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A 236-GHz Fe³⁺ EPR STUDY OF NANO-PARTICLES OF THE FERRO-MAGNETIC ROOM-TEMPERATURE SEMICONDUCTOR Sn_{1-x}Fe_xO₂(x=0.005)

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Abstract

High frequency (236 GHz) electron paramagnetic resonance (EPR) studies of Fe³⁺ ions at 255 K are reported in a Sn_{1-x}Fe_xO₂ powder with x = 0.005 which is a ferromagnetic semiconductor at room temperature. The observed EPR spectrum can be simulated reasonably well as overlap of spectra due to four magnetically inequivalent high-spin (HS) Fe³⁺ ions (S = 5/2). The spectrum intensity is calculated, using the overlap I(BL) + (I(HS1)+I(HS2)+I(HS3)+I(HS4))×e^{-0.00001×B}, where B is the magnetic field intensity in Gauss, I represents the intensity of an EPR line (HS1, HS2, HS3, HS4), and BL stands for the base line. (The exponential factor, as found by fitting to the experimental spectrum, is related to the Boltzmann population distribution of energy levels at 255 K, which is the temperature of the sample in the spectrometer.) These high-frequency EPR results are significantly different from those at X-band. The large values of the zero-field splitting parameter (D) observed here for the four centers at the high frequency of 236 GHz are beyond the capability of X-band, which can only record spectra of ions only with much smaller D values than those reported here.

Keywords

tin oxide; ferromagnetism; electron paramagnetic resonance

I. INTRODUCTION

Tin dioxide (SnO₂) is an attractive system for a wide variety of practical applications [1–6], being a chemically stable transparent oxide semiconductor with a band gap of ~ 3.6 eV. It has been shown that Fe doping produces ferromagnetism in SnO₂ [7], thus making it a promising ferromagnetic semiconductor at room temperature. This material, therefore, has the potential for use in spintronic devices such as spin transistors, spin-LED's, very high-density non-volatile semiconductor memory and optical emitters with polarized output [8–11], in which both the spin and charge of the particles play important roles. It is believed that oxygen vacancies and substitutional incorporation are important to produce ferromagnetism in semiconductor oxides [12], doped with transition metal ions. The details of the synthesis of the sample investigated

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here have been described elsewhere [7]. Transmission-electron-microscopy [7] showed the presence of non-spherical nano-scale particles in these samples. Quantitative magnetometry measurements showed clearly that chemically synthesized $\text{Sn}_{1-x}\text{Fe}_x\text{O}_2$ powders exhibit room-temperature ferromagnetism for $x \leq 0.05$ when prepared in the 350 to 600 °C range, associated with a high Curie temperature, T_c , of 850 K [7]. The present paper reports 236-GHz electron paramagnetic resonance (EPR) investigation at 255 K of the $\text{Sn}_{1-x}\text{Fe}_x\text{O}_2$ ($x=0.005$) sample prepared at 600 °C to study EPR centers characterized by large zero-field splitting (ZFS), which was not possible at X-band EPR as reported by Misra *et al.* [13]. Apart from determining the ZFS parameters, the focus here is to understand how Fe ions are incorporated into the nano-particles in the SnO_2 lattice and their interaction with the environment.

II. RESULTS AND DISCUSSION

EPR measurements at 236 GHz were carried out at 255 K at Cornell University on a spectrometer that uses an induction mode Fabry-Pérot cavity in the warm bore of the superconducting magnet dewar containing liquid helium, where the sample is placed, whose ambient temperature is 255 K. The magnetic field can be varied from 0.0 to 9.0 T. As seen from the experimental EPR spectrum, shown in Fig. 1, there exists an overlap of four substitutionally incorporated high-spin Fe^{3+} ions with the effective spin $S = 5/2$, characterized by rather large zero-field splitting (ZFS). At 255 K, the three Fe^{3+} Kramers doublets ($M = \pm 5/2, \pm 3/2, \pm 1/2$) are still populated, so that all the allowed EPR transitions are observed with reasonable intensities. No broad ferromagnetic line due to ferromagnetically coupled Fe^{3+} ions was observed here, because of the absence of long-range ordering of nano-particles constituting the sample.

