrictive interaction between the defect-induced elastic lattice distortions, which can be expressed mathematically in terms of elastic dipoles [32], and the spontaneous magnetization in the domain wall. Due to the rotation of the magnetization vector within the domain wall, this interaction energy varies over the wall width, so that the driving force for the diffusion is the gradient of the average interaction energy, $\partial \bar{E}/\partial z$. Thus, the diffusion of defects within a domain is described by a modified form of Fick's law,

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left[D_z \left\{ \frac{\partial c}{\partial z} + \frac{c}{kT} \frac{\partial \bar{E}}{\partial z} \right\} \right], \quad (2.23)$$

where D_z is the linear diffusion coefficient parallel to the domain-wall normal, which may be expressed by

$$D_z = \frac{a^2}{\tau} g, \quad (2.24)$$

with a the lattice parameter, τ_0 a characteristic atomic jump time (cf. (2.20)) and $g \leq 1$ a specific geometry constant. $\bar{E}$ is the average interaction energy, defined by

$$\bar{E} = \frac{1}{n_E} \sum_{i=1}^{n_E} E_i. \quad (2.25)$$

Equation (2.23) has a solution of the form [15, 31]

$$c(z, t) = c_0 \left\{ 1 - \frac{\bar{E}(z)}{kT} f \left(\frac{D_z}{\delta_B^2} t \right) \right\}, \quad (2.26)$$

where δ_B is the domain-wall thickness.

For the equilibrium concentration in the limit $t \rightarrow \infty$, the stationary solution of eq. (2.23) with the boundary conditions $c(z, 0) = c(\infty, t) = c_0$ may be written as

$$c^\infty(z) = c_0 \exp(-\bar{E}(z)/kT). \quad (2.27)$$

Since, in the case of a diffusion MAE, the defect has to migrate over considerable distances, the corresponding time constant, τ_D , is larger than that for reorientation, τ_0 (cf. (2.20)), as follows from (2.24) and (2.26):

$$\tau_D = \frac{\delta_B^2}{D_z} \simeq \frac{1}{g} \left(\frac{\delta_B}{a} \right)^2 \tau_0. \quad (2.28)$$

Thus the diffusion time constant, τ_D , is by a factor of $(\delta_B/a)^2$, greater than the time constant, τ_0 , of a reorientation MAE; this factor is typically of the order 10^4 to 10^6 .

Defects which are, at least in principle, capable of exhibiting a diffusion MAE include:

a) All defects which give rise to an orientation MAE, although the corresponding diffusion MAE should occur at a considerably higher temperature.

b) Defects which have the symmetry of the lattice and hence exhibit no orientation MAE.

c) Defects which are unable to reorient in three dimensions, e.g. crowdions.

Diffusion MAEs, as compared to reorientation MAEs, are typically characterized by a larger half-width, ΔT_H , of their relaxation maxima and a reduced convergence of the high-temperature flanks of their family of isochrones (cf. Fig. 5).

2.4.3 Combined after-effect

In general, anisotropic defects will be able to undergo both a reorientation of their symmetry axis and a long-range migration, thus giving rise to a combined MAE. Since, during migration, the defect density may vary, the relaxation strength of the orientation MAE will become correspondingly modified.

Well-known examples of this type of relaxation are the so-called Richter MAEs [15, 19] of C and N in α -Fe which, although generally being considered to be prototypes of classic orientation MAEs, are, strictly speaking, combined MAEs. C and N dissolve interstitially in α -Fe and are located on the centres of elementary cube edges, i.e. in positions of tetragonal symmetry (Fig. 3a). Thus, the anisotropy axis of such an impur-

Fig. 3. Some possible C-intrinsic defect configurations in α -Fe, according to Johnson [67, 68], ($\circ$ Fe, $\bullet$ C, $\square$ monovacancy): a) Interstitially dissolved C atom in α -Fe on an octahedral lattice site with tetragonal symmetry; b) C-di-interstitial configuration; c) C-monovacancy configuration. d) Energy model for the Snoek-Richter MAE. Due to the predominance of the magnetocrystalline interaction, those anisotropic axes enclosing the largest angles with the spontaneous magnetization J , here anisotropies pointing in the x_1 direction, are energetically privileged, cf. level diagram

ity atom is directed along the line joining two next-nearest Fe neighbours, i.e. oriented in a $\langle 100 \rangle$ direction. Based on this concept, Snoek [33] initially proposed the observed Richter MAEs to result from stress-induced ordering of the impurity interstitials due to magnetostrictive interactions with the spontaneous magnetization. Néel [34], however, succeeded in showing that, in fact, magnetocrystalline interactions play the dominant role in the generation of these relaxations. Néel's interpretation was confirmed by measurements of induced anisotropy and time-dependent magnetostriction, performed by de Vries et al. [35]. These authors deduced that the effect of the magnetocrystalline, energy, E_i^K , was far greater than that of the magnetomechanical (magnetostrictive) energy, E_i^M , and, moreover, found that these interactions were of opposite sign.

Under the condition $E_i^K \gg E_i^M$, i.e. dominance of the magnetocrystalline term (cf. (2.17)), we may approximate the effective interaction energy, E_i , in the following way:

$$E_i \approx E_i^K = w\gamma_i^2, \quad (2.29)$$

where γ_i represents the direction cosines between the spontaneous magnetization and the cube axes (cf. Section 2.3.2) and w , in the case of C and N in α -Fe, is a positive interaction constant [35, 36] with the values

$$w_C = 5.24 \times 10^{-4} \text{ eV}, \quad w_N = 3.56 \times 10^{-4} \text{ eV}.$$

For a general direction of the spontaneous magnetization, all three $\langle 100 \rangle$ directions are energetically different. As a result of the positive sign of w , those $\langle 100 \rangle$ cube edges which enclose the largest angles with the local direction of the magnetization become the most heavily populated ones; this situation is sketched in Fig. 3d. Since MAE measurements are performed following a demagnetization of the sample, the starting conditions are such that a domain wall finds itself in a position where all defect orientations are equally populated. The impurity atoms will jump, via thermally activated processes, so as to minimize the interaction energy, E_i . This leads to a reduction in the stabilization energy and thus a decrease in the initial susceptibility. Clearly, such motions of impurity interstitials entail a shift of their centres-of-mass, so that the Richter MAE, in principle, must be regarded as a combined MAE. However, whereas at low temperatures ($T \leq 300 \text{ K}$) the interstitial atoms, after one combined reorientation – diffusion jump, will have attained their new equilibrium positions, only at higher temperatures thermal activation is expected to be strong enough to induce interstitial migration over large distances, thereby producing the diffusion-type component of the combined after-effect.

2.4.4 Cold-work after-effect

The cold-work MAE has been extensively discussed by Kronmüller [15, 37] and we shall not consider in detail this type of MAE here, except where it impinges on results arising from energetic particle irradiation. Briefly, the cold-work MAE arises due to the interactions between dislocations and the magnetostrictive stresses of domain walls. According to the sign of these interactions, dislocations are either attracted to – or repelled from – the wall until positions of minimum energy are attained. This results in a stabilization of the walls, leading to a reduction of their mobility and thus a corresponding increase in reluctivity. After demagnetization, the establishment of equilibrium is delayed, since the dislocation segments must overcome obstacles in their paths, thereby producing a MAE. The following mechanisms of dislocation movement are feasible [38, 39]:

- a) Formation of kink pairs.
- b) Kink motion parallel to the dislocation line.
- c) Jog-dragging accompanied by vacancy and interstitial formation.
- d) Elastic interaction with impurity atoms – especially of interstitial type.

3. Measurement of the Magnetic After-Effect

3.1 Bridge techniques

Any ac-technique which is used to determine the initial susceptibility results in the measurement of a complex quantity. Thus, we may express the complex susceptibility, χ , in terms of its real and imaginary components

$$\chi = \chi' - i\chi'' . \quad (3.1)$$

In practice, it is found that all information on thermally activated processes can usually be obtained from the real component alone and thus attention is mostly confined solely to this term.

A very sensitive technique for the measurement of the MAE is to use a bridge. The sample to be investigated is made the core of a mutual inductance coil which, in turn, is in one of the arms of a mutual inductance bridge. A bridge which in the past proved to be very useful has been that described by Wilde [40] and, in a modified version due to Gerstner and Kneller [41], has been widely applied [2 to 6, 13 to 15, 42]. In the original form of this bridge, both components of the complex permeability had to be balanced by hand and this proved to be extremely tedious and time-consuming [8].

In an attempt to overcome this handicap, various modifications of ac-bridges have been proposed in the past, including circuits based on phase-sensitive detectors which were able to measure both components of the complex susceptibility [43 to 46]. Recently, a modernized version of this phase-locking technique has been described by Blythe [47], allowing both automated data acquisition and control of all measuring procedures using a microcomputer.

3.2 LC-oscillator technique

A highly-sensitive, versatile MAE technique has been developed by Walz [8] in which the sample to be investigated is made the core of a self-inductance coil which, in turn, forms part of an LC-oscillator. In this technique, variations in the susceptibility of the specimen are followed as changes in the resonant frequency of the LC-circuit which, by means of a high-resolution frequency counter, can be measured with great accuracy. This digital data acquisition is the key to the automation of the complete MAE measuring programme, including specimen demagnetization and temperature control, by means of a microcomputer. Both components of the complex susceptibility can be determined from the resonance frequency and the feedback control of the LC-circuit [8], with the advantage that this automated technique allows measurements to be started almost immediately after demagnetization i.e. at $t_1 \leq 1$ s. This has the consequence that, within the shorter period of only up to $t_2 = 180$ s, even more details on isothermal relaxation can be obtained than within the longer time intervals ($0.5 \text{ min} \leq t \leq 30 \text{ min}$), which are typical for the former bridge methods [8]. This gain in time, combined with the inherent sensitivity of the LC-oscillator technique and the complete automation of the measuring programme, allowed us to considerably increase the accuracy and resolu-

tion of fine-structured MAE spectra. All experimental data are electronically stored for the subsequent analysis on the most appropriate computer, be it PC or mainframe. Skin-effect corrections, as discussed, e.g. by Kronmüller [15] and Walz [48], may be included directly into the computer programs for data evaluation. Since its first introduction, the oscillator technique has proved to be so successful that it served as basis for almost all subsequent MAE measurements performed both in Stuttgart and Sheffield [8].

3.3 Analysis of results and application to carbon in α -Fe

The simplest analysis of a set of isochronal relaxation curves is based on eq. (2.22), leading to the following expression for the relaxation time $\tau(T_{\max})$ at the temperature, $T_{\max}$, of the maximum of a single isochrone [5]:

$$\tau(T_{\max}) = (t_2 - t_1) / \ln(t_2/t_1). \quad (3.2)$$

Thus eq. (3.2) may be combined with the expression for the relaxation time (cf. eq. (2.20)),

$$\tau(T_{\max}) = \tau_0 \exp(Q/kT_{\max}), \quad (3.3)$$

so as to yield τ_0 and Q via an Arrhenius plot. This method of analysis, whilst relatively quick and convenient, tends to give values of Q which are too large and of τ_0 which are correspondingly too small.

In the treatment so far, we have assumed that the relaxation of a defect may be described in terms of a single, discrete relaxation time τ . In practice, this of course is not the case. Due to interactions between the defects and the elastic distortion fields of neighbouring other defects, including dislocations and grain boundaries, the potential wells of relaxing defects become locally modified, thereby giving rise to a spectrum of relaxation times. Accordingly, the observed half-widths, ΔT_H , of isochronal relaxation curves are frequently somewhat larger than would be expected from eq. (2.22).

In order to account for a continuous spectrum of relaxation times, we introduce, following Richter [19], a distribution function, $P(\tau)$, where $P(\tau) d\tau$ is the probability of finding the relaxation time τ of a given process in the interval τ and $\tau + d\tau$. This leads to the normalization condition

$$\int_0^{\infty} P(\tau) d\tau = 1. \quad (3.4)$$

The change of reluctivity at constant temperature, following a demagnetization of the specimen, can be described quite generally in the form

$$r(t) = r(0) + \Delta r_s G(t), \quad (3.5)$$

where $r(0)$ is the initial reluctivity immediately after demagnetization, Δr_s the stabilization reluctivity and $G(t)$ the relaxation function. For an ideal orientation MAE, the relaxation function is of exponential type,

$$G(t) = (1 - e^{-t/\tau}). \quad (3.6)$$

In the case of continuous superposition of such processes we obtain, together with eq. (3.4), the following expression:

$$G(t) = \int_0^{\infty} P(\tau) (1 - e^{-t/\tau}) d\tau. \quad (3.7)$$

Fig. 4. Illustration of a Gaussian-shaped (GS) spectrum of relaxation times and its approximation by a rectangular box-type (RB) distribution function

It now proves useful to transform $P(\tau)$ into a second function $p(\tau)$, such that [15, 29, 49]

$$P(\tau) d\tau = p(\ln \tau) d \ln \tau = p(\tau) (d\tau/\tau), \quad (3.8)$$

where $p(\tau)$ as a function of $\ln \tau$ is approximately Gaussian-shaped (Fig. 4). If

we approximate the Gaussian distribution for $\ln \tau$ by a rectangular distribution in the interval $\ln \tau_1 \leq \ln \tau \leq \ln \tau_2$, insertion of eq. (3.8) into the normalization condition eq. (3.4) yields the following relation between the distribution functions:

$$P(\tau) \tau = p(\ln \tau) = \frac{1}{\ln(\tau_2/\tau_1)} = \text{const}. \quad (3.9)$$

This corresponds, via eq. (2.20), to a distribution of activation enthalpies, Q , having a constant probability in the interval $Q_1 \leq Q \leq Q_2$ and, by insertion of eq. (3.9) into eq. (3.7), yields the following expression for $G(t)$:

$$G(t) = \frac{1}{\ln(\tau_2/\tau_1)} \int_{\tau_1}^{\tau_2} (1 - e^{-t/\tau}) \frac{d\tau}{\tau} \quad (3.10)$$

or

$$G(t) = 1 + \frac{1}{\ln(\tau_2/\tau_1)} [\text{Ei}(-t/\tau_2) - \text{Ei}(-t/\tau_1)]. \quad (3.11)$$

In eq. (3.11) the integral eq. (3.10) is expressed in terms of so-called exponential integrals [50, 51], using the notation

$$\text{Ei}(-x) = - \int_x^{\infty} \frac{e^{-u}}{u} du, \quad (3.12)$$

with the substitutions $u = t/\tau$ and $x = t/\tau_i$, $i = 1, 2$.

Insertion of eq. (3.11) via eq. (3.5) into eq. (2.2) yields, in the case of continuous, box-type distributed activation energies, the following expression for the isochronal relaxation between two times t_1 and t_2 :

$$\Delta r(t_1, t_2, T) = \frac{\Delta r_s(T)}{\ln(\tau_2/\tau_1)} \{ [\text{Ei}(-t_2/\tau_2) - \text{Ei}(-t_2/\tau_1)] - [\text{Ei}(-t_1/\tau_2) - \text{Ei}(-t_1/\tau_1)] \}. \quad (3.13)$$

This relation is to be compared with eq. (2.22) for the ideal case of a simple Debye process. It should be borne in mind that the stabilization reluctivity, Δr_s , still represents a temperature-dependent variable which may be approximated by the expression [15]

$$\Delta r_s(T) = \frac{\Delta r_{0,s}}{T}, \quad (3.14)$$

where $\Delta r_{0,s}$ is composed of time- and temperature-dependent parameters of the domain-wall system. The relaxation times, τ_i , in eq. (3.13) are related to the corresponding activation enthalpies, Q_i , via the general Arrhenius equation (cf. eq. (2.20))

$$\tau_i = \tau_{0i} \exp(Q_{i0}/kT). \quad (3.15)$$

Here Q_{i0} is the central activation energy of a continuous, box-type MAE spectrum which is limited by the boundary values Q_{i1} and Q_{i2} (cf. Fig. 5):

$$Q_{i0} = (Q_{i1} + Q_{i2})/2, \quad (3.16)$$

with the half-width of the distribution

$$\Delta Q_i = (Q_{i2} - Q_{i1})/2, \quad (3.17)$$

so that

$$Q_{i2,1} = Q_{i0} \pm \Delta Q_i. \quad (3.18)$$

Fig. 5 shows the experimental, isochronal relaxation spectrum of C in α -Fe where, in order to facilitate dimensionless scaling of the ordinate, Δr has been divided by r_1 , i.e. the reluctivity as measured 1 s after demagnetization of the specimen. This type of scaling may be advantageously applied to data which were obtained from such temperature ranges within which the initial reluctivity, r_1 , itself is only weakly temperature-dependent. The theoretical fit of the data of Fig. 5 is based on eq. (3.13), using a least-squares fitting technique [9 to 11] with the following activation parameters: $Q_0 = 0.84$ eV; $\Delta Q = 0.04$ eV; $\tau_0 = 3 \times 10^{-15}$ s. These values compare favourably with other determinations of the activation parameters for C in α -Fe [6, 8, 28] Section 7.

It is worthwhile mentioning here that, whilst according to our discussion in Section 2.4.2, C in α -Fe should also give rise to a diffusion MAE, no such effect has yet been detected.

Fig. 5. Approximation of a family of C-relaxation isochrones in α -Fe (Richter MAE), as obtained by means of the LC-oscillator technique [8] (Section 3.2), using the numerical analysis described in Section 3.3. Measurements were performed at $t_1 = 1$ s; $t_2 = 2$ s (1), 4 s (2), 8 s (3), 16 s (4), 32 s (5), 64 s (6), 128 s (7), 180 s (8). The activation parameters of this process were determined to be $Q = 0.84$ eV, $\Delta Q = 0.04$ eV, $\tau_0 = 3 \times 10^{-15}$ s, cf. [216]

4. Structural Defects in α -Fe

Detailed calculations of structural defects in α -Fe have been performed by Erginsoy et al. [52] and Johnson [53]. Johnson, who considered a crystallite of 531 atoms embedded in an elastic continuum, used an empirical two-body force potential based on experimental elastic data. Each of the atoms within the crystallite was treated as an independent particle. The resulting Fe-Fe interaction potential was a composite of three cubic equations and was cut-off between second and third nearest neighbours. Further model calculations and re-evaluations of earlier results are reported by Dederichs et al. [54] and Ehrhart et al. [55] (cf. Table 1). Extensive studies have been continued up to the present time by the group around Bacon [56 to 60]. Besides atomic pair potentials, as used by Johnson, Bacon et al. applied for their model calculations especially many-body potentials, as derived by Finnis and Sinclair [61]. Interestingly, in the case of α -Fe, this extended technique did not only justify many of Johnson's former results [53] but, finally, yielded also strong support in favour of the two-interstitial model [60].

4.1 Intrinsic interstitials

From both Johnson's and Bacon's model calculations it was found that there are, from symmetry considerations, six equivalent interstitial configurations (Fig. 6), of which only

Fig. 6. Possible interstitial configurations in α -Fe according to Johnson [53]: a) octahedral, b) tetrahedral, c) $\langle 100 \rangle$ -split, d) crowdion (activated state), e) crowdion ($\langle 111 \rangle$ -split interstitial), f) $\langle 110 \rangle$ -split interstitial (dumb-bell), indicating a first jump composed of migration and a 60° rotation. By a following, second jump the dumb-bell axis may undergo a rotation of 90° relative to its original orientation, g) di-dumb-bell configuration

Table 1
Compilation of data of the most interesting point defects in α -Fe: relative volume variation, $\Delta V/V$; formation enthalpy, H^F ; binding enthalpy, H^B ; migration enthalpy, H^M ; reorientation enthalpy H^R

defect	$\Delta V/V$ [54, 55]	formation enthalpy [53 to 55] H^F (eV)	binding enthalpy [53] H^B (eV)	migration enthalpy H^M (eV)		reorientation enthalpy H^R (eV)	
				theory	experiment ⁺	theory	experiment ^{a)}
				[53]	1IM 2IM	[52, 53]	1IM 2IM
interstitials							
$\langle 110 \rangle$	2.34	4.60	—	0.33	0.27 [87] to 0.32 [106]	0.33	0.32 [106] 0.56
$\langle 111 \rangle$ (crowdion)	2.20	+0.32	—	0.04	—	—	—
$\langle 001 \rangle$	2.22	+1.29	—	—	—	—	0.30 to 0.33
octahedral	1.85	+1.12	—	—	—	—	—
tetrahedral	2.08	+0.85	—	—	—	—	—
di-interstitial	—	—	0.20 [53]	0.66	0.42 [87] <0.5	0.18	0.37
vacancies							
monovacancy	1.37	1.37	—	0.68	0.55 [87]	—	—
divacancy	—	—	0.20	0.66 to 0.78	—	0.78	—

^{a)} cf. Tables 2 to 5.

one is stable [53, 56]. This is the $\langle 110 \rangle$ -split interstitial (Fig. 6f) in which two atoms are split in a $\langle 110 \rangle$ direction about a vacant normal lattice site. This interstitial configuration, which has orthorhombic symmetry, is strongly anisotropic and frequently referred to as a dumb-bell configuration; the direction of the dumb-bell is the line connecting the two interstitial atoms.

The elementary jump of the interstitial is shown in Fig. 6f. The dumb-bell moves its centre by a nearest-neighbour distance and the axis of the dumb-bell rotates by 60° . According to Johnson [53], the migration enthalpy of this process is 0.33 eV, although later on a value of 0.21 eV has been suggested to be more accurate [54], Table 1.

In addition, the dumb-bell may undergo a process of pure reorientation, e.g. from a $\langle 110 \rangle$ to a $\langle 011 \rangle$ direction, thus changing its orientation by 60° . Johnson found the the activation energy of this process to coincide with the migration energy, i.e. $Q^R = Q^M = 0.33$ eV [53], whereas another study yielded a lower value of $Q^R = 0.25$ eV [54]. A second type of reorientation is also possible whereby the axis of the dumb-bell

Fig. 7. a) Possible crowdion (C) reactions upon thermal activation as represented in a (111) plane [7]: (i) direct annihilation with a nearby vacancy; (ii) trapping by an off-line lattice defect (I), enabling the crowdion to jump to and fro between two equilibrium positions A and B, thereby inducing a reorientation-type MAE (cf. Fig. 7b); (iii) strong trapping by a (substitutional) on-line impurity atom (I), immobilizing the crowdion up to temperatures where, after thermal conversion, it may either escape or form a reorientable complex with its trap. b) Potential of the crowdion configuration of Fig. 7a (ii). c) Conversion of an off-line crowdion (C), upon its migration in a (111) plane, into a stable $\langle 110 \rangle$ dumb-bell (D). After thermal activation at elevated temperatures, the dumb-bell, in turn, undergoes migration, thus giving rise to two alternative reactions: a) recombination with a vacancy (V), b) trapping at an impurity atom in, e.g., interstitial position. The combined rotational and translational migration mode of the dumb-bell is schematically illustrated in its projection onto a (100) plane. Actually, in order to achieve the indicated 90° rotation, the dumb-bell has to perform two successive 60° rotations in different (111) planes [15]. For the sake of clarity, the central atoms of the b.c.c. lattice are indicated only in the upper right corner

remains in the same plane and rotates by 90° . Of the other five configurations, the crowdion, Fig. 6e, is found to be the energetically next favourable configuration, Table 1. In terms of the 2IM, this result is a justification for introducing the crowdion as a metastable interstitial into the annealing mechanism of irradiated α -Fe, in addition to the stable dumb-bell configuration (Section 1).

The crowdion is able to induce both diffusion-type and reorientation-like MAEs. The first type of MAE is expected to result from long-range diffusion, ending either by annihilation with a vacancy (on-line crowdion), trapping at an impurity or conversion into the stable dumb-bell configuration (Fig. 7a). A reorientation-like MAE may be induced by a crowdion jumping to and fro between pairs of equilibrium positions, A and B (Fig. 7a (ii) and 7b), which have been shown to exist in the vicinity of point defects of either intrinsic nature (self-interstitials, vacancies) or impurity type [62, 63]. In addition to this behaviour of *on-line crowdions*, Fig. 7c illustrates some typical reactions of *off-line crowdions*, i.e. diffusion and conversion into a stable dumb-bell. After its thermal activation, such a dumb-bell may a) either annihilate with a vacancy or b) become trapped, e.g. at an impurity atom.

There are many possible di-interstitial configurations, although most are unstable. The most stable one consists of two split interstitials parallel to each other and separated by a nearest-neighbour distance, with the dumb-bell axes oriented perpendicular to the line joining their centres (Fig. 6g). Migration would occur via a stepping process in which each dumb-bell shifts its centre to a nearest-neighbour lattice site. The migration energy of the di-interstitial was found to be lower than that of the single interstitial (Table 1) [53].

4.2 Vacancies

The most stable monovacancy, Fig. 8a, was found to be a vacant lattice site and its migration process consists of a jump of a nearest neighbour to the vacant site. Johnson

calculated a migration energy of 0.68 eV [53], Table 1. Such a vacancy has, of course, the symmetry of the lattice and is thus able to give rise to a diffusion MAE, but not to an orientation MAE.

The most stable divacancy, Fig. 8c, consists of two single vacancies on second nearest-neighbour sites and not, as might be at first expected, on nearest-neighbour sites (Fig. 8b). In the divacancy migration process, one of the vacancies moves as a single vacancy. Two processes are im-

Fig. 8. Possible vacancy configurations in α -Fe according to Johnson [53, 66]: a) monovacancy, b) metastable divacancy, c) stable divacancy, d) trivacancy

portant: one where the separation alternates from second nearest neighbour to nearest neighbour and one where the separation alternates from second to third nearest-neighbour positions. Motion by the second of these two processes leaves the orientation of the divacancy unaltered; both these processes have approximately equal migration energies (Table 1). Clearly, a divacancy could give rise to both orientation and diffusion MAEs. Sometimes the split monovacancy is also discussed in the literature [15, 53, 64] as a potential vacancy configuration which, due to its anisotropy, should be able to undergo reorientations, thereby, giving rise to a relaxation. According to Johnson's model calculations [53], however, this vacancy type proves to be unstable and, so far, there has been no experimental evidence of its existence [65].

Beeler and Johnson [66] have investigated tri-vacancies, Fig. 8d, and higher-order vacancy clusters of up to 37 vacancies which they found to be stable with no tendency to form dislocation loops.

4.3 *Intrinsic defects and interstitial impurities*

Johnson's model for α -Fe has also been applied to the problem of C impurities in α -Fe and to their interaction with intrinsic defects [67, 68]. Since no data on the elastic constants of such systems existed at the time, the constants of the cubic interaction potential were varied until agreement was obtained with experimentally determined data on C such as activation energy of migration, activation volume and binding energy of C-vacancy complexes (Section 7). The potential thus determined was then used, together with the known data of the Fe lattice, to calculate the binding energy of the C atom to an Fe interstitial; the position of the C atom in a C-vacancy complex was also calculated using the same technique. Fig. 3b shows the most stable position of a split-interstitial-C complex and Fig. 3c that of a vacancy-C complex. Since the strain fields of these complexes do not have the symmetry of the lattice, they are expected to give rise to relaxation phenomena.

4.4 *Intrinsic defects and substitutional impurities*

Most of the work on the trapping of irradiation-induced interstitials at substitutional impurities has been confined to f.c.c. systems. Dederichs et al. [54] have treated this problem theoretically for f.c.c. structures by assuming that the size of the impurity is the decisive quantity concerning the formation of impurity-interstitial centres.

If one defines the atomic volume, Ω , of a metal or solid solution as the volume of the unit cell divided by the number of atoms contained therein, then one can introduce the concept of the volume size factor, Ω_{SF} , for a substitutional alloy system such that [69]

$$\Omega_{\text{SF}} = \frac{1}{\Omega_{\text{A}}} \frac{\partial \Omega}{\partial c}, \quad (4.1)$$

where $\partial \Omega / \partial c$ is the concentration dependence of the atomic volume of the alloy which, for dilute alloy systems, is found to be a linear variation. Ω_{A} is the atomic volume of the host atom. The Seitz radius, r_0 , may then be expressed as

$$r_0 = \left(\frac{3\Omega_{\text{A}}}{4\pi} \right)^{1/3}. \quad (4.2)$$

Dederichs et al. [54], using both Morse and Born-Mayer potentials, simulated the interaction of an impurity atom by shifting the host-host interaction potential in proportion to the difference, Δr , between the Seitz radii of the host and impurity atoms. The binding energies of mixed dumb-bells, calculated with these approximated potentials, were found to be simply related to the corresponding volume changes, ΔV . Binding only occurred for $\Delta r < 0$, i.e. undersized impurities; for oversized impurities, $\Delta r > 0$, the mixed dumb-bell proved to be unstable due to repulsive interactions between the partners. In addition to mixed dumb-bells, other configurations between interstitials and substitutional impurity atoms have been considered and, again, it was found that oversized impurities form only weak traps for interstitials.

These theoretical results seemed to be in good agreement with the experimental results obtained for several f.c.c. alloy systems. Thus, in irradiated Al alloys, Swanson et al. [70, 71] were able to identify mixed dumb-bells in the presence of impurities with negative size factors, Ω_{SF} , such as Mn (-46.8%), Zn (-5.7%) and Ag ($+0.1\%$) in contrast to the presence of oversized impurities like Sn ($\Omega_{SF} = +2.4\%$) where no mixed dumb-bells were detected. The same situation was observed in Cu alloys where, in the presence of Ag ($+43.5\%$), Sb ($+91.9\%$) and Au ($+47.6\%$), no mixed dumb-bells were observed.

