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Paramagnetic hyperfine splitting in the ^{151}Eu Mössbauer spectra of $\text{CaF}_2:\text{Eu}^{2+}$

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Abstract

^{151}Eu Mössbauer spectra in zero magnetic field of highly dilute (0.1 mol%) Eu^{2+} ions in CaF_2 showed an almost temperature-independent asymmetrically split pattern, arising from the paramagnetic hyperfine interaction **AS. I** in a cubic crystal field with slow electron spin relaxation; in a small external magnetic field B of 0.2 T such that $g\mu_B B > A$ an almost symmetrical pattern was observed. Both the spectra with and without external field are well described using the spin Hamiltonian and previous electron paramagnetic resonance data. A more concentrated (2 mol% Eu^{2+}) sample exhibited a strongly broadened symmetrical resonance line due to an increased Eu-Eu spin relaxation rate; in an external magnetic field of 0.2 T the Mössbauer spectra exhibited further broadening and additional magnetic structures due to the reduced relaxation rate. When a large field of 6 T was

applied such that $g\mu_B B$ is much larger than the crystal field splitting, a fully resolved hyperfine pattern was observed at 2.5 K, with an effective field at the Eu nuclei of -33.7 T; at higher temperatures superimposed patterns originating from excited electronic states were observed in the spectra. The present results on the highly dilute $\text{CaF}_2 : 0.1\% \text{Eu}^{2+}$ sample deliver a straightforward explanation for previous observations of a seemingly large dependence of the Eu^{2+} isomer shift on europium concentration.

I. INTRODUCTION

The divalent europium ion Eu^{2+} is optically active in fluorozirconate-based (FZ) glass ceramics, which are used, for example, as x-ray detectors in medical and other applications.^{1,2} The Eu-doped FZ base glass has already been investigated by electron paramagnetic resonance (EPR)³ and other techniques including ^{151}Eu Mössbauer spectroscopy.⁴ The present ^{151}Eu Mössbauer study on dilute Eu^{2+} in a CaF_2 matrix was motivated by an extremely broad linewidth (up to 18 mm/s) of the Eu^{2+} resonance line observed with this method in Eu^{2+} -doped FZ glasses and FZ-based glass ceramics.⁵ CaF_2 is a much simpler system as it is cubic and does not contain heavy elements, resulting in a relatively low absorption for the 21.5-keV γ rays of ^{151}Eu .

Dilute $\text{CaF}_2:\text{Eu}^{2+}$ systems have previously been studied with paramagnetic resonance spectroscopy,^{6–9} as well as ^{151}Eu Mössbauer spectroscopy.^{10–14} The paramagnetic splitting of dilute Eu^{2+} (0.01%) has been determined at low temperature by EPR by Baker, Bleaney, and Hayes,⁶ and the hyperfine interaction has been measured by electron nuclear double resonance (ENDOR) by Baker and Williams.⁷ Later the temperature and pressure dependence of these parameters have been determined.^{8,9} The first ^{151}Eu Mössbauer studies were performed on more concentrated systems: Maletta *et al.*¹⁰ and Wickman *et al.*¹¹ studied systems with 0.5 to 10% Eu, reporting on a very anomalous variation of the Eu^{2+} isomer shift with concentration. Nitsche *et al.*¹² found a very unusual temperature dependence of the Eu^{2+} isomer shift in $\text{CaF}_2:1\% \text{Eu}$. Lambe and Schroeder¹³ and Schroeder *et al.*¹⁴ extended the Mössbauer studies to lower concentration (0.1% to 10%) and observed an even stronger anomalous variation of the isomer shift with Eu^{2+} concentration from 11.3 mm/s (0.1%) to approximately 13.4 mm/s (1%–10%). In addition, these authors reported on a very broad linewidth (up to ≈ 8 mm/s compared to a common experimental line-width of ≈ 2.5 mm/s) of the Eu^{2+} absorption lines, which they attributed to spin-spin relaxation effects of paramagnetic splitting (known from the above EPR and ENDOR studies). The anomalous shifts were speculatively attributed to oxygen neighbors of the Eu^{2+} ions, with a detailed model for possible O^{2-} configurations.^{13,14}

