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Aim of the work

In this work, we present study of magnetic properties of sample containing nanosize ZnO powders doped with MnO magnetic dopant, by using the magnetic resonance method. The magnetic resonance spectra registered at temperatures in the 4-300 K range will be analyzed in term of three different components and attributed to specific magnetic centers.

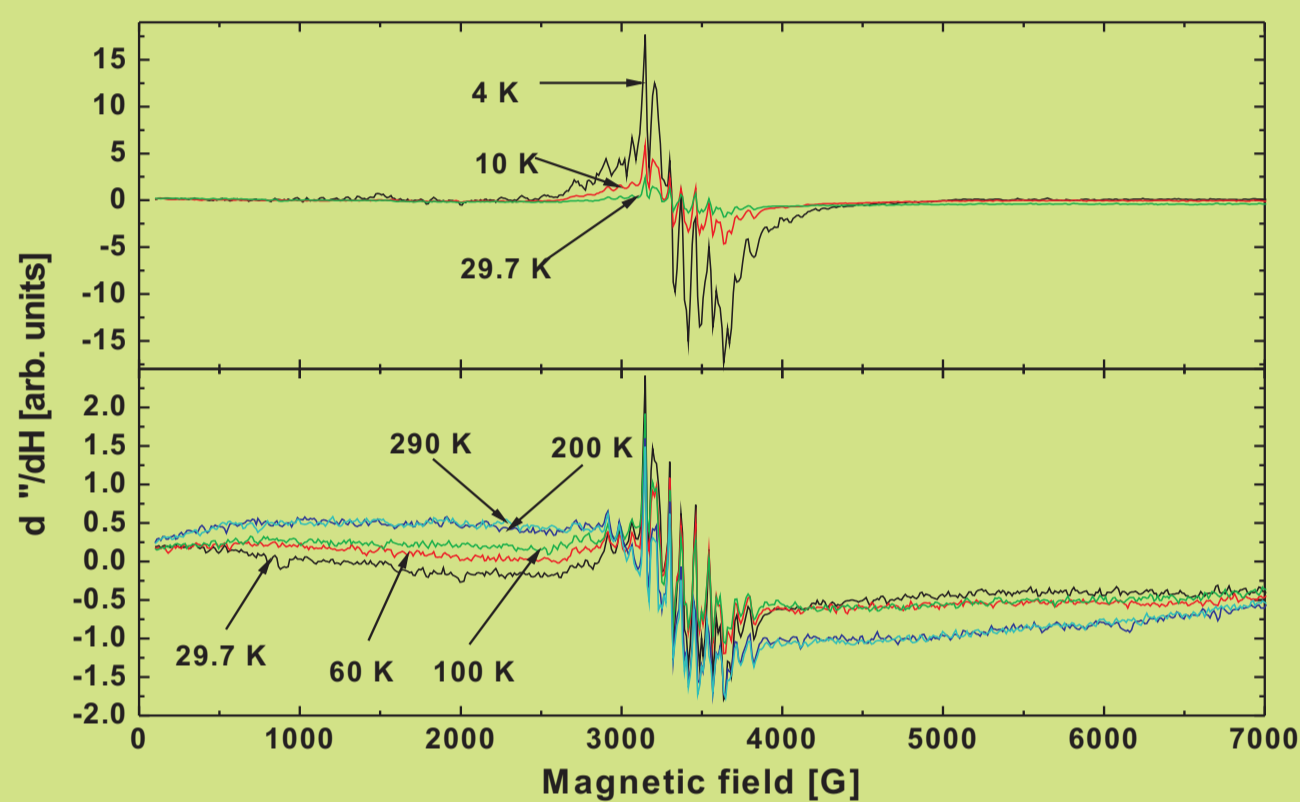


Fig. 1. Examples of registered spectra of nanocrystalline 0.10MnO/0.90ZnO at low (top panel) and high (bottom panel) temperatures.