So far only little information has been available regarding the behaviour of substitutional impurities in b.c.c. crystals [72 to 74] Section 6. However, by drawing an analogy with f.c.c. crystals, we would also expect in b.c.c. crystals mixed dumb-bells to be stable only in the case of undersized impurities, giving rise to the following configurations [54, 55, 75, 76]:

a) $\langle 110 \rangle$ mixed dumb-bells with only slightly modified configurations as compared to those formed in the pure metal, cf. Fig. 6f. Two different motion modes of such dumb-bells may be distinguished:

(i) Reorientation without dissociation of the dumb-bell (Fig. 9a). In this case, following a jump of the impurity interstitial, the mixed dumb-bell rotates by 60° , thereby having the chance to take up one of the four positions shown in Fig. 9a. In this way, the impurity is found to be "caged" and, in fact, its motion is confined to two dimensions since the four equilibrium positions lie on the corners of the rectangle 1-2-3-4 directed along $\langle -110 \rangle$. Thus, we are concerned with a pure reorientation process, without the possibility for long-range migration.

Fig. 9. Elementary jumps of a mixed dumb-bell: $\circ$ Fe atoms, $\bullet$ impurity atoms. a) Pure orientation, without dissociation of the dumb-bell. b) Combined migration and reorientation after dissociation of the dumb-bell

(ii) Reorientation combined with a dissociation of the dumb-bell (Fig. 9b). Here, too, the jump of an impurity atom of the initial $\langle -110 \rangle$ dumb-bell into one of the four equivalent positions 1, 2, 3 or 4, as in the case of its intrinsic counterpart (Fig. 6f), causes a reorientation of the dumb-bell axis by 60° . By a second jump from these positions, back into the original $\langle 100 \rangle$ plane, the dumb-bell may achieve a 90° rotation relative to its initial orientation and, by a continuation of such steps, undergo a series of successive reorientations combined with long-range diffusion.

(iii) After the jump of a host interstitial, the impurity atom may take up a regular lattice site leaving behind a normal dumb-bell formed on a nearest-neighbour site. From this position, the dumb-bell may either migrate further away or, as discussed by Johnson and Lam [76], it may alternatively loop around the impurity there by re-forming, ultimately, a mixed dumb-bell which has been rotated by 180° . The latter case would also lead to a reorientation process, in combination with a long-range diffusion.

(iv) In addition to our models, various alternative motion modes of mixed dumb-bells are discussed in the literature, including 90° rotation, without dissociation, in the $\langle 100 \rangle$ plane and reorientations, requiring intermediate dissociation but leading, nevertheless, to a caged motion of the impurity atom [54, 55, 75, 76].

(b) At sufficiently high impurity concentrations, the formation of impurity–impurity dumb-bells may also be expected.

5. The MAE Spectrum of Pure Fe Following Low-Temperature Irradiation

5.1 Fast-particle irradiation

The most efficient method of introducing sufficiently high concentrations of intrinsic defects, i.e. monovacancies and interstitials, into a metal is to irradiate it with fast particles such as neutrons or electrons [77 to 80]. However, due to their difference in charge and mass, the radiation damage produced by these two types of particles differs characteristically [77]. Whereas energetic neutrons ($E > 1.1$ MeV) are, at their primary knock-on, able to transfer energies of up to several thousand times the threshold energy, electrons of comparable energy are only able to transfer amounts which slightly exceed the threshold energy [79]. Consequently, e^- -irradiation produces the simpler defect spectrum, ranging from close Frenkel pairs to isolated vacancies and interstitials which have been formed via dynamic crowdions at the end of long-range, focussing displacement chains. During n-irradiation, due to the thousand-fold higher energies transferred, cascades of secondary and higher-order knock-ons are produced, which are effective in generating dynamic crowdions at the end of their range. This mechanism, which has been described in detail by Seeger [78], leads to the formation of high local densities of vacant sites, so-called depleted zones, which are surrounded only by a relatively small number of interstitials, whereas most other interstitials have been propagated over large distances as dynamic crowdions. Thus, after n-irradiation, the defect spectrum consists not only of the simple configurations which are typical of e^- -irradiation but, in addition, also includes complexes formed between intrinsic defects, such as di-vacancies (V_2), tri-vacancies (V_3) etc., as well as di-interstitials (I_2), tri-interstitials (I_3) etc. [80].

Since, following n-irradiation, the basic reactions of simple intrinsic defects are, to a large extent, modified by those of higher-order complexes, it is evident that e^- -irradiation is preferable for the classification of the fundamental recovery mechanisms of sim-

ple defects. Nevertheless, since high-energy neutron beams are readily available, many experiments, especially in the early stages of point-defect research, were performed on α -Fe following n-irradiation.

5.2 Classification of the annealing stages

Historically, the search for a deeper insight into the various defect reactions occurring in irradiated α -Fe appears as a sequence of trial and error, the latter arising frequently as a result of using insufficiently pure Fe in the early experiments. It thus seems only fair to acknowledge in the following the many contributions made by various workers to our present understanding of the defect kinetics in high-purity α -Fe. In the later discussions on defect mechanisms in substitutionally (Section 6) and interstitially (Sec-

Fig. 10. Isochronal recovery curves of the electrical resistivity and their derivatives, as obtained in pure Fe following: a) 1.2 MeV electron irradiation at 20 K [16, 84]. b) >1 MeV neutron irradiation at 78 K [16, 84]. c) e^- -irradiation at 20 K (-----) [86], n-irradiation at 4 K (—) [85]

Fig. 11. a) Isochronal recovery curves of the electrical resistivity of high-purity α -Fe after e^- irradiation to various doses, as indirectly indicated by the induced resistivity $\Delta\rho_0$ [87]. b) Derivatives of the RRR curves of a)

tion 7) impurity-doped α -Fe, however, we will leave this historical approach and focus our attention on the most relevant results which have been obtained from recent analyses of MAE investigations.

Initially, the various isochronal recovery stages of the electrical resistivity of an f.c.c. metal, following low-temperature irradiation, were classified in the sequence I to V [81]. Subsequent measurements showed these stages to exhibit considerable structure and they were thus sub-divided into various sub-groups, I_A, I_B, I_C etc. This nomenclature has also been generally adopted for the annealing stages occurring in b.c.c. metals [82]. However, in the MAE, a given isochronal relaxation peak is designated as corresponding to that recovery stage of the electrical resistivity with which its annealing coincides. In order to distinguish between magnetic and other relaxation processes, some authors [83] prefer to denote the corresponding magnetic relaxations with an asterisk.

Figs. 10, 11 show recovery spectra of the electrical resistivity of pure Fe following low-temperature n- [16, 84, 85] and e^- [16, 84, 86] irradiation, which allow to distinguish clearly the recovery stages I_A, I_B and I_C . More recent work by Takaki et al. [87] has been shown there to be six recovery stages in this low-temperature region. However, since it is accepted by supporters of either the 1IM or 2IM that these stages are due to close-pair recombination, which is not able to produce pronounced MAEs, they will not be discussed here any further. Over the years, many measurements have been performed, following either n- or e^- irradiation, on samples which, at that time, were erroneously believed to be pure Fe. Irradiations have been performed over a wide range of temperatures but, since in Fe no annealing occurs until about 100 K (Stage I), the essential features of the relaxation spectrum are not sensitive to the exact temperature of irradiation, provided that the sample temperature throughout irradiation remains well below this critical limit.

5.3 Neutron irradiation

Moser and Dautreppe [88] and Balthesen et al. [89] were the first to report magnetic relaxation measurements made on nominally pure Fe after low-temperature neutron

Fig. 12. Annealing behaviour of the MAEs as observed by Balthesen et al. [89] after n-irradiation at 30 K in terms of the reciprocal initial permeability $1/\mu_i$ ($t_1 = 10$ s, $t_2 = 120$ s)

irradiation. Balthesen et al. irradiated at 30 K in the FRM München to a dose of $8 \times 10^{21} \text{ n m}^{-2}$ ($E > 0.1 \text{ MeV}$). After irradiation, measurements were made by applying a stepwise annealing programme in which the final annealing temperature for each of the successive measuring runs was increased by a constant amount of about 20 K. These authors attempted to correlate the annealing behaviour of the sample with results from other experimental techniques such as, e.g., IF, stored energy, etc. In summary, a total of nine distinct relaxation processes were detected in the temperature range from 4.5 to 300 K; their recovery spectra are shown in Fig. 12.

Moser [44] has also reported detailed measurements after n-irradiation at 78 K. Fig. 13 gives the result of a measuring run during the course of which the sample temperature was increased uniformly at a rate of 0.4 K/min^{-1} . Measurements started 4 s after demagnetization and continued up to 285 s. The dotted and solid curves give the envelopes of measurements made 4 and 285 s after demagnetization. Thus, on account of the relatively slow rate of change of temperature, the difference in amplitude between the two curves may be regarded as an isochronal relaxation spectrum with t_1 and t_2 equal to 4 and 285 s, respectively (cf. Section 3.3). This measuring technique is typical of most of the measurements of the Grenoble group. The results show a very strong

Fig. 13. a) MAE following n-irradiation at 78 K to a dose of $2 \times 10^{21} \text{ n m}^{-2}$ [44]. The dotted and solid curves represent the envelopes of measurements made at, respectively, 4 and 285 s after demagnetization. The various annealing stages are indicated by Roman numbers. b) Recovery of the magnetic relaxation after annealing the sample for 30 min at $T = 475 \text{ K}$

Fig. 14. Isochronal annealing behaviour of the MAEs of Fig. 13

relaxation occurring between 80 and 130 K, a second from 66 to 170 K, which is superimposed on the first process, together with two additional relaxations extending between 170 to 230 K and 230 to 400 K. The recovery spectrum of Fig. 14 shows the growth and decay of these peaks during sample anneal.

More recently, Mensch et al. [83, 90, 91] and Dunleavy and Blythe [92 to 94] have reported measurements on α -Fe irradiated at 30 and 77 K, respectively. These results were obtained by means of a stepwise heating programme as illustrated in Fig. 15, in

Fig. 15. Schematic diagram of temperature profiles during stepwise annealing programmes: a) Individual steps within a series: Δt_1 , control time after a preceding temperature change (typically 300 s); Δt_2 , delay time, before the commencement of the first measurement after demagnetization (typically 1 s); $t_2 - t_1$, period of measuring at stabilized temperature (typically 2×180 s) [8, 89 to 94]. b) Successive measuring series within an extended recovery programme: Δt , total time spent at one temperature (typically 11 min, cf. a); ΔT , increment of the measuring temperature within a series; $\Delta T_{\max}$, increment of the maximum temperature between two successive measuring series. After each run, up to one of the maximum temperatures $T_{\max(1)}$, $T_{\max(2)}$, ..., the sample is cooled down to the initial starting temperature

which, prior to any measurement, the temperature is stabilized to an accuracy of typically $\lesssim 0.02$ K. Then, an isothermal run is started, at the end of which the sample temperature is rapidly incremented by an amount, ΔT , to the next measuring temperature, which again is stabilized before the initiation of a further measurement. This procedure is continued up to a maximum temperature, $T_{\max, i}$, after which the sample is cooled

Fig. 16. a) Magnetic relaxation spectrum of purified α -Fe after n-irradiation at ≤ 18 K to a dose of $3.2 \times 10^{21} \text{ nm}^{-2}$ [83, 91]: $t_1 = 15$ s; $t_2 = 30$ s (1), 120 s (2), 300 s (3), 600 s (4), 1200 s (5). b) Recovery spectrum obtained by systematic annealing of an identical Fe specimen to that of a); $t_1 = 15$ s, $t_2 = 600$ s

down to the original starting temperature. Subsequently, the next corresponding measuring sequence is initiated, ending at an elevated maximum temperature, $T_{\max, i+1}$, etc. Thus, during the course of measurements, the sample spends a total time Δt at any given temperature, leading to a temperature profile as indicated schematically in Fig. 15b. This type of measuring programme, originating from Balthesen et al. [89], is applied by almost all workers, apart from the Grenoble group. Clearly, both programmes give essentially the same results. However, due to the fact that recovery frequently occurs during measurement, the exact location of a relaxation peak depends not only upon the measuring times t_1 and t_2 (Section 3.3), but also upon the values of Δt and ΔT .

Fig. 17. a) Magnetic relaxation spectrum of purified α -Fe after n-irradiation at 77 K to a dose of $2 \times 10^{23} \text{ nm}^{-2}$ [93]: $t_1 = 1 \text{ s}$, $t_2 = 2 \text{ s}$ (1), 4 s (2), 16 s (3), 64 s (4), 180 s (5). The dashed curve corresponds to an identically irradiated, C-charged specimen ($t_2 = 180 \text{ s}$). b) Stepwise annealing sequences obtained for a pure Fe sample, irradiated to a dose of $2 \times 10^{23} \text{ n m}^{-2}$ [93]. On each successive measuring pass the temperature is incremented by about 20 K ($t_1 = 1 \text{ s}$, $t_2 = 180 \text{ s}$). c) Annealing spectrum as determined from b). The amplitude of the 200 K relaxation ($\bullet$) is normalized with respect to that observed after e^- -irradiation (---- [97]) in order to facilitate comparison ($t_1 = 1 \text{ s}$, $t_2 = 180 \text{ s}$); $\blacktriangle$ 200 K (e^-), $\bullet$ 200 K (n), ($t_1 = 1 \text{ s}$, $t_2 = 180 \text{ s}$)

Mensch et al. [83, 90, 91] used, as source material, nominally high-purity Johnson Matthey α -Fe, which they purified by anneal in hydrogen prior to irradiation. Samples were irradiated at 20 K in the FR2 reactor of the KFZ Karlsruhe and, at temperatures below 25 K, transferred to a measuring cryostat; a bridge technique was used for measurements [91]. Fig. 16 shows the results of a measurement made in a single-pass from 20 to 300 K on a sample irradiated to a dose of $3 \times 10^{21} \text{ n m}^{-2}$ [83]. These measurements were performed with the parameters $\Delta T \simeq 2 \text{ K}$ and $\Delta t \simeq 30 \text{ min}$, thus giving an effective temperature rise of 0.067 K min^{-1} . The annealing behaviour of the various MAEs is given in Fig. 16b; these measurements were correlated with IF measurements made on similarly irradiated samples [83, 90].

Dunleavy and Blythe [92 to 94] irradiated samples in the liquid nitrogen cryostat facility of the "Herald" reactor AWRE, Aldermaston, to doses of $2 \times 10^{22} \text{ n m}^{-2}$. Measurements were performed using the LC-oscillator technique (Section 3.2). Fig. 17a shows the results of a single-pass from 30 to 300 K; the temperature profile of the sample was obtained with $\Delta T \simeq 2 \text{ K}$ and $\Delta t \simeq 11 \text{ min}$. Fig. 17b gives the results of a stepwise annealing programme in which the maximum temperature for subsequent measuring runs was incremented by some 20 K; the corresponding recovery spectra of the observed processes are represented in Fig. 17c. It is gratifying to observe that there is almost complete agreement between the results of Mensch et al. [83, 91] and those of Dunleavy and Blythe [92 to 94] (cf. Figs. 16a, 17a and Figs. 16b, 17c); a slight discrepancy exists in the amplitude of the relaxation centred at 110 K. However, as will be discussed later (Section 6.2), the amplitude of this relaxation depends strongly on sample purity, which may have differed in both experiments; e.g. Blythe and Dunleavy reported their nominally pure Fe to contain about 25 at ppm Ni.

5.4 Electron irradiation

Magnetic relaxation measurements after low-temperature e^- -irradiation were first reported by Verdone et al. [95]; these workers irradiated at 22 K with 3 MeV electrons and used a measuring technique similar to that reported by Moser [44]. Fig. 18 shows the observed isochronal recovery [88] of the various relaxation zones. Schaefer et al. [96] have reported measurements on Fe containing about 15 at ppm substitutional impurities and 10 to 15 at ppm carbon and oxygen. Fig. 19 shows the relaxation spectrum after irradiation at 27 K to a dose of about $10^{22} \text{ e}^- \text{ m}^{-2}$ with 2.5 MeV electrons; these measurements were correlated with simultaneous measurements of the electrical resistivity of the samples. Walz et al. [97] performed measurements on nominally pure Fe,

Fig. 18. Isochronal recovery of MAEs as observed by Verdone et al. [95] after irradiation at 22 K with 3 MeV electrons ($t_1 = 3 \text{ s}$, $t_2 = 166 \text{ s}$)

Fig. 19. MAE spectrum of α -Fe after e^- -irradiation at 27 K, according to Schaefer et al. [96], ($t_1 = 15$ s, $t_2 = 300$ s)

irradiated at $\lesssim 77$ K with 3 MeV electrons to doses between 2×10^{22} and $2 \times 10^{23} \text{ e}^- \text{ m}^{-2}$ in the van-de-Graaff generator of the RWTH Aachen. The results of a series of measuring passes, using the annealing technique described in Section 5.2, are shown in Fig. 20; here the annealing parameters were $\Delta T \simeq 2$ K, $\Delta t \simeq 11$ min. More recently, Blythe et al. [98] have reported measurements made after 3 MeV irradiation to a dose of $10^{23} \text{ e}^- \text{ m}^{-2}$ at ≤ 44 K in the low-temperature van-de-Graaff accelerator facility at the Forschungszentrum (formerly KFA) Jülich. Here, samples were prepared from high-purity Johnson Matthey Fe containing a total of less than 4 at ppm metallic impurities. Fig. 21a gives the isochronal relaxation spectrum obtained in a single measuring pass from 30 to 300 K with $\Delta T \simeq 2$ K and $\Delta t \simeq 11$ min. The various sequences of a stepwise annealing programme, together with the corresponding recovery spectra, are

shown in Figs. 21b and c, respectively. Similar MAE measurements on e^- -irradiated, high-purity α -Fe have been performed by Walz [99], Figs. 22a, b. Most recent results obtained by MAE investigations on high-purity ($\text{RRR} \simeq 2300$), low-temperature e^- -irradiated α -Fe are reported by Schwendemann et al. [100] and Hirscher et al. [101, 102]. In these experiments, e^- -irradiation was performed in the dynamitron accelerator of the University of Stuttgart at temperatures kept below 80 K by cooling with liquid nitrogen. In order to investigate

Fig. 20. Isochronal anneal of nominally pure α -Fe after 3 MeV e^- -irradiation at $T = 60$ K to a dose of $2 \times 10^{23} \text{ e}^- \text{ m}^{-2}$ [97], ($t_1 = 1$ s, $t_2 = 180$ s)

Fig. 21. a) Isochronal, single-pass, relaxation spectrum of high-purity α -Fe after 3 MeV e^- -irradiation at $T < 45$ K to a dose of $10^{23} \text{ e}^- \text{ m}^{-2}$ [98]; $t_1 = 1$ s, $t_2 = 2$ s (1), 4 s (2), 8 s (3), 16 s (4), 180 s (5). b) Annealing sequences of an identical sample to that presented in a). The maximum temperatures are increased by about 20 K in each successive pass ($t_1 = 1$ s, $t_2 = 180$ s). c) Recovery spectra deduced from the successive measuring sequences of b), ($t_1 = 1$ s, $t_2 = 180$ s); it should be noted that the 110 K process has a different scaling factor

Fig. 21. c)

the dose dependence of both the relaxation and the recovery spectra, the integrated doses were varied from 2.7×10^{21} to $8.5 \times 10^{22} \text{ e}^- \text{ m}^{-2}$. From these investigations, detailed information has been obtained about the annealing mechanisms of the processes occurring in Stages I_E and III. This was achieved by using refined least-squares fitting techniques, taking into account simultaneously both the kinetics of the relaxation process and its possible recovery during measurement (Figs. 23 to 26).

5.5 The fundamental relaxation spectrum in irradiated α -Fe

Despite the differences in the damage produced by either n- or e^- -irradiation (cf. Section 5.1), there exists a striking similarity between the corresponding isochronal relaxation spectra (Figs. 16, 17, 21, 22). These spectra also illustrate convincingly the advantages of the isochronal data representation (cf. Section 2.2), which clearly resolves the various processes and separates them from any background relaxation. As a characteristic feature, the relaxation spectra of the various Fe samples of different degrees of impurity (cf. Sections 5 to 7) are composed of pronounced peaks at about 50, 110, 125 and 200 K. These processes are, therefore, regarded as being of intrinsic nature and therefore attributed to simple, intrinsic defect configurations whose interpretations, however, differ according to the recovery model being adopted. Thus, in the 2IM the peaks at 110 and 200 K are related to metastable crowdions and dumb-bell interstitials, respectively, whereas in terms of the 1IM these peaks are attributed to dumb-bells and monovacancies. The process at 125 K, in both models, is associated with small clusters of self-interstitials which are formed by the trapping of single interstitials during recovery of the 110 K process. The 50 K relaxation peak, together with further peaks at about 80 and 90 K, is identified as resulting from residual impurity trapping (Section 6.2) and hence is assigned to mixed interstitial clusters.

5.5.1 The process at 110 K (Stage I)

Of the peaks occurring in the MAE spectrum of α -Fe, the relaxation centred at 110 K (I_E) is the most prominent and therefore has attracted the interest of many authors, cf. Table 2.

Fig. 22. a) Annealing sequences of high-purity α -Fe after 3 MeV irradiation at $T < 45$ K to a dose of $8 \times 10^{22} \text{ e}^- \text{ m}^{-2}$ ($t_1 = 1$ s, $t_2 = 180$ s) [99]. With $3000 < \text{RRR} < 3500$, this Fe — which was kindly supplied by H. Matsui — is believed to have the highest value of RRR investigated so far by the MAE technique. b) Recovery of the various processes occurring in the annealing sequences of a), ($t_1 = 1$ s, $t_2 = 180$ s)

After n-irradiation (Figs. 16, 17) the 110 K relaxation is found to be accompanied by a minor, low-temperature satellite at 100 K (I_D) which after e^- -irradiation, however, could hardly be detected (Figs. 21, 22). Moreover, whilst in the MAE I_E appears with maximum strength, in RRR measurements I_D is found to be the dominant process [86, 87], being composed of further substages [87, 103], Figs. 10, 11. Hirscher et al. [102, 104], using a modified LC-oscillator technique, were able to follow simultaneously the annealing of both the MAE and the RRR in the same e^- -irradiated Fe sample and found the total recovery in Stage I to be distributed between about 70% in Stage I_D and $\leq 30\%$ in Stage I_E .

Whereas in RRR measurements the recovery of Stage I is governed by an activation enthalpy of 0.27 eV [87], in most MAE measurements the enthalpies for reorientation (H^R) and recovery (H^M) of the Stage I_E defect are found to be close together and of the order $H^M > H^R \geq 0.3$ eV (Table 2). Lower values, reported from earlier measurements [44, 89, 95] resulted, most probably, from poor sample purity. Thus, for instance, the MAE recovery spectra of n-irradiated α -Fe of Balthesen et al. (Fig. 12) and Moser (Fig. 13) are characterized by the occurrence of pronounced peaks in the

Fig. 23. Numerical fit of the Stage I relaxation isochrones following low-temperature ($T < 80$ K) e^- -irradiation to a dose of $3 \times 10^{22} e^- m^{-2}$ [102]. The measuring times were $t_1 = 1$ s, $t_2 = 2$ s (1), 5 s (2), 10 s (3), 20 s (4), 30 s (5), 60 s (6), 90 s (7), 120 s (8) and 180 s (9). The fitting was performed under the assumption of a reorientation-type relaxation which recovers during measurement and thereby obeys second-order kinetics. Experimental data are represented by symbols, continuous lines correspond to the numerically approximated isochrones. The dashed envelope indicates the shape of the 180 s isochrone for the hypothetical case that no recovery were to occur during measurement. In addition, the recovery of relative defect concentration, $c(T)/c_0$ is indicated

Fig. 24. Numerical fit of the relaxation occurring at 125 K after low-temperature e^- -irradiation and successive anneal up to 150 K [98]. Experimental data are represented by symbols, theoretical isochrones are indicated by continuous lines; $t_1 = 1$ s, $t_2 = 2$ s (1), 4 s (2), 8 s (3), 16 s (4), 32 s (5), 64 s (6), 128 s (7), 180 s (8)

Fig. 25. Numerical fit of the relaxation spectrum of the 50 K process in pure α -Fe following n-irradiation at 77 K and successive anneal up to 125 K [92]. Experimental data are represented by symbols, theoretical curves are indicated by continuous lines; $t_1 = 1$ s, $t_2 = 2$ s (1), 4 s (2), 16 s (3), 64 s (4), 180 s (5)

temperature ranges of 90, 60 and 11 K. By means of detailed analyses on e^- -irradiated Ni-doped α -Fe (Section 6.3.1), these peaks have been shown to occur only in the presence of impurity atoms. From the relative strengths of these impurity peaks, a Ni content of about 500 at ppm may be estimated in these early Fe samples [105]. The presence of impurity atoms, such as Ni, influences the recovery kinetics of intrinsic Fe interstitials in several ways: (i) due to attractive interactions, the annealing may be accelerated, thus resulting in a reduced effective enthalpy, H^M , and a modified reaction order. (ii) Mixed interstitial complexes are formed, in addition to the defect configurations arising in high-purity α -Fe. Frequently, these impurity-induced extra-effects have

Fig. 26. Numerical fit of the Stage III relaxation in low-temperature ($T < 45$ K), e^- -irradiated ($8 \times 10^{22} \text{ e}^- \text{ m}^{-2}$), high-purity ($\text{RRR} > 3000$) α -Fe after anneal at 210 K [100]. The analytical technique was identical to that described in Fig. 23. Experimental data are indicated by symbols, theoretical isochrones by continuous lines. The dashed envelope corresponds to the 180 s isochrone in the hypothetical case that no recovery were to occur during measurement. Additionally, the recovery of the relative defect concentration, $c(T)/c_0$, is indicated. The same measuring times as in Fig. 23 have been used

Table 2

Summary of activation parameters of the Stage I (110 K) relaxation, as determined by various authors: peak temperature, T_{peak} ; reorientation enthalpy, H^R , pre-exponential factor, τ_0 ; migration enthalpy, H^M , reaction order, γ

ref.	T_{peak} (K)	H^R (eV)	τ_0 (s)	H^M (eV)	γ	anneal. temp. range (K)	irradiation dose	irradiation temp. (K)	designation
Hirscher et al. [102]	110	0.30 ± 0.2	$10^{-12 \pm 1}$	0.31 ± 0.02	$\neq 1, 2$	100 to 150	2.7×10^{21} to $8.5 \times 10^{22} \text{ e}^-/\text{m}^2$	78	I_E
Walz et al. [97]	110	0.33 ± 0.04	$10^{-13.5 \pm 1.5}$	Coinc.	~ 2	100 to 160	$2 \times 10^{23} \text{ e}^-/\text{m}^2$	60	I_E
Schaefer et al. [96]	110	0.30 ± 0.01	10^{-12}	Coinc.	~ 2	100 to 140	$5 \times 10^{21} \text{ e}^-/\text{m}^2$	27	I_E
Verdone et al. [95]	108	0.23 ± 0.03	—	Coinc.	2	120	$8 \times 20^{21} \text{ e}^-/\text{m}^2$	20	I_E
Dunleavy and Blythe [93]	110	—	—	—	—	100 to 130	$2 \times 10^{22} \text{ n/m}^2$	77	I_E
Mensch and Diehl [83]	105	0.32 ± 0.01	$10^{-13.7 \pm 0.5}$	Coinc.	—	100 to 130	$3 \times 10^{21} \text{ n/m}^2$	20	I_E^*
Balthesen et al. [89]	101	0.19 ± 0.01	10^{-12}	Coinc.	—	—	$8 \times 10^{21} \text{ n/m}^2$	30	—
Moser [44]	108	0.25 ± 0.02	—	0.27 ± 0.015	2	115	$2 \times 10^{21} \text{ n/m}^2$	28	I_E

been ignored in the past and thus delayed the correct interpretation of experimental results. From magnetic anisotropy measurements, using a torque magnetometer, Verdone et al. [106] derived a reorientation enthalpy for the Stage I_E defect of $0.32 \pm 0.015 \text{ eV}$, which fits well with the more recent MAE results of Table 2.

In an attempt to determine the symmetry of the relaxing defects by means of IF measurements on single crystals, Chambron et al. [107] were able to exclude $\langle 100 \rangle$ symmetry for the Stage I_E interstitials. Thus, they assumed $\langle 110 \rangle$ symmetry for these defects, in agreement with the dumb-bell configuration to which they had previously [108] been assigned. Weller et al. [109, 110] and subsequently Wolf et al. [111, 112], continued these symmetry investigations by means of IF and Fe single crystals and found their results to be compatible with an $\langle 111 \rangle$ anisotropy of the Stage I defect, as would be expected for the crowdion interstitial configuration (cf. Section 4.1).

From RRR measurements [84, 87] the recovery kinetics of the I_E defect has been deduced to be close to second order. Evaluating MAE measurements, however, Hirscher et al. [102] found it impossible to describe the I_E recovery, over the whole stage of annealing, by one single reaction order. Irrespective of the e^- -irradiation dose, only the central recovery range was found to be governed by reactions close to second order, whereas for high- or low-dose irradiation – especially at the beginning and the end of recovery – significant deviations from the second-order process were observed.

Measurements of the RRR sometimes have been interpreted in terms of a 1IM, by arguing that the observed second order kinetics was an indication of a recovery due to the recombination of *freely migrating interstitials* with randomly distributed vacancies [84 to 87, 113, 114] – in con-

trast to first-order annihilation kinetics between *one-dimensionally migrating crowdions* and on-line vacancies, as proposed in terms of the 2IM recovery model [1, 115 to 118].

Inspection of the detailed MAE spectra, however, reveals that the RRR-based explanation is too simple, since the recovery in Stage I_E, already in high-purity, low-dose irradiated, and even more so in impurity-doped, strongly irradiated, α -Fe, is composed of a variety of different reactions (cf. Figs. 21c, 22b).

