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Influence of magnetic ordering on the resistivity anisotropy of α-MnS single crystal

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Abstract

The resistivity, the optical absorbtion spectra of single crystal α-MnS are studied in the temperature range 80–300 K along two directions [100] and [111]. Strong anisotropy of resistivity, shift of absorbtion spectra band edge below $T < 160$ K are explained in terms of model delocalized holes in 3d-band manganese ions interacting with localized spins by using sd-model. © 2003 Published by Elsevier Ltd.

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The problem of spin dependent transport of electrons, magnetic ordering is one of the new and unsolved problems of condensed matter physics and magnetism. It is important to study the influence of magnetic structure on the transport properties of magnetic semiconductors. Sulfide α-MnS shows the antiferromagnetic (AF) ordering of the second kind constituted from ferromagnetic arranged spins into plane [111] and AF spin ordering along cube edges. According to the Hall measurements [1] the conductivity occurs by holes in 3d-band of manganese ions and the mobility of the holes is not thermally activated. The holes concentration per manganese ion is $n \sim 0.1$ at $T = 435$ K.

The electronic and magnetic properties of α-MnS have been studied at the density functional level of theory by solving the Kohn-Sham equations self-consistently [2]. First principle calculations confirm the hole character of conductivity. So the Mn 3d orbitals are populated with 5.5 electrons, where the e_g and t_{2g} spin down states consist $0.14e^-$ and $0.36e^-$, respectively, while the 3d orbitals of sulfur are practically unoccupied (0.01 electron) [2]. The bandwidths of Mn states of e_g and t_{2g} are ~2.5, ~1 eV and t_{2g} band structures corresponding to the spin up and spin down electron states are separated by ~2.7 eV. Fermi level allocates at the bottom of band t_{2g} with spin down. The states of the valence band are occupied by electrons of both p sulfur and d manganese orbitals and the gap value is ~1.5 eV. These results indicate that the low-energy electronic properties are due to holes at t_{2g} and symmetry hole band is in accordance with symmetry of ferromagnet ordering localized spins of manganese ions in plane [111].

The conductivity is proportionate to holes concentration in the paramagnetic phase. At $T < T_N$ the contribution of holes (n) with spin $\sigma = \downarrow$ in plane [111] with ferromagneting ordering localized spins $S = \uparrow$ in the conductivity decreases and holes with spin $\sigma = \uparrow$ move free. As a result the intensities of bands with different spin orientation become not the same. The chemical potential changes and resistivity may increase. The resistivity does not change along [100] if concentration n satisfies the condition derived for manganites [3] $n < n_c = 12\pi^4[J(2S+1)^{3/2}/6t]^3$, where t is the hopping matrix element, J is exchange. We consider a simple model interacting holes with localized spins in plane [111].

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α-MnS single crystal were obtained using the liquid manganese saturation with sulfur at $T \sim 1245$. X-ray diffraction analysis was performed with a DRON-2.0 diffractometer in the monochromatic Cu Kα—radiation at a temperature range of 80–300 K. The resistance measurements were made in the directions [111] and [100] in the same temperature range. Fluorescence spectroscopy is made with SPARK-1 spectrometer. According to X-ray analysis data, synthesized α-MnS sample is single crystals with an NaCl cubic lattice with the cell parameter $a = 5.22$ A. The optical measurements were carried out in a flowing quartz cryostat in a temperature range of 86–300 K measured with an accuracy of ± 1 K and in an interval of energies of 8×10^3–22×10^3 cm^{-1}.

The measurement of resistivity in the directions [111] and [100] reveals the anisotropy $lg(\rho_{111}/\rho_{100}) \simeq 2$ for $T < T_N$, were Neel temperature is $T_N = 150$ K. The temperature dependence of resistivity anisotropy normalized on the anisotropy value at $T = 126$ K is presented in Fig. 1. The activation energy of conductivity in the [111] is $E_a = 0.04$ eV and in the [100] is equal to zero in the temperature range 80 K $< T <$ 150 K. The anisotropy of the optical absorption bands are also observed [4]. The optical gap (peak A($^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$) and peak B($^6A_{1g} \rightarrow {}^4T_{2g}(^4G)$) is decreased by 0.08 eV along [111] at increasing temperature from 80 to 160 K. The some optical absorbtion spectra are shown in Fig. 2. The relative change of lower absorbtion band edge $(W_b(T) - W_b(T = 300\ \text{K}))/W_b(T = 80\ \text{K})$ normalized on the band edge at $T = 80$ K along [111] is plotted in Fig. 3.

