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ORBITAL ORDERING PROBED BY ELECTRON-SPIN RESONANCE METHOD IN MAGNETIC SEMICONDUCTORS*

The temperature dependence of the electron-spin resonance in the 80…300 K range temperature and magnetic field up to 5 kOe has been investigated in the substance of $Co_xMn_{1-x}S$ solid solutions. From the temperature dependence of linewidth and g-value the orbital order is determined. The temperature hysteresis of ESR intensity in $Co_xMn_{1-x}S$ is found at the cooling in the magnetic field and without it.

Keywords: magnetically ordered materials, spin-orbit efiects, electron-spin resonance, sulfides.

The electron-spin resonance (ESR) can be used to detect orbital-ordering (OO) and to monitor the evolution of the OO parameter. Probing the spin of the non-integer filled d shell of $Mn^{(2+\delta)}$ ions by ESR, the anisotropy and temperature dependence of g-value and linewidth ΔH provide clear information on orbital order via spin-orbit coupling. Promising materials are $Co_xMn_{1-x}S$ solid solutions, which assume orbital ordering [1–3]. The $Co_xMn_{1-x}S$ solid solutions can be attributed to the multiferroic class. In the temperature ranges of $T \sim$ (110…120) K and T ~ (230…260) K, the correlation between the magnetic and electric subsystems has been found [3]. The presence of this correlation is confirmed by the magnetic field dependence of the temperature variation of the permittivity having maximum at these temperatures. The first maximum in the low-temperature range is caused by the change in the orbital ordering for cobalt ions surrounded with manganese ions; the second maximum is related to the orbital order in the manganese system.

The reduced ordered moment $\mu_0 = 4.4\mu_B$ in the AF structure of MnS may be the result of change of manganese ion valency $Mn^{2\pm\delta}$ or repartition of electron density between e_g- and t_{2g}-orbitals. In any case the number of t_{2g} the orbital occupancy is not equal to $n_{tg} = 3$. The uniform orbital occupancy at every site is formed at some high temperature. The MnS_6 octahedra distortion is small and essentially undetectable in X-ray experiments on MnS. The crystal field acting on the $Mn^{2\pm\delta}$ ion is therefore nearly cubic, and heuristically one expects unquenched orbital moment. The spin dynamics of MnS are highly sensitive to the orbital occupancy and can provide important information in this regard.

The aim of the study is to bring to light on mechanism of origin of the correlation between the magnetic and elastic subsystems [3; 4], to establish the role of orbital fiuctuations on the dynamical properties $Co_xMn_{1-x}S$ sulfides in the wide frequency range.

The crystal structure of the $Co_xMn_{1-x}S$ sulfides was studied with a DRON-3 facility in monochromatic CuKα-radiation at a temperature of 300 K. According to the X-ray difiraction data, the $Co_xMn_{1-x}S$ samples with $0 < x < 0.4$ have the NaCl-type face-centered cubic (FCC) lattice. With an increase in concentration of cation substitution (x), the lattice parameter linearly decreases from 5.222 E (x = 0) to 5.204 E (x = 0,4), which evidences the formation of the б-MnS-based solid solutions in the system [2].

The degree of inhomogeneity of the magnetic system, the efiect of the orbital magnetic moment, and the relaxation mechanism can be established by an ESR method. Cobalt and its compounds are characterized by a high g-factor ($g > 3$), which is not observed in the compound under study. This confirms magnetic homogeneity of the $Co_xMn_{1-x}S$ solid solutions. The magnetic resonance measurements were performed with a Bruker Elexsys 580 spectrometer at X-band frequency, using a continuous gas-fiow cryostat for He. The sample was cooled from 300 K down to 80 K in zero magnetic field and in the field H = 5 kOe. It enables to establish the dependence of the local magnetic characteristics of the sample on its magnetic prehistory and existence of degeneration on the orbital magnetic moment.