In order to clarify the contradicting results and interpretations in these previous Mössbauer studies of $\text{CaF}_2:\text{Eu}^{2+}$ systems, we performed the following series of ^{151}Eu Mössbauer studies: (i) $\text{CaF}_2:\text{Eu}^{2+}$ with an Eu doping level of only 0.1% was studied at different temperatures between 4.2 and 295 K without an external field; (ii) $\text{CaF}_2 : 0.1\% \text{Eu}^{2+}$ was studied in a relatively small external magnetic field of 0.2 T at 295 K; (iii) $\text{CaF}_2:\text{Eu}^{2+}$ with 2% Eu was studied between 4.2 and 295 K without an external magnetic field; (iv) $\text{CaF}_2:2\% \text{Eu}^{2+}$ was studied in an external magnetic field of 0.2 T between 10 and 295 K (to elucidate the impact of an external magnetic field on the observed paramagnetic line broadening) and, in addition, in a large external field of 6 T between 2.5 and 10 K.

II. EXPERIMENTAL DETAILS

Single crystals of Eu-doped CaF_2 were grown in the crystal-growth laboratory at the University of Paderborn using the Bridgman method with a vitreous carbon crucible, argon atmosphere, and a CaF_2 powder to which 0.1 and 2 mol% of EuF_2 were added, respectively.

The ^{151}Eu Mössbauer spectra of these powdered crystals were measured using 100 mCi $^{151}\text{Sm}_2\text{O}_3$ and $^{151}\text{SmF}_3$ sources. Intrinsic germanium detectors were used to detect the 21.5-keV γ rays. The source energy was varied using triangular and sinusoidal waveforms. Experiments at various low temperatures were performed in a cryostat with the source and absorber at the same temperature (0.1% Eu sample) or with the source at room temperature (2% Eu sample). An Oxford Instruments superconducting magnet was used to apply fields up to 6 T at temperatures between 2.5 and 10 K. The velocity scale was calibrated using an iron foil absorber and ^{57}Co source at room temperature.

The spectra were fitted as described below using either the spin Hamiltonian of the paramagnetic splitting or standard Mössbauer fitting programs for the ^{151}Eu (21.5 keV) resonance. The resulting isomer shifts (relative to EuF_3) and linewidths (full width at half maximum=FWHM) are summarized in Table I.

III. EXPERIMENTAL RESULTS

A. CaF_2 : 0.1%Eu crystals

1. In zero field—For very dilute CaF_2 :Eu crystals the electron-spin relaxation times are slow enough to resolve the hyperfine interaction, as shown from the ENDOR measurements on CaF_2 : 0.01%Eu at 13 K⁷ or EPR studies on samples with 0.1 mol% Eu.⁹ ^{151}Eu Mössbauer studies on such dilute Eu-doped samples are difficult and time consuming because of the low Eu concentration and the resulting small resonance effects as in the present case with a CaF_2 : 0.1%Eu crystal. Using a relatively thick absorber, which reduced the normal transmission of the 21.5-keV γ rays to about 20% by photoabsorption of the CaF_2 matrix, resonance effects of $\approx 0.6\%$ at 4 K [Fig. 1(a)] and $\approx 0.2\%$ at 295 K [Fig. 1(c)] were obtained. The analysis of the spectra in Fig. 1 with the spin Hamiltonian (see Sec. IV) reveals that Eu^{2+} ions are located in sites with zero quadrupole interaction, i.e., they are on regular Ca^{2+} sites. This excludes the possibility of oxygen neighbors, which had been tentatively postulated to explain the observed “anomalous” isomer shifts in these systems.^{12,13} Such regular lattice sites are also a prerequisite for the successful analysis of the paramagnetic hyperfine splitting in the ENDOR⁷ and EPR studies,^{8,9} as well as in the present Mössbauer spectra.

We should mention that we initially performed exploratory ^{151}Eu Mössbauer measurements over a velocity range of 20 mm/s and observed a broadened resonance line centered around -11 mm/s, resembling the previous reports on an anomalous concentration dependence of the Eu^{2+} isomer shift^{12,13} at these low concentrations. Since the resonance line was, however, asymmetric with some additional structures apparent, in all further studies the source velocity was increased to ± 35 mm/s and important additional features appeared at higher resonance velocities. The resulting spectra are shown in Fig. 1; at all temperatures they exhibited an asymmetric shape with two major dips at -11 mm/s and -24 mm/s. These dominant spectral features were initially fitted by two broad resonance lines, which yield an average isomer shift of -13.4 mm/s, exactly the value obtained previously for more concentrated systems^{10–13} and in the present work (see below) for the CaF_2 : 2%Eu sample. This was the first proof that we indeed observed a resolved paramagnetic splitting. The theoretical background for a more detailed fit of these asymmetric spectra by $144 (= 8 \times 18)$ transitions, arising from the Hamiltonian of the paramagnetic hyperfine splitting of isolated Eu^{2+} ions in a cubic surrounding, will be given in Sec. IV.