In Fig. 1 a selection of the registered magnetic resonance spectra of 0.10MnO/0.90ZnO are presented. In the upper panel in Fig. 1 three spectra obtained at $T < 30$ K are shown, in the bottom panel a few spectra taken at higher temperatures are presented. At low temperatures the spectra of two components are easily to recognized. One component forms a collection of many narrow lines that are presumably the result of a hyperfine structure (hfs) of manganese ion and will be further designated as component S1. The other component constitutes a single, broader line that is superimposed on the S1 spectrum. That component will be designated as S2. Both components are visible in all spectra registered in 4-300 K range. At temperatures $T > 30$ K yet another component is visible – a very broad line that spans the whole range of magnetic field. This component will be designated as S3.

Spectrum S1

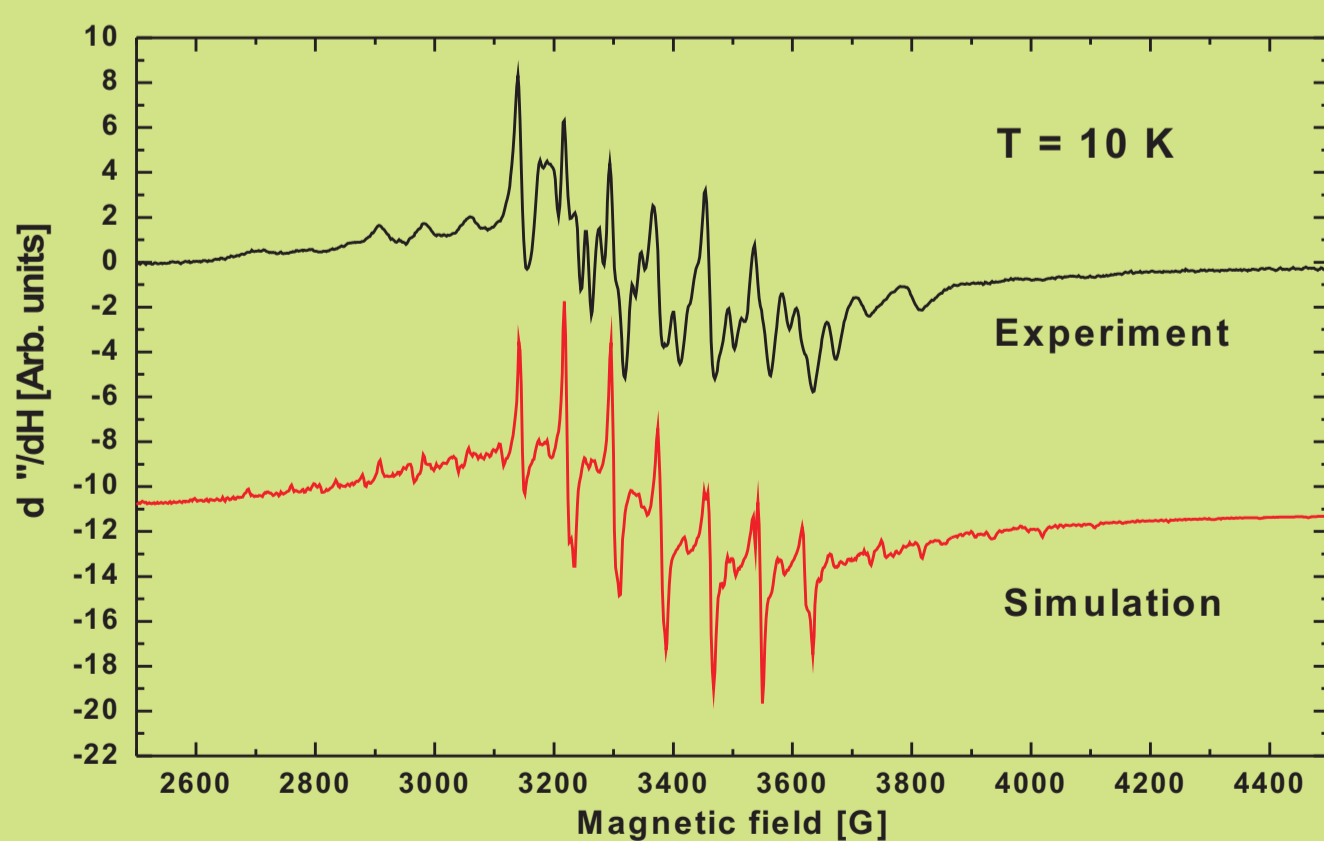


Fig. 3. Experimental (black) and simulated (red) magnetic resonance spectra of nanocrystalline 0.10MnO/0.90ZnO at 10 K. Only S1 and S2 spectra components were included in the simulation.