It thus seems more realistic to regard any analytically determined reaction order in this stage as merely the numerical average over the various processes which contribute to the total recovery with relative proportions depending on specific experimental parameters, such as impurity content and irradiation dose.

5.5.2 The relaxation process at 200 K (Stage III)

The identification of the Stage I defect may be facilitated by comparing its recovery behaviour with that of the lattice defect migrating in Stage III. There, at 200 K, a well-developed MAE peak is observed in all previously investigated Fe systems, ranging from high-purity α -Fe to various substitutional and interstitial Fe alloys (Sections 6, 7), following either low-temperature n- or e⁻-irradiation. This is a feature which, as in the case of the 110 K relaxation, is characteristic of an elementary, intrinsic defect. Moreover, this magnetic relaxation is found to correlate with IF measurements [90, 109 to 112]. The 200 K process, similar to the 110 K relaxation, recovers rapidly during measuring (Figs. 21, 22, 26), in the temperature range of Stage III, parallel to the RRR. Again, the detailed recovery mechanism depends strongly on the purity of the Fe, so that the results of earlier measurements, where this purity could not be realized, were frequently incorrectly interpreted. Thus, Moser [44], following n-irradiation found considerable structure in the 200 K relaxation, which he classified into two subgroups II_A and II_B, situated at 183 and 233 K. His analysis yielded activation enthalpies for reorientation of 0.55 and 0.70 eV, respectively. Both subgroups were found to recover concomitantly in a first stage from 200 to 280 K, followed by a second stage from 350 to 400 K. Following RRR measurements the recovery at 200 K, on the other hand, was tentatively interpreted as Stage II_C [119, 120]. Blythe and Kronmüller [121 to 123] also detected two groups of reorientation-type relaxation processes in the temperature range from 200 to 300 K following n-irradiation. One of these groups was identified with Moser's subgroup II_B, whereas the other was tentatively associated with the relaxation of residual C and N in the matrix [124, 125].

From repeated experiments on α -Fe of increasingly higher purity, on the one hand, and of systematically doped impurity contents (cf. Sections 6 and 7), on the other hand, it turned out finally that these early subgroups represent satellites of the intrinsic 200 K relaxation, resulting from reorientable complexes formed by trapping of mobile Stage III defects at impurity atoms.

Regarding the nature of the intrinsic defect migrating in Stage III, the following statements hold:

1. The occurrence of a pronounced reorientation-type relaxation in Stage III, both in MAE [83, 91, 92, 96 to 102] and IF [90, 110, 111] measurements, points to an anisotropic defect.
2. The Stage III defect recovery immediately during the relaxation measurements. Together with statement 1., this indicates defect recovers via a motion mode of com-

Table 3
Summary of activation parameters of the Stage III (200 K) relaxation, as determined by various authors; the same notations are used as in Table 2

authors	T_{peak} (K)	H^R (eV)	τ_0 (s)	H^M (eV)	γ	anneal. temp. range (K)	irradiation dose	irradiation temp. (K)	irradiation designation
Hirscher et al. [101]	200	0.56 ± 0.03	2×10^{-13}	0.56	2	$T \geq 200$ K (during meas.)	$3 \times 10^{22} \text{ e}^-/\text{m}^2$	78	III
Schwendemann et al. [100]	200	0.56 ± 0.03	5×10^{-13}	0.56	2	$T \geq 200$ K (during meas.)	$10^{22} \text{ e}^-/\text{m}^2$	<45 K	III
Walz et al. [97]	200	$0.6 < Q$ < 0.75	—	—	—	$T \geq 200$ K (during meas.)	$2 \times 10^{23} \text{ e}^-/\text{m}^2$	60	III
Mensch [91]	{ 189 203 }	0.57 ± 0.04	1×10^{-13}	—	—	$T > 200$ K (during meas.)	$2 \times 10^{21} \text{ n}/\text{m}^2$	18	III*
		0.65 ± 0.05	2×10^{-14}	—	—	$T > 200$ K (during meas.)	$2 \times 10^{21} \text{ n}/\text{m}^2$	18	III*
Moser [44]	195	0.6	—	0.6	compl.	$T \geq 200$ K (during meas.)	$5 \times 10^{21} \text{ n}/\text{m}^2$	78	III

bined reorientation and migration, in agreement with the observed coincidence of the activation energies for relaxation and recovery (cf. Table 3).

3. The recovery follows a second-order reaction, as has been determined both from the observed shift of the recovery to lower temperatures with increasing radiation dose and from the recovery kinetics of long-time MAE isotherms [102].

The above arguments allow us to exclude definitely the monovacancy as a possible candidate for the Stage III defect: (i) The monovacancy possesses the cubic symmetry of the Fe host lattice and is therefore unable to produce the reorientation-type relaxations observed in the MAE and IF of Stage III. (ii) The second-order reaction, observed for the recovery of Stage III, is incompatible with the assumption of migrating vacancies in this stage since, at least within the framework of the 1IM, at this temperature a comparable number of anti-defects necessary to enable annihilation no longer exists. According to the 1IM, all interstitials have already either annihilated or agglomerated into larger complexes during annealing in the preceding Stages I and II. This incompatibility of second-order kinetics within the framework of the 1IM also remains valid for alternative vacancy configurations, sometimes discussed as possible Stage III defects, such as divacancies and split monovacancies [87, 65], cf. Section 4.2. The same is true for an early proposal of Moser [44] to associate the recovery in Stage III with the dissociation of interstitial– or vacancy–impurity complexes, since this reaction would be characterized by first-order kinetics.

Divacancies, or higher-order vacancy complexes, can also be excluded as sources of the recovery in Stage III by

the following reasoning: (i) if they had already been formed during irradiation, the corresponding Stage III amplitudes should differ drastically after either e^- - or n -irradiation, due to the more efficient vacancy formation mechanism of the latter irradiation (Section 5.3). Such a difference, however, is not observed, cf. Figs. 16 to 22. (ii) The formation of divacancies in Stage III, due to thermally activated trapping, is excluded since this would imply a quadratic, rather than the observed linear, dependence of the MAE on the radiation dose [101].

An additional, serious argument against vacancy migration in Stage III has been developed by Decker et al. [116] by considering the migration enthalpy of monovacancies as the difference between their respective enthalpies of self-diffusion and formation,

$$H_{IV}^M = H_{IV}^{SD} - H_{IV}^F. \quad (5.1)$$

In high-purity α -Fe, the right-side terms of this equation can be quantitatively determined, i.e., H_{IV}^{SD} from measurements of high-temperature tracer self-diffusion [126 to 128], and H_{IV}^F from positron annihilation (PA) in thermal equilibrium [129, 130], in addition to muon spin resonance (μ SR) below the Curie temperature ($T_C = 1043$ K) [131]. The initially determined value of $H_{IV}^{SD} = 2.88$ eV by Hettich et al. [126] has been essentially confirmed by subsequent measurements [127, 128] to yield the presently accepted best value for self-diffusion in iron [118, 132],

$$H_{IV}^{SD} = 2.91 \pm 0.04 \text{ eV}. \quad (5.2)$$

Similarly, from consideration of the results obtained on high-purity α -Fe by means of both PA [129, 130] and μ SR [131], the best value for the vacancy formation enthalpy is regarded to be [132]

$$1.61 \text{ eV} \leq H_{IV}^F \leq 1.75 \text{ eV}. \quad (5.3)$$

Inserting these values into (5.1) leads to a monovacancy migration enthalpy of [116, 131, 132]

$$H_{IV}^M = 1.24 \pm 0.13 \text{ eV}. \quad (5.4)$$

This high value, being qualitatively supported also by recent model calculations [59], is clearly incompatible with the recovery enthalpy of the Stage III process, $H_{III} = 0.56$ eV, so that the corresponding lattice defect cannot be identified with the monovacancy.

5.5.3 Efficiency of the 2IM in α -Fe

Having excluded monovacancies and vacancy complexes as possible defects which migrate in Stage III, the question arises as to which interstitial-type defect may be appropriate to explain the recovery in this stage. With regard to the linear dose dependence of the relaxation strength in Stage III and the second-order reaction of its recovery, it is evident – from the same arguments used above against multi-vacancy migration – that *interstitial complexes* are to be excluded and that, instead, only a simple, freely migrating self-interstitial configuration may be able to explain the obtained experimental results. Furthermore, taking into account the observed coincidence of the activation enthalpies for reorientation and migration, the most promising candidate, able to explain this and the other features of the Stage III reaction, may be seen in the $\langle 110 \rangle$ dumb-bell interstitial configuration as described in detail by Johnson [53]. Since there exists general agreement that the defect becoming mobile in Stage I_E is of interstitial type,

another interstitial configuration, besides the dumb-bell, has to be considered for this low-temperature relaxation. The envisaged configuration must be able to explain the RRR recovery enthalpy of 0.25 to 0.27 eV [44, 87, 102], together with the enthalpies, $H^R = 0.30$ eV and $H^M = 0.31 \pm 0.02$ eV [97, 102], for reorientation and migration, respectively, as determined from the MAE.

An appropriate configuration, able to meet all these conditions, is the metastable $\langle 111 \rangle$ crowdion (cf. Section 4.1). In terms of the 2IM, it is assumed that in Stage I_D these crowdions become mobile with activation enthalpies of about 0.27 eV. In pure α -Fe most crowdions (70%) will have the chance to recombine, as so-called on-line crowdions, with their own vacancy (cf. Fig. 7a (i)), thereby giving rise to a first-order reaction, in agreement with RRR results [87].

A smaller fraction of off-line crowdions (30%), however, will become trapped during their one-dimensional migration by immobile defects of either intrinsic (vacancy, dumb-bell) or impurity nature. These crowdions are able to induce reorientation-like MAEs by jumping to and fro, relative to the trapping centre, on their migration-line with an activation enthalpy of 0.3 eV (Fig. 7a (ii)) which is of the order of the free migration energy of the crowdion. Upon further annealing, the crowdions become activated to escape from these rather weak initial traps, with a slightly increased enthalpy of 0.31 eV. Such crowdions may undergo reactions of different order: a) first-order annihilation with vacancies, or b) stronger, second-order trapping at on-line defects such as, e.g., substitutional impurity atoms or stable interstitials (Fig. 7a (iii)). Strongly-trapped crowdions are immobilized and, upon further annealing, converted into stable dumb-bells which, in the temperature range of Stage III, may either escape from or form reorientable complexes with their traps (Fig. 7c). In addition to the described thermal crowdion conversion, athermal conversion is also feasible under the action of defect-induced stresses, even during irradiation and in dependence on the integrated dose.

This discussion illustrates that the crowdion model is not only able to explain, in a consistent way, the various activation enthalpies observed for various point-defect mechanism in Stage I, but also the mixed-order of their respective reaction kinetics.

5.5.4 *The relaxation processes at 50 and 125 K (Stage II)*

The relaxation processes occurring at 50 and 125 K are discussed under the above heading since they are both attributed to the reorientation of small clusters of intrinsic interstitials which recover in Stage II ($125 \text{ K} < T < 200 \text{ K}$). Closer inspection reveals that the 125 K relaxation results from a purely intrinsic defect configuration, whereas the occurrence of the 50 K relaxation is related to the presence of impurity atoms (Section 6.3.1). This is deduced from the observation that in pure α -Fe the 125 K relaxation, in contrast to the 50 K process, is present immediately after either neutron (Fig. 17) or electron irradiation (Figs. 21, 22) with considerably greater amplitude than the 50 K process. Since the strength of the 125 K relaxation is further increased during annealing in Stage I, the corresponding defect configuration is assumed to develop by trapping of Stage I_E defects (crowdions) in the form of di-crowdion complexes which are stabilized at an intrinsic defect, i.e. vacancy or dumb-bell. Evidently, this configuration is also simple enough to be athermally formed during irradiation. An analysis of the 125 K relaxation, as performed by Blythe et al. [98] after annealing up to 150 K, is shown in Fig. 24. Diehl et al. [83] were able to detect the corresponding IF relaxation and to

Table 4

Summary of activation parameters of the relaxation process at 125 K, as determined by various authors; the same notations are used as in Table 2

ref.	T_{peak} (K)	H^R (eV)	τ_0 (s)	anneal. temp. range (K)	irradiation dose	irradiation temp. (K)	designation
Hirscher ⁺	125	0.34	5.5×10^{-13}	170	$8.5 \times 10^{22} \text{ e}^-/\text{m}^2$	77	II _C
Blythe et al. [98]	125	0.35	2.4×10^{-14}	170 to 215	$1 \times 10^{23} \text{ e}^-/\text{m}^2$	44	II _C
Walz et al. [97]	125	0.37 ± 0.04	$10^{-13.5 \pm 1.5}$	150 to 270	$2 \times 10^{23} \text{ e}^-/\text{m}^2$	60	II _C
Dunleavy and Blythe [93]	126	0.39 ± 0.01	2×10^{-14}	170 to 215	$2 \times 10^{22} \text{ n/m}^2$	77	II _C
Mensch and Diehl [83, 91]	116	0.38 ± 0.015	4×10^{-15}	160 to 207	$3 \times 10^{21} \text{ n/m}^2$	20	II*
Balthesen et al. [89]	121	0.29 ± 0.02	$\sim 10^{-14}$	150 to 200	$8 \times 10^{21} \text{ n/m}^2$	30	II
Moser [44]	123	0.34	—	180 to 240	$2 \times 10^{21} \text{ n/m}^2$	28	II

⁺) Diploma-Thesis, 1984 (unpublished)

Table 5

Summary of activation parameters of the relaxation process at 50 K, as determined by various authors; the same notations are used as in Table 2

ref.	T_{peak} (K)	H^R (eV)	τ_0 (s)	anneal. temp. range (K)	irradiation dose	irradiation temp. (K)	designation
high-purity α -Fe [97 to 102]	process too weakly developed for analysis after e^- -irradiation						II _A
Blythe et al. [105] (Fe + 0.1 at % Ni)	45	0.134 ± 0.01	1.88×10^{-14}	140 to 190	$10^{23} \text{ e}^-/\text{m}^2$	44	II _A
Mensch [91]	46.9	0.136 ± 0.01	2.5×10^{-13}	gone by 170 K	$3.2 \times 10^{21} / \text{m}^2$	18	II*
Dunleavy and Blythe [93]	52	0.16 ± 0.01	10^{-14}	gone by 165	$2 \times 10^{22} \text{ n/m}^2$	77	II _A
Balthesen et al. [89]	57	0.13 ± 0.02	$\sim 10^{-14}$	gone by 190 K	$8 \times 10^{21} \text{ n/m}^2$	30	II _A
Moser [44]	60	0.17	—	gone by 180 K	$2 \times 10^{21} \text{ n/m}^2$	78	II _A
Blythe et al. [105]	46	0.13 ± 0.01	3.2×10^{-14}	100 to 140	$2 \times 10^{21} \text{ n/m}^2$	78	II _A
(Fe + 0.25 at % Ni)	52	0.15 ± 0.01	3.2×10^{-14}	140 to 190	$2 \times 10^{22} \text{ n/m}^2$	78	II _A

correlate it with magnetic measurements. The numerical parameters of this process, as determined by a series of workers over a period of years, are compiled in Table 4.

Inspection of the 50 K process (Figs. 16, 17) shows that this also appears immediately after n-irradiation, although with considerably reduced strength as compared to the 125 K relaxation (Fig. 17). Following e^- -irradiation (Figs. 21, 22), however, it is not found to develop before annealing in Stage I, yielding only relatively small amplitudes. Our detailed studies of systematically alloyed Fe systems, particularly on **FeNi** (Section 6.3.1), reveal that the corresponding defect configuration must be composed of both *intrinsic* defects and *impurity* atoms. Since, following e^- -irradiation, this process develops in the temperature range where the Stage I_E crowdions leave their primary 110 K traps (Figs. 21, 22) and interact with one another, we tentatively relate it to di-crowdion complexes, trapped at an impurity site. In view of the nominally pure Fe systems under discussion, this interpretation is in agreement with the relatively small 50 K amplitudes observed. The analysis shows that the 50 K relaxation is of pure reorientation type (Fig. 25); its activation parameters, as obtained by various authors, are summarized in Table 5.

Whereas, at first glance, the interpretation of the processes at 50 and 125 K in terms of small intrinsic interstitial complexes might appear to be feasible equally well in terms of either the 1IM or the 2IM (Section 5.5), closer inspection, particularly of alloyed Fe systems (cf. Sections 6, 7), shows that a consistent interpretation of all observations is only possible within the framework of a 2IM.

5.6 Assessment of the alternative recovery models

MAE measurements on irradiated pure α -Fe, providing us with straightforward arguments against any vacancy migration in Stage III (cf. Sections 5.5.1 to 5.5.3), present a strong support in favour of the 2IM. In contrast to this, the conclusions in favour of a 1IM – which are derived from results obtained by means of less discriminating, non-relaxation techniques – are rather indirect and sometimes ambiguous, as discussed in detail previously [7, 12]. This is reflected by the following, most serious, objections of 1Im adherents against the 2IM:

1. The questioning of the numerical values of the activation enthalpies for formation H_{V1}^M , and self-diffusion, H_{V1}^{SD} , of vacancies – which, via (5.1), yield a monovacancy migration enthalpy of $H_{V1}^M = 1.28$ eV [87, 114, 133, 134]. It has been argued that the extrapolation of the self-diffusion data from above to below the Curie temperature may entail such uncertainties as to make feasible a vacancy migration enthalpy of only 0.56 eV, as is actually determined for the Stage III defect. In addition, the presence of even low impurity concentrations, i.e. 1 to 10 at ppm C, has been regarded as effective in masking the true vacancy migration enthalpy, particularly if the impurity–vacancy binding energy were, as assumed, of the order $H_{V1}^B \geq 0.5$ eV [134].

These arguments in favour of vacancy migration in Stage III can be refuted, however, in view of high-precision measurements of the enthalpies H_{V1}^{SD} and H_{V1}^F [128, 131] which yield, via (5.1) in any case a minimum possible vacancy migration enthalpy of $H_{V1}^M > 1.0$ eV, cf. (5.4). Moreover, no significant modifications in the Stage III MAE recovery spectra have been observed in **FeC** alloys containing up to 100 at ppm C [7], for which the binding energy of monovacancy–carbon complexes (V_1C_1) has been determined to be about only 0.1 eV [135].

2. Attempts have been undertaken to deduce vacancy migration in Stage III using a semi-empirical scaling rule, based on the elastic properties of b.c.c. metals [136]. In the past, similar attempts were made to deduce the properties of intrinsic lattice defects from macroscopic parameters, such as melting points [137, 138], elastic constants and surface energy [139, 140]. However, all these empirical rules, useful as they may be for *a posteriori* ordering of experimental data, are unable to predict reliable quantitative results [80]; this is particularly true in the extremely delicate situation of the Stage III dilemma [7].

3. Positron annihilation (PA) experiments on electron-irradiated high-purity α -Fe have been regarded as ultimate proof of vacancy migration in Stage III [174, 175, 232]. The decrease of the positron lifetime, τ_1 , from 170 to 115 ps in this stage, together with the occurrence of a second lifetime component, τ_2 , of 300 ps has been explained in terms of migrating *monovacancies* which thereby mainly annihilate, but also, to a minor extent, agglomerate into small clusters [141 to 143]. Especially the appearance of the long life-time component τ_2 was regarded as strong evidence for vacancy migration in Stage III. Frank et al. [144, 145], however, pointed to the efficiency of positron trapping at small *intrinsic interstitial complexes* which, in terms of the 2IM, are expected to agglomerate in Stage III into specific configurations so as to enclose “super-vacancies”. This model allows us to explain conveniently all features of PA experiments in terms of a 2IM, thereby yielding, also with respect to the other experimental results, greater consistency than attainable within the framework of the 1IM [141 to 143], cf. Section 6.3, 7.4, 8.4.

There exists a large amount of further, less specific, measurements on both pure and impurity-alloyed α -Fe, obtained by various techniques, such as RRR [87, 114], PA [141 to 143, 174, 175], stored Energy (SE) [72, 146], Muon Spin Resonance (μ SR) [147], High-Voltage Electron Microscopy (HVEM) [148 to 151], Perturbed Angular Correlation (PAC) [152, 153], Mössbauer Spectroscopy (MS) [154], Huang Scattering [155, 156], etc., all of which have been interpreted in terms of the 1IM by their respective authors; some of these interpretations have been already critically discussed in previous papers with respect to MAE results [7, 12]. In the following, our analyses of substitutionally and interstitially alloyed α -Fe will provide us with additional, convincing arguments against vacancy migration in Stage III. We shall therefore postpone any further discussion regarding these two alternative recovery models until our MAE results on impurity-alloyed α -Fe have been presented in Sections 6 and 7.

6. MAE Spectra in Substitutionally Doped α -Fe

Many data have been accumulated on point defect reactions in substitutional Fe alloys. In addition to our MAE measurements [73, 74, 157 to 164], further studies on substitutionally alloyed Fe have been performed by various other authors, using MAE [16, 72, 141, 165 to 168], RRR [167, 169 to 172], SE [72, 173], PA [174, 175], μ SR [176, 177] and PAC [152, 178]. In addition to the alloys listed in Table 6, Vigier [72] has also reported MAE measurements on **FeCo** ($\Omega_{\text{SF}} = +1.54\%$), **FeSb** ($\Omega_{\text{SF}} = +36.4\%$) and **FePt** ($\Omega_{\text{SF}} = +10\%$). RRR investigations on these same alloys have been performed by Minier-Cassayre [169], whereas Maury et al. have investigated **FeNi**, **FeCo**, **FeMn** [171], **FeAu** ($\Omega_{\text{SF}} = +44\%$) and **FeSi** [170]. PA results have been also reported on **FeCo**, **FeMn**, **FeSi**, **FeAu** and **FeSb** [175].

Table 6

Compilation of data for those binary Fe alloys which have been most thoroughly investigated by means of MAE measurements. Included are the characteristic parameters for impurity trapping in terms of the size-factor model. The following notations are used: c_A , solute concentration in the alloy; c_S , saturation concentration of the solute [69]; Ω_{SF} , size-factor of the solute [69]; VLF, Vegard's law factor, indicating the deviation from a linear volume–concentration dependence [69]; ϵ_d , average energy of d-band electrons – for non-transition elements the s-band energy, ϵ_s is quoted in [180]

alloy	C_A (at %)	C_S (at %)	$10^2 C_A/C_S$	Ω_{SF} (%)	VLF (%)	ϵ_d (eV)
Fe	–	–	–	–	–	16.54
FeBe	–	20.0	–	–26.2	+ 6.9	8.17 (ϵ_s)
FeSi	0.51	10.0	≈ 5	– 7.9	–45.8	13.55 (ϵ_s)
FeNi	0.25	5.0	5	+ 4.7	+12.6	18.96
FeMn	1.0	10.0	10	+ 4.9	+ 1.2	15.27
FeV	0.5	30.0	1.7	+10.5	– 6.3	12.55
FeAl	0.25	25.0	1	+12.8	–19.3	10.11 (ϵ_s)
FeTi	1.0	1.8	56	+14.4	–23.7	11.04
FeCu	≥ 0.7	0.7	≈ 100	+17.5	+17.2	20.14

Since, however, in comparison with the MAE, the information available on defect reactions in Fe systems by other techniques is rather limited (Section 1) [7, 12], we shall in the following base our arguments primarily on MAE results obtained by means of the highly-sensitive LC-oscillator technique (Section 3.2). Conclusions drawn from investigations using alternative techniques will only be discussed in the context of results obtained from MAE measurements.

6.1 Survey of basic trapping reactions

The changes produced in the MAE spectrum of high-purity α -Fe (Section 5) in the presence of substitutional impurities may, to a first approximation, be discussed in terms of geometrical size-factor arguments (Section 4.4).

6.1.1 Impurities with large positive size-factors ($\Omega_{SF} > 10\%$)

For dilute Fe alloys of this type (Table 6), the geometrical hardsphere size-factor model predicts repulsive forces between self-interstitials and impurities which should give rise to relatively simple MAE

Fig. 27. a) MAE-recovery spectrum of Fe + 0.5 at % V after irradiation at $T \leq 45$ K with 3 MeV electrons to a dose of $10^{23} \text{ e}^- \text{ m}^{-2}$ [74]. b) High-temperature ($T_a > 250$ K) recovery sequence of the alloy of a), after annealing to above Stage III [158], ($t_1 = 1$ s, $t_2 = 180$ s)

Fig. 28. a) MAE-recovery spectrum of Fe + 0.25 at % Al after irradiation at $T \leq 45$ K with 3 MeV electrons to a dose of $10^{23} \text{ e}^- \text{ m}^{-2}$ [73]. b) High-temperature ($T_a > 250$ K) recovery sequence of the alloy of a), after annealing to above Stage III [164], ($t_1 = 1$ s, $t_2 = 180$ s)

spectra, i.e. similar to those observed in high-purity α -Fe (Figs. 21, 22). From a first inspection of the MAE spectra of **FeV**, **FeAl** [157] and **FeTi** and **FeCu** [158] (Figs. 27 to 31), this assumption seems to be basically correct. As in pure Fe, the annealing spectra of these alloys start with a pronounced stage I relaxation at 110 K, the decay of which, in most cases, is found to be accompanied by the formation of relatively small, secondary processes near 50, 80 and 125 K. On anneal-

ing up to $T_a \geq 200$ K, the well-known Stage III relaxation is observed. Closer examination, however, reveals the influence of, at least residual, impurity trapping. This may be deduced from the increased strengths of the relaxations near 80 K and, in the

Fig. 29. MAE-recovery spectrum of Fe + 70 at ppm Ti after irradiation at $T \leq 45$ K with 3 MeV electrons to a dose $10^{23} \text{ e}^- \text{ m}^{-2}$ [74, 158], ($t_1 = 1$ s, $t_2 = 180$ s)

Fig. 30. MAE-recovery spectrum of Fe + 1 at % Ti, e^- -irradiated under the same conditions as the alloy of Fig. 29 [74, 158], ($t_1 = 1$ s, $t_2 = 180$ s)

case of **FeTi** and **FeCu** also 50 K, in addition to the occurrence of various satellite processes after annealing above Stage III (Figs. 29b to 31b). Evidently, the effect of increasing Ti concentration is to enhance the impurity trapping (Fig. 30b), thus giving rise to the formation of additional, high-temperature relaxations and, of particular interest, a relaxation at 16 K.

Fig. 31. MAE-recovery spectrum of Fe + 1 at % Cu after irradiation at $T \leq 45$ K with 3 MeV electrons to a dose of $10^{23} e^- m^{-2}$ [74, 158], ($t_1 = 1$ s, $t_2 = 180$ s)

Fig. 32. a) MAE-recovery spectrum of Fe + 0.5 at % Si after irradiation at $T \leq 45$ K with 3 MeV electrons to a dose of $10^{23} \text{ e}^- \text{ m}^{-2}$ [73], ($t_1 = 1$ s, $t_2 = 180$ s). b) Isochronal low-temperature relaxation spectrum occurring in the above alloy after corresponding irradiation and subsequent annealing at $T_a = 175$ K. The measuring times were: $t_1 = 1$ s; $t_2 = 2$ s (1), 4 s (2), 8 s (3), 16 s (4), 32 s (5), 64 s (6), 128 s (7), 180 s (8) [157]. The dashed line corresponds to the numerical fitting of the 180 s isochronal by means of eq. (3.13) yielding values for Q , ΔQ and τ_0 of, respectively, 2 meV, 3 meV and 10^{-5} s

6.1.2 Impurities with negative size-factors

For this type of alloy, the simple size-factor model predicts increased trapping of self-interstitials at impurity sites as is, indeed, observed in **FeSi** ($\Omega_{\text{SF}} = -7.9\%$ [73]) and **FeBe** ($\Omega_{\text{SF}} = -26.2\%$ [159], Figs. 32 to 35). Thus, in **FeSi** the initial Stage I relaxation, which is dominant in pure Fe, is found to be completely suppressed in favour of strongly increased processes at 63, 83 and 122 K.

Further impurity trapping is seen on annealing above Stage III ($T \geq 200$ K) particularly by the formation of a characteristic, low-temperature relaxation ($T = 17$ K) together with a process near 300 K. In **FeBe** too, impurity trapping is indicated by a strong reduction of the initial stage I relaxation, together with the formation of additional satellite processes at 84 and 50 K. Moreover, the influence of impurity trapping is further emphasized by the appearance of a series of additional processes, not observed in the spectrum of pure Fe, of which those near 17, 75 and 165 K are of major interest (Figs. 33 to 35, Section 6.3.3.1).

6.1.3 Impurities with small positive size-factors ($\Omega_{\text{SF}} < 5\%$)

Whereas the simple size-factor model is in qualitative agreement with the MAE spectra observed in Fe alloys with impurity atoms of sufficiently *large positive* ($\Omega_{\text{SF}} > 10\%$) or *negative* size factors, it obviously fails completely for impurities with *small positive* size factors such as **FeNi** ($\Omega_{\text{SF}} = +4.7\%$) and **FeMn** ($\Omega_{\text{SF}} = +4.9\%$), Table 6 [74]. Particu-

Fig. 33. MAE-recovery spectra of Fe + 20 at ppm Be, following irradiation at $T \leq 45$ K with 3 MeV electrons to a dose of $10^{-23} \text{ e}^- \text{ m}^{-2}$ [159], ($t_1 = 1$ s, $t_2 = 180$ s)

larly in FeNi alloys, following either n- or e^- -irradiation, extremely strong impurity trapping is observed, giving rise to the most complex MAE spectra observed in any Fe system so far investigated (Figs. 36 to 39, Section 6.3.1). This behaviour is clear evidence that geometric size-factor considerations alone are unable to explain trapping mechanisms in all alloy systems and that additional interactions, e.g. of an electronic nature [16, 74], have to be taken into account.