Paramagnetic hyperfine splitting has previously been observed in the ^{151}Eu Mössbauer spectra of EuO -doped borate glasses.¹⁵ Due to the different local surroundings of the Eu^{2+} ions in the glass matrix, a consistent fit of the spectra was not possible. Broadened Eu^{2+} absorption lines, attributed to unresolved paramagnetic hyperfine splitting, have been observed in magnetically diluted Eu-Ca hexammines¹⁶ for Eu^{2+} ions in zeolites¹⁷ and for Eu^{2+} ions isolated in an Ar

matrix.¹⁸ The present observation of a resolved paramagnetic hyperfine splitting of Eu^{2+} in CaF_2 even at room temperature, which can be convincingly described by the hyperfine structure parameters of the previous ENDOR and EPR studies of this system,^{7–9} is a new finding and offers immediately a consistent interpretation of the previously reported “anomalous” behavior of the Mössbauer isomer shift in the $\text{CaF}_2:\text{Eu}$ system.

Paramagnetic relaxation has also been previously resolved in Mössbauer studies of other rare-earth ions such as Er^{3+} or Yb^{3+} in dilute systems, but only at very low temperatures.^{19–23} These ions exhibit fast spin-lattice relaxation at higher temperatures due to their orbital angular momentum L . By contrast Eu^{2+} is in a S state with $L=0$, hence the relaxation is determined by the spin-spin interaction.²⁴

2. In a small magnetic field—The Mössbauer spectrum measured at room temperature in a field of 0.2 T, applied by a permanent magnetic array perpendicular to the γ -ray direction, is shown in Fig. 2. It is considerably different from the spectra measured in zero field (Fig. 1) as the two dips transmute to a broad line around -13.5 mm/s with additional structures on either side of the main resonance. As will be described in Sec. IV, the magnetic field B affects the hyperfine interaction AS_zI_z by suppressing the fluctuating (off-diagonal) terms $A(S_xI_x+S_yI_y)$. If $g\mu_B B \gg A$ the interaction reduces to AS_zI_z , i.e., it becomes an effective field proportional to the value of the spin quantum number m_S of the Eu^{2+} ions. The spectrum then consists of overlapping hyperfine patterns arising from the states $|m_S=-7/2\rangle$, $|m_S=-5/2\rangle$ up to $|m_S=+7/2\rangle$ as described in Sec. IV.

B. $\text{CaF}_2:2\%\text{Eu}$ crystals

1. In zero field—The ^{151}Eu Mössbauer spectra of $\text{CaF}_2:2\%\text{Eu}$ at 295, 90, and 10 K are shown in Fig. 3. They are drastically different from those of the 0.1% Eu-doped system of Fig. 1 in that they exhibit only a symmetrically broadened single line at -13.4 mm/s. This agrees with the isomer shift reported in the previous Mössbauer studies for this concentration range.^{10–13} Apart from the expected increase in the absorption depth by $\approx 100\%$ between 295 K and 10 K, the spectra are virtually independent of temperature. For 2% Eu concentration in CaF_2 , the electron-spin relaxation rates are much larger than in the 0.1% Eu-doped system, where resolved hyperfine splitting was observed, but not high enough to lead to a normal Mössbauer linewidth, as observed for instance in the concentrated systems EuF_2 and EuS with $\text{FWHM}_{\text{exp}}=2.5$ mm/s. The observed linewidth of (7.7 ± 0.3) mm/s at 10 K remains practically constant up to 295 K.