$$H \quad g \quad HS \quad D S_z^2 \quad 1/3 S S \quad 1 \quad E S_x^2 \quad S_y^2 \quad ASI$$

$$g=2,00232, A=80 \text{ G}, D=225 \text{ G}, E=15 \text{ G},$$

$$\text{Gaussian-shape line, peak-to-peak linewidth} \quad B=8 \text{ G}$$

Conclusions

Temperature study of the magnetic spectrum of 0.10MnO/0.90ZnO nanocomposite revealed the existence of three kinds of magnetic centers. Two components of the observed spectra, designated as S1 and S2, are connected with defects in magnetic structure of the ZnMnO₃ nanoparticles: the S1 spectrum displaying hfs is formed by isolated Mn²⁺ ions, while the S2 line is attributed to the clusters of the exchange-coupled Mn⁴⁺. Both paramagnetic centers are probably located on the surfaces of ZnMnO₃ nanoparticles. The FMR line S3 is produced by the ZnMnO₃ nanoparticles in a superparamagnetic phase.

Experimental

The investigated sample was synthesized by the wet chemical method. Initially, from an aqueous solution of nitrates the mixture of manganese hydroxides and zinc hydroxides was obtained. Then the obtained hydroxides were filtered, dried at the temperature of 70°C and calcined 1 hour at 300°C. The final sample contained 10 wt.% MnO and 90 wt.% ZnO. The phase composition was determined by X-ray diffraction (CoK_α radiation, X'Pert Philips). It was found that the sample contains only two phases: ZnO and ZnMnO₃. The mean crystallite size of magnetic ZnMnO₃ was calculated by using Scherrer's formula and was found to be 9 nm.

Magnetic resonance spectra were obtained on a conventional X-band ($\nu = 9.4$ GHz) Bruker E 500 spectrometer with the 100 kHz magnetic field modulation. The measurements were carried in the 4 – 290 K temperature range using an Oxford Instrument helium-flow cryostat. The registered spectra are the first derivative of the absorption curve with respect to the sweeping field H.

Attribution of the spin system to the S1, S2, and S3 spectra

The S1 spectrum is ascribed to isolated Mn²⁺ ions which appear as defects in the ZnMnO₃ structure. They might appear on the surface of the nanograins or inside the grains. Simulation of the hfs of S1 lines as produced by the Mn⁴⁺ ($S=3/2$) ion was not successful. For the broad S2 spectrum clusters of the exchange-coupled Mn⁴⁺ ions are responsible. The hfs structure is not visible in S2 spectrum because it was washed out by a stronger interaction between neighboring ions. The very broad line of the S3 spectrum is most likely attributed to the magnetic ZnMnO₃ nanoparticles. Thus the S3 spectrum is the ferromagnetic resonance (FMR) line originating in a system of magnetic nanoparticles in the superparamagnetic state. FMR line vanishes from the spectrum before the magnetic structure of nanoparticles freezes at T_f . Because the S2 and S3 spectra display similar changes at the same temperature 75 K thus the magnetic clusters of Mn⁴⁺ ions must be influenced by the magnetic field of a nanoparticle. A possible connection will be that the S2 clusters are formed on the surface of a nanoparticle thus ensuring a close interaction of both systems.