The fact that size-factor considerations alone are insufficient for a complete understanding of the properties of diluted alloys becomes directly evident from the observation that most binary systems are in disagreement with Vegard's law (Table 6) [69]; this postulates that the macroscopic volume of a dilute alloy should change in strict proportion to both the concentration and the size-factor of the alloyed constituent. The observed deviations suggest that, in addition to geometrical factors, electronic interactions

Fig. 34. MAE-recovery spectra of Fe + 0.3 at % Be after irradiation at $T \leq 45$ K with 3 MeV electrons to a dose of $10^{23} \text{ e}^- \text{ m}^{-2}$ [159], ($t_1 = 1$ s, $t_2 = 180$ s)

between solvent and solute atoms are responsible for the effective volume of an alloy [179, 180]. Thus, it is tempting to associate the strong interstitial trapping in **FeNi** and **FeMn** with the fact that the electronic d-band energies of Ni, Mn and Fe lie within a narrow range [180], Table 6. This close relationship may enable electron transfer to take place between host and impurity atoms resulting in an electrostatic attraction between both partners [74].

Fig. 35. MAE-recovery spectra of Fe + 1.5 at % Be after irradiation at $T \leq 45$ K with 3 MeV electrons to a dose of $10^{23} \text{ e}^- \text{ m}^{-2}$ [159], ($t_1 = 1$ s, $t_2 = 180$ s)

6.2 Analysis of defect configurations in irradiated Fe alloys

In the following, we shall try to associate the modified MAE spectra observed in substitutional Fe alloys with specific defect configurations composed of intrinsic defects and impurity atoms. Since it is generally accepted that the defect migrating in Stage I of α -Fe is of interstitial type (cf. Section 1) – be it crowdion (2IM) or dumb-bell (1IM) – the secondary peaks arising during the decay of the 110 K process, are interpreted – according to either annealing model – as resulting from the trapping of Stage I *interstitials* at various types of sinks. Clearly, the 2IM offers the greater number of different interstitial configurations, since it takes into account both metastable crowdions and stable dumb-bells. Thus, the numerous interstitial-based, *simple* reorientation-type relaxation processes arising in FeNi (Figs. 36 to 39) in the low-temperature Stages I to III

Fig. 36. a) Annealing sequences with stepwise increased maximum temperatures, as obtained for Fe + 0.25 at % Ni after n-irradiation under liquid nitrogen to a dose of $2 \times 10^{22} \text{ n m}^{-2}$ [161]. b) MAE-recovery spectra of the processes observed in the above alloy, as constructed from the annealing sequences of Fig. 36a, ($t_1 = 1 \text{ s}$, $t_2 = 180 \text{ s}$)

Fig. 37. a) Annealing sequences as obtained for Fe + 0.01 at % Ni after irradiation at $T \leq 45$ K with 3 MeV electrons to a dose of $10^{23} \text{ e}^- \text{ m}^{-2}$ [105]. b) MAE-recovery spectra of the processes observed in the above alloy, as constructed from the annealing sequences of Fig. 37a, ($t_1 = 1 \text{ s}$, $t_2 = 180 \text{ s}$)

may be regarded, *per se*, as qualitative support for the 2IM. If, alternatively, in terms of the 1IM, we were to try to identify the various relaxation processes with *simple* interstitial clusters, we should soon run out of reasonable defect configurations, since it seems rather speculative to argue in terms of complexes composed of more than, say, four interstitials. In the 2IM, however, the numerous processes may be interpreted consistently in terms of small interstitial clusters, comprising not more than three interstitials of either crowdion or dumb-bell type. In addition, due to impurity interactions, athermal conversion from metastable crowdions into stable dumb-bells may also be considered.

If one compares the complexity of the MAE spectra in the various alloys, it becomes evident that, as in pure Fe, only the processes at 110, 125 and 200 K are due to intrinsic defects (Section 5.5), whereas the minor relaxations at 50, 80 and 90 K (Fig. 22) result from interstitial trapping at impurity sites.

The rapid decay of the reorientation-type MAE in Stage III ($T \geq 200 \text{ K}$) gives rise to the formation of satellite processes situated both above and below the peak temperature of the Stage III relaxation. Unlike the MAEs occurring during the anneal in Stages I and II, the processes which develop above Stage III are frequently no longer of pure Debye-type. Such a feature is typical for MAEs induced by mobile, high-order

Table 7

a) Compilation of representative, numerically determined activation parameters for the relaxation processes occurring in e⁻-irradiated FeNi alloys [105]

T_p (K)	45 (46)	59 (62)	78 (82)	91 (89)	107 (108)	122 (128)	11	205
T_a (K)	160	177	<77	120	146	177	215	210
Q (eV)	0.134	0.17	0.23	0.22	0.27	0.34	25×10^{-3}	0.55
ΔQ (eV)	0.013	0.01	0.02	0.02	0.01	0.03	1.0×10^{-3}	0.03
τ_0 (s)	1.88×10^{-14}	1.98×10^{-14}	1.59×10^{-14}	5.32×10^{-14}	1.53×10^{-14}	2.4×10^{-13}	1.72×10^{-11}	4×10^{-13}

b) Representative, numerically determined activation parameters for the relaxation processes occurring in n-irradiated FeNi alloys [161]

T_p (K)	46	52	62	82	89	108	128
T_a (K)	77	77	171	125	154	154	240
Q (eV)	0.13	0.13	0.17	0.211	0.26	0.32	0.35
ΔQ (eV)	0.011	0.01	0.012	0.02	0.001	0.001	0.036
τ_0 (s)	3.2×10^{-14}	2.4×10^{-13}	3.2×10^{-14}	2.4×10^{-13}	4×10^{-14}	4×10^{-14}	1.4×10^{-14}

T_p denotes the peak temperature of each process and T_a the temperature of the preceding anneal. The values for T_p in brackets, give the positions of corresponding relaxation peaks following n-irradiation

Fig. 38. a) Annealing sequences as obtained for Fe + 0.1 at % Ni after irradiation at $T \leq 45$ K with 3 MeV electrons to a dose of $10^{23} \text{ e}^- \text{ m}^{-2}$ [105]. b) MAE-recovery spectra of the processes observed in the above alloy, as constructed from the annealing sequences of Fig. 38a, ($t_1 = 1 \text{ s}$, $t_2 = 180 \text{ s}$)

complexes due to (i) a reduction of anisotropy with increasing number of constituents and (ii) the occurrence of various relaxation modes with only slightly differing activation enthalpies.

These general considerations, in addition to the definitive results obtained in pure α -Fe (Section 5.5.3), support the 2IM which will, therefore, in the following serve as a basis for the discussion of the various defect reactions occurring in substitutional Fe alloys. Since FeNi reveals the most refined recovery spectra of all Fe alloys, the detailed analysis of the MAEs arising in this system also offers the decisive key to an understanding of the reaction mechanisms occurring in other alloys, Section 6.3.

6.2.1 MAE spectra of FeNi

On account of its interesting recovery behaviour, this alloy is the one which has been investigated in most detail, i.e. for various Ni contents following both n- (0.25, 0.5 at% Ni [161]) and e^- - (0.002, 0.01, 0.05, 0.1, 0.25, 1.0 at% Ni [162 to 164]) irradiation (Figs. 36 to 39). Earlier, less detailed measurements on this system ($0.02 < c_{\text{Ni}} < 0.5 \text{ at\%}$), following either n- or e^- -irradiation, were performed by Vigier et al. [72, 165 to 167]. Fig. 39 shows the effect of increasing Ni content on the strengths of typical reorientation type MAEs occurring in FeNi (i) immediately after e^- -irradiation (Fig. 39a) and (ii) after subsequent annealing up to their maximum amplitudes (Fig. 39b, c). The activation parameters of these processes are summarized in Table 7.

Fig. 39. a) Influence of varying Ni content on the amplitudes of characteristic relaxation processes in FeNi alloys, occurring immediately after irradiation to a dose of $10^{23} \text{ e}^- \text{ m}^{-2}$; the corresponding processes are indicated by their peak temperatures. b, c) Influence of varying Ni content on the maximum amplitudes of characteristic processes in FeNi alloys, occurring in the course of annealing; the corresponding processes are indicated by their peak temperatures, ($t_1 = 1 \text{ s}$, $t_2 = 180 \text{ s}$), cf. [105]

(i) *Defect reactions in Stage I.* As in the case of pure Fe (Section 5.5), we interpret the primary 110 K process, which occurs in most Fe systems, as arising due to one-dimensional “Fe crowdions”, bound to intrinsic lattice defects, e.g., “off-line” vacancies or dumb-bells. Upon thermal activation, the crowdion may escape from its primary trap and either annihilate with “on-line” vacancies or be trapped at other, more strongly binding lattice defects such as impurity atoms. A typical product of such impurity trapping is the process which develops near 80 K both in FeNi and in most other Fe alloys after annealing above 110 K. Due to the presence of residual impurities, this process may be detected even in high-purity Fe (Figs. 21, 22). In our recovery model, we attribute this process to a modified crowdion relaxation, where the crowdion is tightly bound to an “off-line” impurity, i.e. a Ni atom (Fig. 39a, b), as opposed to an intrinsic defect in the case of the 110 K relaxation, cf. Fig. 7.

In dilute FeNi systems, the transformation sequence $110 \text{ K} \rightarrow 80 \text{ K}$ has been found to be governed by a reaction order close to 1 [72]. With increasing Ni content, this transformation sets in athermally during irradiation (Fig. 39a). Thus, in Ni-rich alloys ($c > 0.5 \text{ at}\%$)

the 110 K relaxation following either e^- - or n -irradiation is found to be strongly (Fig. 38b) or even completely (Fig. 36) suppressed. Consequently, the annealing spectra in these alloys start with a prominent peak at 80 K, rather than with that one at 110 K.

It is interesting to note that, in contrast to pure Fe, during the decay of the 110 K process in dilute **FeNi** alloys, almost no 125 K peak develops (cf. Figs. 38, 39b). This suggests that in **FeNi**, trapping reactions between intrinsic interstitials in Stage I are completely suppressed in favour of impurity trapping. The 80 K process proves, in turn, to be thermally unstable and, following anneal up to about 150 K, transforms into a further process, situated again near 110 K with comparable strength as the original 80 K process (Figs. 38, 39b). The activation parameters of this new relaxation (Table 7) are indistinguishable from those of the primary 110 K process, which usually appears immediately after irradiation. It is most unlikely, however, that a defect which at lower temperatures has been found to be thermally unstable and transforms into a new configuration should, after annealing at higher temperatures, become re-established and stabilized. We therefore propose the defect configuration of this second 110 K process to be closely related to the one giving rise to the original 110 K relaxation, i.e. to a Ni crowdion – instead of an Fe crowdion – bound to an “off-line” vacancy (Section 4.1). This modified defect type is assumed to result from the thermally activated interchange between a Fe crowdion and a substitutional Ni atom. Such an exchange seems feasible on account of the close relationship between Fe and Ni atoms and their strong electronic interactions in the Fe matrix (Section 6.2). A similar exchange mechanism, although within the context of the 1IM, has been proposed by Vigier and Moser [165] in order to explain their MAE results on e^- - and n -irradiated **FeNi** and **FeSi** alloys.

(ii) *Defect reactions in Stage II.* In order to understand the subsequent recovery sequence of the MAE spectrum, we must look in some detail at the relaxation processes which develop near 50 K in various systems:

a) In pure, n -irradiated α -Fe, prior to anneal, a relaxation process is observed at 52 K (Figs. 16, 17).

b) In pure, e^- -irradiated Fe, the development of a minor relaxation at 52 K is only observed on anneal in Stage I, during the decay of the primary 110 K process (Figs. 21, 22).

c) In e^- -irradiated **FeNi** alloys, a relaxation process is observed at 46 K immediately after irradiation. The amplitude of this relaxation increases with increasing Ni content (Fig. 39a). During annealing in Stage II ($T > 150$ K), a strong increase of the 46 K peak is observed simultaneously with the decay of the secondary 110 K process (Figs. 38a, b).

d) In n -irradiated **FeNi** alloys, a minor relaxation occurs at 50 K prior to any annealing (Fig. 36). This is found to be composed of two separate processes situated at 46 and 52 K [159]. The relative amplitudes of these two relaxations depend on the Ni content such that, in the alloys with the higher Ni concentrations, the amplitude of the 46 K peak is increased relative to that of the 52 K peak.

From these observations, we deduce both that the 52 and 46 K processes must be closely related and that the 52 K relaxation may be transformed into the 46 K process either athermally, in the presence of attractive impurities, or by thermal activation. The growth of the 52 K process in e^- -irradiated Fe during recovery in Stage I, where only crowdions are expected to escape from their primary traps (Section 6.3.1), is related to the formation of small interstitial clusters formed, e.g., by two Fe crowdions trapped at an impurity site. The growth of the 46 K relaxation in n -irradiated **FeNi** during anneal

is attributed to the thermal conversion of the 52 K complex. Since, in e^- -irradiated **FeNi**, the 46 K relaxation is formed during the decay of the secondary 110 K process, which is related to Ni crowdions trapped at vacancies, we tentatively attribute the 46 K relaxation to a di-Ni-crowdion configuration which may be trapped at a lattice defect, e.g. an impurity site or a vacancy.

The different formation rates of the 52 and 46 K complexes during n- or e^- -irradiation are associated with the different defect production mechanisms (Section 5.1). During e^- -irradiation, lower-energy collision chains may be preferentially stopped at substitutional impurity atoms, thereby producing a relative excess of Ni crowdions. During n-irradiation, however, high-energy collision chains may be able to create, in the course of their propagation, comparable numbers of both Fe and Ni crowdions. Consequently, following e^- -irradiation, the Ni crowdion cluster at 46 K would have the greater formation probability, whereas, following n-irradiation, both Fe and Ni crowdion clusters should be created with comparable concentrations, thus giving rise to a broad relaxation peak composed of the individual processes at 46 and 52 K. Upon further annealing to temperatures above 160 K, the simultaneous recovery of both the 46 K and the residual 110 K relaxation coincides with the occurrence of two new processes: a prominent one near 60 K and a smaller one at 125 K (Figs. 36b, 38 b, 39 b, c), cf. [74].

In agreement with its formation kinetics (Figs. 36, 38), we interpret the 60 K relaxation as arising from a slight modification of the "46 K configuration" which is induced by thermal conversion of, e.g., the di-Ni-crowdion complex into a mixed Fe-Ni-crowdion cluster bound to a vacancy. Similar transformations may also take place during the decay of the secondary 110 K relaxation, thereby producing di-Fe-crowdion clusters which give rise to the 125 K relaxation. This interpretation is supported by the modified annealing sequence observed in the dilute **FeNi** alloy containing only 0.01 at% Ni (Fig. 37). At this concentration, in contrast to all other **FeNi** alloys, the decay of the 80 K process is not directly related to the formation of a secondary 110 K relaxation. Instead, an additional process first develops at 155 K, the rapid decay of which then gives rise to the secondary peak at 110 K. The thermally induced decay of this 110 K process contributes to the formation of smaller peaks near 125 and 60 K. This modified annealing behaviour may be regarded as the consequence of an increased recombination rate between interstitials and vacancies, both in Stage I and during the decay of the 80 K relaxation. Thus, only a reduced number of small interstitial complexes and free vacancies, as compared to more concentrated alloys, is expected to survive. In this situation, radiation-induced dumb-bells may be important in trapping the Ni crowdions, released from the 80 K defect configuration, thereby giving rise to the intermediate 155 K relaxation. The minor 46 K peak, formed during the decay of the 80 K process, indicates a reduced number of effective trapping centres – i.e. Ni atoms or vacancies – in this dilute alloy.

The break-down of the secondary 110 K process, due to thermally released Ni crowdions which may partly reconvert into Fe crowdions, gives rise to the formation of relaxations at 125 and 60 K which are attributed to di-Fe-crowdions [Fe_cFe_c] and mixed Fe-Ni-crowdions [Fe_cNi_c], possibly trapped at vacancies (V).

The decay of the 60 K process, which in concentrated alloys partly overlaps with the beginning of the recovery of the 200 K process, is accompanied by the formation of new processes at 11 and 90 K (Figs. 38b, 39c) [160, 163]. In view of the configuration

assigned above to the 60 K process, its break-down may initiate the following reactions:

- (i) $[\text{Fe}_\text{C}\text{Ni}_\text{C}]_\text{V} \rightarrow \text{Fe}_\text{C}\text{V} + \text{Ni}_\text{C} \rightarrow (\text{NiFe})_\text{D}$
- (ii) $[\text{Fe}_\text{C}\text{Ni}_\text{C}]_\text{V} \rightarrow \text{Ni}_\text{C}\text{V} + \text{Fe}_\text{C} \rightarrow (\text{NiV})_\text{FP} + (\text{FeFe})_\text{D}$
- (iii) $[\text{Fe}_\text{C}\text{Ni}_\text{C}]_\text{V} \rightarrow \text{Fe}_\text{C} + \text{Ni}_\text{C} + \text{V} \rightarrow (\text{FeFe})_\text{D} + (\text{NiFe})_\text{D} + \text{V}$.

Thus, we expect the formation of mixed Ni-Fe dumb-bells $(\text{NiFe})_\text{D}$, Ni – vacancy Frenkel pairs $(\text{NiV})_\text{FP}$, which may also convert into vacancy-bound mixed dumb-bells, $(\text{FeNi})_\text{D}\text{V}$, and intrinsic $(\text{FeFe})_\text{D}$ dumb-bells. The NiV and $(\text{NiFe})_\text{D}\text{V}$ complexes, in contrast to normal Frenkel pairs (FeV), are assumed to also remain stable at higher temperatures ($T_\text{a} \geq 200$ K), due to attractive forces between the Ni interstitial and the Fe matrix, which prevent spontaneous annihilation with the vacancy.

The relaxations occurring at 90 and 11 K are proposed to result from reorientations of the following defect types: i.e., freely rotating mixed dumb-bells $(\text{NiFe})_\text{D}$ and Ni interstitials, possibly also in the form of mixed dumb-bells, bound to a vacancy. The 200 K (Stage III) process is itself associated with the combined reorientation and migration of Fe dumb-bells, which have been formed both athermally during irradiation and also by thermal conversion of crowdions during the course of anneal.

On annealing just above 200 K, both the 11 and 90 K processes recover; the bound Ni interstitials due to annihilation with their vacancies and the free mixed dumb-bells due to either further trapping and/or annihilation with residual vacancies.

Within the modified annealing sequence of the dilute **FeNi** system ($c_\text{Ni} = 0.01$ at%), we find the 60 K relaxation to be more stable than in the systems with higher Ni concentrations (Fig. 37b). This may be explained by reduced interactions between the potential trapping centres and the constituents of these complexes in the dilute alloy. Moreover, since annihilation between interstitials and vacancies within the assumed $[\text{Fe}_\text{C}\text{Ni}_\text{C}]_\text{V}$ complexes is inhibited below the crowdion conversion temperature, delayed recovery is observed for the 60 K complex on annealing above 220 K. Since, in this temperature range, the configurations of the 11 and 90 K relaxations are, as discussed above, already thermally unstable, these processes have no longer a chance for development during the recovery of the 60 K relaxation.

(iii) *Defect reactions in and above Stage III.* Near 200 K we observe in all **FeNi** alloys – as in the case of most other Fe systems, including high-purity α -Fe – a pronounced relaxation which is of an intrinsic nature (Section 5.7) and, depending on the Ni content, recovers rapidly during annealing in the temperature range $200 \text{ K} < T_\text{a} < 250 \text{ K}$. In terms of the 2IM, as established from the results obtained on pure Fe (Section 5.5) and therefore applied throughout the preceding discussion, the relaxation in Stage III is attributed to the combined reorientation and migration of the stable, second intrinsic interstitial type in the Fe matrix, the dumb-bell. Accordingly, the processes which develop on further annealing near 250 and 270 K (Figs. 36 to 39c) are identified as resulting from further trapping reactions between Fe and possibly mixed FeNi dumb-bells, thereby giving rise to the formation of di- and higher-order interstitial clusters.

After annealing up to $T \geq 520$ K, all lower-temperature processes have disappeared. In terms of the 2IM, this is expected to result from the annihilation between vacancies, becoming mobile in Stage IV (≥ 500 K), and residual interstitial clusters. On annealing above 520 K, a minor, unstructured relaxation is observed near 550 K (Fig. 40), which in the higher-temperature range ($T_\text{a} \geq 650$ K) partly recovers. Such high-temperature relaxations, which are no longer of Debye-type and also occur in other Fe alloys, are

Fig. 40. High-temperature annealing sequence of an Fe + 1 at % Ni alloy irradiated at $T \leq 45$ K with 3 MeV electrons to a dose of $10^{23} \text{ e}^- \text{ m}^{-2}$ and subsequently annealed above Stage III [164], ($t_1 = 1$ s, $t_2 = 180$ s)

attributed to thermally activated creep of residual dislocations which are pinned by radiation-induced obstacles such as, e.g., immobile interstitial clusters.

Before we enter into a detailed discussion regarding the two alternative recovery models with respect to specific defect reactions (cf. Section 6.3), it may be instructive to first present the bulk of MAE spectra obtained on further substitutionally alloyed Fe systems.

6.2.2 MAE spectra of strongly oversized impurities in α -Fe

In this category, we include alloys containing impurity atoms with positive size-factors of $\Omega_{\text{SF}} > 10\%$: i.e. **FeV** (+10.5%), **FeAl** (+12.5%), **FeTi** (+14.4%) and **FeCu** (+17.5%). Of these, the alloys **FeV** and **FeAl** exhibit very similar MAE spectra, of the high-purity α -Fe type, so that we shall discuss them both under the one heading.

6.2.2.1 MAE spectra in FeV and FeAl

Both spectra start with a relatively strong Stage I relaxation which, on decay, gives rise to a minor relaxation near 80 K (Figs. 27, 28). A small 120 K process, which has been formed athermally during irradiation, recovers in the temperature range of Stage II. In Stage III, only a strongly reduced 200 K relaxation occurs which recovers rapidly. Above Stage III no further, distinct relaxation processes are observed. Only weak, unstructured MAEs of the type occurring also in **FeNi** above 520 K, which have been assigned there to dislocation-induced relaxations, can be resolved (Figs. 27b, 28b).

As expected from the hard-sphere model, the MAE spectra of oversized alloys show only weak interstitial trapping, in favour of enhanced recombination between interstitials and vacancies.

Beyond the basic relaxations, no indication of additional processes, as observed in **FeNi**, can be detected. Consequently, in terms of the **FeNi** recovery model (Section 6.2.1), we are concerned here only with simple vacancy- (110 K) and impurity- (80 K)

trapped crowdions, di-crowdions (120 K) and dumb-bells (200 K). The Stage I relaxation in **FeV** appears with a somewhat increased maximum temperature (114 K) and retarded decay, both features probably being due to reduced trapping in this alloy.

6.2.2.2 MAE spectra in FeCu

In **FeCu** relatively stronger impurity trapping, as in **FeV** and **FeAl**, may be deduced to occur. This is inferred from the appearance of well-developed relaxation processes at 82, 48 and 35 K in combination with the decay of the 110 K process (Fig. 31). In terms of the recovery model developed for **FeNi**, we would attribute these processes to the relaxation of single crowdions (82 K) and di-crowdions (48 K) trapped at impurities. Correspondingly, the 35 K process would be associated with a modified di-crowdion – impurity configuration, where one, or both, of the Fe crowdions are replaced by Cu crowdions. No 125 K relaxation develops in this alloy. Instead, a minor relaxation at 170 K which, similarly to the corresponding 150 K process in **FeNi**, may be attributed to a crowdion trapped at an immobile dumb-bell. This would explain the simultaneous recovery of the 170 and 200 K relaxations in Stage III, where – again as observed in **FeNi** – a new relaxation develops at 257 K. This latter process is attributed to the reorientation of Stage III interstitials trapped at Cu sites. Upon decay of the 257 K relaxation, a further process develops at 327 K which, in turn, is followed by relaxations at 370 and 425 K. These higher-temperature processes are again associated with interstitial clusters of increasing complexity, formed by continued interstitial trapping.

6.2.2.3 MAE spectra in FeTi

In this system, alloys containing 0.007 and 1.0 at% Ti have been investigated. Whereas the dilute alloy displays the typical “standard spectrum” of oversized alloys (Section 6.1.1), the concentrated alloy is characterized by a strongly modified recovery behaviour.

a) Fe + 70 at ppm Ti. Here we observe the “classic” annealing sequence, starting with the rapid decay of the 110 K relaxation in combination with the formation of a relatively strong 80 K and a weak 50 K process (Fig. 29a). Both these processes recover within the temperature range of Stage II. A small 125 K process, probably formed athermally during irradiation, is observed to increase simultaneously with the decay of the 80 and 50 K processes just below 200 K, thereby being able to survive up to temperatures above 220 K. Due to interactions with the interstitial-type constituents released by the 125 K process, the 200 K relaxation, in turn, is observed to undergo delayed recovery. As in the case of the Ni-rich alloy (Section 6.2.1), we associate this delay with the additional production of dumb-bells due to the conversion of crowdion-type constituents released from the 125 K configuration. Thus, the recovery reactions observed in Stage III of dilute **FeTi** provide further support in favour of interstitial, as opposed to vacancy migration at 200 K.

Associated with the decay of the 200 K process, only one further pronounced relaxation is observed to develop at 218 K (Fig. 29b). In agreement with the analyses of the other Fe systems, this relaxation is attributed to mixed **FeTi** dumb-bells (Section 6.2.1).

b) Fe + 1.0 at% Ti. A completely different annealing behaviour is observed in this system as compared to the preceding 70 at ppm Ti alloy (Fig. 30). The recovery starts with a Stage I relaxation which has only half the amplitude of the dilute alloy and is

shifted to lower temperatures (104 K), Fig. 30a. After an initial rapid decay, accompanied by the formation of weak relaxations at 83 and 48 K and a pronounced process at 118 K, the 104 K relaxation is found to increase again and to pass through a maximum just below Stage III ($T_a \leq 180$ K). On account of its large initial amplitude, we assume the 118 K process to have partly formed athermally, already during irradiation, by an aggregation of two crowdions. If we also consider the reduced development of the 80 and 48 K relaxations, which are usually attributed to impurity-trapped crowdions (Section 6.3.1), it is evident that, in this alloy, the interactions between intrinsic interstitials dominate over impurity trapping. These modified interactions are also reflected in the observed shifts of the relaxations in Stage I (104 K, instead of 110 K) and Stage II (118 K, instead of 125 K). On annealing above 150 K, the decay of the 104 K process is retarded and reversed into a growth, probably due to the simultaneous break-down of the 118 K relaxation. As in the case of **FeNi** (Section 6.2.1), we associate this re-established 104 K process with a slightly modified defect configuration of higher stability, i.e. Ti crowdions which have been formed by an exchange between Fe interstitials and impurity atoms. Both the modified 104 and 200 K relaxations recover with comparable amplitudes in Stage III, being followed by further processes arising at 233 and 277 K (Fig. 30b). Again, as also discussed for **FeNi**, these processes are associated with the trapping of pure and mixed dumb-bells at Ti atoms, the latter configuration being assumed to result from thermal conversion of Ti crowdions. Upon recovery of these processes at temperatures >250 K, mixed dumb-bells are released and subsequently trapped at vacancies, thereby giving rise to a new, simple Debye-type MAE at 16 K. As in the similar situation of **FeNi** (Section 6.3.1), these complexes are assumed to be protected from spontaneous annihilation due to attractive interactions between Ti interstitials and the Fe atoms of the matrix. This relaxation recovers by annihilation of the dumb-bells with their vacancies, after annealing at temperatures $T_a > 320$ K. No further significant relaxation processes are found to develop in this alloy during anneal at higher temperatures.

6.2.3 MAE spectra in typical undersized alloys

Within this category we have investigated the systems **FeBe** ($\Omega_{SF} = -26.2\%$) and **FeSi** ($\Omega_{SF} = -7.9\%$); Table 6, Figs. 32 to 35. From first inspection it is evident that in these alloys increased impurity trapping takes place, as it is expected from the simple size-factor model.

6.2.3.1 MAE spectra in **FeBe**

In this alloy impurity trapping becomes apparent, particularly for the higher Be concentrations ($c_{Be} = 0.3$ and 1.5 at%), by the occurrence of modified reaction sequences and characteristic peak shifts of familiar processes. As a typical feature of these alloys, on annealing above 160 K, no series of discrete processes is developed but rather a “wave” of transient relaxations which – upon continued annealing – decrease in amplitude and shift to higher temperatures (Figs. 33b to 35b). With the exception of a single prominent peak at about 160 K arising in the alloys with 0.002 and 0.3 at% Be, these recovery spectra are relatively unstructured. It therefore no longer seems meaningful to associate these various transient peaks with the distinct processes occurring in the spectra of other Fe alloys at comparable temperatures.

a) Fe + 20 at ppm Be. The MAE spectrum of this alloy (Fig. 33) starts with a large Stage I (108 K) process which, on recovery, gives rise to a fairly strong 84 K and a weak 50 K process. The origin of a rapidly decreasing relaxation at 125 K – whether formed during irradiation or following the decay of the 108 K process – cannot be definitely resolved. In terms of our recovery model (Section 6.3.1), these processes are attributed to single crowdions trapped at vacancies (108 K) or impurities (84 K) and to either free (125 K) or impurity-trapped di-crowdion configurations (50 K). On its decay, the 125 K process evidently supports the 84 K relaxation in undergoing a delayed recovery up to temperatures $T_a \leq 180$ K. On anneal above 140 K, the 125 K process stabilizes at a reduced level, apparently due to the decay of a further process centred at 168 K. Since this 168 K process, on its thermally activated dissociation, contributes to the relaxations at 125, 84 and 50 K – all of which formed from crowdions – we assign this process to a configuration, also discussed for FeNi (Section 6.3.1), which is composed of a crowdion trapped at an immobile dumb-bell.