The efiective g-factor value $g_{eff} = h\text{н}/(\mu_B H_{res})$ is determined from the resonance field, which sharply increases in the temperature range 150 K< T < 180 K as shown in Fig. 1.

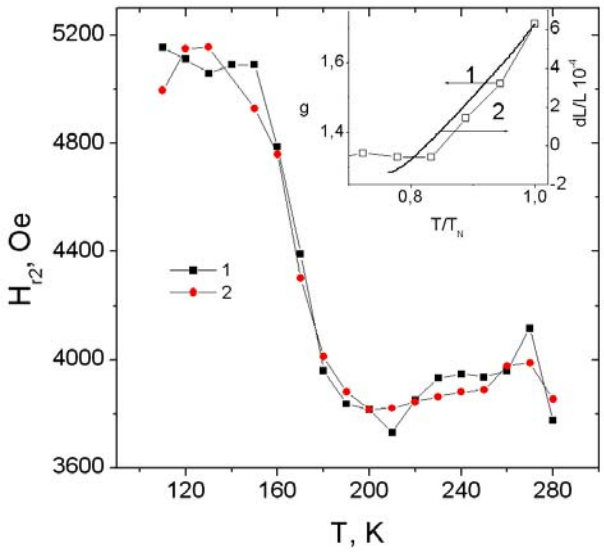

Fig. 1. Temperature dependences of the resonance field upon cooling in zero magnetic field (ZFC – 1) and in the field H = 5 kOe (FC – 2) for $Co_{0.05}Mn_{0.95}S$. The inset shows the temperature dependence of g-factor (1) and relative extension of sample dL/L (2)

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At $T < 150$ K, the g-factor is nearly temperature-independent and takes a value of about 1.3, whereas in the temperature range 190 K< T < 280 K its value varies within 1,7…1,75. Based on our data, we estimate $\Delta g/g \sim 0.15$, where g is the free-electron Lande factor and Δg is its shift in the crystalline environment.

In the absence of any appreciable static Jan–Teller distortion as observed experimentally by the X-ray difiraction data [2], one expects that the spin-orbit interaction splits the t_{2g} multiplet of the cubic crystal field Hamiltonian into a quadruple degenerate ground state and a higher-lying Kramers doublet. Even if a static JT distortion at the limits of the experimental error bars is included, the orbital contribution to the moment remains significant to the spin moment [5].

Antiferromagnetic long-range order causes the splitting d_{xz}- and d_{yz}-orbitals as a result of spin-orbital interaction at $T < T_N$, that leads to deformation octahedra. The temperature dependence of relative deformation $\Delta L/L$ for the $Co_xMn_{1-x}S$ with $x = 0.05$ is similar to $g(T)$ value as shown in insert to Fig. 1. These data prove a close relationship between spin and orbital magnetic moments, lattice deformation. The orbital ordered phase is characterized by an anisotropy of ΔH, which for polycrystalline samples reduces to a broad maximum in $\Delta H(T)$ [6]. For doped and pure $LaMnO_3$ the expression for the linewidth ESR due to crystal-field efiects and accounting only for the rotations of octahedral were obtained [7]. This theoretical approach is summarized in the formula [8]:

$$\Delta H_{\theta,\varphi}(T) = \frac{\chi_0(T)}{\chi(T)} \times$$

$$\times \left[\tau^{2\beta} \left(\Gamma_{CE} f_{reg}(\theta,\varphi) + \Gamma_{CFD} \left(\frac{T_N}{6(T-T_N)} \right)^{\alpha} \right) f_{div}(\theta,\varphi) \right] \quad (1)$$

with the free Curie susceptibility $\chi_0 \sim 1/T$, the static susceptibility $\chi(T)$, and $\tau = 1 - T/T_{JT}$. The first and second term describes the regular and divergent crystal field contributions, respectively. Only the latter diverges for $T \to T_N$ with an exponent α, whereas both terms decrease for $T \to T_{JT}$ with a critical exponent 2β. For polycrystalline compounds the averaging of angular factors $f_{reg}(\theta, \varphi)$, $f_{div}(\theta, \varphi)$ gives constant. We neglected here angular dependence $\Delta H(\theta, \varphi)$ and the linewidth is well fitted by

