An X- and Q-band Fe^{3+} EPR study of nanoparticles of magnetic semiconductor $Zn_{1-x}Fe_xO$

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ABSTRACT

EPR studies on two types of nanoparticles of Fe^{3+} doped, 0.1–10%, ZnO, NL and QJ, prepared using similar chemical hydrolysis methods, in diethylene glycol, and in denatured ethanol solutions, respectively, were carried out at X-band ($\sim$9.5 GHz) at 77 K and at Q-band ($\sim$34.0 GHz) at 10, 80, and 295 K. To interpret the experimental results, EPR spectra were simulated by exact diagonalization of the spin-Hamiltonian matrix to identify the Fe ions at different magnetically active sites in these samples. The simulation for NL samples revealed that they contained (i) Fe^{3+} ions, which substituted for Zn ions, the zero-field splitting (ZFS) parameter which has a large distribution over the sample due to oxygen vacancies in the second coordination sphere; (ii) EPR signal from surface oxygen defects; and (iii) ferromagnetically (FM) coupled Fe ions with concentration of Fe more than 1%. The EPR spectra for QJ samples are very different from those for NL samples, exhibiting only rather intense FM EPR lines. The FM and EPR spectra in NL and/or QJ samples are found to vary strongly with differences in the surface morphology of nanoparticles.

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1. Introduction

Dilute magnetic semiconductors (DMSs), containing a small percentage of transition-metal (TM) cations, lead to many new functionalities, resulting from the carrier–cation magnetic exchange. Oxide semiconductors, such as ZnO, have been recently shown to be amongst the most promising host systems to exhibit ferromagnetism (FM) above room temperature [1,2]. Fe^{3+} is among the most appropriate TM ions to exhibit strong FM due to its high magnetic moment of $\sim$5.92μ_B or $\sim$1.73μ_B, expected in the high spin ($S=5/2$) or low spin ($S=1/2$) states, respectively.

Fe-doped ZnO nanoparticles are at present considered to be prospective DMS candidates, and have recently been investigated extensively. The various mechanisms for producing ferromagnetism in ZnO nanoparticles are as follows. Dietl et al. [1] first proposed a double-exchange interaction, wherein magnetic ions are coupled by free carriers, resulting in ferromagnetism [3], rendering these materials DMS. A mechanism of bound magnetic polarons (BMPS) has also been proposed to explain magnetic ordering in ZnO [4]. Further investigations revealed that defects could induce ferromagnetic interactions between the dopant Fe ions. On the other hand, antiferromagnetic coupling dominates in neutral defect-free clusters [5].

The ferromagnetic interaction is stabilized in n-type ZnO semiconductors by electron doping [6]. Detailed theoretical studies revealed that the presence of O and Zn vacancies produces ferromagnetism. Ultimately, it was shown that in order to achieve long-range half-metallic ferromagnetism, Zn-vacancies are more crucial than O-vacancies [7]. Finally, the nature of ferromagnetism in DMS is not uniquely established yet. A review of recent advances in the interpretation of ferromagnetism in ZnO was published by Snure et al. [8].

Ferromagnetic interactions exist in these samples near the surface region (within 10 nm) that possess higher Fe concentration, enriched with Zn and O vacancies [9]. Fe^{3+} ions dominate on the surface region, with the ferromagnetism originating from the exchange interaction between an unequal numbers of Fe ions occupying two sets of inequivalent positions in the surface region of 2–3 nm [10]. Karmakar et al. [11] found that the magnetic system of Fe ions becomes converted from the ferromagnetic state to the spin-glass state at $T>450$ K due to canting of disordered surface-spins in the nanoparticles. The Fe^{3+} ($S=5/2$, 3d^5) state becomes stabilized in these samples, because XPS studies showed the presence of only Fe^{3+} ions and did not show any significant presence of Fe^{2+} ions [12]. Thus, most of the doped Fe ions are incorporated as Fe^{3+}. As-grown ZnO nanoparticles are n-type semiconductors due to their native defects, which are specifically O- and Zn-vacancies. However, this O-vacancy is too deep in a donor and, therefore, the carriers are not easily excited from donor levels to the conduction band, and a Zn-vacancy is too mobile to be stable, and thus it is not a stable source of carriers.