The Mössbauer spectra of the $\text{CaF}_2:2\%\text{Eu}$ sample show that 98% of the doped Eu ions are in the Eu^{2+} state, only 2% showing up at 0 mm/s, an isomer shift typical for Eu^{3+} ions. Such small Eu^{3+} contents, eventually stabilized by oxygen neighbors, are difficult to avoid and were also observed in other studies of $\text{CaF}_2:\text{Eu}$ systems.¹⁴

2. In a small magnetic field—Figure 4 shows the Mössbauer spectra of the $\text{CaF}_2:2\%\text{Eu}$ sample at 295, 90, and 10 K in a magnetic field of 0.2 T, applied by a permanent magnet parallel to the γ -ray direction. The spectra change considerably and consist now of one dominant ($\approx 77\%$) line at -13.4 mm/s, the same isomer shift as without an external field, but somewhat more broadened ($\text{FWHM}=8.2$ mm/s at 10 K), together with another broad feature (21%) in the wings, indicating a magnetic splitting. The spectra have been fitted to the sum of a single line and a magnetically split pattern with the same isomer shift, a line-width of 5.0 mm/s, and an almost temperature-independent magnetic hyperfine field of $B_{\text{hf}}=(-27.2 \pm 0.5)$ T. There is also a small (2%) contribution from an Eu^{3+} impurity as in the zero-field spectra (see Table I).

As observed for the 0.1% Eu sample, the application of a small external magnetic field suppresses the fluctuating terms in the hyperfine coupling, and extra lines of magnetic origin are resolved in the wings of the spectrum.

3. In a large magnetic field—In a large magnetic field of 6 T applied perpendicular to the γ -ray direction at low temperatures, the full hyperfine interaction is observed at 2.5 K [Fig. 5 (a)]. This spectrum is, in a first approach, similar to that observed in magnetically ordered Eu^{2+} systems, e.g., EuS or EuF_2 .²⁵ It may be fitted with an effective hyperfine field arising (beside transferred and external fields) from the $|m_S = -7/2\rangle$ ground state of the ordered Eu^{2+} $4f$ moments resulting in 18 transitions from the $I_g = 5/2$ nuclear ground state to the $I_e = 7/2$ nuclear excited state, and exhibits now a narrow linewidth of (2.3 ± 0.1) mm/s. From the relative intensities of the four main lines (each consisting of three transitions), as well as from the somewhat less intense lines at the wings (e.g., around +6 mm/s), one immediately recognizes a polarization dependence, according to the external perpendicular field, enhancing the $\Delta m_f = 0$ transitions by a factor of two. If the small contribution from the excited $|m_S = -5/2\rangle$ and other states is ignored, the observed effective field at the Eu nuclei, $B_{\text{eff}} = B_{\text{hf}} + B_{\text{ext}}$ is (-27.7 ± 0.2) T, which leads for an external magnetic field of 6 T to a hyperfine field of $B_{\text{hf}} = (-33.7 \pm 0.2)$ T. This value of B_{hf} is close to the value of -33.3 T found in EuF_2 crystals below the antiferromagnetic transition temperature of 1.0 K,²⁵ and to the value of -34.0 T deduced from ENDOR results (see discussion).

The spectra at 5 and 10 K [Fig. 5(b) and 5(c)] are more complicated and cannot be fitted by the magnetic spectrum of the ground state only. Additional contributions to the spectra originating from the excited m_S sublevels ($m_S = -5/2, -3/2, -1/2, \dots$) of the $S = 7/2$ $4f$ moment with different hyperfine fields have to be considered. They contribute to the Mössbauer spectrum according to their Boltzmann populations (see Fig. 6 and theoretical background to the fits given in Sec. IV).

Finally, it should be mentioned that early ^{151}Eu Mössbauer studies of CaS:Eu (1% and 4%)²⁴ and Eu-Ca hexammines¹⁶ in various external fields yielded similar spectra to the present ones observed for $\text{CaF}_2\text{:2\%Eu}$ in small and large magnetic fields. Analysis with a paramagnetic relaxation theory yielding relaxation rates strongly dependent on concentration, temperature, and external fields with similar dependencies as discussed here.

IV. INTERPRETATION AND DISCUSSION

In a paramagnet the hyperfine interaction is a tensor, and in general cannot be described by an effective magnetic field, which is found in magnetically ordered materials.