$$\Delta H(T) = \frac{T + T_{CW}}{T} \times$$

$$\times \left[\tau^{2\beta} \left(\Gamma_{CE} + \Gamma_{CDF} \left(\frac{T_N}{6(T-T_N)} \right)^{\alpha} \right) \right]. \quad (2)$$

As shown in Fig. 2 (solid line) a qualitative description was obtained by fitting the $\Delta H(T)$ data with $\Gamma_{CE} = 1.8$ kOe, $\Gamma_{CFD} = 0.4$ kOe and $\beta = 0{,}14(2)$, $\alpha = 1{,}3(5)$ with fixed $T_N = 165$ K, $T_{CW} = 460$ K, $T_{JT} = 280$ K. The critical indexes have been satisfactory agreement with estimates $\beta = 0.16(1)$, $\alpha = 1.8$ for polycrystalline $LaMnO_3$ [8].

Below the Neel temperature, one more weak resonance with $g = 2.03$ is observed in the field H_{r1} whose intensity is lower than the main resonance intensity (I_{r2}) by three orders of magnitude (insert in Fig. 2). This resonance may be associated with spin of conductivity electron of impurity ion Co^{+2} and magnons that formative spin polaron. Spin polaron density disappears at $T > T_N$. The ESR linewidth in the field $H_{r1} = 3.35$ kOe below the Neel temperature is also temperature-independent and may be related to localization of an spin-polaron with a small radius. The relaxation time is determined as $1/T_1 = \omega_{LS}^2 ac/x$ [9], where ω_{LS} is the energy of the spin-orbital interaction of electron, x is the Fermi velocity of an electron ($x \sim 10^6$ m/s), a is the size of an localized area close to the lattice constant, and c is the concentration of the spin polaron. For example, at $c = 0.001$ the spin-orbital interaction is $\omega_{LS} = 10^{12}$ Hz.

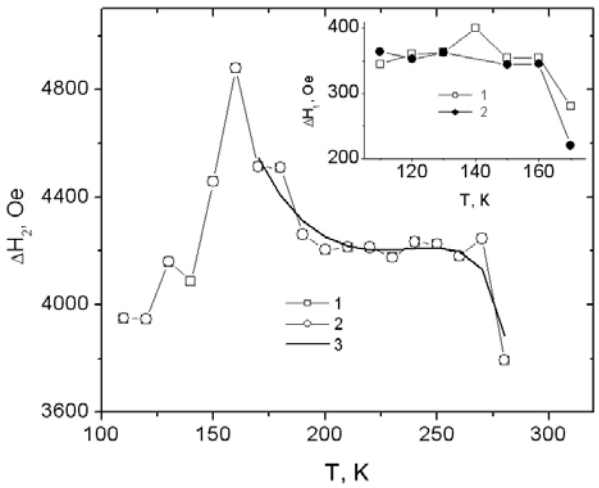

Fig. 2. Temperature dependences of the linewidth for the resonance field H_{r2} upon cooling in zero magnetic field (ZFC – 1) and in the field $H = 5$ kOe (FC – 2) , fitting curve (3) according to Eqn. 2 for $Co_{0.05}Mn_{0.95}S$.
The inset shows temperature dependence of the linewidth for the resonance field H_{r1} upon cooling in zero magnetic field (ZFC – 1) and in the field $H = 5$ kOe (FC – 2)