During anneal in Stage III, the 168 K process transforms into a reduced relaxation centred at 155 K, tentatively associated with a mixed FeBe dumb-bell, trapped, i.e., at a Be site. Upon dissociation of this 155 K process, during annealing above Stage III ($T_a \geq 240$ K), dumb-bells are expected to become released and thereby to give rise to a new process centred at 100 K.

Whilst it appears futile to try to identify the sequence of continuously shifted peaks occurring above 200 K (Fig. 33b) with specific defect configurations, it remains a question of central importance as to what types of defects, interstitials or vacancies, constitute these configurations. On account of the survival of the interstitial-type relaxations at 155, 84 and 50 K – in addition to the formation of a new process at about 100 K – during annealing up to $T_a \geq 240$ K (Fig. 33a), vacancy migration in Stage III can again be excluded in favour of interstitial migration. Consequently, we attribute the higher temperature relaxations (Fig. 33b) to reorientations of interstitial clusters which, upon annealing, grow in complexity due to continued interstitial trapping.

b) Fe + 0.3 at% Be. At first glance, this recovery spectrum differs from that of the 20 at ppm Be alloy by a strongly reduced Stage I (105 K) relaxation and an almost completely suppressed 125 K process (Fig. 34). Both effects indicate increased impurity trapping, possibly accompanied by subsequent conversion of crowdions into immobilized dumb-bells, since no corresponding growth of the lower-temperature relaxations is observed. Instead, the processes at 84 and 50 K are found to have developed here, mainly athermally during irradiation, as deduced from their constant initial amplitudes (Fig. 34a). During recovery of the 105 K process, the 84 K relaxation goes through a weak maximum with a retarded decrease at higher temperatures ($T_a \leq 180$ K), possibly caused by the simultaneous decay of a relatively strong 165 K relaxation. This 165 K decay, moreover, gives rise to new processes at 120, 75 and 100 K, of which the latter two undergo further growth during anneal in Stage III (Fig. 34a). If we associate, as in the former alloy, the 165 K relaxation with crowdions bound to dumb-bells, we expect their dissociation – besides supporting the 84 K relaxation – to be accompanied by a formation of di-crowdion complexes (120 K) in addition to – after crowdion conversion in Stage III – either free (100 K), Be-bound (75 K) mixed dumb-bells or di-interstitials of dumb-bell type (145 K).

On thermally activated dissociation of these complexes ($T_a \geq 250$ K), some of the mixed dumb-bells will become trapped at vacancies, without being spontaneously anni-

hilated, thereby giving rise to a characteristic low-temperature relaxation at 17 K ($T_a \geq 360$ K). In addition, further low-temperature, interstitial-type relaxations are developed – i.e. at 80 K ($T_a \geq 320$ K) and 50 K ($T_a \geq 400$ K), (Fig. 34a) – with configurations assumed to differ from the original ones in that mixed dumb-bells replace the initial crowdions.

On annealing above Stage III, as in the dilute alloy, we observe a series of transient relaxations, which transform from one into another after successive annealing steps. There is, however, no doubt as to the basic interstitial-type character of all these relaxations in view of the additionally developed distinct lower-temperature processes which, in turn, are unambiguously identified as being of interstitial-type.

Thus, once again, interstitial, rather than vacancy migration in Stage III is indicated.

c) *Fe + 1.5 at% Be*. Strong impurity trapping is suggested by the recovery spectrum of this alloy (Fig. 35), which is characterized by an even greater reduction of the processes occurring at 105 and 165 K, in addition to the complete suppression of the 125 K relaxation. Again, the 84 and 50 K processes have been formed athermally during irradiation, as follows from their constant initial amplitudes which recover here immediately on annealing at the end of Stage I. In addition, the 17 K process – observed also in the preceding alloy – appears with pronounced strength immediately after irradiation. As above, we associate this process with a mixed dumb-bell – vacancy configuration, which reorients with a small activation energy and is protected from spontaneous annihilation with its vacancy due to the attractive interactions between the Be half dumb-bell and the surrounding Fe atoms. On annealing in Stage II ($T_a \leq 160$ K), this process undergoes further growth, probably due to trapping of irradiation-induced mixed dumb-bells which are situated within the capture radius of a vacancy but are able to form the 17 K configuration only after weak thermal activation.

On further anneal above 170 K, we observe the decay of the 165 K process, known from the above systems, (a) and (b), to be related with the following effects:

- (i) A slow but steady decrease of the 17 K relaxation.
- (ii) The formation of a relatively strong process at 100 K.
- (iii) The formation of a small 120 K process.

Attributing the 165 K process, as before, to a crowdion which is bound to a dumb-bell, the above reactions may be explained as follows:

(i) Crowdions, released from the 165 K configuration, may be trapped at 17 K complexes and, after conversion into stable interstitials, annihilate with their vacancies. Such annihilations destroy the 17 K configuration, thereby releasing mixed dumb-bells which may contribute to the 100 K relaxation.

(ii) Mixed dumb-bells may also be formed after trapping and successive conversion of released “165 K crowdions” at Be sites, thereby further supporting the 100 K process.

(iii) In addition to reactions (i) and (ii), released “165 K crowdions” may also interact with one another to form di-crowdion complexes which give rise to the 120 K relaxation. On anneal in Stage III, these complexes become unstable and, after transformation, give rise to a process at 145 K; this may tentatively be ascribed, like the 155 K process in (a), to mixed dumb-bells trapped at Be sites.

With regard to the recovery mechanisms activated in Stage III, it is of great importance that, upon annealing in this temperature range, we observe not only the *survival* of characteristic, clearly interstitial-type, low-temperature relaxations, i.e. those at 17 and 145 K, but also the further strong *growth* of such processes, i.e. the one at 84 K (Fig. 35).

On further anneal, the 84 K complexes are modified, e.g. by conversion of their crowdions into mixed dumb-bells and/or additional trapping of a Stage III dumb-bell, thus causing a lowering of the original peak temperature to 75 K. Similarly, trapping of Stage III interstitials may convert some of the 17 K complexes into 75 K configurations, thereby causing the retarded decay of the 17 K amplitude across this temperature range (Fig. 35).

Annealing above 230 K causes a rapid decay of the 75 K relaxation, probably due to further interstitial trapping. After an intermediate stabilization at lower level, this process finally disappears on anneal above 340 K, presumably due to thermally activated dissociation. This final recovery of the 75 K process is accompanied by a re-growth of the 17 K amplitude and a simultaneous increase of the 50 K relaxation. Both effects may be associated with a trapping of the constituents of the 75 K process at vacancies and Be atoms to form, e.g., additional $(\text{FeBe})_{\text{D}}\text{V}$ (17 K) and $\text{di-Fe}_{\text{D}}\text{Be}$ (50 K) complexes, respectively.

In addition to the recovery behaviour of these distinct, low-temperature processes, we observe in this alloy, once again, a continuous series of unspecified relaxations which, upon further annealing ($T_{\text{a}} \geq 200$ K), transform continuously from one into another with steadily increasing peak temperatures. Their interstitial-type character is manifested by the survival and further growth of additional, unambiguously interstitial-type complexes – i.e. those at 84/75, 17, 120/145 and 50 K – which had initially formed in Stages I and II. These reaction sequences present further, strong evidence in favour of interstitial, as opposed to vacancy migration in Stage III.

6.2.3.2 MAE spectra in FeSi

In terms of the simple size-factor model (Section 4.4), strong interstitial trapping is expected at Si sites in the Fe matrix. This, indeed, is indicated by a suppression of the 110 K relaxation in favour of some low-temperature processes – at 83, 63 and 4.2 K – which have apparently been athermally formed during irradiation (Fig. 32). By analogy with **FeNi** (Section 6.3.1), the 83 and 63 K processes are associated with crowdions trapped at Si sites and mixed di-crowdions, $(\text{FeSi})_{\text{C}}$, stabilized by off-line vacancies, respectively. On anneal up to 120 K, rapid growth of the 83 K process, as compared to a slower increase of the 63 and 4.2 K relaxations, is observed. Above 120 K, the 83 K process decreases, evidently due to thermal dissociation, thereby giving rise to a rapid growth of the 63 K relaxation, together with the formation of a new process at 122 K. The 83 K defects, upon partly transforming into Si crowdions, may give rise to the formation of both mixed, $(\text{FeNi})_{\text{C}}$ at 63 K, and pure, $(\text{FeFe})_{\text{C}}$ at 122 K, di-crowdion complexes. The 122 K process shows remarkable stability, undergoing further growth during the decay of the 63 K relaxation above $T_{\text{a}} = 160$ K. On annealing above 200 K, a characteristic Debye peak is found to develop at 17 K. This attains an initial maximum at the end of Stage III ($T_{\text{a}} \leq 250$ K) where the 213 and 122 K relaxations undergo rapid decay. As in the similar case of **FeNi**, this relaxation is related to the reorientation of mixed dumb-bells, formed by constituents released from the 200 and 122 K processes, which are trapped at vacancies.

On further anneal above 250 K, a new process appears near 300 K which, upon its subsequent decay, gives rise to continued growth of the 17 K relaxation, thus indicating its interstitial-type character. A further process, which develops at 70 K during the de-

cay of the 300 K relaxation, is tentatively attributed to the reorientation of mixed dumb-bells trapped at Si sites.

In addition to the orientation-type point-defect relaxations already discussed, a non-Debye process also occurs below 7 K (Fig. 32b, [157]), which was observed also by Vigier [72]. This is characterized by a plateau-shaped relaxation extending into the temperature range below 3 K. Similar plateau-type relaxations exhibiting logarithmic time dependence have been observed in the low-temperature ($T < 20$ K) MAE spectra of magnetite, Fe_3O_4 . There, they have been identified as resulting from electron tunnelling between neighbouring Fe^{2+} and Fe^{3+} ions. Due to the corresponding polarity changes of adjacent Fe ions, local variations of the magnetic anisotropy are induced which are regarded as the source for the observed MAEs [20 to 22]. Similarly, the low-temperature relaxation in **FeSi** may be attributed to tunnelling processes, induced by an overlap between the electronic wave functions of closely neighboured Fe and Si atoms within an interstitial-type defect configuration. Increased spin-orbit coupling may be induced via an activation of electronic states, leading to reduced domain-wall mobility which, in turn, gives rise to the observed low-temperature MAE. Since the relaxations at 4.2 and 63 K (Fig. 32) are present immediately after irradiation, thus indicating athermal formation, it is tempting to identify the Si crowdions of the 63 K configuration as being initially responsible for the occurrence of the 4.2 K process. On further anneal, during the rapid decay of the processes at 83 K ($T_a > 140$ K) and 63 K ($T_a > 160$ K), the 4.2 K relaxation undergoes rapid growth up to $T_a \leq 180$ K, as may be expected from increased Fe-Si interactions due to the released constituents of thermally destabilized interstitial-type defect configurations. In particular, immobile mixed dumb-bells, $(\text{FeSi})_D$, formed after conversion and subsequent trapping of released Fe (83, 63 K) and Si crowdions (63 K), may possibly contribute to the 4.2 K relaxation by inducing magnetic anisotropy via electron tunnelling between neighbouring Fe and Si ions. During anneal in the temperature range of Stage III, these mixed dumb-bells start to migrate, thereby becoming partly trapped at vacancies. This reaction causes both the recovery of the 4.2 K relaxation – via the suppression of electron tunnelling – and the formation of $(\text{FeSi})_DV$ complexes, which are assumed to induce the 17 K process.

6.2.4 MAE spectra in *FeMn*

Despite its small positive size-factor (Section 6.1.3), dissolved Mn, like Ni, gives rise to rather complicated MAE recovery spectra. The similarity of magnetic interactions in these two alloys confirms a well-established metallurgical rule stating the close relationship between **FeMn** and **FeNi** systems [179].

The MAE spectrum of **FeMn** starts with a rapidly decaying 110 K relaxation, giving rise to two strong processes at 116 and 95 K, in addition to a small relaxation at 82 K. By analogy with the systems already discussed, we assign the 82 K process to crowdions trapped at Mn-sites, instead of at off-line vacancies (110 K). On account of its proximity to 120 K, we associate the 116 K relaxation with Fe di-crowdions (Section 6.3.1) and the 95 K process with a modified configuration built up of mixed Fe-Mn crowdion pairs.

During the initial recovery of the 110 K relaxation, the 95 K process is found to develop preferentially whereas, above 120 K, the formation of the 116 K process is dominant and the 95 K relaxation, in turn, becomes somewhat reduced. After passing through a

maximum, the 116 K process recovers rapidly on annealing above 130 K, thereby giving rise to a strong re-growth of the 95 K relaxation. Both the recovery of the 116 K process and the re-development of the 95 K relaxation may be associated with the thermally activated conversion of pure (116 K) into mixed (95 K) di-crowdion complexes.

On further anneal, the 95 K process recovers rapidly as a result of thermally activated dissociation; its released constituents – Fe and Mn crowdions – give rise to the formation or re-growth of a series of well-known processes at 64, 82, 52 and 108 K. In analogy to the situation in **FeNi**, Section 6.3.1, the re-growth of the 82 K relaxation is related to additional trapping of crowdions at Mn sites. Due to corresponding trapping reactions, growth is also observed for the processes at 52 and 64 K, associated with pure and mixed di-crowdions trapped at vacancies and the 108 K relaxation, assigned to Mn crowdions trapped at vacancies. During the almost simultaneous recovery of the processes at 64, 82 and 52 K, the appearance of a new, rapidly decaying relaxation is observed at 90 K. This latter, like a similar process occurring in the MAE spectrum of **FeNi**, is assigned to a combined reorientation and migration of mixed dumb-bells which have been formed by reactions between the released constituents of preceding processes.

In contrast to **FeNi**, on anneal of **FeMn** in Stage III, no low-temperature relaxation ($T_a \leq 20$ K) or survival of any relaxation process, formed in Stages I or II, is observed. This modified recovery behaviour in **FeMn** reflects weaker interactions between host and impurity atoms, thus pointing to reduced electronic exchange (Section 6.2). Consequently, in Stage III more interstitials are able to recombine with vacancies, whereas only a smaller number becomes trapped at Mn sites, thereby giving rise to a series of weaker, transient relaxation processes with continuously increasing peak temperatures upon successive annealing steps (Fig. 41a). This situation resembles that observed in **FeBe** (Section 6.3.3.1), where it was considered futile to identify such transient pro-

Fig. 41. MAE-recovery spectra of Fe + 1 at % Mn following irradiation at $T \leq 45$ K with 3 MeV electrons to a dose of $10^{23} \text{ e}^- \text{ m}^{-2}$ [74, 158], ($t_1 = 1$ s, $t_2 = 180$ s)

cesses with specific defect configurations. Once more, however, our analysis leaves no doubt about the fundamental interstitial-type character of the related defect configurations. Therefore, the corresponding MAEs are attributed to reorientable interstitial clusters of increasing complexity, formed in Stage III by continued trapping of interstitials becoming released from thermally destabilized defect configurations.

6.3 Model-relevant defect reactions in substitutional Fe alloys

Our survey on the MAEs in irradiated, binary substitutional Fe alloys may be concluded by a summary of those defect reactions which proved to be most informative in discriminating between the two recovery models. The corresponding MAE spectra may be classified under the following aspects:

1. MAE spectra which are so closely related to those occurring in pure α -Fe that, although fully supporting the 2IM interpretations deduced from the Fe results (Section 5.5), they are, nevertheless, unable to provide us with further new arguments in favour of any recovery model. Spectra of this type occur preferentially in dilute alloys with strongly oversized ($\Omega_{\text{SF}} > 10\%$) solute atoms, i.e. V, Al, Cu, Ti (Section 6.2.2).

2. MAE spectra which, on account of their large number of different, simple Debye-type relaxation processes occurring in the low-temperature Stages I to III, suggest an interpretation in terms of a 2IM, rather than a 1IM. The inherent weight of this argument may be, possibly, only under-estimated by workers on such techniques which, on account of their limited resolving power, are *a priori* unable to reveal the wealth of specific processes available to the MAE [7, 12]. The prime example of this type of alloy may be seen in **FeNi** (Section 6.2.1). However, also **FeMn** and the alloys with undersized solute atoms, i.e. **FeBe** and **FeSi** (Section 6.2.3), are typical representatives of this category of systems.

3. MAE spectra which, on annealing in and above Stage III, are characterized by the survival of typical interstitial-type relaxations which have already been formed in Stages I and II. Typical representatives of this category are the undersized alloys **FeSi** (Fig. 32) and **FeBe** (Figs. 33 to 35). In terms of the 1IM, in contrast to the observed survival, elimination of these processes would be expected in Stage III due to de-stabilization and annihilation in the course of vacancy trapping.

4. MAE spectra which, on anneal in and above Stage III, are characterized by the pronounced growth of relaxation processes which had earlier been formed in Stage II and thus, unambiguously, are of interstitial type. As already outlined in item 3., if vacancies were to migrate in Stage III, instead of further growth, accelerated elimination of these peaks would be expected. A prototype for this class of reactions is the 58 K peak occurring in dilute **FeNi** (Fig. 37b), in addition to the 122 K peak in **FeSi** (Fig. 32) and the peaks at 75 and 100 K in **FeBe** (Fig. 34a).

5. MAE spectra characterized by a shift of Stage III to somewhat elevated temperatures. The fact that such shifts are observed only in Fe alloys with pronounced interstitial trapping, i.e. **FeSi** (213 K, Fig. 32), **FeNi** (205 to 210 K, Figs. 36b, 38b) and **FeMn** (205 K, Fig. 41b) is regarded as further support for the 2IM.

6. MAE spectra characterized by an uninterrupted transformation of lower- into higher-temperature peaks starting from a first, unambiguously interstitial-type configuration formed in Stage II up to temperatures far above Stage III ($T > 400$ K). This behaviour typically occurs not only in **FeBe** alloys (Figs. 33 to 35), but also in **FeMn**

(Fig. 41a) and **FeCu** (Fig. 31b). In the case of vacancy migration in Stage III, in contrast to the observed continuous peak genealogy, a qualitative change between the defect reactions below and above Stage III would be expected.

7. MAE spectra characterized by pronounced, Debye-type low-temperature relaxations ($T_p < 20$ K) which typically develop on annealing at temperatures in or above Stage III. Examples of such processes are found in **FeNi** (11 K), **FeSi** (17 K), **FeBe** (17 K) and **FeTi** (16 K). On account of their correspondingly low activation enthalpies (Table 7), their respective defect configurations must be so easily reorientable as is only feasible in the presence of vacancies. However, these defect configurations cannot have been formed by trapping of mobile vacancies in Stage III since then they all should have developed at *one* definite temperature, i.e., at about 200 K. Instead, we observe a wide spread of formation temperatures, extending from 200 K in **FeNi** (Fig. 38b) to $T > 250$ K in **FeSi** (Fig. 32a) and **FeTi** (Fig. 30b) up to 340 K in **FeBe**. (Fig. 34a, 35a) Accordingly, the defect genealogies deduced above for these alloys (cf. aspects 2. to 6.) point to a formation of these low-temperature relaxations by trapping of mobile interstitial-type defects at immobile vacancies. Such interstitial trapping may occur either immediately during their initial migration in Stage III or, upon continued annealing at elevated temperatures, after the release of interstitials from thermally de-stabilized defect configurations.

7. MAE Spectra in Interstitially Doped α -Fe

7.1 General aspects

The question as to whether a given impurity atom dissolves substitutionally or interstitially in α -Fe may be answered initially from consideration of its size-factor. Thus, elements with ratios of atomic radii less than 0.7, relative to Fe, are located preferentially on interstitial sites [179, 181, 182]. Elements of this type are those with small atomic numbers, at the beginning of the Periodic Table, i.e., H, He, B, C, N, O. Of these, only H, C, N, O have been investigated to any extent by means of IF and MAE techniques. Since our interests are focused on the interactions between radiation-induced intrinsic defects and impurity atoms, we consider in the following only dilute Fe systems which do not tend to form precipitation-induced ordered phases [179, 181, 182].

As compared with substitutional alloys, interstitially dissolved impurity atoms offer great advantages in discriminating between various defect interactions in Fe. This is due to the fact that interstitial impurity atoms, themselves, become thermally mobilized – in the case of C and N at temperatures above Stage III, near room temperature – thereby giving rise to characteristic MAEs of the so-called Richter type [15, 19]. In radiation-damaged α -Fe, this mobilization of impurity atoms is accompanied by a series of additional reactions, such as continued growth and/or re-dissolution of mixed intrinsic–impurity defect configurations. A most interesting problem arising in this context is the question of whether simple impurity–interstitial–vacancy complexes are formed in Stage III by the trapping of *mobile vacancies* at *immobile impurity atoms* (1IM) or, vice-versa, at temperatures above Stage III ($T_a > 250$ K) by the trapping of *mobile impurity interstitials* at still *immobile vacancies* (2IM). The following discussion will reveal that, in the case of **FeC** and **FeN**, only the latter interpretation is compatible with our experimental results (Section 7.3.1.2), which thus serve as convincing support for the 2IM.

7.2 MAEs in FeO and FeH alloys

We discuss these two alloys under the one heading since, up to the present time, no well-developed Richter MAEs due to either O or H have been detected.

7.2.1 MAE in FeO

It has been known for a long time that the solubility of O in α -Fe is very small [179, 182 to 190]. This fact has served as an explanation for the absence of any distinct Snoek relaxation of O in α -Fe [185, 186]. In an attempt to consolidate the experimental data available at that time, Frank et al. [187, 188] determined the migration energy of interstitially dissolved O in α -Fe to be 0.98 ± 0.01 eV. From these calculations, the solubility of O near the γ -transition of Fe (1180 K) is expected to range between 0.4 and 12 at ppm. Due to this small solubility level, the O content retained in the Fe matrix after quenching is below the detection limit of the MAE [191], whose relaxation maxima should be located in the temperature range 220 to 320 K [188, 189]. More recently, Földeaki et al. [192] have reported MAEs in O-charged pure Fe and dilute Fe alloys. These MAEs, however, were not of definite Richter type and, in so far as they were O-induced, should rather be attributed to cold-work type interactions of O with dislocations or reorientations of small impurity clusters [192].

7.2.2 MAEs in FeH

Many attempts have been made in the past to resolve a Snoek-Richter type relaxation of H interstitials in α -Fe by means of IF and MAE techniques. As in the case of O, one major problem for the observation of such processes arises from the small solubility of H in Fe [179, 189, 190]; this is less than 1 at ppm in the low-temperature range ($T < 50$ K) where, on account of the high mobility of H [186, 189, 193, 194], the respective relaxations are expected to occur. For some time, confusion arose concerning the role of H in various relaxation processes below 150 K. Thus, Heller [195] and Gibala [196] identified an IF peak – which, depending on the measuring frequency, occurs at 30 K (1 Hz) or 48 K (80 kHz) – with the Snoek effect of H interstitials. By means of MAE measurements, Au and Birnbaum [197, 198] resolved a series of peaks near 30 K which they interpreted as reorientations of single H interstitials, H–H pairs and H interstitials trapped at impurity sites. Subsequent MAE measurements of Kronmüller et al. [194, 199 to 201], however, revealed that these relaxations also occur in high-purity, H-free α -Fe after plastic deformation and should therefore be associated rather with dislocation-induced interactions. This conclusion was further supported by the fact that charging with hydrogen, following plastic deformation of the crystal, produced complete suppression of the low-temperature relaxation in favour of an additional, strong relaxation at 180 K. On annealing within the temperature range $200 \text{ K} < T_a < 450 \text{ K}$, this 180 K peak was found to be reduced in strength and shifted to lower temperatures [202 to 205]. All these various reactions are most consistently explained within the following scheme:

- a) 10 to 30 K: so-called α -peak, resulting from thermally activated formation of double-kinks on non-screw dislocations [194, 204, 206, 207].
- b) 70 to 180 K: H cold-work relaxations, induced by interactions between dislocations and H interstitials [200 to 205].
- c) 250 to 400 K: so-called γ -peaks, which are produced by the formation of double-kinks on screw dislocations [204, 206, 208, 209].

From inspection of these results, it becomes apparent that, up to now, no Snoek-Richter – type relaxation has been observed as yet in H-charged α -Fe [196, 201, 204, 207]. This is also true for a recent investigation, performed by Hirscher [210] on H- and deuterium (D)-charged, unirradiated and e^- -irradiated α -Fe. In unirradiated, H-charged Fe, all basic dislocation-induced relaxations, known from preceding studies, have been found to re-appear. Similarly, in e^- -irradiated, H-charged Fe, due to the high mobility of H, only minor modifications of the high-purity e^- -irradiated Fe spectrum could be detected:

a) All peaks appeared with slightly reduced amplitudes. This effect was related to the presence of dislocations, which had probably been introduced during electrolytic H charging and which may have acted as trapping centres for intrinsic interstitials.

b) Only one additional point defect relaxation, as compared to high-purity α -Fe, has been observed at 60 K (H) or 80 K (D). These processes have been associated with reorientations of mixed H (D) – intrinsic interstitial clusters. Also quantum-mechanical tunnelling of H and D atoms has been discussed, on account of the relatively large pre-exponential factors of the relaxation times determined for these processes.

The repeated failure to discover any indication of a Snoek-Richter type relaxation in H-charged α -Fe may be explained by the following arguments:

a) Due to the negligibly small solubility of H in Fe below room temperature, practically all H atoms have been precipitated, e.g. in the form of H_2 molecules, at dislocation cores, micro-cracks, grain boundaries and similar lattice defects.

b) The non-cubic lattice distortions induced by individual H interstitials, in comparison to those produced by C or N, may be too small to produce detectable MAEs.

c) Due to the high mobility of H, the corresponding reorientation-type relaxations may be activated at temperatures below 4 K.

d) The assumed low-temperature reorientation may be induced by tunnelling, rather than by thermally activated jumping, thus giving rise to modified relaxation mechanisms.

In view of the vanishing interactions observed between H and irradiation-induced intrinsic interstitials [210], on the one hand, and the rather complicated interactions between H and dislocations, giving rise to pronounced cold-work peaks [196 to 205], on the other hand, the **FeH** system appears to be not very helpful in the solution of the Stage III problem. In the following, therefore, our attention will be confined to the two remaining interstitial alloy systems: **FeN** and **FeC**.

7.3 Magnetic relaxations in **FeN** and **FeC**

Dilute **FeN** and **FeC** alloys represent the classic b. c. c. systems which exhibit well-developed, magnetic and anelastic relaxation processes due to thermally activated reorientations of solute interstitials.

The Richter MAE in **FeC** and **FeN** – similar to its mechanical analogue, the IF Snoek effect [186, 211] – can be used to obtain valuable information on low-temperature diffusion data of N and C [6, 7, 109, 212 to 214], dissolved interstitial concentrations [215, 216], details of the precipitation kinetics [217 to 221] and interactions with lattice imperfections [7, 15, 217].

In order to investigate the influence of interstitially dissolved C and N on the MAE spectra of irradiated α -Fe, measurements have been performed on alloys with varying

Table 8
Initial impurity contents of the Fe used as source material in the various investigations. The different Fe basis material has been individually analyzed by JM (Johnson Matthey Chemical Lim., U.K.) and at the MPI (Max-Planck-Institut für Metallforschung); (ND means not detected)

elements	Ag	Al	Ca	Cr	Cu	Mg	Mn	Mo	Ni	Pb	Si	analysis
Blythe et al. [92 to 94]	—	—	1	1	2	—	2	—	25	—	1	JM
Mensch et al. [90, 91]	<1	2	—	—	2	2	3	2	2	—	4	MPI
Walz et al. [7, 214, 219 to 221]	ND	<1	1	<1	<1	<1	<1	ND	ND	ND	1	JM
Walz et al. [97, 213]	ND	ND	<1	ND	20	<1	<1	ND	ND	2	<1	JM

impurity contents ($20 \text{ at ppm} \leq c_{\text{C,N}} \leq 400 \text{ at ppm}$) and irradiation doses ($10^{22} \leq \phi t_{\text{e,n}} \leq 2 \times 10^{23}$). The particular interest in these systems results from their *dual* role in being able to support defect clustering: (i) by trapping of intrinsic interstitials at immobile impurity atoms, at temperatures below Stage III, and (ii) by trapping of thermally activated impurity interstitials, at temperatures $T \geq 250 \text{ K}$, at immobile intrinsic defect configurations. These two mechanisms are clearly distinguishable from one another and are thus extremely useful for the identification of the various constituents involved in the formation of specific defect configurations. **FeC**, in contrast to **FeN**, has the additional advantage that those relaxations which have been formed by trapping of *mobile C* at *intrinsic* traps occur at temperatures well *below* their respective recovery stages. This allows us to conveniently correlate the original constituents with their resulting clusters. Consequently, defect reactions in **FeC** can be identified with higher accuracy than in any other Fe system so far investigated. We shall therefore begin our review of MAEs in interstitially doped α -Fe with this alloy.

