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journal homepage: [www.elsevier.com/locate/jmmm](http://www.elsevier.com/locate/jmmm)An X- and Q-band  $\text{Fe}^{3+}$  EPR study of nanoparticles of magnetic semiconductor  $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ Sushil K. Misra<sup>a,\*</sup>, S.I. Andronenko<sup>b</sup>, A. Thurber<sup>c</sup>, A. Punnoose<sup>c</sup>, A. Nalepa<sup>d</sup><sup>a</sup> Physics Department, Concordia University, Montreal, QC, Canada H3G 1M8<sup>b</sup> Physics Institute, Kazan Federal University, Kazan 420008, Russian Federation<sup>c</sup> Department of Physics, Boise State University, Boise, ID 83725-1570, USA<sup>d</sup> Max-Planck-Institut für Chemische Energie Konversion, Stifstrasse 34-36, 45470 Mülheim an der Ruhr, Germany

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## ABSTRACT

EPR studies on two types of nanoparticles of  $\text{Fe}^{3+}$  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)  $\text{Fe}^{3+}$  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].  $\text{Fe}^{3+}$  is among the most appropriate TM ions to exhibit strong FM due to its high magnetic moment of  $\sim 5.92\mu_B$  or  $\sim 1.73\mu_B$ , 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, anti-ferromagnetic coupling dominates in neutral defect-free clusters [5].

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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].  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  ( $S=5/2$ ,  $3d^5$ ) state becomes stabilized in these samples, because XPS studies showed the presence of only  $\text{Fe}^{3+}$  ions and did not show any significant presence of  $\text{Fe}^{2+}$  ions [12]. Thus, most of the doped Fe ions are incorporated as  $\text{Fe}^{3+}$ . 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 band, 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.