MAGNETISM
AND FERROELECTRICITY

Anisotropy of Optical Absorption of α-MnS Single Crystal

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Abstract—The optical absorption spectra of an α-MnS single crystal and their temperature behavior in the range from 86 to 300 K are investigated for the (100) plane in the energy range from 8×10^3 to 22×10^3 cm^{-1} for the first time. Comparison of these spectra with those for the (111) plane reveals an essential absorption anisotropy in unpolarized light. The anisotropy is manifested in a much stronger splitting of the lowest energy band for the (100) plane in comparison with that for the (111) plane. With decreasing temperature, the splitting becomes smaller. Possible mechanisms for the anisotropy revealed are proposed. © *2001 MAIK "Nauka/Interperiodica".*

The discovery of colossal magnetoresistance in $Fe_x Mn_{1-x} S$ solid solutions [1] revived interest in investigating the physical properties of manganese monosulfide, which is the base component of these substances. An α-MnS single crystal possesses an NaCl-type face-centered cubic lattice which undergoes a rhombohedral distortion along the cube diagonal in the (111) plane with decreasing temperature. The structural transition in α-MnS is observed at $T_s = 162 \pm 2$ K [2]; the antiferromagnet–paramagnet phase transition occurs at $T_N = 150$ K [3]. In the paramagnetic phase, the α-MnS monosulfide is a *p*-type semiconductor with a conductivity activation energy $E_a = 0.3$ eV. A sharp change in the activation energy is observed in the antiferromagnetic region: E_a is virtually zero at $T < 150$ K, and the resistivity ρ is 10^8 Ω cm [3, 4]. Optical measurements have been carried out for an α-MnS single crystal in the (111) plane [2, 5]. Three absorption peaks associated with single-ion transitions in Mn^{2+} were revealed, and a blue shift of the fundamental absorption edge was observed with decreasing temperature.

The absorption spectra of an α-MnS single crystal produced by saturation of liquid manganese with sulfur were investigated in this work.

Two α-MnS single-crystal plates parallel to the (111) and (100) planes were produced for optical measurements. The plates were about 40 μm thick, and their area was about 2 × 2 mm. Measurements were conducted in a gas-flow quartz cryostat at temperatures from 86 to 300 K with an accuracy of ±1 K within the energy range 8×10^3–22×10^3 cm^{-1}.

Figure 1 shows the optical absorption spectra obtained for the (111) and (100) planes of the α-MnS single crystal at room temperature. Figure 2 shows the spectra for these planes at three different temperatures. An essential difference between these spectra can be

seen in Fig. 2. The spectra for the (111) plane (curve *1* in Fig. 1; Fig. 2a) are, in general, identical to those obtained in [2, 5]. Two maxima corresponding to the electron transitions of the Mn^{2+} ions are observed: the *A* peak ($^6A_{1g} \longrightarrow {}^4T_{1g}(^4G)$) and *B* peak ($^6A_{1g} \longrightarrow {}^4T_{2g}(^4G)$). A third maximum, *C* ($^6A_{1g} \longrightarrow {}^4A_{1g}, {}^4E_g(^4G)$), was also observed in [2]; we could record only its long-wavelength edge. Probably, this is because our samples were thicker than those used in [2, 5]. For the same reason, we could not reveal the fundamental absorption edge either.

The shape of the spectrum does not change with a decrease in temperature, the energy of peak *A* ($E =$
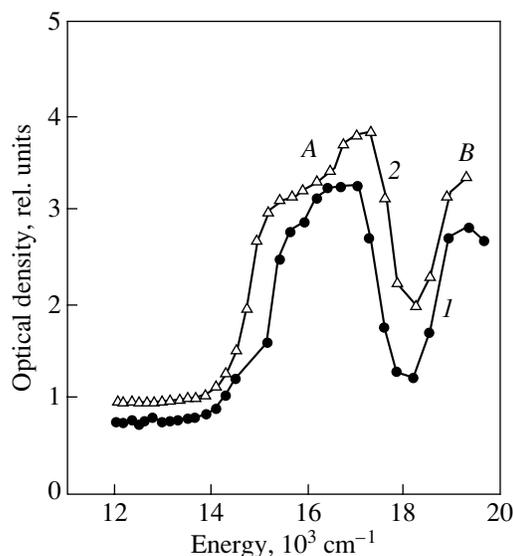
Fig. 1. Optical density $D = \ln(I_0/I)$ for an α-MnS single crystal at $T = 300$ K (I_0 and I are the intensities of incident and transmitted light, respectively). The light beam is perpendicular to (*1*) the (111) plane and (*2*) the (100) plane.
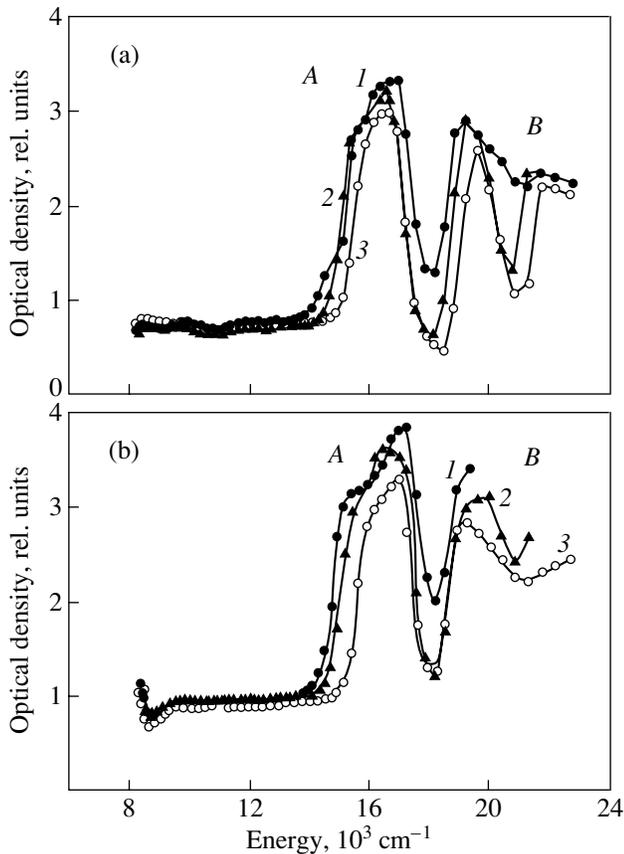
Fig. 2. Spectra of the optical density of an α-MnS single crystal at (*1*) 300, (*2*) 160, and (*3*) 86 K. The light beam is perpendicular to (a) the (111) plane and (b) the (100) plane.

