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An X- and Q-band Fe³⁺ EPR Study of Nanoparticles of Magnetic Semiconductor Zn_{1-x}Fe_xO

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EPR studies 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 % Fe³⁺, were carried out at X-band (9.5 GHz) at 77 K and at Q-band (34 GHz) at 10, 80, 295 K. To interpret the experimental results, EPR spectra were simulated by exact diagonalization of the spin-Hamiltonian matrix, in order to identify the presence of Fe ions at different magnetically active sites in these samples. The simulation of EPR spectra for NL samples revealed that they contained (i) Fe³⁺ ions, which substituted for Zn ions, exhibiting trigonal Fe³⁺ EPR spectrum in crystalline ZnO, the zero-field splitting (ZFS) parameter for which has a large distribution over the sample due to oxygen vacancies in the second coordination sphere; (ii) Fe³⁺ ions characterized by very small ZFS; and (iii) ferromagnetically (FM) ordered Fe ions in samples with concentration of Fe more than 1%. ZnO nanoparticles. The EPR spectra for QJ samples are very different from those for NL samples, clearly exhibiting Fe³⁺ EPR spectra belonging to localized ions. The ferromagnetism and EPR spectra are found to vary strongly with differences in the surface morphology of nanoparticles.





The main conclusions of our EPR investigations of ZnO nanoparticles are as follows:

(i) The observed EPR spectra provide clear evidence for the presence of both paramagnetic Fe^{3+} ions exhibiting sharp lines, as well as ferromagnetically coupled Fe ions producing a single broad signal. Both the paramagnetic Fe^{3+} ions and the ferromagnetic components are present in NL samples with Fe concentration of more than 2.5%.

(ii) The EPR spectrum for localized Fe^{3+} ions has been successfully interpreted here by taking into account the Gaussian distribution of the zfs (b_2^0) parameter. Both sets of EPR signals, HS1 and HS2, became more intense with increasing Fe concentration.

(iii) The paramagnetic fraction of the doped ions does not contribute to the ferromagnetic coupling. This explains the smaller magnetic moment observed in NL samples. QJ samples, on the other hand, only exhibit FM resonance signals, suggesting that all the doped Fe ions in them are magnetically coupled. This accounts for their stronger ferromagnetism.