Therefore, additional doping with Group III ions (B, Al, Ga and In) is required to enhance n-type conductivity in ZnO samples [13]. DMSs are usually formed in $Zn_{1-x}Fe_xO$ nanoparticles at a low concentration (x) of Fe ions, from 0.01% to 0.09%. The disappearance of ferromagnetism at higher concentrations means that Fe ions become incorporated in the secondary magnetic phase, $ZnFe_2O_4$, which is antiferromagnetic at $T_N < 10$ K and paramagnetic at room temperature [14,15]. Alternatively, it can also be ascribed to a transition to the antiferromagnetic state of the $Zn_{1-x}Fe_xO$ phase [16]. On the other hand, if ferrimagnetic Fe_3O_4 ($T_c < 858$ K) is formed as the secondary phase, the magnetic moment increases.

One of the main problems in the study of DMS is the ability to separate the true DMS phase and to avoid the formation of secondary magnetic phases, taking into account the solid-solubility limit of the magnetic dopant. X-ray diffraction (XRD) is not an unequivocal method for the determination of secondary phases in nano-sized particles due to the limited length of Bragg's diffraction. Because of their different crystallographic orientations with respect to the host crystal, secondary-phase nano-particles are very difficult to detect by a simple Bragg–Brentano scan in some cases [3]. With increasing Fe doping, the lattice parameters a and c, and lattice volume V, were determined using suitable pairs of (100), (102), (110) and (103) peaks (and using peak deconvolution as necessary). Usually, several secondary phases were revealed in the $Zn_{1-x}Fe_xO$ system depending on the synthesis method and initial chemical reagents, such as $ZnFe_2O_4$ [15,17], α-Fe [18,19] and Fe_3O_4 [4]. α-Fe and Fe_3O_4 are ferromagnetic and ferrimagnetic, respectively, at room temperature and can mask the true DMS behavior. Therefore, control of secondary magnetic phases is very important in the investigation of DMS. Electron Paramagnetic Resonance (EPR) is a very effective technique in such cases, because it is capable of unambiguously separating the contributions from different sources of magnetism, even for the smallest nanoparticles.

The EPR technique can be used in the investigation of localized Fe impurity ions [10,20,21], localized defects [22–25], and ferromagnetic phases [26] in ZnO nanoparticles. It is a powerful tool to detect secondary magnetic phase formation. The influence on EPR linewidth by charge carriers in semiconducting ZnO [27] provides important information on the mechanism of producing a DMS state. Influence of nanoparticle size and surface defects on magnetic properties of ZnO nanoparticles has been investigated by EPR [28]. Weak exchange interactions of Co^{2+} pairs have also been investigated in ZnO [29]. Controlled formation of defects is a very important step to render Fe-doped ZnO a ferromagnetic semiconductor (DMS) at room temperature, which can be exploited to develop spintronic devices, whose operation depends on both spin and charge of the constituents. Furthermore, several new devices, such as spin transistors and spin-LEDs, have very high-density non-volatile semiconductor memory and optical emitters with polarized output can be fabricated using spintronic materials.

Many EPR investigations of nanoparticles have been reported recently [30–47]. The purpose of this paper is to report detailed EPR studies at X-band ($\sim$9.5 GHz) at 77 K and at Q-band ($\sim$34 GHz) at 10, 80, and 295 K on two types of nanoparticles of ZnO, NL and QJ, prepared using similar chemical hydrolysis methods, in diethylene glycol, and in denatured ethanol solutions, respectively, doped with 0.1–10% Fe^{3+} to advance further the information available on nanoparticles from EPR.