16667 cm^{-1}) changes only insignificantly, and the energy of peak *B* (E = 19 608 cm^{-1} at T = 300 K) increases slightly. The intensity of both peaks decreases.

Figures 1 (curve 2) and 2b show the absorption spectra for the (100) plane. Optical investigations have not yet been carried out for this plane. A wide band is observed at energies from 14×10^3 to 18×10^3 cm^{-1}; it is split into at least two components. It should be noted that negligible splitting of band *A* is also observed for the (111) plane. With decreasing temperature, the split components become closer to each other. In this case, the low-energy component undergoes a substantially larger shift to the high-energy side. The amplitudes and widths of both components decrease. At the minimum temperature used, band *A* remains appreciably asymmetric for the (100) plane, while for the (111) plane, the band asymmetry almost vanishes. At low temperatures, the spectral position of band *A* for the (100) plane corresponds to the position of band *A* for the (111) plane. For this reason, the high-energy component of the band can be attributed to the transition $^6A_{1g} \longrightarrow {}^4T_{1g}(^4G)$ in the Mn^{2+} ion. The low-energy component, which undergoes a shift to higher energies with a decrease in

temperature, can be associated either with the splitting of the $^6A_{1g} \longrightarrow {}^4T_{1g}(^4G)$ band or with electron excitations of another nature.

In the energy range $(18–20) \times 10^3$ cm^{-1}, the band corresponding to band *B* in the spectrum for the (111) plane does not appear at room temperature. (In this energy range, the sensitivity of the photodetector decreases in comparison with the energy of approximately 16×10^3 cm^{-1}, where band *A* is observed.) Band *B* is observed beginning from $T \approx 160$ K. For the (100) plane, the intensity of the absorption bands is noticeably larger than for the (111) plane. In the window region near 18×10^3 cm^{-1}, the absorption is significantly larger for the (100) plane. Perhaps, due to these two circumstances, there is a difference between the colors of the crystals cut from the same block along different planes. In contrast to the green color typical to the (111) plane of the α-MnS crystal, the α-MnS single crystal cut in the (100) plane looks yellow. The energy of peak *B* observed for the (100) plane corresponds to the energy of peak *B* in the spectrum for the (111) plane only at low temperatures.

Thus, anisotropy of the optical absorption in unpolarized light is observed in the α-MnS single crystal. The difference in the splitting of the low-energy absorption band and in the intensities of the bands for the (100) and (111) planes are the most striking manifestations of this anisotropy.

The anisotropy revealed and the splitting of the low-energy band can be explained in a different manner. The splitting can be associated with the dynamic Jahn–Teller effect [6–8]. On the other hand, the formation of a magnetic polaron due to the exchange interaction between the charge carriers and electrons of the *d* shell of the Mn^{2+} ion (*c–l* exchange) [9] can be supposed; this exchange is observed in Cd$_x$Mn$_{1-x}$Te [10, 11]. At $T = 0$, according to [9], the spin-polaron state coincides with the band state, while at finite temperatures, they become essentially different. With increasing temperature, the spin-polaron band shifts to the high-energy side; the shift in the paramagnetic state can be as large as 60% of the shift in the magnetically ordered state and can be equal to ~0.1 eV [9]. To explain the anisotropy itself, it is necessary to take into account the characteristic features of the band structure of the crystal and its change at phase transitions. Additional measurements are being carried out to interpret the anomalies more clearly.

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