Analysis of experimental data is carried out in term of model delocalized holes in 3d-band manganese ions interacting with localized spins by using sd-model. So wave functions of Mn t_{2g}–t_{2g} may be overlapped in plane [111]. The on-site Coulomb repulsion of holes can be neglected because the holes concentration is $n \ll 1$.

We consider a model Hamiltonian:

$$H = H_{\text{kin}} + H_{\text{int}} + H_{\text{ex}} \quad (1)$$

$$H_{\text{kin}} = -\sum_{i,j,\sigma} t_{i,j} a^+_{i\sigma} a_{j\sigma}$$

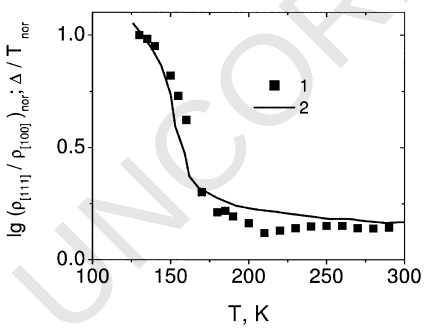

Fig. 1. The temperature dependence of resistivity anisotropy $lg(\rho_{111}/\rho_{100})(T)/lg(\rho_{111}/\rho_{100})(T = 126\ \text{K})(1)$ normalized on the anisotropy value at $T = 126$ K in the [111] and temperature gap dependence $126\Delta(T)/(T\Delta(T = 126\ \text{K}))(2), \Delta = E_F - \mu$.

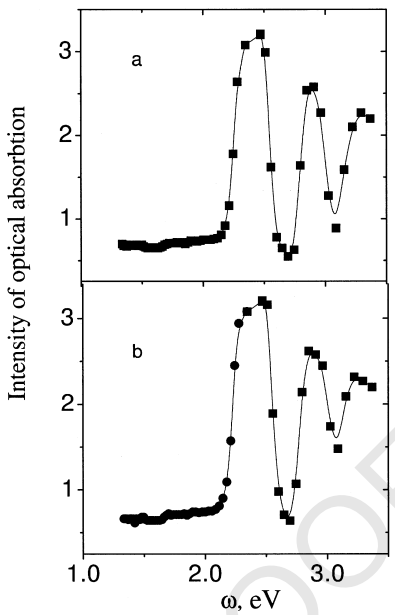

Fig. 2. The optical absorbtion spectra in the [111] for $T = 130$ K (a), 170 K (b).

$$H_{\text{int}} = -1/2 J_H \sum_i S^z_i (a^+_{i\uparrow} a_{i\uparrow} - a^+_{i\downarrow} a_{i\downarrow})$$

$$H_{\text{ex}} = -\sum_{i,j} J_{i,j} S_i S_j - \sum_{i,l} K_{i,l} S_i S_l,$$

where t is the hopping matrix element, $a_{i\sigma}$ is projected fermion annihilation operator, J_H is Hund's exchange, $J < 0, K < 0$ are the nearest-neighbors and next nearest-neighbors exchanges, S_i is classic spin as a function of angles $S(\theta, \varphi)$, S^z_i is spin operator. We used adiabatic approximation. Magnetic structure factor, spin–spin correlation functions are calculated by Monte Carlo method on the lattice $20 \times 20 \times 20$ with 30 000 MC/spin for exchange ratio $K/J = 1.85$ [5] by using Hamiltonian H_{ex}. Equations for estimation of chemical potential μ, half-bandwidth of

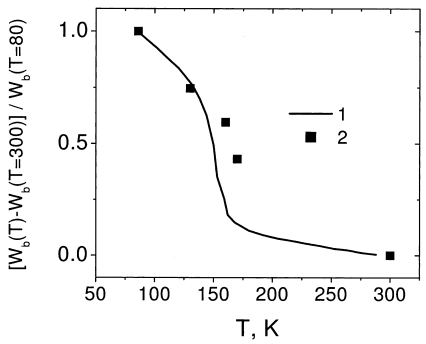

Fig. 3. The relative change of lower optical absorbtion band edge $(W_b(T) - W_b(T = 300\ \text{K}))/W_b(T = 80\ \text{K})$ (2) normalized on the band edge at $T = 80$ K in the [111] and change of lower holes band edge (1) versus temperature.