2. Experimental details

2.1. Synthesis

Special attention is required to synthesize ZnO nanoparticles with controllable surface morphology and size, as the room-temperature ferromagnetism in the $Zn_{1-x}Fe_xO$ system is not stable due to poor reproducibility of defects on the surfaces of ZnO nanoparticles. Two

main procedures to grow ZnO nanoparticles have been developed: solid state reactions and solvothermal method [48]. For the latter, two solvents have been used, ethanol [49,50] and diethylene glycol [50], to modify the surfaces of ZnO nanoparticles. Use of diethylene glycol as a solvent produces ellipsoidal (rod-like) samples [51], whereas use of ethanol produces spherical particles [52]. The influence of benzyl alcohol as a solvent on magnetic properties of ZnO was investigated in detail by Clavel et al. [53]. They found that different solvents and capping agents can change the ZnO state from ferromagnetic to paramagnetic. On the other hand, total absence of ferromagnetism in the $Zn_{1-x}Fe_xO$ system for any Fe concentrations was also found [54], whereas the presence of ferromagnetism in pure Wurtzite ZnO phase [20] has also been reported. Thus, the exact mechanism of ferromagnetism in the $Zn_{1-x}Fe_xO$ system is not well understood so far. It is noted in this context that methods of modification of the surface properties and surface charge, strongly influencing the saturation magnetization of ZnO nanoparticles, have been proposed recently [55,56].

Nanoparticle samples of Fe-doped ZnO were synthesized using the chemical hydrolysis of zinc(II) and iron(II) acetate precursors. Two sets of iron-doped zinc oxide nano-samples were prepared using similar chemical hydrolysis methods, one in diethylene glycol, and another in denatured ethanol solutions, hereafter referred to as NL and QJ samples, respectively. The samples were prepared from the same zinc and iron acetate dihydrate precursors. The nano-samples so prepared possess different surface structure/groups depending on the solvent used for synthesis. The dopant concentration, referred to as x, is given by the molar ratio of [Fe]/([Fe]+[Zn]).

2.2. X-ray diffraction (XRD) characterization and transmission electron microscopy (TEM) images

X-ray diffraction was employed to investigate the structural properties and crystallite size, as well as to rule out the presence of undesired impurity phases. The XRD patterns (Fig. 1) show only the Wurtzite ZnO phase with no indication of the presence of other phases even with up to 10% Fe doping. The XRD peak positions showed gradual changes with Fe doping, revealing significant variations in the unit cell volume, V, which initially increased due to Fe doping by up to 5%. This can be understood qualitatively by realizing the fact that interstitial incorporation of Fe ions results in an expansion of the lattice. This, in turn, causes a rearrangement of neighboring oxygen and/or Zn^{2+} ions for charge neutrality. The relatively mild changes in V for Fe doping > 5% may indicate additional incorporation of dopant ions in both substitutional and interstitial sites, as reported in some host systems, since the Fe^{3+} ionic radius is smaller than that of Zn^{2+}, causing somewhat similar structural changes in the lattice parameters [57]. The average primary crystallite length, L, of the doped $Zn_{1-x}Fe_xO$ nano-samples was calculated using the width of the (102) peak and the Scherrer relation giving $L = 6.8 \pm 1.5$ nm. It was found to be similar for both NL and QJ samples. The sizes of nanoparticles were determined directly by transmission electron microscopy (TEM). Details of size distribution of these nanoparticles were reported by Johnson et al. [12], showing the TEM images of ZnO nanoparticles doped with Fe ions. Studies of such samples by Johnson et al. [12] and by Thurber et al. [58] clearly showed that these samples were nano-sized. As well, they established the intrinsic nature of ferromagnetism in ZnO powder in these samples.

2.3. Saturation magnetization

As seen from the dependence of the saturation magnetization on Fe concentration [58], the saturation magnetization for NL sample with x = 10% Fe is almost equal to the saturation magnetization for QJ sample with x = 2.5% Fe. Only when s > 2.5% Fe does