Since CaF_2 has a cubic crystal structure the hyperfine structure is isotropic and the nuclear quadrupole interaction is zero. The Ca^{2+} and thus the Eu^{2+} site has O_h symmetry, and the energy levels are given by the spin Hamiltonian

$$\mathcal{H} = g\mu_B \mathbf{B} \cdot \mathbf{S} + \frac{1}{60} b_4 (O_4^0 + 5O_4^4) + \frac{1}{1260} b_6 (O_6^0 - 21O_6^4) + A \mathbf{S} \cdot \mathbf{I} - g_N \mu_N \mathbf{B} \cdot \mathbf{I}, \quad (1)$$

where the parameters b_k describe the strength and the operators O_k^q define the symmetry of the crystal field. Although the $^8S_{7/2}$ state is unsplit in first order by the crystal field, higher-order interactions produce a small splitting. The first term in Eq. (1) represents the electron Zeeman interaction, the next two the effects of the crystal field of cubic symmetry, and the last two the hyperfine interaction with the nuclear dipole moment and the nuclear Zeeman interaction. g and μ_B are the electron g factor and Bohr magneton, and g_N and μ_N are the nuclear g factor and

nuclear magneton, respectively. For Eu^{2+} in CaF_2 the cubic splitting parameters b_4 and b_6 are -176.12 MHz and $+0.78$ MHz; the g value is 1.9926 and the hyperfine interaction parameter $A(^{151}\text{Eu})$ is -102.9 MHz.⁷ The hyperfine field calculated from

$$B_{\text{hf}} = \frac{AI}{g_N \mu_N} \quad (2)$$

is equal to -34.0 T.

To compute the expected spectra it is necessary first to calculate the energy levels of the ground and excited nuclear states from the spin Hamiltonian. The transition energies are then the differences between these energies, and the dipole transition probabilities involve the Clebsch-Gordan coefficients.

The energy levels for the nuclear ground state ($I_g=5/2$) of the $S=7/2$ Eu^{2+} ion were calculated from the spin Hamiltonian [Eq. (1)] by diagonalizing the $(2S+1)(2I_g+1) \times (2S+1)(2I_g+1) = 48 \times 48$ matrix and are shown as a function of applied magnetic field in Fig. 6.

In the absence of a magnetic field the $^8S_{7/2}$ ground state of Eu^{2+} is split by the cubic crystal field into a doublet, Γ_6 , a quartet, Γ_8 , and another doublet, Γ_7 , at energies $-14|b_4|$, $2|b_4|$, and $18|b_4|$, respectively. Thus the overall splitting is $32|b_4|$, i.e., 5.636 GHz. The wave function of each level contains mixtures of eigenstates whose m_S differ by ± 4 . The hyperfine interaction ($A_g = -0.102$ GHz for the ground state) further partially removes the 2-, 4-, and twofold electron degeneracies. For the excited nuclear state $I_g=7/2$ the spin Hamiltonian is a 64×64 matrix and $A_e = -0.054$ GHz. The transition energies are then the differences between the energies of the ground and excited states. To simulate the spectra we use the A values from Baker *et al.* converted from MHz to mm/s, i.e., $A_g = -5.91$ mm/s and $A_e = -3.12$ mm/s.

The intensities of each transition are obtained from the Boltzmann populations of the states multiplied by the dipole matrix element between the states and weighted by the transition probabilities. Since the energy levels in each state are asymmetrical, it follows that the spectrum is asymmetrical, as is seen in Fig. 1, for the crystal containing 0.1% Eu. The thin-line solid curve in Fig. 1(a) is constructed with an unphysically narrow linewidth of 0.23 mm/s to indicate in stick-diagram form the energy positions of the 18 possible transitions. The solid curve is the fitted spectrum with a more realistic linewidth of 5.3 mm/s and is seen to explain the main features of asymmetric paramagnetic splitting. The contribution from the absorber to this linewidth is about three times the natural value, indicating that the spin-spin relaxation rates are not infinitely slow. Since the crystal field splitting is small ($b_4/k = 0.3$ K), the Boltzmann factors are close to unity for all the states and the spectra are practically independent of temperature, as observed.