Table 9
Compilation of interesting parameters of the various alloys investigated, i.e. residual resistivity ratio (RRR), integrated doses of n- and e^- -irradiation (ϕt), concentration of induced Frenkel pairs, C_{FP} , using a specific value of $3.0 \times 10^{-11} \Omega\text{m/ppm}$ [87], and interstitially dissolved C (C_{C}). Irradiations have been performed in the “Herald” Reactor AWRE, Aldermaston (U. K.) [92 to 94, 222], in the reactor “FR2”, KFZ Karlsruhe (Germany) [90, 91] and in the van-de-Graaff accelerators of the KFA Jülich (Germany) [7, 220] and the Institut für Allgemeine Metallkunde und Metallphysik der RWTH Aachen (Germany) [7, 213]

specimens	RRR	$\phi t \text{ (} 10^{22} \text{ m}^{-2} \text{)}$		C_{FP} (at ppm)			C_{C} (at ppm)	$C_{\text{FP}}/C_{\text{C}}$ (200 K)
		n	e^-	as-irr.	$T \leq 200 \text{ K}$			
Blythe et al. [92 to 94]	—	2		560	140		>300	0.47
Mensch et al. [90, 91]	>1600	3×10^{-1}		84	21		140	0.15
Walz et al. [7, 220]	1600		8	300	30		50	0.6
Walz et al. [7, 220]	1600		8	300	30		100	0.3
Walz et al. [7, 213]	>1200		2×10^1	750	75		25	3
Walz et al. [7, 213]	>1200		2	75	7.5		25	0.3

Table 10

Compilation of activation parameters of individual relaxations, determined by various authors in n- (n_I : [94, 222]; n_{II} : [90, 91]) and e⁻ [7, 213, 220] irradiated C-charged α -Fe. The following notations are used: peak temperature of processes (T_p), annealing temperature, following which the processes are fully developed (T_a), activation enthalpy (Q), half-width of activation energy spectrum ΔQ , pre-exponential factor (τ_0) of Debye-type relaxation times $\tau = \tau_0 \exp(Q/kT)$. The MAE peaks in the n-irradiated experiments are shifted to somewhat lower temperatures due to different measuring times, i.e., $t_1 = 1$ s; $2 \text{ s} \leq t_2 \leq 180 \text{ s}$ following n_I - [94, 222] and $t_1 = 15$ s; $15 \text{ s} < t_2 \leq 600 \text{ s}$ after n_{II} -irradiation [91]. In the text, peak temperatures of n_{II} experiments are given by the n_I "standard-temperatures" with the corresponding n_{II} values in brackets, e.g. 320 (298) K

T_p (K)			T_a (K)			Q (eV)			$\pm \Delta Q$ (eV)			τ_0 (10^{-13} s)		
n_I	n_{II}	e ⁻	n_I	n_{II}	e ⁻	n_I	n_{II}	e ⁻	n_I	n_{II}^*	e ⁻	n_I	n_{II}	e ⁻
18	17	18	473	396	500	0.047	0.048	0.042	0.002	(1)	0.003	$10^{1.5 \pm 0.5}$	$10^{0.9 \pm 0.2}$	$10^{2 \pm 1}$
—	47	50	—	116	80	—	0.138	0.138	—	(1.1)	0.006	—	$10^{0.4}$	$10^{\pm 1}$
—	81	84	—	116	140	—	0.266	0.25	—	(1.15)	0.02	—	$10^{-1.4}$	$10^{-1 \pm 1}$
—	103	110	—	18	110	—	0.32	0.32	—	(1.2)	0.02	—	$10^{-0.7}$	$10^{\pm 1}$
—	115	115	—	316	240	—	0.36	0.36	—	(1.15)	0.03	—	$10^{-0.4}$	$10^{-0.5 \pm 1}$
120	116	125	240	154	180	0.31	0.36	0.40	0.01	(1.2)	0.03	$10^{+0.3}$	$10^{-0.5}$	$10^{-1 \pm 1}$
—	135	140	—	220	140	—	0.45	0.34	—	(1.2)	0.03	—	$10^{-1.1}$	$10^{1 \pm 1}$
—	147.7	155	—	316	355	—	0.48	0.48	—	1.05	0.03	—	$10^{-1.2}$	$10^{-0.5 \pm 1}$
—	156	170	—	18	223	—	0.5	0.53	—	—	0.04	—	10^{-1}	$10^{-0.5 \pm 1}$
190	176	—	315	220	—	0.57	0.56	—	0.03	(1.1)	—	$10^{-0.4}$	$10^{-0.7}$	—
—	189	200	—	18	210	—	0.57	0.56	—	(1.17)	0.02	—	1	$10^{0.5 \pm 0.5}$
225	203	215	315	18	223	0.67	0.65	0.64	0.02	(1.2)	0.04	$10^{-0.4}$	10^{-1}	$10^{-0.5 \pm 0.5}$
265**	253	265	593	18	265	0.87	0.80	0.85	0.02	(1.08)	0.03	10^{-2}	$10^{-0.7}$	$10^{-1.8 \pm 1}$
—	298	325	—	356	385	—	0.97	1.07	—	(1.4)	0.04	—	$10^{-1.2}$	$10^{-1.5 \pm 1.5}$

* Following a modified numerical technique due to R. M. Fuoss and J. G. Kirkwood (J. Am. Chem. Soc. **62**, 385 (1941)), [211], increased halfwidths in the n_{II} -irradiated alloys are described by a parameter $W \geq 1$.

** C-MAE

7.3.1 MAE spectra in irradiated C-charged α -Fe

Detailed investigations of the MAE spectra which occur in **FeC**, following n-irradiation, have been performed by Blythe et al. [94, 123, 222] and Mensch et al. [90, 91, 212, 223] and following e⁻-irradiation by Walz et al. [7, 12, 213, 220]. The relevant parameters of these systems, such as initial sample purity, introduced C content, temperature, irradiation doses etc. are compiled in Tables 8 and 9. The numerically determined activation parameters of the various observed relaxation processes are summarized in Table 10.

The most systematic measurements have been performed on two series of e⁻-irradiated **FeC** (cf. Table 9) after, respectively, irradiation of *differently C-charged* alloys to the *same dose* [7, 220] and irradiation of *identically C-charged* alloys to *different doses* [7, 213]. Especially the results obtained from these two systems will serve us in the following as a valuable basis for a discussion of the recovery kinetics in e⁻-irradiated **FeC**.

7.3.1.1 Characteristics of the recovery spectra in irradiated FeC

The classification of the recovery spectra of irradiated **FeC** is developed in analogy to that deduced for irradiated, high-purity (Section 5) and substitutionally alloyed α -Fe

Fig. 42. Stepwise annealing sequence of α -Fe containing 100 at ppm C, following low-temperature irradiation to a dose of $8 \times 10^{22} \text{ e}^- \text{ m}^{-2}$: a) temperature range ($80 \text{ K} \leq T_a \leq 380 \text{ K}$), b) temperature range ($400 \text{ K} \leq T_a \leq 620 \text{ K}$) [7, 220]. The annealing programme shown is also representative for the other **FeC** alloys discussed, ($t_1 = 1 \text{ s}$, $t_2 = 180 \text{ s}$)

(Section 6). Thus, the spectra shown in Figs. 42 to 48, which are representative of irradiated **FeC**, may be associated with the following defect configurations:

a) *Primary defects.* This defect type gives rise to the MAEs at 110 K (Stage I: intrinsic interstitials), at 200 K (Stage III: second intrinsic interstitial type (2IM) or vacancy (1IM)) and at 265 K (C-Richter MAE).

b) *Clusters formed by trapping of intrinsic defects.* Defect configurations of this type are responsible for the processes occurring at 50/55, 84, 125/115, 140, 170 and 215 K. Similarly as in high-purity and substitutionally alloyed α -Fe, the 125 K, and possibly also the 50 K relaxation, may be associated with intrinsic interstitial clusters, whereas the processes at 84 and 55 K are associated with mixed intrinsic-impurity interstitial clusters. The processes occurring at 115, 140, 170 and 215 K do not appear in pure α -Fe and are therefore attributed to small clusters of intrinsic interstitials trapped at C.

c) *Clusters originating from trapping of C interstitials.* Clearly, configurations of this type induce the processes occurring at 155 and 320 K (Figs. 43, 45, 49), which can be straightforwardly associated with small clusters formed by trapping of *mobile C* at *immobile vacancies* (cf. Section 7.3.1.2.d).

d) *Vacancy migration.* On annealing above 400 K (Stage IV), in e^- -irradiated **FeC** a pronounced, well-defined Debye-type relaxation is developed at 18 K (Figs. 43, 45, 49c). In terms of the 2IM, this relaxation can be conveniently attributed to small clus-

Fig. 43. Annealing spectra of a) the alloy of Fig. 42, as constructed from the annealing sequences, and b) an identically e^- -irradiated alloy, charged with 50 at ppm C [7, 220]; API stands for “amplitude prior to irradiation” of the C-Richter MAE, ($t_1 = 1$ s, $t_2 = 180$ s)

ters formed by trapping of *thermally mobilized monovacancies* at C–vacancy complexes of type c), which had formed during previous annealing at $T_a > 270$ K, cf. Section 7.3.1.2.d.

7.3.1.2 MAEs in e^- -irradiated FeC

a) *Stage I* (≈ 110 K). In the “as-irradiated”, dilute **FeC** systems, containing 100 and 50 at ppm C, the concentrations of intrinsic self-interstitials exceed that of C by factors of about 3 and 6, respectively (Table 9). We thus expect simple I_nC_1 complexes ($n \geq 1$)

Fig. 44. Comparison of the recovery behaviour of the relevant processes of the MAE spectra shown in Fig. 43a (high C content): (—) and Fig. 43b (low C content): (---), ($t_1 = 1$ s, $t_2 = 180$ s)

to develop from the trapping of intrinsic interstitials at immobile C. In contrast to substitutionally alloyed Fe, for instance **FeNi** (Section 6.3.1), the processes occurring at 84 and near 50 K are only slightly modified during annealing in Stage I. Instead, relatively strong, C-specific relaxations develop at 140 and 170 K (Figs. 43a, b) which, however, recover rapidly on annealing in Stage II. These relaxations are attributed to small, mixed interstitial clusters resulting from trapping of Stage I interstitials at C. In addition to these C-dominant reactions, similar to the situation in pure Fe (Section 5.5), small, reorientable self-interstitial clusters are assumed to give rise to the relaxations at 125 and near 50 K. Further trapping of intrinsic interstitials at sinks of either residual substitutional or C-interstitial type is indicated by a minor growth of the relaxations at 84 and 55 K.

b) Stage II (130 K < T < 180 K). The relaxation processes which occur in this temperature range are assumed, in either recovery model, to result from rearrangements of primary, interstitial-type defect configurations which had previously formed in Stage I.

Evidently, despite the rapid decay of the strong processes at 140 and 170 K, no additional defect configurations develop in this temperature range. Since the amplitudes of the primary processes at 50/55, 84 and 125 K, too, are only weakly affected, the mobile self-interstitials must either annihilate with vacancies or agglomerate at C sites to form clusters which, at these temperatures, remain immobile and thus cannot be detected.

c) Stage III (≈ 200 K). Here we are faced with the striking fact that the 200 K relaxation appears with *identical amplitude* in the two **FeC** alloys which differ in C concentration by a factor of two (cf. Table 9), but were low-temperature e^- -irradiated ($T < 40$ K) to the same dose (Figs. 43, 44). In order to discriminate between the two recovery models which predict, controversially, the migration of either vacancies (1IM) or self-interstitials (2IM) in this stage, the decisive question to be answered is: which one of the two elementary defect types has the better chance for surviving up to Stage III, with *identical concentration*, in these two alloys?

Fig. 45. Recovery spectra of Fe + 25 ppm C alloys, following low-temperature irradiations to doses of a) 2×10^{23} and b) $2 \times 10^{22} \text{ e}^- \text{ m}^{-2}$ [7, 213, 220], ($t_1 = 1 \text{ s}$, $t_2 = 180 \text{ s}$)

(i) Identical concentrations of monovacancies in Stage III?

A priori, one could argue that an identical vacancy content in the two different specimens would be *rather unlikely*. In the stronger C-charged sample, self-interstitials should predominantly become trapped at C atoms in Stages I and II, thus leaving behind them a larger vacancy content exceeding, say, by about a factor of two that of the lower C-charged specimen, where annihilation between interstitials and vacancies plays the major role. In agreement with this argument, the Richter MAE, when observed for the first time after irradiation, is found to be, by a factor of two, more reduced in the higher (-6%) than in the lower (-3%) C-charged alloy (cf. Fig. 43a, b). In order to completely confirm this above “*a priori*”-conclusion, however, we must ascertain that

Fig. 46. Comparison of the recovery behaviour of the relevant processes of the MAE spectra shown in Fig. 45a (high-dose irradiation) (—) and Fig. 45b (low-dose irradiation) (---), ($t_1 = 1$ s, $t_2 = 180$ s)

this reduction did not occur in Stage III, but already previously at lower temperatures, i.e. by *interstitial* trapping at C atoms. This proof can, indeed, be furnished as follows:

α) Due to the continued, strong recovery during annealing up to Stage III, the absolute content of intrinsic defects may be estimated to have reduced by factors of about 3 to 6 below that of the dissolved C (Table 9). Thus, the trapping rate at C sites is determined essentially by the number of migrating Stage III defects which – on account of

Fig. 47. Recovery spectrum of low-temperature ($T \leq 18$ K), low-dose (3×10^{21} n m $^{-2}$) irradiated α -Fe charged with 140 at ppm C [91], as observed for the isochromals with $t_1 = 15$ s and $t_2 = 600$ s

Fig. 48. Recovery spectrum of low-temperature ($T < 78$ K), high-dose ($2 \times 10^{22} \text{ n m}^{-2}$) irradiated Fe charged with >350 at ppm C [94]. The dashed curves show (i) the recovery of the 18 K relaxation for a corresponding FeC alloy after n-irradiation to the same dose at $T = 320$ K [94] and (ii) a simulation of the recovery of the 150 K peak which, due to experimental shortcomings, in these measurements has not been observed, ($t_1 = 1$ s, $t_2 = 180$ s)

the equal heights of the two 200 K peaks – proves to be equivalent in both alloys. Consequently, also the amounts of the respective reaction products should be comparable and if these were, in terms of the 1IM, C – monovacancy complexes, the Richter MAE should be reduced by *comparable* rates in both alloys – in contrast to the actually observed *factor of two difference*.

This evident discrepancy can be reconciled only by assuming *different rates of defect trapping at C atoms* already in the *lower recovery stages* (I and II), which are clearly dominated by reactions of *mobile interstitials*. Thus, it is only consequent to conclude that after annealing up to Stage III – due to C-induced, varying interstitial–vacancy recombination rates at lower temperatures – the two specimens *must* have *unequal vacancy contents*, differing, i.e., by about a factor of two between the lower and higher C-charged sample. Thus, following our argumentation, vacancy migration in Stage III can be definitely excluded.

β) If, despite our above arguing (α), vacancies were to migrate, in Stage III, elementary C_1V_1 complexes should have formed which, in terms of the 1IM interpretations [87, 141 to 143] would possess a pronounced anisotropy and thus induce a *new*, specific relaxation peak in the MAE spectrum. Moreover, due to vacancy trapping at other defects, drastic modifications of the residual interstitial type processes – i.e. those at 125/115, 50/55, 170 K – would be expected, culminating in their de-stabilization and final dissolution. On further C trapping, in and above the C-Stage ($T_a \geq 300$ K), the original C_1V_1 clusters would be expected to transform into a series of further multi-C–vacancy complexes, e.g. C_2V_1 , C_3V_1 , ..., C_nV_1 . Such higher-order complexes, however, are generally characterized, by (i) a reduction of anisotropy – and hence relaxation strength – with increasing n , and (ii) a broadening of corresponding peaks, due to the occurrence of various relaxation modes with slightly different activation enthalpies.

Fig. 49. Least-squares fitting of the important relaxation processes occurring in the MAE spectra of the e^- -irradiated alloys of Figs. 42, 43, and 45. Data points and theoretical curves are shown for the following times (cf. Section 2.2): $t_1 = 1$ s, $t_2 = 2$ s (1), 4 s (2), 8 s (3), 16 s (4), 32 s (5), 64 s (6), 128 s (7) and 180 s (8). a) 155 K, together with 125 K, relaxation after annealing at $T_a = 322$ K. b) Residual C Richter MAE (265 K) with 320 K relaxation, after annealing at $T_a = 360$ K. c) 18 K relaxation after annealing to $T_a = 500$ K [213], ($t_1 = 1$ s, $t_2 = 2$ s (1), 8 s (2), 32 s (3), 180 s (4))

In contrast to this 1IM-based scenario of feasible reaction sequences in Stages III and in the C-Stage, a completely opposite annealing behaviour is observed (Figs. 43, 44): in Stage III, *no* pronounced, new relaxation process is developed and all still surviving interstitial-type clusters (50/55, 115, 170 K) undergo further growth instead of dissolution. In the C-Stage, however, a completely new relaxation process develops at 155 K. On account of its prominence, simple Debye-type and formation kinetics (cf. d)),

we associate this process with an elementary defect configuration such as, for example, the V_1C_1 cluster, having been formed by trapping of migrating C interstitials at immobile vacancies. Thus, the clear answer to the initial question of (i) is: “no”. At the beginning of Stage III, the vacancy content in the higher C-charged sample exceeds by a factor of about two that of the lower charged one.

(ii) Identical concentrations of mobile interstitials in Stage III?

The assumption of equivalent contents of mobile interstitials, as opposed to vacancies (i), up to Stage III is compatible within the framework of the 2IM. Assuming, that in the two alloys comparable amounts of *on-line crowdions* are lost in Stages I and II by either annihilation with vacancies (dominant in the lower C-charged sample) or trapping at C atoms (dominant in the higher C-charged sample), *comparable amounts of off-line crowdions* may be retained which, during anneal in Stage II, convert into dumbbells. These, together with the directly irradiation-induced, initially immobile dumbbells, will start to migrate in Stage III, thereby giving rise to comparable relaxation amplitudes for the 200 K process in both alloys.

(iii) Interpretation of the reaction mechanisms in Stage III

The 2IM, in contrast to the 1IM, is able to conveniently explain the recovery behaviour observed in Stage III (Figs. 43a, b) by assuming trapping of Stage III interstitials at various sink types. In addition to continued trapping at C sites and residual interstitial clusters – giving rise to growth (50/55, 170 K), new development (170, 215 K) or transformation (125/115 K) of processes – further annihilation of Fe interstitials at vacancies has to be envisaged.

Of these processes, the reactions observed for the 125 K relaxation in the two differently C-charged alloys are of particular interest. Although occurring initially with different strengths, after annealing up to 200 K the amplitude of this process – due to thermal destabilization – is reduced to about the same level in both samples (Figs. 43a, b) and its peak temperature shifted to 115 K. On further anneal in Stage III, this 115 K relaxation increases again, however, with about a factor of two greater amplitude in the stronger – as compared to the lower – C-charged sample. On continued annealing, up to the C-Stage, these amplitudes are only moderately affected; in the C-Stage, however, a rapid decay is observed being accompanied by a shift of the peak back to its original temperature of 125 K. The reaction kinetics of this process, too, are best comprehensible in terms of the 2IM: the initial 125 K relaxation, arising at the end of Stage I in various Fe systems (Sections 5, 6), is attributed to a simple intrinsic interstitial complex of, i.e., I_2 -type. In pure α -Fe, this relaxation is usually observed to disappear at the end of Stage II due to thermal dissociation of the corresponding clusters. In the present FeC alloys, however, such complexes are able to survive, albeit at a reduced level, i.e. in form of I_2 clusters, being trapped and thereby stabilized at C atoms. These modified complexes are assumed to relax at the lower temperature of 115 K. The fact that in Stage III these *interstitial-type* complexes undergo further growth, instead of dissolution, indicates that the migrating Stage III defects, upon trapping at C atoms, form similar defect configurations which, consequently, must also be of *interstitial type*. Characteristically, these clusters become de-stabilized in the temperature range where C interstitials undergo thermal activation giving rise to a process located, again, at 125 K. This interesting observation points to the following interpretation: after release from their carbon traps, the intrinsic interstitials relax again, in their initial configuration, at the temperature of the primary Stage II clusters, i.e. at $T_p = 125$ K.

This interpretation in terms of migrating *self-interstitials*, rather than vacancies, in Stage III is also in agreement with the corresponding growth of the weaker, interstitial-type complexes at 50/55 and 170 K and the formation of a minor satellite of the original 200 K process at 215 K (Fig. 43).

d) *Diffusion of carbon in irradiated α -Fe (C-migration stage)*. On annealing in the C-Stage ($T \geq 300$ K), a pronounced relaxation peak develops at 155 K which, because of its particular features, proves to be of decisive importance in discriminating between the different recovery models:

(i) Due to its development in the C-Stage, it is evident that this peak results from trapping reactions between *thermally mobilized* C interstitials and *immobile* lattice defects.

(ii) The extraordinary distinct Debye-type of this process points to the reorientation of a simple anisotropic defect configuration [7].

(iii) The characteristic 4:1 amplitude ratio, observed in two identically e^- -irradiated alloys containing by a factor of two different C contents (Figs. 43, 44; Table 11) indicates definitely a second-order reaction between two elementary defect species, i.e. monovacancies and C interstitials, both being expected to exist with a factor of two differing contents in the two samples.

In order to describe the formation of the 155 K process in terms of the 1IM, the simplest feasible trapping centres for C interstitials, would be small clusters of, e.g., V_1C_1 or residual I_nC_1 -type, which had formed in, or below, Stage III. As a result of C trapping a series of higher-order complexes would be expected to develop, for example of the type C_2V_1 , C_3V_1 , ..., C_nV_1 . Such higher-order complexes, however, are not only less likely to produce such well-defined, simple Debye-type relaxations, as the one occurring at 155 K (item c. i. β) but, moreover, are also incompatible with the observed 4:1 amplitude ratio in the two alloys and hence with their reaction kinetics both in the C-Stage and in and below Stage III (item c.iii [220]).

The 2IM, however, in contrast to the 1IM, even in the temperature range of the C-Stage, is still able to offer an elementary, *immobile*, lattice defect, namely the monovacancy, as trapping centre for C interstitials, thereby allowing the formation of a new, simple, anisotropic defect configuration, i.e. the C_1V_1 pair.¹⁾ Evidently, the formation of these complexes is governed by second-order reaction kinetics, cf. Table 11, [220] so that the occurrence of the 4:1 amplitude ratio for the 155 K peak is only a natural consequence of the fact that the two respective alloys differ, as discussed above, by a factor of two in both C and monovacancy content (Figs. 43, 44; cf. item c).

The additional observation that the 155 K peak appears with comparable strength in the two equally lower C-charged, but differently e^- -irradiated samples (Figs. 45, 46) is also compatible with the bi-molecular reaction discussed in the C-Stage. One has only to assume that, in both alloys, the concentration of one reaction partner is always reduced by such an amount as to allow comparable probabilities for pair reaction. Inspection of the respective recovery spectra shows (Figs. 45, 46) that, due to the relatively small C content, only reduced interstitial trapping takes place during anneal in Stages I and II. Nevertheless, the amplitude of the Stage III relaxation in the higher irradiated sample exceeds that of the lower irradiated one by a factor of about 5.

¹⁾ Similarly, in quenched α -Fe the occurrence of a RRR recovery step near 380 K has been attributed to the precipitation of thermally *mobilized* C-interstitials at still *immobile* vacancies [224].

Table 11

Best values of parameters of reaction kinetics in **FeC**, as determined from numerical analysis of all important processes indicated in Figs. 43a, b and 45a, b [220]. The following notations are used: central annealing temperature of processes (T), reaction order (γ), activation enthalpy (Q), effective reaction constant ($K_{1,2}^0$, cf. [220, 221])

type of reaction	temperature T (K)	parameters	characterization of specimens by their C content (at ppm)		
			100	50	25
precipitation of C	320	γ	1	1	1
		Q (eV) K_1^0 (10^8 s $^{-1}$)	0.82 ± 0.04 $10^{1.44 \pm 1}$	0.82 ± 0.04 $10^{1.3 \pm 1}$	0.82 ± 0.04 $10^{1.35 \pm 1}$
	470	γ	1		
		Q (eV) K_1^0 (10^8 s $^{-1}$)	1.26 ± 0.04 $10^{1.35 \pm 0.5}$		
release of C	<550	γ		1	1
		Q (eV) K_1^0 (10^8 s $^{-1}$)		1.28 ± 0.04 $10^{\pm 0.5}$	1.26 ± 0.04 $10^{1 \pm 0.5}$
	>550	γ			1
		Q (eV) K_1^0 (10^8 s $^{-1}$)			1.54 ± 0.04 $10^{2.7 \pm 1}$
155 K process formation	320	γ	2	2	2
		Q (eV) K_2^0 (10^8 s $^{-1}$)	0.84 ± 0.04 1.2	0.84 ± 0.04 1.1	0.83 ± 0.04 1.1
dissociation	350	γ	1	1	1
		Q (eV) K_1^0 (10^8 s $^{-1}$)	0.95 ± 0.04 $10^{2.15}$	0.95 ± 0.04 $10^{2.2}$	0.93 ± 0.04 $10^{2.3}$
325 K process decay	400	γ	2		
		Q (eV) K_2^0 (10^8 s $^{-1}$)	1.1 ± 0.04 $10^{0.5 \pm 1}$		
18 K process formation	450	γ	2		
		Q (eV) K_2^0 (10^8 s $^{-1}$)	1.26 ± 0.04 $10^{1.7 \pm 0.05}$		
dissociation	530	γ	1		1
		Q (eV) K_1^0 (10^8 s $^{-1}$)	1.32 ± 0.04 $10^{0.84 \pm 0.5}$		1.32 ± 0.4 $10^{1.25 \pm 0.5}$

This result is incompatible with the 1IM since, from the similar interstitial clustering observed in Stages I and II, we would expect also comparable contents of vacancies to survive in the two samples – by assuming the surplus of Frenkel pairs in the stronger irradiated specimen to become reduced, via direct annihilation of interstitials at vacancies in Stages I and II, to the level of the less irradiated sample. Consequently, the residual vacancies in both specimens upon migration in Stage III, should give rise to comparable MAE amplitudes.

In terms of the 2IM, however, this difference of the relaxation amplitudes in Stage III is explained by assuming that during irradiation of the high-dose sample, a correspondingly greater number of crowdions become athermally converted into dumb-bells. Consequently, in this alloy a greater number of interstitials start to migrate in Stage III, giving rise to the increased 200 K amplitude, which on its decay, in turn, induces further

reactions with other lattice defects. Such possible reactions include trapping of intrinsic interstitials at C-sites – giving rise to satellite relaxations at 215 and 170 K – and at residual interstitial clusters, i.e. at the 125 K complex which thereby transforms into the modified configuration with the respective peak temperature shifted to 115 K.

In view of these reactions, one may assume that the free C atom content in the higher-irradiated sample is reduced, due to increased interstitial trapping in Stage III, to about the level of the surviving monovacancies in the low-irradiated sample. Under this aspect, in the C-Stage, similar numbers of C_1V_1 clusters are expected to develop in both alloys by trapping of C at immobile vacancies. Assuming C-trapping at $T_a \geq 300$ K in the low-dose irradiated alloy to occur mainly at monovacancies, the concentration of vacancies contributing to the assumed V_1C_1 relaxation at 155 K may be estimated, from the corresponding reduction of the C Richter MAE of $\approx 1\%$ (Fig. 45b), to be about 5 at ppm [216]. This is in reasonable agreement with the vacancy concentrations expected above Stage III (Table 9). In the high-dose irradiated alloy both the stronger C precipitation and the rather small amplitude of the 155 K relaxation suggest that mobile C interstitials only react to a lesser extent with monovacancies, thereby forming simple 155 K clusters of C_1V_1 -type, whereas to a larger extent, C is expected to be trapped at residual interstitial type complexes dating from earlier recovery stages, thereby forming also, possibly, immobile clusters.

On anneal at only slightly higher temperatures, the 155 K relaxation recovers, being followed by a minor peak at 325 K which, again, appears with comparable amplitudes in both alloys. This secondary process may be identified as being due to a reaction product between the constituents of the de-stabilized 155 K (C_1V_1) complexes, e.g., in the form of C_2V_1 clusters.

e) Stage IV. During annealing in this temperature range ($T_a \geq 450$ K), a pronounced simple Debye-type relaxation process develops at 18 K (Fig. 49c). Both its high formation temperature and distinct, simple reorientation type are atypical for a higher-order V_1C_n complex ($n > 2$), as might be expected to result from continued C trapping at primary V_1C_1 or V_1C_2 clusters formed in the C-Stage (Figs. 43, 45). All features of this relaxation are strongly indicative of a further, simple defect configuration which, on account of its low peak temperature, is able to reorientate its anisotropy axis with the utmost ease (Table 10).

Only the 2IM is still able to offer, at this stage, another simple defect configuration which has not yet been invoked during the preceding anneal. This is the V_2C_1 cluster which may have formed by trapping of thermally activated vacancies at V_1C_1 (155 K) or de-stabilized V_1C_2 (325 K) complexes [7]. This reaction is in agreement with the thermal overlap between the recovery of the processes at 155 and 325 K and the formation of the 18 K relaxation (Figs. 43, 45). Moreover, this configuration is expected to be sufficiently elementary to exhibit both the anisotropy and ease of reorientation which characterize the 18 K relaxation.