Spectrum S2

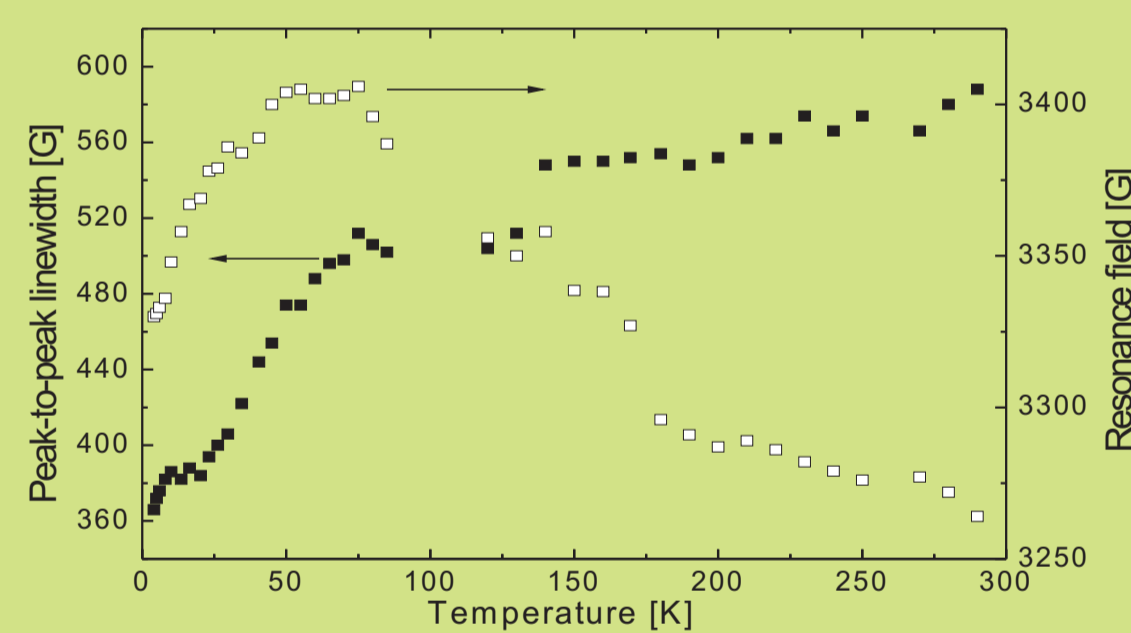


Fig. 4. Temperature dependence of the resonance field (open squares, right axis) and the peak-to-peak linewidth (filled squares, left axis) for the S2 spectrum component.

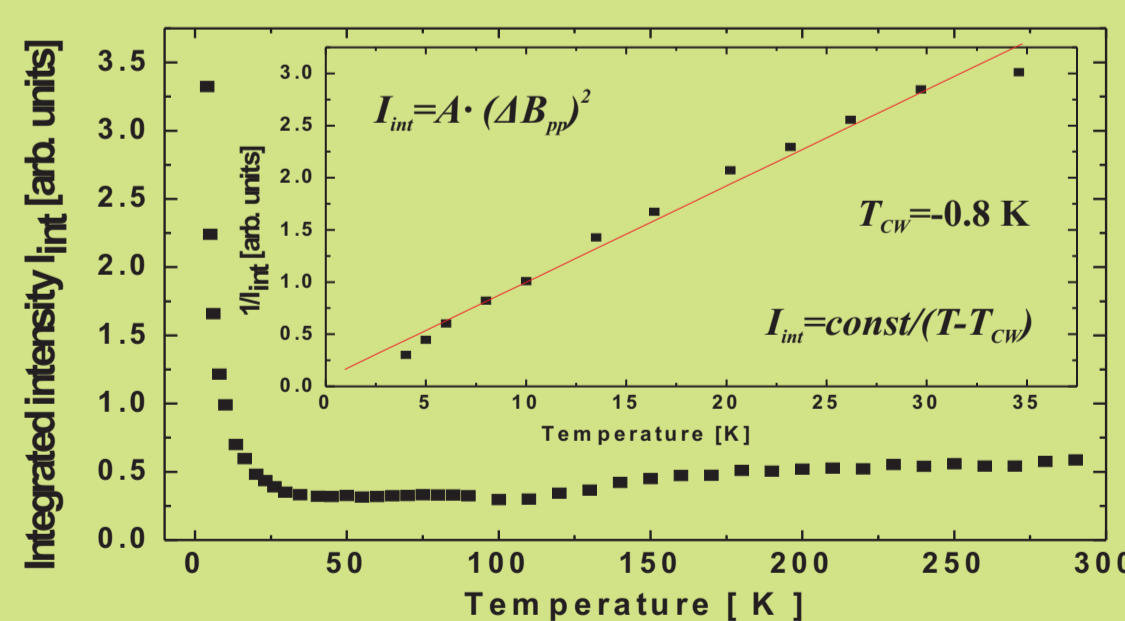


Fig. 5. Temperature dependence of the integrated intensity of the S2 spectrum component. The inset shows the temperature dependence of the inverse of the integrated intensity. The straight line in inset is the best fit to the Curie-Weiss law.