The spin-Hamiltonian characterizing the spin-5/2 state: $H_S = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + D [S_z^2 - S(S+1)/3] + E [S_x^2 - S_y^2]$, with $\mathbf{B}$, $\mathbf{g}$ and μ_B being the magnetic-field intensity, $\mathbf{g}$ -matrix and the Bohr magneton, respectively, is used to describe the EPR spectrum due to individual Fe^{3+} ions localized in substitutional or interstitial positions with defects around them. The spectra were simulated using Win-EPR software (Bruker). The baseline had the semblance of a spin-1/2 EPR line, described by the Zeeman interaction, $\mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S}$. The overall spectrum due to the various centers, HS1, HS2, HS3, HS4 and the baseline (BL), was calculated using the overlap $I(\text{BL}) + (I(\text{HS1}) + I(\text{HS2}) + I(\text{HS3}) + I(\text{HS4})) \times \exp(-0.00001 \times B)$, where the exponential factor is related to Boltzmann population distribution of the energy levels, I is the relative intensity of a center, and B is in Gauss. The simulated spectra are shown in Fig. 1, with the values of the spin-Hamiltonian parameters and relative intensities being listed in Table 1. The baseline seemed to fit well to an $S = 1/2$ EPR spectrum. It has not been identified to be a ferromagnetic resonance line, because there is not expected any long-range order in nano-particles due to varying sizes of the nano-particles in the sample; it is the characteristic of the magnetic-field sweep over a rather long range of 9 T. There is seen a good general agreement of the simulated spectrum with the experimental one. The differences in the simulated and observed line positions are due to the neglect of the fourth-order parameters in the spin Hamiltonian, whose inclusion would have certainly improved the agreement considerably. However, it would have required an exorbitant effort to vary three additional fourth-order parameters in the brute-force trial-and-error fitting carried out here. Some of the lines constituting the multitude of lines about the $g = 2.0$ region are due to the Fe^{3+} centers characterized by much smaller ZFS parameters (D , E) than those considered here to simulate the high-frequency spectrum, as detected in the X-band EPR spectrum [13]. No effort has been made to simulate them here; they have been addressed in [13].

In SnO_2 , each tin ion is octahedrally surrounded by six oxygen ions at equal distances. When a 3d impurity ion, like Fe^{3+} , substitutes for the Sn^{4+} ion, it causes an axial distortion due to the difference in the size and charge. Further, this creates vacancies due to charge compensation

caused by the difference in the charge of the impurity Fe^{3+} ions which substitute for Sn^{4+} ions in SnO_2 , preferably at the octahedral sites. Dusausooy *et al.* [14] reported EPR spectra due to four Fe^{3+} sites in single crystals of Fe^{3+} -doped SnO_2 due to different charge compensation mechanisms, deducing that three of these four centers are due to substitutional Fe^{3+} ions, whereas the fourth Fe^{3+} center is situated at an interstitial site. In the high-frequency EPR spectrum reported here, there are observed two Fe^{3+} spectra associated with very low field lines ($\sim 14,000$ G and $\sim 18,000$ G), described by rather large D parameters greater than 1.5 cm^{-1} (Table 1). This is due to the Fe^{3+} ions being situated in interstitial positions in close proximity to the surfaces of nano particles in the sample, surrounded by oxygen defects, which play a leading role in determining the magnetic properties of the sample. In addition to these EPR spectra, there are observed two other EPR spectra due to Fe^{3+} ions in substitutional positions with relatively smaller D parameters, although still quite large. One of them, (HS3) is close to that for the I1 Fe^{3+} EPR center reported by Dusausooy *et al.* [14], who assigned that center to Fe^{3+} ions in substitutional positions, where OH^- replaces O^{2-} , and the second one (HS4) is close to that for the SN Fe center reported by Dusausooy *et al.* [14], the site for which was not deduced. The sign of the D parameter is chosen here to be positive in accordance with the published value [14].

At the nano-scale, the role of the nano particles on the surface is enhanced significantly; thus, additional effects in the EPR spectrum different from those in the bulk form are expected. The occurrence of the observed EPR lines at lower fields and changes in the linewidth are related to the anisotropy in non-spherical particles with a statistical distribution of sizes and shapes [15-17].

III. CONCLUSIONS

The EPR measurements and simulations presented here bring an understanding of the environments of the isolated Fe^{3+} ions incorporated into the SnO_2 lattice in nano-particles at substitutional and interstitial positions. No ferromagnetic lines were observed, because a long-range ordering is not expected when there are present nano-particles of varying shapes and sizes in the sample. The Fe^{3+} EPR spectrum reported here reveals evidence for strong influence of surface proximity and oxygen defects. A detailed microscopic analysis of the observed spectra will require an exorbitant effort which is not warranted over and above the main conclusions deduced here.

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Figure 1.

Simulated and experimentally recorded first-derivative EPR absorption spectrum recorded at 236 GHz at 255 K for the 0.005% Fe^{3+} -doped SnO_2 sample prepared at 600 °C. The individually simulated spectra, as well as their overlap to describe the experimental spectrum, have been displayed.

Table 1

Spin-Hamiltonian parameters employed to simulate the EMR spectrum. Here BL stands for baseline

$\text{Fe}^{3+}/\text{Sn}_{1-x}\text{Fe}_x\text{O}_2$ (x=0.005)	Center/BL	g_x	g_y	g_z	D (cm^{-1})	E (cm^{-1})	Relative intensity	Linewidth (G)
S = 5/2	HS1	2.0	2.0	2.0	1.541	0.0	2.0	40
	HS2	2.0	2.0	2.0	1.634	0.0	0.25	40
	HS3	2.004	2.003	2.006	1.276	0.049	0.125	180
	HS4	2.003	1.998	2.006	0.856	0.101	0.45	360
BL (S = 1/2)	BL	5.2	5.2	5.2			0.25	28000