The concept of a V_2C_1 complex formation in Stage IV is further supported by an analysis of the reaction kinetics of the 18 K process [220], Table 11. Its development is found to be governed by an activation enthalpy of 1.26 eV, which agrees fairly well with the migration enthalpy of monovacancies as predicted by the 2IM [116, 132]. Moreover, the observed reaction order, $\gamma = 2$, is in agreement with comparable concentrations of both reaction partners, i.e. monovacancies and C_1V_1 clusters. The 18 K relaxation recovers with an activation enthalpy of 1.32 eV and obeys first-order kinetics. This indi-

cates thermal dissociation of the corresponding cluster with an enthalpy composed of the binding enthalpy of the complex, H_{CV}^B , and the migration enthalpy of its most mobile partner, H_{MP}^M , according to the relation:

$$H_{CV}^{Diss} = H_{CV}^B + H_{MP}^M. \quad (7.1)$$

Our discussion so far has clearly shown that the most mobile partner is the C interstitial, with $Q = 0.84$ eV (Table 10, Section 3.3, Fig. 5) [6 to 8, 225, 226]. The binding enthalpy of 0.48 eV, determined in this manner for the 18 K process, is typical of the order of magnitude of binding enthalpies ($0.1 \text{ eV} < H_B < 0.65 \text{ eV}$) of vacancy–impurity interstitial complexes as obtained from analyses of various C- and N-charged α -Fe systems [67, 68, 219 to 221, 227 to 229].

Table 11 presents a concise compilation of the process parameters of all reactions observed during the precipitation and subsequent re-solution of C in e^- -irradiated **FeC** [220].

7.3.1.3 MAE in n-irradiated FeC

In comparison with e^- -irradiation, far less is known about the annealing behaviour of magnetic relaxations in **FeC** following n-irradiation. In fact, only two sets of data exist on n-irradiated samples which cover a sufficiently wide temperature range (Figs. 47, 48). These measurements were performed by two groups using either bridge [90, 91, 223] or LC-oscillator techniques (Section 3), [94]. The MAE spectra obtained by various authors on different **FeC** systems yield consistent results with respect to most parameters such as peak temperatures, activation enthalpies, etc. Only the absolute peak heights of the various processes are sometimes found to differ; these, however, depend on the individual sample geometry and sensitivity of the measuring system employed. Thus, from comparison of the spectra in n-irradiated **FeC** the following conclusions may be drawn:

a) Stage I. As in the e^- -irradiated alloys, the low-temperature spectra are dominated by the rapid decay of a huge relaxation peak at 110 K. This is accompanied by the growth of further processes at 53, 84 and 125 K (Figs. 47, 48). Unlike in e^- -irradiated systems, however, these latter processes are already present with appreciable amplitudes during a first measuring pass, thus indicating their athermal formation during irradiation. By analogy with the previous interpretation, these secondary processes are attributed to small clusters formed from either intrinsic interstitials and impurity atoms (53, 84 K) or solely intrinsic interstitials (125 K), i.e. of I_2 -type.

b) Stage II. On first inspection, the recovery which occurs in this temperature range appears very similar to that in the other Fe systems (Figs. 47, 48) and is characterized by: (i) disappearance of some minor processes which can be resolved more distinctly in the low-dose sample (Fig. 47), (ii) growth of some peaks at the expense of others, e.g. the one at 81/84 K concomitantly with the decay of those at 103/110 K and 116/125 K, (iii) transformation of primary into secondary processes, for example those at 135 and 176 K which result from the decay of the relaxations at 81, 116 K and possibly 156 K (Fig. 47). Closer inspection, however, reveals that the amplitudes of the processes near 84 and 125 K exceed those in e^- -irradiated alloys. This same phenomenon is also observed in both n- and e^- -irradiated **FeN** and will be discussed in more detail in Section 7.3.2.

c) Stage III and the C-migration stage. The decay of the Stage III relaxation is accompanied by the development of a series of satellite processes (Figs. 47, 48). The most promi-

nent of them (at 215 (203) and 190 (176) K), initially decrease but then re-grow in the C-migration stage, together with low-temperature processes, especially the one which transforms from 107 to 115 K (Fig. 48). In the C-Stage the formation of the important process at 155 (147.7) K, cf. Figs. 47, 48, is again observed, being followed, upon further anneal, by the 320 (298) K relaxation. However, in contrast to the e^- -irradiated samples, no conclusive interpretation of these processes is possible, since no additional measurements exist on related systems with systematically varied C concentrations and/or irradiation doses. Following the analysis of e^- -irradiated alloys, these processes are associated with reorientations of C_1V_1 (155 K) and C_2V_1 (320 K) complexes (cf. Section 7.3.1.2, item d).

Mensch et al. [91, 223], who employed *both IF and MAE*, gave a different interpretation of these processes on the basis of the following assumptions: (i) within the family of possible C_1V_1 complexes, the C_1V_1 complex should be regarded as the one of highest anisotropy and stability. (ii) Since only the 320 K process appears in *both MAE and IF* – the 150 K process being most resolved in IF – the former one is identified with the C_1V_1 (C–X) configuration. (iii) Following these arguments, the 155 K MAE is associated with a higher-order defect configuration of reduced elastic anisotropy (cf. Section 7.3.1.2), resulting from trapping of mobile C at residual mixed C–intrinsic interstitial clusters of the type I_mC_n .

These assumptions and the ensuing deductions, however, are not necessarily conclusive: (i) as regards the MAE, their arguments are based on only one spectrum, obtained for a medium C-charged (140 at ppm), low-dose n-irradiated ($3 \times 10^{21} \text{ nm}^{-2}$) alloy [91], Fig. 47. Corresponding IF measurements, although being performed on some additional alloys, following either n- or e^- -irradiation [223], have not been systematically varied with respect to both impurity content and irradiation dose, as described above for e^- -irradiated FeC (Section 7.3.1.2). (ii) Thus, all that can reliably be said about n-irradiated FeC is that the elastic anisotropy of the 155 K defect is, possibly, below the detection limit of the IF, whereas the magnetic anisotropy of this defect is strong enough to induce a pronounced MAE. Such a behaviour seems well compatible with the simple C–vacancy configuration of C_1V_1 type, as discussed above which, indeed, is feasible to be mechanically less anisotropic than, say, mixed C–intrinsic interstitial complexes. (iii) On the other hand, higher-order C_1V_1 complexes may be mechanically more anisotropic and thus contribute to the IF spectra, for example by giving rise to the 320 K relaxation, which we associated above with C_2V_1 complexes.

To summarize, our detailed analysis of reaction kinetics in e^- -irradiated FeC clearly favours the assumption of simple C_1V_1 clusters, rather than higher-order impurity–intrinsic vacancy (or interstitial) complexes, as origins of the 155 K relaxation. As concerns the 320 K process, the analysis of e^- -irradiated FeC is more compatible with the assumption of a C_2V_1 than with the C_1V_1 cluster proposed from IF measurements.

d) *Stage IV.* The formation kinetics of the 18 K process are found to be somewhat modified as compared to the situation in e^- -irradiated FeC: in a high-temperature, n-irradiated alloy (Fig. 48) [222], this relaxation starts to grow, beginning from a constant level, during anneal between 320 and 440 K. In the low-temperature, n-irradiated alloy, the growth of the 18 K peak occurs at still lower temperatures, $T_a \geq 320 \text{ K}$, and is evidently correlated with the recovery of the 155 K relaxation [91] (Fig. 47).

Several arguments may be advanced in order to explain these different formation kinetics in e^- - and n-irradiated FeC: (i) depending on the type of irradiation, modified defect structures are introduced into the lattice. Thus, following n-irradiation, higher

concentrations of intrinsic defect clusters, including divacancies are expected to be present. In terms of the model proposed in Section 7.3.1.2, at temperatures near 300 K, migrating C interstitials may be trapped at, still immobilized, divacancies, thereby forming the C_1V_2 complexes which, above, have been attributed to the 18 K relaxation (cf. Section 7.3.1.2). (ii) Following n-irradiation, vacancies may be assumed to migrate with reduced activation enthalpies within the heavier radiation-damaged lattice, particularly in the neighbourhood of depleted zones, thereby giving rise to an accelerated formation of the 18 K peak. (iii) In a previous discussion [7] it has also been argued that the accelerated formation of the 18 K relaxation may be due to an increased Si content, particularly in the low-dose n-irradiated sample (Table 1). As discussed in Section 6.3.3.2, in irradiated **FeSi** alloys, after annealing near 300 K, a characteristic relaxation develops at about the same temperature (17 K). The corresponding defect configuration has been associated with anisotropic Si_1V_1 clusters, resulting from trapping of mobile Si at immobile monovacancies [7, 74, 150]. Unfortunately, in the low-dose n-irradiated specimen, annealing has not been continued to temperatures above 400 K (Fig. 47), where further growth of the 18 K relaxation would have been expected, due to vacancy migration, as it was observed in e^- -irradiated **FeC**.

7.3.2 MAE spectra in irradiated N-charged α -Fe

The first investigations of n-irradiated **FeN** systems are due to Stanley [228], using IF; and to Wuttig et al. [218], who applied the technique of magnetic disaccommodation. These authors were mainly interested in the mechanism of N precipitation in irradiated **FeN** which is induced above 255 K by trapping of migrating N interstitials at intrinsic defects. Details of the precipitation kinetics in unirradiated **FeN** have recently been resolved by means of the MAE [219] and compared with former results, obtained by alternative techniques, concerning the problem of N clustering in **FeN**. Here, as in the preceding sections, we are interested in the reaction kinetics within the complete family of MAE spectra, extending over the temperature range $4\text{ K} < T_a < 650\text{ K}$, within which N precipitation is only one amongst a range of other processes.

7.3.2.1 Characteristics of the recovery spectra in **FeN**

As in the case of **FeC** (Section 7.3.1.1), we are able to distinguish between specific defect types which contribute to the MAE spectra of **FeN** (Figs. 50, 51):

a) *Primary defects* of intrinsic or impurity type: these give rise to simple reorientation MAEs at 110 K (Stage I: self-interstitials), at 200 K (Stage III: second self-interstitial type (2IM)), and at 255 K (N Richter MAE, initiating the N precipitation stage).

b) *Small interstitial clusters*: these arise due to trapping of Stage I interstitials in the temperature range $110\text{ K} < T_a < 200\text{ K}$ (Stage II), of both purely intrinsic (125 K) and mixed intrinsic-impurity interstitial composition (50, 84 K). Recovery in Stage III is accompanied by the formation of satellite processes, related to the initial Stage III relaxation, at 210/220 and 145 K, Fig. 51.

c) *Mixed nitrogen clusters*: these are formed at $T_a > 255\text{ K}$ (N-Stage) by trapping of migrating N at intrinsic defects and give rise to MAEs at 295, 310, 370 and 425 K (Figs. 51a, c).

d) *Release of N* at temperatures $T_a > 400\text{ K}$ (Stage IV): this is due to de-stabilization of mixed clusters of type c), thereby causing a re-growth of the N Richter MAE in less-

Fig. 50. Stepwise annealing sequence of a low-temperature, e^- -irradiated ($9 \times 10^{22} e^- m^{-2}$) **FeN** alloy, containing 120 at ppm N [214]. This annealing programme, similar to that of Fig. 42, in the case of **FeC**, may be taken as representative for all other **FeN** alloys, ($t_1 = 1$ s, $t_2 = 180$ s)

damaged specimens (Figs. 51a, b). In the heavier-damaged specimen (Fig. 51c), accelerated dissociation of the most stable 425 K cluster is indicated by a shift of its recovery to lower temperatures by about 70 K (cf. Fig. 51a, c), [219].

7.3.2.2 MAEs in e^- - and n-irradiated **FeN**

a) Basic reactions of Stage I interstitials. Both the strength of the primary 110 K process and its annealing behaviour point to different defect production mechanisms during e^- - and n-irradiation (Section

5.1). The amplitude of this process is found to be largest after e^- -irradiation, but appears with more or less reduced strength following high- or low-dose n-irradiation, respectively (Figs. 51a to c). On anneal of the e^- -irradiated specimen, secondary, previously absent processes appear at 84, 125 and 50 K. This is in contrast to n-irradiation, where these processes are present immediately after irradiation, thus indicating their athermal formation. The recovery of the 110 K relaxation and its influence on these secondary processes may be most consistently described in terms of the crowdion model discussed in Section 4.1 (Fig. 7). After thermal dissociation of the initial configuration, i.e., a crowdion trapped at an intrinsic off-line defect and exhibiting the reorientation-like 110 K relaxation, the released crowdions may undergo the reactions described in Section 4.1.

- (i) Annihilation with on-line vacancies.
- (ii) Stronger trapping at an off-line defect of either intrinsic or impurity type, i.e. interstitially dissolved N, thereby forming anisotropic configurations of somewhat elevated reorientation enthalpies.
- (iii) Strong trapping at an impurity-type defect, thereby immobilizing the crowdion until it may convert, at higher temperatures, into either a three-dimensionally reorientating complex or, after release from its trap, undergo free dumb-bell migration.
- (iv) As a special case of (iii), crowdion immobilization may be achieved also by spontaneous conversion into the dumb-bell configuration which, in turn, becomes mobile only in Stage III.

Fig. 51. Recovery spectra of the relaxation processes, characterized by their peak temperatures, as constructed from their respective annealing sequences (Fig. 50). a) e^- -irradiated ($9 \times 10^{22} \text{ e}^- \text{ m}^{-2}$), charged to 120 at ppm N. b) Low-dose (10^{21} n m^{-2}) and c) high-dose ($5 \times 10^{22} \text{ n m}^{-2}$) n-irradiated alloys, charged to 120 at ppm N [214]. Similarly as in Fig. 43 the pre-irradiation amplitudes of the N-Richter MAE (255 K) are indicated, ($t_1 = 1 \text{ s}$, $t_2 = 180 \text{ s}$)

Table 12

Compilation of relevant parameters of the **FeN** alloys. The Fe source material for these experiments was identical with that given in Table 8 under Walz [220, 221], characterized by a RRR of 1600 (cf. Table 9). All notations in this table are consistent with those used in Table 9, the given data have been determined in [214, 221]

Φt (10^{22} m^{-2})		c_{FP} (at ppm)		c_{N} (at ppm)	$c_{\text{FP}}/c_{\text{N}}$
e^-	n	ass-irr.	$\leq 200 \text{ K}$		($\leq 200 \text{ K}$)
9		320	60	120	0.5
	10^{-1}	28	12	120	0.1
	5	1070	500	120	4.2

b) Stage I relaxation and its satellites

(i) *The relaxations at 84 and 125 K.* The contributions of the above-mentioned reactions to the MAE spectra of **FeN** are modified by both the type and dose of the irradiation. Thus, the most complicated relaxation spectrum is observed following high-dose n-irradiation (Fig. 51c), whereas after e^- - and low-dose n-irradiation less complicated, similar spectra are found to develop (Figs. 50, 51a, b). Minor differences, however, are also observed between these latter two: as may be deduced from the strength of the 110 K relaxation and the degree of N precipitation at $T_a \geq 255 \text{ K}$ (Figs. 51a, b), the radiation-induced, overall defect concentration is greater in the e^- -irradiated specimen (Table 12). Nevertheless, after low-dose n-irradiation, the 125 K process is already well-developed in the as-irradiated state. This observation again indicates the modified defect production mechanism during n-irradiation, allowing athermal interstitial clustering, i.e. of I_2 -type, to which the 125 K relaxation has been related (Section 5.6). Accordingly, high-dose n-irradiation gives rise to an even stronger, athermally developed 125 K process (Fig. 51c).

Following e^- - and low-dose n-irradiation, the 84 K process displays comparable, moderate strength whose recovery extends over a wide temperature range up to the end of Stage II (Figs. 51a, b). High-dose n-irradiation, however, increases the amplitude of the 84 K relaxation by an order of magnitude, of which considerable part has been formed athermally already during irradiation (Fig. 51c). This indicates that during high-dose n-irradiation, a drastically increased number of crowdions will be able to interact with N atoms, for example via reactions mentioned under item a)–(ii), to form the larger number of Fe_1N_1 interstitial clusters.

(ii) *The 50 K relaxation.* Whereas after e^- - and low-dose n-irradiation this process appears with reduced strength, in high-dose n-irradiated samples it is strongly developed immediately after irradiation. During annealing in Stage I this process grows at the expense of both the 110 K and the 84 K relaxation (Fig. 51c). This behaviour would be compatible with the trapping of an additional self-interstitial, released from the destabilized 110 K configuration, at an Fe_1N_1 interstitial cluster (84 K), thereby producing mixed Fe_2N_1 complexes. For a given N concentration, this reaction rate is proportional to the self-interstitial content and will thus occur preferentially following high-dose n-irradiation. On recovery above 120 K, probably by dissociation, the 50 and 125 K clusters support the formation of further 84 K complexes (Fig. 51c) which, in turn, recover in the temperature range of Stage III.

c) *Stage II* ($130\text{ K} < T_a < 180\text{ K}$). In this temperature range, the processes formed in Stage I exhibit further variations in amplitude which are associated with continued interstitial-type reactions with preformed clusters. Typically, in the e^- -irradiated specimen the processes at 50, 84 and 125 K have completely recovered towards the end of Stage II whereas, especially after high-dose n-irradiation, the recovery of the latter two is shifted to higher temperatures, thus overlapping with Stage III.

In addition to these peaks formed previously in Stage I, following e^- - and low-dose n-irradiation a relaxation appears at 155 K which recovers rapidly during the measurement (Figs. 51a, b). At about the same temperature (145 K), after high-dose n-irradiation, a minor, more stable relaxation develops which, during annealing in Stage III, recovers in favour of another stable process located at 135 K (Fig. 51c). Since both these processes are absent in high-purity α -Fe, we associate them with a further diatomic interstitial complex, composed of, for example, crowdions trapped at N sites. These crowdions, on further annealing, may either de-trap and subsequently recover (e^- -irradiation) or convert into dumb-bells (n-irradiation) and thereby give rise to modified relaxations (cf. Section 4.1, Fig. 51).

d) *Stage III*. The strength of the Stage III relaxation is found to depend on both type of irradiation and dose (Figs. 50, 51). In **FeN** and **FeC**, comparable 200 K amplitudes are observed following e^- -irradiation to equal doses, thus pointing to similar defect reactions in both systems (Figs. 43, 51a). Following high- or low-dose n-irradiation the strength of the Stage III relaxation is increased or decreased, respectively, by a factor of about two relative to the amplitude after e^- -irradiation (Figs. 51a to c). In contrast to **FeC**, however, no definite conclusions can be drawn from these amplitude dependences as to the type of defect migrating in Stage III. The occurrence of minor satellite relaxations at 210 K following e^- - and low-dose n-irradiation, and at 180 and 220 K, after high-dose n-irradiation (Figs. 51a to c), has its analogue in the formation of corresponding satellites during annealing in Stage I_E, where they could be unambiguously identified with trapping of self-interstitials at various types of lattice defects. Corresponding Stage III satellites, occurring also in substitutionally alloyed Fe systems (Section 6) and in **FeC** (Section 7.3.1) have been shown to be compatible with the migration of intrinsic interstitials, rather than with migrating vacancies. The adoption of this interpretation, also in the case of **FeN**, is supported by an obviously interstitial-type relaxation at 145 K (Fig. 51c), which starts to develop in Stage II ($T_a > 150\text{ K}$) and continues to grow during annealing in Stage III. If it were vacancies which migrate in Stage III, the annihilation of the corresponding 145 K interstitial-type complexes would be expected, rather than their further growth. At the onset of N migration ($T_a > 255\text{ K}$), this 145 K relaxation vanishes in favour of an apparently modified process at 135 K (Fig. 51c).

e) *N-migration stage*. During annealing in the temperature range $T_a > 260\text{ K}$, the strength of the N Richter MAE in the various samples diminishes rapidly in proportion to the radiation-induced damage. This N precipitation initiates the formation of a series of small clusters – with peak temperatures at 295, 310, 370 and 425 K – by trapping of N at immobile intrinsic defects, i.e. vacancies (Figs. 51a to c) [221]. At the end of these reactions, the remaining levels of the respective N Richter MAEs in the various systems are only little affected during further annealing up to 400 K. However, depending on the type of irradiation and dose, at higher temperatures ($T_a > 400\text{ K}$) a different behaviour is observed: In the e^- - and low-dose n-irradiated samples, the Richter MAE

Fig. 52. Least-squares fitting of the important relaxation processes occurring in the MAE spectra of irradiated **FeN** (Figs. 50, 51) [214]: a) Satellite processes at 180 and 220 K, as observed in high-dose n-irradiated ($5 \times 10^{22} \text{ n m}^{-2}$) **FeN** following anneal in Stage III. b) 310 K relaxation, together with residual N Richter MAE, in e^- -irradiated ($9 \times 10^{22} \text{ e}^- \text{ m}^{-2}$) **FeN** after annealing at 340 K. c) 425 K relaxation, observed in alloy b) following anneal at 470 K. The measuring times are as indicated in Fig. 49, ($t_1 = 1 \text{ s}$, $t_2 = 180 \text{ s}$)

starts to recover, presumably due to the release of N from the thermally de-stabilized clusters which had been formed in the N-Stage. In contrast, in the high-dose n-irradiated sample, the N Richter MAE becomes further reduced, thus indicating continued precipitation of released N at extended, radiation-induced sinks, such as, e.g., depleted zones.

The identification of both the formation sequence and composition of these small N-Stage clusters is complicated, since their relaxation temperatures are well *above* their respective formation temperatures. This is in contrast to the situation in **FeC**, where the reversed location of relaxations and corresponding formation stages facilitates the iden-

Fig. 53. Precipitation and re-solution of N in a) supersaturated ($c_N = 320$ at ppm) and b) dilute ($c_N = 120$ at ppm) unirradiated **FeN**, as monitored by the N Richter MAE; both effects (a) and (b) are reversible [219, 221], ($t_1 = 1$ s, $t_2 = 180$ s)

tification of respective clusters (Section 7.3.1). However, our above discussion of defect reactions in Stage III, together with further analogies between the recovery of **FeC**, and **FeN**, support the view that monovacancies, indeed, do act as traps in the formation of these N-stage clusters [214, 219, 221]. The most prominent of these related N-stage relaxations is the one occurring at 425 K (Figs. 51, 52c). In view of both the strength and obvious reorientation type of this relaxation, it might tentatively be associated with the most elementary defect configuration of, i.e., N_1V_1 type. However, since the forma-

Fig. 54. a) Extended relaxation zone, observed in supersaturated ($c_N = 320$ at ppm), unirradiated **FeN** after precipitation of the α'' -phase (Fe_8N) [219]. Symbols correspond to measured data, lines represent least-squares approximations to measurements by means of superposition of the processes shown in b): I corresponds to a long-range diffusion ($H^D = 0.92$ eV, $\tau_{0,1} = 10^{-9}$ s), II to reorientation ($H^R = 1.36$ eV, $\tau_{0,2} = 5 \times 10^{-15}$ s) of N interstitials and $\sigma(T)$ is the temperature-dependent order parameter governing the existence of the metastable nitride phase. Reference times are given in a) by $t_1 = 1$ s, $t_2 = 2$ s (1), 10 s (2), 60 s (3), 180 s (4) and in b) by $t_1 = 1$ s, $t_2 = 180$ s

Table 13

Compilation of activation parameters of principal processes occurring in the MAE spectra of e^- - and n-irradiated FeN [219, 221]. The same notations are used as in Table 10

T_p (K)	T_a (K)	Q (eV)	$\pm \Delta Q$ (eV)	τ_0 (10^{-13} s)
50	150	0.13 ₈	0.06	1.6
84	165	0.24 ₅	0.07	2.6×10^{-1}
110	100	0.30	0.03	3.0
125	180	0.35	0.02	6.3
145	225	0.40	0.001	1.2
135	330	0.42	0.01	6.0×10^{-2}
200	195	0.56	0.02	4.0
180	225	0.53	0.04	4.2×10^{-1}
220	225	0.64	0.04	4.2×10^{-1}
255	N-MAE	0.76	0.04	2.0×10^{-1}
295	310	0.87	0.04	1.5×10^{-1}
310	340	0.94	0.08	1.0×10^{-1}
370	—	—	—	—
425	470	1.40	0.04	1.0×10^{-2}

tion of this family of relaxations starts with a transient process at 295 K, which is regarded as resulting from immediate N trapping, and is therefore assumed to be of simple N_1V_1 type, the higher temperature relaxations are associated with reaction products of further N trapping at these initial V_1N_1 clusters. Since the 295 K relaxation immediately transforms into the 310 K process (Figs. 51a, c, 52b), we tentatively associate the latter with a V_1N_2 configuration. Consequently, the higher-temperature relaxations at 370 and 425 K are identified with higher-order configurations such as V_1N_3 (370 K) and V_1N_4 (425 K) [221]. This interpretation of the 425 K process as a higher-order defect

Table 14

Best values of the reaction parameters governing the process kinetics in FeN, as determined from numerical analyses of the processes shown in Figs. 51 and 54; n (1) and n (2) correspond to high- and low-dose n-irradiation, respectively. The same notations are used as in Table 11, [221]

processes	FeN type	T (K)	γ	Q (eV)	$K_{1,2}^0$ ($10^8 s^{-1}$)
precipitation of N	e^-	300	1	0.77 ± 0.02	$10^{1.3 \pm 0.5}$
	n (1)	280	1	0.77 ± 0.02	$10^{2.3 \pm 0.5}$
	n (1)	430	1	1.17 ± 0.04	$10^{2.5 \pm 0.7}$
	n (2)	300	2	0.78 ± 0.04	$10^{\pm 0.7}$
	unirr.	390	1	0.95 ± 0.04	$10^{0.3 \pm 0.5}$
resolution of N	e^-	410	2	1.05 ± 0.04	$10^{0.4 \pm 0.7}$
	e^-	500	1	1.24 ± 0.04	$10^{0.9 \pm 0.7}$
	unirr.	470	2	1.25 ± 0.04	$10^{0.3 \pm 0.5}$
dissociation					
295 K	n (1)	340	2	0.85 ± 0.04	$10^{-1 \pm 0.7}$
310 K	e^-	420	2	1.01 ± 0.04	$10^{-0.7 \pm 0.7}$
370 K	n (1)	420	2	1.09 ± 0.04	$10^{0.7 \pm 0.7}$
425 K	e^-	500	1	1.22 ± 0.04	$10^{0.5 \pm 0.7}$
	n (1)	430	1	1.17 ± 0.04	$10^{2.5 \pm 0.7}$

configuration is in agreement with corresponding relaxation characteristics observed in unirradiated **FeN** [219] and irradiated **FeC** [220]:

(i) After precipitation of the α'' -phase (Fe_8N) in supersaturated, unirradiated **FeN** (Fig. 53), an extended relaxation zone is observed in the temperature range $350\text{ K} < T < 480\text{ K}$ (Fig. 54). This was found to be composed of a diffusion ($H^D = 0.92\text{ eV}$, $\tau_{0,1} = 10^{-9}\text{ s}$) and a reorientation-type ($H^R = 1.36\text{ eV}$, $\tau_{0,2} = 5 \times 10^{-15}\text{ s}$) relaxation. The activation parameters of this latter process, according to Table 13, are very close to those of the 425 K relaxation. The reorientation-type process in unirradiated **FeN** has been interpreted as being composed of two reactions: a) the release and b) the subsequent jump of an N interstitial on the surface of the precipitate, thus yielding a reorientation enthalpy, H_N^R , which is composed of both binding, H_N^B , and migration, H_N^M . From the proximity between the activation parameters of this α'' - and the 425 K process, it seems feasible to assume similar relaxation mechanisms in both cases. The similarity between these two processes is reflected also by their recovery kinetics: the metastable Fe_8N phase is found to dissociate in the same temperature range ($T_a > 450\text{ K}$) with reaction parameters similar to those of the 425 K clusters in e^- -irradiated **FeN** (Fig. 52, Table 14).

(ii) The association of the 425 K relaxation with a higher-order defect configuration is also in agreement with the more easily recognizable situation in **FeC**, where the simpler clusters were found to relax at lower temperatures (Section 7.3.1) [7, 220].

Based on these arguments, the following correlation between peak temperatures and defect configurations of higher-temperature clusters in **FeN** has been proposed [221]: 295 K (V_1N_1), 310 K (V_1N_2), 370 K (V_1N_3), 425 K (V_1N_4).

The reaction parameters which control the kinetics of formation ($T_a > 260\text{ K}$) and dissociation ($T_a > 400\text{ K}$) of these clusters have been determined previously [221] and are compiled in Table 14. Their binding enthalpies, H_{VN}^B , have been obtained – similarly as in the case of **FeC**, cf. Sect. 7.3.2.1 d – as the difference between the numerically determined dissociation enthalpy, H_{VN}^D , and the migration enthalpy, H_{MP}^M , of the more mobile partner in the cluster,

$$H_{\text{VN}}^B = H_{\text{VN}}^D - H_{\text{MP}}^M. \quad (7.2)$$

Yielding values within the range $0.09\text{ eV} < H_B < 0.5\text{ eV}$ which compare well with the data determined by other means [68, 221, 225, 226].

As, according to our analysis, these clusters have been formed by trapping of migrating N at immobile, elementary intrinsic defects, it is clear that in these clusters, N interstitials are the constituents with the lowest activation enthalpies of $H_{\text{MP}}^M = H_N^M = 0.76\text{ eV}$ (Table 13), [221, 225, 226]. Since our analysis suggests to identify the initial, immobile formation centres for these mixed N-type clusters with monovacancies, the migration enthalpy of these vacancies, H_V^M , must be greater than 0.76 eV – in the analogous case of **FeC** we have deduced that H_V^M must be greater than 0.84 eV , cf. Sect. 7.3.1.2 d, 7.4. This value, however, which is considerably greater than the activation enthalpy of the intrinsic defect which becomes mobile in Stage III, allows us to exclude vacancy migration in Stage III.

f) *Stage IV.* During annealing at $T_a > 450\text{ K}$, we observe the dissolution of all mixed clusters which were formed during the precipitation of N above 260 K. The de-stabilization of these clusters may be initiated by thermal activation of their nuclei, i.e. monovacancies, thereby allowing the more mobile N interstitials to break off and to escape

rapidly. The observed temperature range of de-stabilization ($400\text{ K} < T_a < 600\text{ K}$) agrees with Stage IV of vacancy migration, in terms of the 2IM. In the high-dose, n-irradiated alloy the accelerated dissociation of the 425 K cluster (Fig. 51c) is ascribed to the presence of surviving, radiation-induced extended sinks, i.e., depleted zones, which may produce attractive gradients for interstitial migration, thereby further reducing the stability of mixed clusters. Accordingly, converse reactions of released N interstitials are observed in the differently damaged specimens:

Following e^- - and low-dose n-irradiation, re-solution of N in the matrix is indicated by a strong increase of the Richter MAE which almost attains its original strength prior to irradiation (Fig. 51a). In contrast to this behaviour, after high-dose n-irradiation, all N is precipitated at additional intrinsic sinks, as may be deduced from the almost complete decay of the N Richter MAE during annealing up to 500 K (Fig. 51c).