As demonstrated in Fig. 6(a), application of a (small) magnetic field splits the eigenstates of the paramagnetic splitting, removing the degeneracy of the nuclear substates and reducing the admixture of different electronic spin states. The energy levels are becoming increasingly pure m_S eigenstates and more, but not completely, symmetrical for an external field of 0.2 T. This behavior is reflected in the spectrum of Fig. 2, where only contributions from the highest and lowest states with $m_S = +7/2$, $+5/2$, and $m_S = -7/2$ can still be seen in the wings of the slightly asymmetric main component. For a field of 0.2 T the Boltzmann factors of the m_S states are still close to one so all components contribute equally at room temperature. The slightly reduced linewidth in comparison to the spectra in zero field might indicate a further slowing down of the relaxation rate.

In the spectra of the $\text{CaF}_2\text{:2\%Eu}$ sample, the Eu-Eu spin-flip rates are considerably larger due to the 20 times larger Eu concentration. In this fast relaxation range the paramagnetic splittings are randomized and are only documented in the width of the perfectly Lorentzian-shaped absorption lines. As shown in the early Mössbauer studies on dilute paramagnetic Eu^{2+} ions in different hosts,^{11,16} application of a simple relaxation theory derives relaxation rates in the 100 MHz range at that Eu concentrations. Because the Boltzmann factors of the electronic sublevels are close to one, the spectra are almost independent of temperature, as documented in the constant linewidth between 10 and 295 K (see Table I).

Application of a small external field of 0.2 T results, beside the change in the paramagnetic splitting shown in Fig. 6(a), in a slowing down of the Eu spin relaxation rate, as demonstrated by the increase in the width of the central line from 7.7 to 8.2 mm/s and the appearance of symmetric magnetic structures at the shoulders of this line, which can be attributed to the $m_S = \pm 7/2$ states, eventually with some admixtures from the $m_S = +5/2$ state, which have less cross relaxation with the other m_S states. This argument is supported by the magnitude of the hyperfine field, $B_{\text{hf}} = (-27.2 \pm 0.5)$ T, adjusted to the magnetic structures in the spectra in Fig. 4. These observations are similar to the above-mentioned Mössbauer studies of dilute Eu^{2+} systems,^{11,16} where a small external field resulted in the appearance of additional structures in the wings of the broadened lines.

In a very large external magnetic field of 6 T, the electronic levels are now approximately 30 times more split and equally spaced [Fig. 6(b)]. At 2.5 K, the lowest temperature used, the $m_S = -7/2$ state lies well below the others and contributes with 96.2% to the well-resolved magnetic hyperfine splitting, while the $m_S = -5/2$ state contributes with only 3.8% to the spectrum. Hence, the full hyperfine field is resolved [Fig. 5(a)] with a narrow linewidth (2.3 mm/s) of the 18 nuclear transitions, indicating that any relaxation effects are switched off at these extreme conditions. As the temperature is raised the population of the higher states becomes significant and is included in Figs. 5(b) and 5(c). Slow fluctuations among these states are now possible, giving rise to increased linewidths in the spectra (see Table I).

V. CONCLUSIONS

Isotropic paramagnetic hyperfine interaction AS_zI_z , manifested by an asymmetrically split pattern, has been observed in the zero-field Mössbauer spectrum of dilute (0.1 mol%) Eu^{2+} in cubic CaF_2 . The absorber linewidth, almost constant in the temperature range investigated, is about three times the natural value, indicating that the spin-spin relaxation rates are slow but appreciable. In an applied magnetic field of 0.2 T the spectrum changes drastically toward a more symmetrical pattern, indicating that the AS_zI_z term gets dominant and that the off-diagonal terms of the hyperfine interaction matrix are suppressed.

For the $\text{CaF}_2\text{:2\%Eu}$ sample, the relaxation rates are much faster yielding a collapsed, but still broadened symmetric line, as observed previously. In a small magnetic field the relaxation rate slows down, and extra structures appear in the wings of the spectrum, mainly originating from the $|m_S = \pm 7/2\rangle$ electronic states. In a large magnetic field of 6 T and at low temperatures (2.5 K), only the $|m_S = -7/2\rangle$ ground state is populated (by 96.2%), so the relaxation rate is practically switched off. The resulting hyperfine field of -33.7 T derived from a well-resolved magnetic spectrum agrees with the paramagnetic hyperfine parameter A determined by previous EPR and ENDOR studies. At higher temperatures (5 K and 10 K) contributions from excited states are observed and line broadening occurs as the relaxation rates become faster.