According to XRD study the only magnetic phase is ZnMnO₃ and it appears as nanoparticles with an average size of 9 nm. ZnMnO₃ has a T_C higher than 300 K and exhibits a spin-glass behavior with the freezing temperature $T_f=15$ K. The other important information is that most of manganese ions in ZnMnO₃ is in Mn⁴⁺ oxidation state.

Spectrum S3

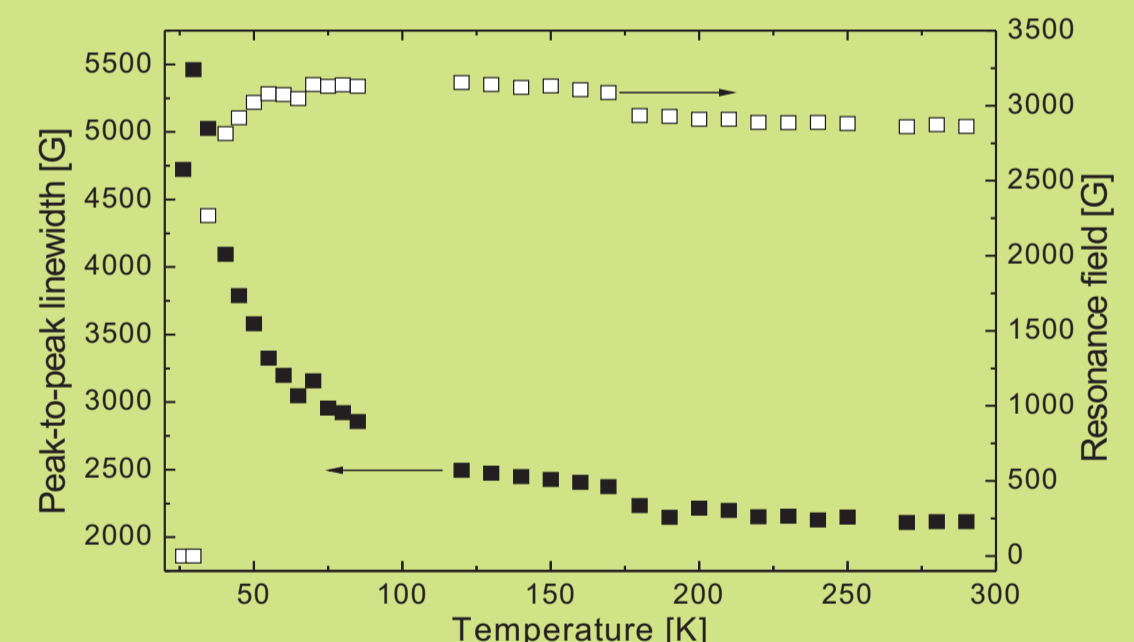


Fig. 6. Temperature dependence of the resonance field (open squares, right axis) and the peak-to-peak linewidth (filled squares, left axis) for the S3 spectrum component.