7.4 Summary

(i) The most informative MAE spectra are obtained from the interstitial alloys **FeC** and **FeN**, rather than from high-purity or substitutional alloys. This is due to the fact that in alloys with impurity interstitials, a greater number of different processes is contributing to the MAE spectra: in addition to the relaxations induced by *mobile intrinsic* defects, which are characteristic of all Fe systems, additional processes occur which result from interactions between *mobile impurity interstitials* and intrinsic defects. This increased number of defect reactions gives rise to more varied MAE spectra which, in turn, enable us to deduce even finer details of the corresponding relaxation mechanisms.

(ii) The most systematic investigations have been performed on **FeC**: these include both variations of radiation doses for given C contents and variations of the C content under given irradiation conditions. Detailed analyses of the reaction kinetics reveal clearly that the relaxation in Stage III is incompatible with vacancy migration. One major argument in this sense is deduced from the fact that various relaxation processes of, indubitably, interstitial-type – i.e., those localized at 50/55 K, 125/115 K and 170 K, having been formed in Stages I and II – experience further growth in Stage III and the ensuing temperature range, instead of becoming dissolved due to reactions with their anti-defects, i.e. vacancies, as to be expected in terms of the 1IM.

(iii) This conclusion is corroborated by a detailed analysis of the processes occurring in the C migration-stage at $T_a > 265\text{ K}$. The key process of this relaxation family gives rise to a pronounced peak at 155 K. Both its pure Debye character and its specific reaction kinetics point to a very simple defect configuration, i.e., of C_1V_1 type, which has been formed by trapping of *mobile C* at *immobile monovacancies*.

(iv) Above the C-Stage, continued precipitation of C at nuclei of intrinsic defects, i.e., monovacancies, leads to the formation of C_iV_1 -type complexes ($i \geq 1$). Only the smaller ones of these give rise to MAEs, whereas the larger ones remain immobile. Reaction analyses of these configurations lead to dissociation enthalpies within the range of $0.95\text{ eV} \leq H_{CV}^D \leq 1.6\text{ eV}$ and to binding enthalpies between $0.1\text{ eV} \leq H_{CV}^B \leq 0.65\text{ eV}$, cf. [7, 220]. The lower of these values have been shown to be representative of small complexes, whereas the higher values are typical of more extended C_iV_k clusters, with $i \geq 3$; $k \geq 1$. Since MAE experiments reveal directly that C interstitials, rather than monovacancies, are the more mobile constituents of these clusters, the migration enthalpy of vacancies must be greater than that of C interstitials, i.e., $H_V^M > 0.84\text{ eV}$. This result, in turn, excludes migration of monovacancies in Stage III,

since the defects migrating there are characterized by activation enthalpies of only $H^M \leq 0.56$ eV.

(v) The relatively high formation enthalpy (1.26 eV) of a second *crucial process* in FeC, i.e. a characteristic Debye process which develops in Stage IV ($T_a > 500$ K) at 18 K, is identified, in terms of the 2IM, with the migration of monovacancies. During their migration, these vacancies are assumed to react with residual C_1V_1 complexes, thereby forming the easily-reorientable 18 K configuration of, as deduced, C_1V_2 type.

(vi) These rather direct deductions, obtained in FeC from the analysis of defect reactions in and above Stage III, are fully supported by the investigation of corresponding N-vacancy reactions in FeN. Here, too, clustering and dissociation is found to be governed by the smaller migration enthalpy of N, $H_N^M = 0.76$ eV, and the binding enthalpies of the various complexes ($0.09 \text{ eV} < H_{NV}^B < 0.5 \text{ eV}$). Thus, from these analyses, too, the vacancy must be excluded as possible Stage III defect, since its estimated activation enthalpy, $H_V^M > 0.76$ eV is, once more, considerably higher than the values of the former one, $H_{III}^M \leq 0.56$ eV.

8. Recovery Mechanisms in α -Fe as Deduced from Non-MAE Techniques

In the past, experimental results, even when obtained by similar techniques on comparable Fe systems, have been frequently interpreted in terms of controversial recovery models. Closer inspection reveals, however, as pointed out already in Section 5.6, that most of these other, *non-relaxation* techniques — such as i.e., positron annihilation (PA), residual resistivity (RRR), etc. — lack the high selective power, necessary to definitely discriminate between the controversial 1IM and 2IM models. In this situation many authors found it convenient and sufficient to interpret their relatively restricted — as compared to MAE spectroscopy — data sets in terms of the less detailed 1IM and, there-upon, often forgot that this deliberate choice was, by itself, not as yet a firm proof for the uniqueness of the chosen model.

The formal basis for this preference of the 1IM recovery model, in the eyes of its adherents, is provided by the pretendedly unassailable interpretation of the PA-revealed annealing behaviour in e^- -irradiated α -Fe. Since this technique is characterized by a selective sensitivity to vacancy-induced variations of positron lifetimes in the lattice, corresponding lifetime alterations occurring in Stage III of e^- -irradiated high-purity α -Fe have been interpreted in terms of *vacancy migration* and subsequent *vacancy-induced defect reactions*.

For a correct understanding of the recovery mechanisms in α -Fe it is therefore of paramount importance to check the reliability of these PA-based arguments. To this purpose we shall revise in the following the relevance of those PA studies which widely are regarded as protagonists in favour of the 1IM.

8.1 Positron annihilation in e^- -irradiated, pure α -Fe

8.1.1 Different types of positron trapping centres

In low-temperature e^- -irradiated pure α -Fe, during annealing up to 200 K, an increased positron lifetime, τ_t , of about 175×10^{-12} s (175 ps) is observed, as compared to the lower value, τ_b , of only 110 ps in well-annealed α -Fe, cf. Fig. 55. This difference is ex-

Fig. 55. Typical PA annealing spectrum of pure, low-temperature e^- -irradiated α -Fe, showing bifurcation and evolution of the various positron lifetime parameters ($\circ$ increased lifetime, τ_i , due to trapping of positrons at irradiation-induced vacancies; $\times$ short lifetime component, τ_1 ; ∇ long lifetime component, τ_2 ; τ_f , lifetime of free, thermalized positrons in the undisturbed lattice, I , overall intensity) [175, 230]

plained in terms of radiation-induced *monovacancies* which, due to their reduced electron density, are locations of diminished annihilation between positrons and free electrons, thereby contributing to increased positron lifetimes [175, 230].

Accordingly, the occurrence of two lifetime components upon annealing in Stage III (200 K), $\tau_1 \approx 110$ ps and $\tau_2 > 200$ ps (Fig. 55), has been assigned, respectively, to two concomitantly occurring reactions: (i) *annihilation of monovacancies* – leading again to the initial value τ_f of the undisturbed lattice – and (ii) *clustering of monovacancies* giving rise, due to enhanced shielding of positrons against spontaneous annihilation, to further increased lifetimes.

Although this concept may provide a basically correct description of the annealing mechanisms in Stage III – as far as they are detectable by means of PA – the subsequent conclusion, on the other hand, that *vacancies* necessarily also play the *active* part in these processes must be regarded as premature, since: (i) annihilation between vacancies and interstitials – giving rise to the short-time component, τ_1 – may be achieved *equally well* by means of a) *either vacancies* migrating to immobile interstitial-type anti-defects (1IM) or b), reversely, by means of *mobile interstitials* recombining with immobile vacancies (2IM). (ii) The formation of extended vacancy complexes is

Fig. 56. Model for the nucleation of {001} interstitial dislocation loops, being accompanied by the formation of supervacancies, in a b.c.c. metal [145]

Fig. 57. Average number $\langle n \rangle$ of interstitials agglomerated in clusters, which have formed in α -Fe after low-temperature neutron irradiation ($\triangle 2 \times 10^{18}$, $\bullet 3 \times 10^{18}$ n cm $^{-2}$) and subsequent annealing, [231]

not at all confined to the process of *vacancy clustering* but, instead, may be achieved as well by means of *interstitial clustering*, as pointed out by Frank et al. [145]. In terms of their model, interstitials may be located on the cube edges of the unit cell (cf. Fig. 56), thereby enabling the transformation of a tri-interstitial complex into a “supervacancy”, i.e., into an interstitial configuration enclosing a free volume which is larger than that of a normal monovacancy. Once this nucleus has been formed, each trapping of *one* further interstitial increases the number of agglomerated supervacancies by one.

The validity of Frank et al.’s. model, within the framework of the 2IM, has been supported recently by means of diffuse X-ray scattering experiments on n-irradiated, pure α -Fe [231]. In these specimens *interstitial agglomeration* has been observed to take place in Stages I and III, thereby yielding irradiation-dependent cluster sizes of up to $n \geq 3$ interstitials ($\phi \simeq 3 \times 10^{18}$ n/cm 2), cf. Fig. 57, which may be regarded as nuclei for the above mentioned supervacancy formation.

8.1.2 Positron lifetimes in the light of various models

It must be considered as a handicap that, in terms of the PA model, [174, 232], large vacancy complexes, V_n , of up to $n \geq 10$ have to be assumed in order to explain the spontaneous increase of the positron lifetime immediately after annealing in Stage III [175], cf. Fig. 58. In view of the strongly reduced defect concentration having survived

Fig. 58. Dependence of the positron lifetime τ on the number $\langle n_v \rangle$ of vacancies constituting of three-dimensional clusters in α -Fe and Al. The points represent the results of theoretical calculations [174, 232], the solid lines are drawn to indicate the general trend

up to this stage [87] – after the intense, interstitially dominated recovery processes in Stages I and II – the formation of such extended vacancy clusters in Stage III appears rather unlikely. Here again the 2IM-based supervacancy formation mechanism of Frank et al., cf. Section 8.1.1, appears as the more realistic alternative: the *already existing interstitial clusters*, I_n , having formed in preceding recovery stages, are more likely to further grow in Stage III to complexes of up to $n \geq 4$ by continued *interstitial trapping*. After transformation into supervacancies, such complexes may contribute to the spontaneous increase of the positron lifetime.

Another explanation of the lifetime growth in Stage III, avoiding the assumption of large intrinsic defect agglomerations, may be given by regarding τ_i , as observed in low-temperature e^- -irradiated α -Fe, not as the *monovacancy-specific* lifetime but rather as a *dynamic average*, τ_i^* , being established by continuous trapping and defect-induced de-trapping of positrons at vacancies [233]. This view compares well with the observation that low-temperature positron lifetimes may vary considerably in differently damaged Fe lattices, i.e., following cold-work ($\tau_i = 165$ ps [142]) or n-irradiation ($\tau_i = 140$ ps [143]), thus indicating a shift to shorter lifetimes due to increased de-trapping rates in the more damaged lattices. In terms of this latter model, the increase of the positron lifetime upon annealing in Stage III is due to the considerable overall defect recovery, causing a strong reduction of corresponding defect-induced positron de-trapping. The finally attained maximum positron lifetime, of the order of 400 ps, in this picture corresponds to the “true” – viz. free from any defect induced detrapping – lifetime of isolated monovacancies and/or small vacancy clusters, as being typically left over in e^- -irradiated α -Fe after annealing up to about 500 K (Fig. 55).

8.2 Positron annihilation in dilute, substitutional Fe alloys

As shown exemplarily in the following, PA lifetime spectra in e^- -irradiated, substitutional Fe alloys may be subdivided into two groups [142, 174, 175]: (i) Spectra which

Fig. 59. Evolution of the positron lifetime parameters τ_0 , τ_1 , τ_2 , I (same notation as in Fig. 55) upon annealing in low-temperature e^- -irradiated a) FeMn and b) FeCo, with alloyed partners of 0.04 at%, respectively, [175]

are similar to those occurring in e^- -irradiated, pure α -Fe like, for instance, those of **FeMn** and **FeCo** (Fig. 59a, b) and (ii) spectra which, in contrast to (i), are characterized by an increased persistence of the trap-dependent lifetime τ_1 (175 ps) up to temperatures, T_S , well above Stage III, cf. Fig. 60a to d with, e.g., $T_S \simeq 300$ K (**FeSi**, **FeCu**), 350 K (**FeTi**) and about 600 K in **FeSb**. At these critical temperatures, τ_1 usually becomes bifurcated into two components, τ_1 and τ_2 , of shorter and longer positron lifetime, respectively. The appearance of a *bifurcation* of the positron lifetime is a most interesting phenomenon, per se, indicating that – at whatever temperature taking place – there exists an intimate correlation between two different processes: (i) recovery of vacancies and (ii) trapping of positrons at lifetime-extending defect configurations.

Fig. 60. Evolution of the positron lifetime parameters τ_0 , τ_1 , τ_2 , I (same notation as in Fig. 55) upon annealing in low-temperature e^- -irradiated a) **FeSi**, b) **FeTi**, c) **FeCu** and d) **FeSb**, with alloyed partners of 0.04 at%, respectively, [175]

8.2.1 The role of bifurcation in the view of the 1IM

In terms of the 1IM this observation is explained in a completely *vacancy-related* way: irradiation-induced *monovacancies* are responsible for the occurrence of an increased positron lifetime τ_1 (175 ps) in the low-temperature range up to ≥ 200 K. In Stage III these monovacancies are assumed to migrate, thereby immediately initiating, in *pure α -Fe* and substitutional alloys of type (i), lifetime bifurcation due to two simultaneously occurring reactions: a) annihilation with interstitial-type defects and b) clustering into large vacancy complexes, V_n , with $n \geq 10$ (cf. Fig. 55, 58, Section 8.1.2).

In *substitutionally impurity-doped α -Fe* of type (ii) – i.e. **FeSi**, **FeCu**, **FeTi**, cf. Section 8.2 – in terms of this model, too, monovacancies are suggested to migrate in Stage III being hindered there, however, in producing any bifurcation because of their preferential trapping at impurity atoms. The observed persistence of the long positron lifetime component τ_1 , up to temperatures above Stage III in these alloys, is explained by the questionable argument that this trapping of vacancies is achieved in such a way that – independent of the specific attracting impurity – their capabilities for positron trapping remain completely unaffected as compared to the unbound situation. Only at elevated, impurity-dependent temperatures, T_S , (cf. Section 8.2) do these complexes become unstable thereby enabling reactions of the released vacancies, similar to those ascribed to Stage III in pure α -Fe: (i) Annihilation with interstitial-type antidefects, thereby re-establishing the short lifetime component τ_1 and (ii) clustering into complexes of the – unrealistically – high number of up to $n \geq 10$ vacancies which are regarded as origin of the long lifetime component τ_2 , cf. Section 8.1.2.

In contrast to these 1IM-based interpretations in type (ii) alloys in the temperature range departing from Stage III, one rather would expect that (i) due to specific, impurity-dependent interactions of, e.g., steric, electrostatic and magnetic nature the “free-vacancy” volume would be characteristically modified, i.e. constrained, so as to yield a considerable impurity-specific *reduction* of the positron lifetime. (ii) As already pointed out in Section 8.1.2, the formation of the assumed large vacancy clusters V_n , with $n \geq 10$, at Stage III and higher temperatures, is most unlikely whereas, in the considered systems, at lower temperatures (Stages I and II), undoubtedly enhanced interstitial clustering is taking place.

These 1IM-inherent incompatibilities between PA and corresponding MAE results are conveniently eliminated when arguing in terms of the 2IM.

8.2.2 Bifurcation in the light of the 2IM

Comparison with the corresponding MAE spectra suggests to relate the occurrence of two types of bifurcated PA spectra, cf. Section 8.2, with the survival or non-survival up to Stage III of small complexes, having been formed during annealing in Stages I and II by *interstitial trapping*.

a) Spectra of type (i) typically occur in such systems in which magnetic low-temperature relaxations undergo strong recovery during annealing up to Stage III – like, i.e., pure α -Fe and **FeMn** (cf. Sections 5.5 and 6.2.4) – and in which, due to the subsequent absence of trapping centers, no further relaxation processes are developed upon further annealing. b) PA spectra of type (ii), on the other hand, are observed in such alloys as **FeSi**, **FeCu**, and **FeTi** where – as revealed in the MAE spectra – low-temperature *interstitial-type* complexes are able to survive up to Stage III – and to react there with

the intrinsic defects which become mobile at this temperature. The fact that, upon migration of Stage III defects, these *interstitial-induced*, low-temperature relaxations are observed to further grow and/or to give rise to new relaxation processes is clear evidence that the Stage III defects, in turn, too, are of *interstitial type* (cf. Section 6.2).

Thus, once more, the 2IM offers the more conclusive interpretation of the positron lifetime behaviour in e^- -irradiated Fe alloys: surviving interstitial-type complexes act as trapping centers for the related interstitial-type lattice defects (dumb-bells) becoming mobile in Stage III. Assuming this interstitial clustering to prevail over the annihilation with vacancies, the persistence of the increased lifetime component τ_1 up to temperatures above Stage III reflects only the fact that *vacancies*, in these alloys, are still *immobile in Stage III* and, thus, remain almost unaffected by the dominant *interstitial reactions*.

Conversely, in sample where the low-temperature complexes have already strongly recovered during annealing up to Stage III, the dominant reaction of the Stage III dumb-bells – due to the absence of other trapping centers – consists in the recombination with *immobile* vacancies, thereby reducing the effective positron lifetime to its value in the ideal lattice, i.e., $\tau_f = 110$ ps. The concomitant appearance of a second, long positron-lifetime component, with strongly reduced intensity, may be attributed alternatively to either Frank et al.'s supervacancy formation or to the annealing-dependent reduction of de-trapping at simple vacancy configurations, cf. Section 8.1.2.

8.3 Positron annihilation in interstitially impurity doped α -Fe

Our following considerations will be confined to e^- -irradiated FeC, as the system being most thoroughly investigated by means of both PA [142] and MAE (cf. Section 7.3.1.2). PA measurements were performed on three differently charged specimens containing 750, 50 and 5 at ppm C, respectively, cf. Fig. 61, 62. Immediately after irradiation, up to annealing in Stage III, the positron lifetime in all three samples is about 175 ps, as in

Fig. 61. Evolution of the positron lifetime parameters τ_0 , τ_1 , τ_2 , I_2 upon annealing in low-temperature e^- -irradiated carbon (C)-doped α -Fe: a) $6 \times 10^{18} e^- cm^{-2}$, 5 at ppm C; b) $3 \times 10^{19} e^- cm^{-2}$, 50 at ppm C; c) $3 \times 10^{19} e^- cm^{-2}$, 750 at ppm C, [142]

Fig. 62. Compilation of the annealing behaviour of the short lifetime component τ_1 , as extracted from Fig. 61a to c

e^- -irradiated pure or substitutionally alloyed α -Fe, cf. Section 8.2. Upon further annealing, this lifetime undergoes characteristic variations which will be discussed now in terms of the two opposing recovery models.

8.3.1 Annealing-dependent lifetime variations in terms of the IIM

(i) At 200 K the positron lifetime becomes split into the short-time component τ_1 and the long-time component τ_2 . Depending on the various C contents – of, i.e. 750, 50 and 5 at ppm – the short-time component is lowered to different levels of 160, 135 and 120 ps, respectively (cf. Fig. 61a to c, Fig. 62), whereas the long-time component jumps abruptly to values of about 300 ps. The different levels of τ_1 , attained in Stage III, are ascribed to the corresponding equilibria established by the concurring processes of *vacancy trapping* at carbon atoms and *annihilation* with interstitial-type anti-defects: thus, the lower the C content the more predominant the annihilation and hence the smaller the time component τ_1 . In the case of the C-rich specimen almost all vacancies are assumed to become trapped at C atoms [142] and the observed lifetime of 160 ps considered to be typical for positrons trapped in such C-vacancy pairs. An interesting aspect of this IIM-interpretation is the fact that *interstitial impurity*-vacancy pairs, in contrast to *substitutional impurity*-vacancy pairs, are assumed to cause a lowering of the lifetime τ_1 , as compared to free monovacancies, cf. Section 8.2.1.

(ii) At temperatures near 350 K, where the carbon atoms become thermally mobilized, a further decrease of the lifetime component τ_1 is observed in all specimens, ending at about 120 ps for the highly C-charged (750 at ppm) and being close to $\tau_1 = 110$ ps – the value of the undisturbed lattice – for the lower C-doped samples. This further drop is explained by continued trapping of C atoms at C-vacancy pairs which thereby, due to decoration, lose their efficiency in positron trapping.

(iii) At temperatures above 400 K, in the strongly C-doped specimen, a re-growth of the component τ_1 to about 140 ps is observed, which is attributed to positrons captured

in C-stabilized vacancy clusters, having formed, departing from Stage III, by continuous trapping of diffusing vacancies.

(iv) Upon annealing above 500 K, again a reduction of the τ_1 values close to the lower limit of $\tau_f = 110$ ps, is observed which is attributed to the thermally induced dissociation of residual vacancy clusters.

(v) The long-lifetime component τ_2 , in the two lower C-charged specimens, increases steadily upon further annealing up to values of about 400 ps, in contrast to the stronger C-charged specimen where τ_2 decreases from its initially attained maximum to values ≤ 300 ps (cf. Fig. 61a to c). The continuous increase in the former two specimens is attributed to vacancy clusters which, by trapping of diffusing vacancies, undergo steady growth during annealing. In the latter specimen, however, such growth is expected to be suppressed in favour of enhanced vacancy trapping at carbon interstitials.

8.3.2 Annealing-dependent lifetime variations in terms of the 2IM

The striking variations of positron lifetime (i) to (v) during annealing, discussed above, when considered in combination with the information obtained from MAE investigations on corresponding systems, can be explained straightforwardly in terms of the 2IM:

(i) The bifurcation of the positron lifetime in Stage III results from a) recombination of mobilized interstitials with immobile vacancies (τ_1) and b) clustering of interstitials, resulting in the formation of supervacancies (τ_2). The discrete levels of reduced τ_1 , observed in dependence on the dissolved C content, are associated with correspondingly differing rates of interstitial-induced vacancy annihilation, in competition with interstitial trapping at C atoms and interstitial-type complexes having survived from previous annealing stages, cf. Section 7.3.1. Similarly, as in substitutionally alloyed α -Fe, these latter complexes are regarded as efficient nuclei for the formation of τ_2 -inducing supervacancies, cf. Section 8.1.2.

The 1IM-specific interpretation of the reduced component τ_1 (160 ps), observed in the strongly C-doped sample in Stage III (Fig. 61c, 62), as the characteristic lifetime of positrons trapped in C-vacancy pairs – formed in Stage III between mobile vacancies and immobile C-interstitials – is *incompatible* with the corresponding MAE observations: such complexes, due to their life-time-reducing interaction, are suggested to be anisotropic and therefore should give rise to considerable relaxation effects. Nothing of them, however, is detectable in the MAE spectra occurring in the temperature range of Stage III.

(ii) In the C-Stage (350 K), on the other hand, exactly this type of simple Debye-like magnetic relaxation, missing in Stage III, is developed at 150 K, cf. Section 7.3.1. In terms of the 2IM, we therefore ascribe the further reduction of the lifetime component τ_1 in the C-Stage, in contrast to the 1IM, to the trapping of migrating C atoms at immobile vacancies, thereby forming simple, anisotropic C-vacancy (C_1V_1) pairs which, upon thermal activation (at 150 K), give rise to a pronounced Debye-type reorientation process, cf. Section 7.3.1.2, item d).

(iii) Led by the concomitant occurrence of a further simple Debye-type relaxation at 18 K (cf. Section 7.3.1), we associate the re-growth of the component τ_1 , during annealing in the temperature range above 400 K, to the free migration of vacancies. Upon becoming trapped at the C-stage complexes, they give rise to the formation of further, lifetime-enhancing, easy-reorientable defect configurations at 18 K of, e.g., C_1V_2 -type, cf.

Section 7.3.1. The fact that both the re-growth of the τ_1 component (PA) and formation of the characteristic 18 K relaxation (MAE) occur only at elevated C contents is in agreement with the assumption that only in such samples – due to preferential interstitial trapping at C atoms in Stage III – a sufficient amount of vacancies can survive up to Stage IV where, upon thermal activation, they are able to undergo the reactions described.

(iv) The decrease of τ_1 upon annealing above 500 K, being accompanied by the disappearance of the small-cluster relaxations in the MAE spectra, is associated in both models with the thermally activated dissociation of corresponding carbon–vacancy complexes (cf. Sections 7.3.1 and 8.3.1). The observation in MAE spectroscopy, however, that after this dissolution the carbon Richter MAE remains almost completely suppressed (cf. Fig. 43a) points to the fact that after this annealing, the irradiation-induced defects have not at all fully recovered, as yet, but survive in the form of large, carbon-stabilized complexes being unable to induce any further noticeable positron trapping or magnetically sensitive reorientations.

(v) The different saturation values of τ_2 observed in the alternatively C-charged specimens (i.e. $\tau_2 \leq 400$ ps for 5 and 50 at ppm C and ≤ 300 ps for 750 at ppm C) point to different sizes of the interstitially induced supervacancy clusters in these specimens. Thus, evidently, in the higher C-charged specimen, due to predominant interstitial trapping at C atoms, the maximum cluster size is smaller than in the lower C-doped samples where trapping between intrinsic defects is more likely to occur. In terms of our alternative trapping/de-trapping model, cf. Section 8.1.2, one would suggest that in the lower C-doped samples, due to their higher recovery rates upon annealing to temperatures above Stage III (cf. item (iv)), defect-induced positron de-trapping is considerably reduced, thus leading to relatively increased lifetimes τ_2 .

8.4 Concluding remarks

Our above review of the most relevant results obtained on α -Fe by means of positron annihilation, the protagonist of various other *static techniques* in point-defect research (cf. Section 1), shows that their interpretation, when *restricted on themselves*, may be achieved – according to one's preference – in terms of either the one- or two-interstitial model. Confrontation, however, with the more detailed observations available, on corresponding systems, by means of higher resolving techniques – like the *dynamic MAE spectroscopy* – reveals clearly that only in terms of the 2IM all aspects of the rich experimental findings can be understood satisfactorily.

Thus the strongest arguments, deduced from MAE spectroscopy, in favour of a 2IM-based interpretation of defect recovery in radiation-damaged α -Fe are the following ones:

1. The *clear identification* of the defect migrating in Stage III, as being of *self-interstitial type*. The deduction is based on:

- a) Detailed investigations of the reaction kinetics of point defects introduced, by means of low-temperature e^- or n-irradiation, into a large variety of different Fe-systems, ranging from *highest purity* to numerous *substitutionally* or *interstitially* alloyed α -Fe samples.

- b) The observation that trapping of Stage III defects, in both substitutionally and interstitially alloyed α -Fe, causes the growth and re-development of reorientable complexes which had been formed already in the preceding annealing Stages I and II, un-

doubtedly, by trapping reactions between intrinsic interstitials. Were it vacancies, instead of interstitials, which migrate in Stage III, these complexes, instead of growing, should undergo rapid dissolution and disappearance due to reactions with their anti-defects.

2. The stringent *exclusion of vacancies* as feasible defect types migrating Stage III, which is based on the following results obtained on *interstitially* alloyed α -Fe:

a) The nuclei of small clusters, having been formed by trapping of interstitial atoms (C, N), after their thermally activated migration at temperatures $T > 260$ K, could be identified as simple, immobile intrinsic lattice defects of, unequivocally, monovacancy-type. The analysis of the dissociation kinetics of these clusters yields – besides their respective binding enthalpy data – the important result that of their constituents the impurity–interstitial atoms are the more mobile ones, with the lower migration enthalpies. Consequently, the enthalpy of the monovacancy must obey the relation H_N^M (0.76 eV) $< H_C^M$ (0.84 eV) $< H_{V1}^M$; this means, however, that the monovacancy is disqualified as a possible candidate for the defect migrating in Stage III with an enthalpy of $H_{III}^M \leq 0.56$ eV.

b) The fact that in interstitially C-doped α -Fe in the C-Stage (350 K) a simple defect configuration, characterized by a well-defined reorientation-type Debye relaxation at 150 K, develops. The formation of this complex follows a well-resolved second-order trapping reaction between thermally mobilized carbon and an immobile elementary intrinsic defect. By consideration of the clear-cut reaction kinetics of this process in combination with the bulk of additional information accumulated during our systematic MAE studies on various Fe systems (cf. item 1.), it is evident that the immobile partner in this trapping reaction can be nothing other than the monovacancy (cf. Section 7.3.1) so that the respective defect configuration is identified as a simple C_1V_1 pair.

c) The formation of a further striking, elementary defect configuration in Stage IV, near 500 K, is shown to result from trapping of thermally activated monovacancies at, i.e., C_1V_1 pairs. During this reaction, the next simple defect configuration of, i.e., C_1V_2 type is formed, which is regarded as being both sufficiently anisotropic and easily reorientable to produce the corresponding well-developed Debye-process situated at 18 K.

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