No evidence was found for the rapid change in isomer shift at low Eu concentrations, as previously reported by other authors.^{10,11,13,14} This can be unambiguously attributed to the fact that the resolved paramagnetic hyperfine splitting, observable even at room temperature

(as demonstrated in the present study), has not been recognized in the earlier studies and therefore not considered in the analysis of the spectra. The present study solves a longstanding puzzle in ^{151}Eu Mössbauer spectroscopy.

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FIG. 1.

Mössbauer spectra of $\text{CaF}_2 : 0.1\% \text{Eu}^{2+}$ at (a) 4 K, (b) 125 K, and (c) 295 K. The solid curves are fits as described in Sec. IV; for the thin solid curve in (a) a linewidth of 0.23 mm/s was used in order to show the positions of the transitions.

FIG. 2.

Mössbauer spectrum of $\text{CaF}_2 : 0.1\% \text{Eu}^{2+}$ at 300 K in an external magnetic field of 0.2 T applied perpendicular to the γ rays. The solid curve is a fit as described in Sec. IV.

FIG. 3.
 (Color online) Mössbauer spectra of $\text{CaF}_2:2\%\text{Eu}^{2+}$ at (a) 10 K, (b) 90 K, and (c) 295 K.

FIG. 4.

(Color online) Mössbauer spectra of $\text{CaF}_2:2\%\text{Eu}^{2+}$ at (a) 10 K, (b) 90 K, and (c) 295 K in an external magnetic field of 0.2 T applied perpendicular to the γ rays.

FIG. 5.

(Color online) Mössbauer spectra of $\text{CaF}_2:2\%\text{Eu}^{2+}$ at (a) 2.5 K, (b) 5 K, and (c) 10 K in an external magnetic field of 6 T perpendicular to the incident γ rays. The solid curves are fits as described in Sec. IV.

FIG. 6.

(Color online) Energy levels of the ground state ($I_g=5/2$) of $^{151}\text{Eu}^{2+}$ in CaF_2 as a function of magnetic fields applied along the cubic c axis (a) from 0 to 0.2 T and (b) 0 to 6 T. For the high fields the hyperfine levels are too close to be resolved in the diagram. The energies corresponding to temperatures of 0.25 K and 5 K are included so that the Boltzmann factors can be visualized.

TABLE I

Fitting parameters of the ^{151}Eu Mössbauer spectra of 0.1% and 2% Eu-doped CaF_2 . Fixed parameters are given without error bars. The isomer shifts are relative to EuF_3 .

doping level (%)	external magnetic field (T)	temperature (K)	isomer shift (mm/s)	line width (mm/s)	fraction (%)	ion
0.1		295	-13.5 ± 0.2	5.0	100	Eu^{2+}
		125	-13.4 ± 0.2	5.0	100	Eu^{2+}
		4	-13.4 ± 0.3	5.3 ± 0.3	100	Eu^{2+}
0.1	0.2	295	-13.5 ± 0.2	4.5	100	Eu^{2+}
2		295	-13.5 ± 0.2	7.6 ± 0.3	98	Eu^{2+}
			0.0	3.0	2	Eu^{3+}
		90	-13.3 ± 0.2	7.8 ± 0.3	98	Eu^{2+}
			0.0	3.0	2	Eu^{3+}
		10	-13.3 ± 0.2	7.7 ± 0.3	98	Eu^{2+}
			0.0	3.0 ± 0.2	2	Eu^{3+}
		295	-13.5 ± 0.2	8.3 ± 0.3	77	Eu^{2+}
			-13.5	5.0 ± 0.2	21	Eu^{2+}
			0.0	3.0	2	Eu^{3+}
		90	-13.4 ± 0.2	8.2 ± 0.3	77	Eu^{2+}
2			-13.4	5.2 ± 0.2	21	Eu^{2+}
			0.0	3.0	2	Eu^{3+}
		10	-13.4 ± 0.2	8.2 ± 0.3	77	Eu^{2+}
			-13.4	5.2 ± 0.2	21	Eu^{2+}
			0.0	3.0 ± 0.2	2	Eu^{3+}
		10	-13.2 ± 0.2	3.8 ± 0.2	100	Eu^{2+}
		5	-13.3 ± 0.1	3.1 ± 0.2	100	Eu^{2+}
		2.5	-13.4 ± 0.1	2.3 ± 0.1	100	Eu^{2+}