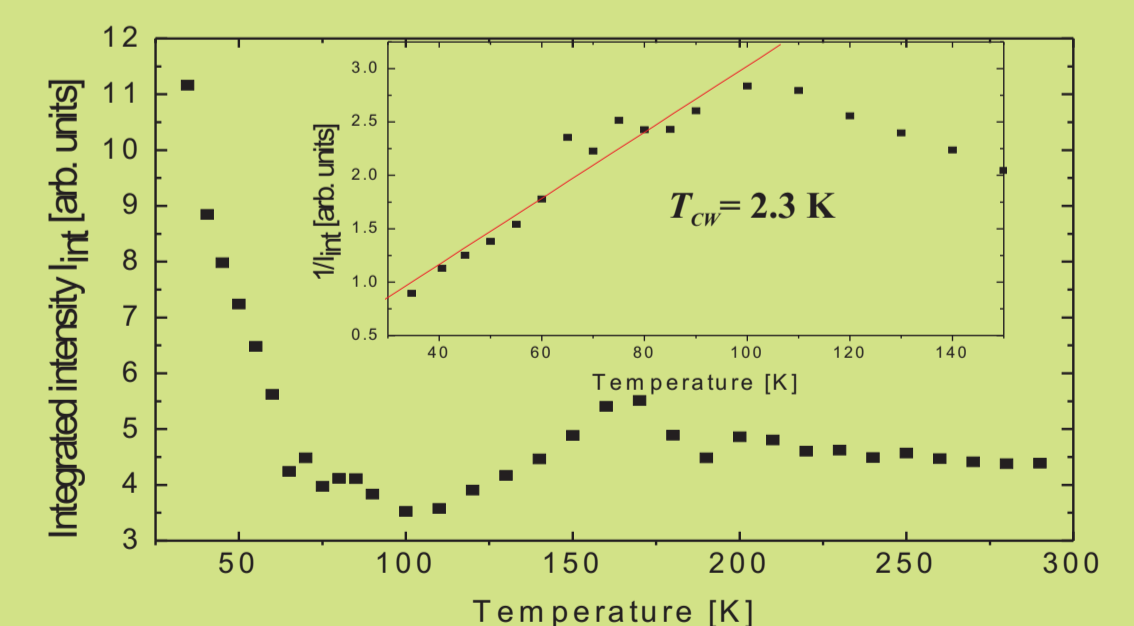


Fig. 7. Temperature dependence of the integrated intensity of the S3 spectrum component. The inset shows the temperature dependence of the inverse of the integrated intensity. The straight line in inset is the best fit to the Curie-Weiss law.

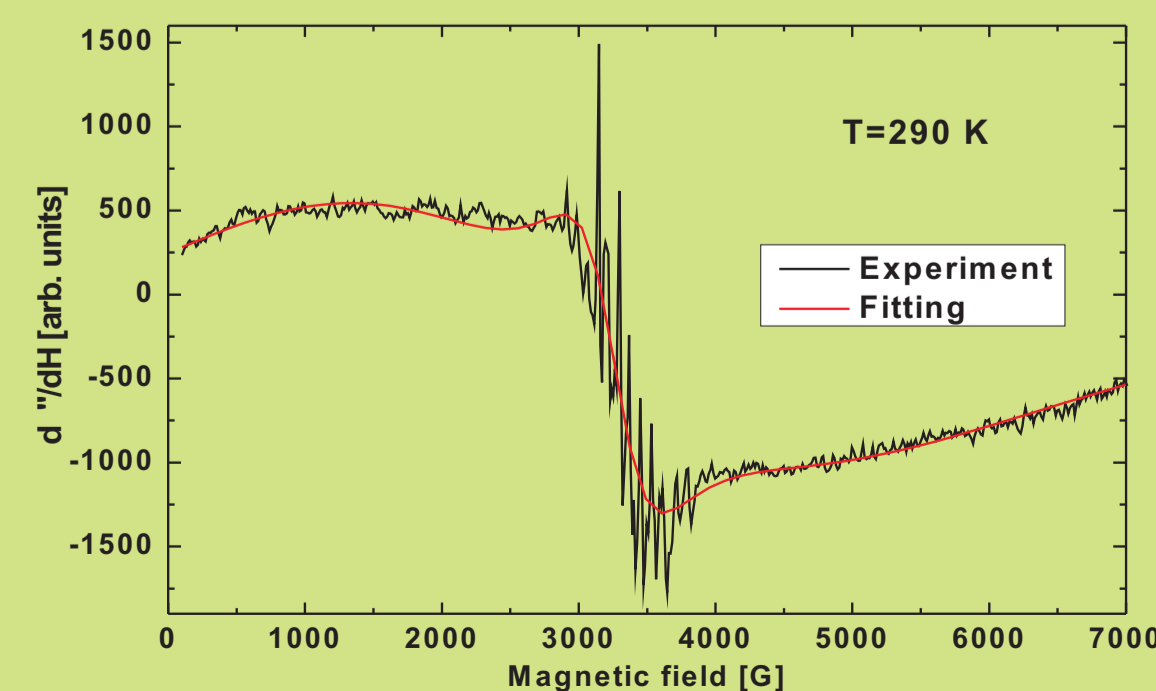


Fig. 2. Experimental (black) and fitted (red) magnetic resonance spectra of nanocrystalline 0.10MnO/0.90ZnO at 290 K. The fitting included only S2 and S3 spectra components.