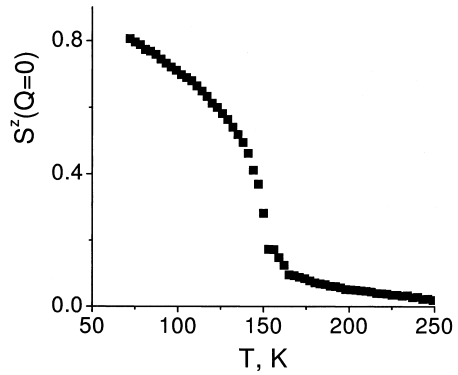

Fig. 4. The temperature dependence of magnetic structure factor $S(Q=0) = 1/N \sum_{r\in[111]}^{N} \langle S^z(0) S^z(r)\rangle$ calculated in plane [111].

correlated holes a_σ and holes concentration n as a function of average value of localized spin m^d have been obtained by Izyumov and Letfulov [6] in the limit $z \to \infty$ by using Hamiltonian $H = H_{kin} + H_{int}$ and dynamic mean field approximation:

$$m^d = \tanh \frac{1}{2} \lambda_F \tag{2}$$

$$\lambda_F = \frac{1}{\pi} \int_0^\infty dt \ln \frac{1 + \exp \beta(\mu_r - \nu - a_\uparrow \cos t)}{1 + \exp \beta(\mu_r + \nu - a_\downarrow \cos t)}$$

$$m^s = nm^d + (1 - (m^d)^2) \sum_\sigma \sigma \frac{1}{\pi} \int_0^\pi dt \sin^2 tf(a_\sigma \cos t + \sigma\nu)$$

$$n = \sum_\sigma (1 + \sigma m^d) \frac{1}{\pi} \int_0^\pi dt \sin^2 tf(a_\sigma \cos t + \sigma\nu),$$

where $\mu_r = \mu + I_h n/2, n = \langle n_{i\uparrow}\rangle + \langle n_{i\downarrow}\rangle$, $m^s = \langle n_{i\uparrow}\rangle - \langle n_{i\downarrow}\rangle, \nu = 1/2 I_h m^s$, $a_\sigma^2 = 1/8 W^2 (1 + \sigma m^d), \sigma = \pm 1, \beta = 1/T$, f, Fermi distribution function [7]. I_h, is theory parameter to be equal to ~ 0.01 eV. The bandwidth of free holes $W \simeq 0.93$ eV is determined from known holes concentration $n \sim 0.1$ at $T = 435$ K [1]. The average value of localized spin m^d in plane [111] is calculated from magnetic structure factor $(m^d)^2 = 1/N \sum_{r\in[111]}^{N} \times \langle S^z(0) S^z(r)\rangle$ that is shown in Fig. 4. As a result of hole spin interaction with localized spin the bandwidth of holes splits as plotted in Fig. 5. The change of lower band edge $\Delta W \simeq 0.11$ eV at $70\ \text{K} < T < 160$ K agrees with shift of optical band ~ 0.08 eV. The relative band edge shift is exhibited in Fig. 3. At $T < T_N$ the holes concentration changes and chemical potential decreases as shown in Fig. 5. The gap at the Fermi level opens and is equal to ~ 0.05 eV at $T = 70$ K that satisfactory agrees with the activation energy ~ 0.04 eV because resistivity is related to gap by $\rho \sim (\Delta/T)$. The relative temperature change of gap $\Delta(T)$,

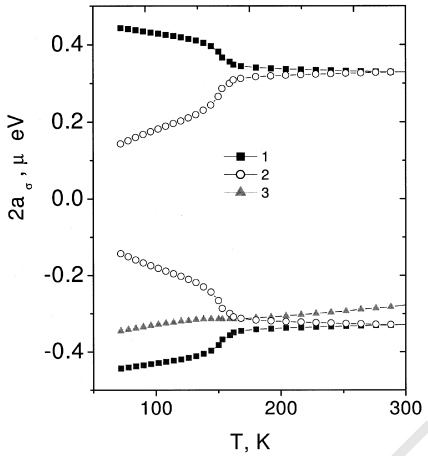

Fig. 5. Spin splitting of holes band $2a_\sigma, \sigma = 1(1), -1(2)$ and chemical potential $\mu(3)$ as a function of temperature.

$\Delta = E_F - \mu$, (E_F, Fermi level) is plotted in Fig. 3 and agrees with experimental data.

In conclusion, we summarize the main results. The resistivity anisotropy of single crystal of α-MnS below Neel temperature results from decreasing of chemical potential of holes in plane [111] and opening gap on the Fermi level. Spin splitting of hole band leads to shift of optical absorption band.

Acknowledgements

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