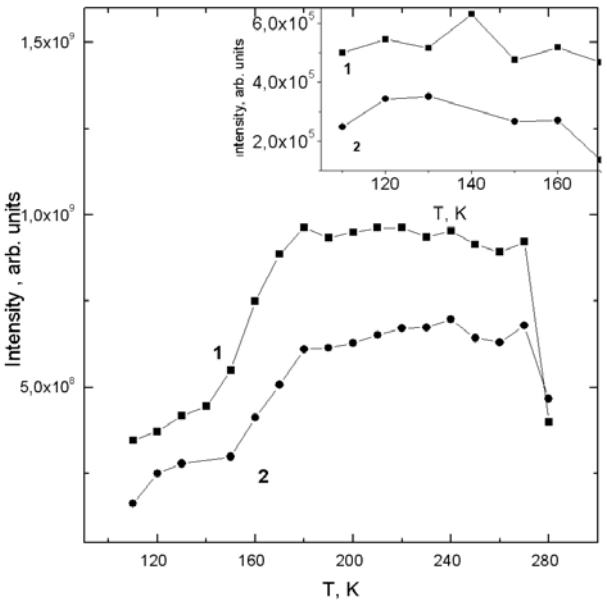

Fig. 3. Temperature dependences of the ESR spectra intensity for $Co_{0.05}Mn_{0.95}S$ sample upon cooling in zero magnetic field (ZFC – 1) and in the field $H = 5$ kOe (FC – 2) in resonance field H_{r2}.
The inset shows temperature dependences of the ESR spectra intensity sample upon cooling in zero magnetic field (ZFC – 1) and in the field $H = 5$kOe (FC – 2) in resonance field H_{r1}

The intensity of the magnetic resonance line is determined as a product of signal amplitude and a square of linewidth H_p obtained from the distance between the absorption derivative peaks. In Fig. 3 the intensities ESR are shown to depend on the prehistory of sample. In the sample cooled in the external magnetic field H = 5 kOe, the signal intensity decreases approximately by 40…60 %. It may be explained by change of direction of magnetic moments in the unaxial antiferromagnet in the vicinity of spin-fiop field. At cooling in the field the vector AF is parallel to alternating magnetic field, that leads to absence of ESR in linear approximation.

Intensity I_{r2} of the ESR in field H_{r2} decreases with temperature across the phase transition paramagnetic-antiferromagnetic. In particular, in the magnetically ordered phase the ESR intensity is directly proportional to a number of magnons, $I \sim n \sim (S - < S^z >)$ or, in normalized units, $I/I_0 \sim (1 - m)$, where m is the sublattice magnetization normalized to spin.

The absence of the temperature dependence of the linewidth (Fig. 2) in the range 190 K < T < 270 K allows one to consider the spin-orbital interaction to be the fundamental mechanism of spin relaxation and formation of short range orbital order.

Two frequencies of ESR are found in $Co_xMn_{1-x}S$ solid solution below Neel temperature. These resonances are ascribed to spin polaron and spin of localized electrons. Temperature independent behavior of the ESR linewidth and temperature hysteresis of the intensity reveal at the cooling in the external magnetic field and without it in the paramagnetic state at T < 280 K, that is accounted for by formation of orbital disordered state.

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ОБНАРУЖЕНИЕ ОРБИТАЛЬНОГО УПОРЯДОЧЕНИЯ МЕТОДОМ ЭЛЕКТРОННОГО ПАРАМАГНИТНОГО РЕЗОНАНСА В МАГНИТНЫХ ПОЛУПРОВОДНИКАХ

На твердых растворах $Co_xMn_{1-x}S$ проведены исследования электронного спинового резонанса в интервале температур 80…300 К и магнитных полей до 5 кЭ. Из температурных зависимостей ширины линии и величины g-фактора определено орбитальное упорядочение. В $Co_xMn_{1-x}S$ найден температурный гистерезис интенсивности электронного спинового резонанса, измеренной при охлаждении в магнитном поле и в нулевом магнитном поле.

Ключевые слова: магнитно упорядоченные материалы, спин-орбитальный эффект, электронный спиновый резонанс, сульфиды.