Magnon mode in α-MnS Raman spectrum

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Raman spectra of manganese monosulphide (α-MnS) with NaCl structure in the temperature range 5–300 K are presented. A new peak at 22 cm^{-1} has been found at low temperatures. The temperature dependence of this peak made possible to attribute it to the magnon mode at $k = 0$. This is in good agreement with the magnon wavenumber calculated with Munich SPRKKR-package.

Keywords: Raman spectroscopy, soft mode, single-magnon scattering, exchange interaction, manganese monosulphide, α-MnS.

1 INTRODUCTION

For decades manganese oxides and chalcogenides belonging to the systems with strong electron correlations have been drawing the attention of researchers for their optical, magnetic and transport properties [for example [1,2]]. State-of-the-art equipment capable of recording the Raman scattering signal makes possible to produce data on scattering by plasmons, polaritons, and magnetic excitations. Spin waves or magnons in pure antiferromagnetic are low-energy excitations associated with oscillations of *z*-component of the spins near their ordered orientations in the two sublattices structure. Elementary excitations usually comprise both sublattices and in the simplest case yield doubly degenerate spin branch. Such degeneration can be eliminated by anisotropy or some external field. At the Brillouin zone boundary, the spin wave propagates over one of the sublattices only and its energy is defined by the Hamiltonian components.

In α-MnS structure both manganese and sulfur ions form face-centered cubic lattices; these two lattices combine and the nearest neighbors of the metal are sulfur ions only, and conversely (NaCl-type structure).

Magnetic structure of the crystal consists of two sublattices magnetized opposite to each other, and the Neel temperature of α-MnS is $T_N \sim 152$ K [3]. In this magnetic structure, the spins of ions in planes (111) of the face-centered cubic lattice are parallel, and the spins of ions in the adjacent layers are antiparallel. It is obvious that the moments of ions are compensated and the crystal, on the whole, is not spontaneously magnetized. Simulations of magnetic excitations in MnS predicted two magnon branches, while experimentally at $k = 0$ in infrared absorption spectra only one magnon was observed[5-7]. Earlier the spectrum of spin waves in MnS was studied by Raman scattering [8], but in the wavenumber region, where the antiferromagnetic resonance was found at k=0 the magnon was not observed [9]. Large interest to the magneto-optic application considered, this work experimentally studied the Raman scattering spectra of spin waves in α-MnS antiferromagnetic at temperatures $T < T_N$.

2 EXPERIMENTAL METHODS

The method of synthesizing manganese monosulfide single crystals is presented in [10, 11]. The powdered α-MnS single crystal was tested with the D8 ADVANCE (Cu-Kα – radiation) diffractometer with a VANTEC linear detector. The experiments were carried out at 298 and 83 K in Anton Paar TTK450 temperature camera. The Raman scattering spectra were produced with LabRAM HR Evolution spectrometer in the back scattering geometry excited by 488 nm line of Ar^+ ion laser. The spectral resolution of the instrument was 1.2 cm^{-1}. The laser power on the surface of the crystal at ~2 μm spot was less than 1 mW. Fourier spectrometer VERTEX 80V (BRUKER, Germany) was used to obtain the far IR (infrared) absorption spectra. Absorption spectra of the compound were obtained in a polyethylene matrix The tablets were prepared as follows: the compound under study was thoroughly ground in a mortar with 0.1 g of fine polyethylene at 1:100 ratio. Raman spectra were obtained from non-oriented single crystals in a back scattering geometry. To record the spectra at different temperatures the sample was wrapped in indium foil and placed on the cooling medium coil in closed cycle helium cryostat. It should be noted that strong absorption of the exciting light heats the sample at the laser spot; the resulting difference between the temperature of the cooling medium coil and the actual temperature at the spot was estimated by Stokes/anti-Stokes intensity ratio.

3 RESULTS AND DISCUSSION

According to the X-ray data, at room temperature, the structure of samples is NaCl-type face-centered cubic (FCC) (sp. gr. *Fm*–3*m*) typical for α-MnS with the lattice parameters a = 5.224(7) Å at 298 K and a = 5.211(4) Å at 83 K. At 83 K (the antiferromagnetic state) the peaks and superstructural peaks were not observed to split to indicate lack of distortion in the lattice, so the refinement carried out was similar to the refinement at room temperature with the *Fm*–3*m* space group. The bond length at room temperature d(MnS) is 2.612 Å and at 83 K d(MnS) is 2.606 Å.

According to the group theory analysis for α-MnS (point symmetry group O_h), the vibrational representation at the center of the Brillouin zone is as follows: $\Gamma_{vibr} = 2T_{1u}$, and one of the triply degenerate modes is acoustic, while the other is the optical one, active in IR spectra. This peak was observed in the room temperature IR spectrum at ω = 226 cm^{-1} and its position agrees well with numerical simulations[6,12]. Temperature dependence of the IR spectrum down to 4.2 K shown no sharp anomalies confirming the absence of any structural transition.

Raman spectra in a cubic NaCl lattice should be forbidden, but these forbidden lines could be activated by lattice non-stoichiometry and vacancies, as it was observed in the α-MnS crystal at room temperature earlier[12] and agrees well with our results. Fig. 1 shows the Raman spectrum of manganese sulfide at 5 K in the range of 100–500 cm^{-1}. The same line emerges here, but it is split into LO–TO doublet; it's LO component doesn't show in IR spectra. Positions of this doublet remain practically stable under cooling.

When the temperature decreases below 200 K in the low wavenumber region of the spectrum a weak wing emerges which below 120 K transforms into an intensive asymmetric band with a maximum at 22 cm^{-1} at T = 5 K (Fig. 2). The difference between the actual temperature of the crystal at the registration point calculated from the Stokes/anti-Stokes intensity ratio and the temperature of the cooling medium coil measured by an integrated sensor

was about 20 K, i.e. emergence of the first signs of low wavenumber spectrum formation should be attributed to 140–150 K, and at ~150 K the antiferromagnetic transition in α-MnS is observed.[3]

The frequency and half-width of excitation inducing the observed scattering were found with the soft mode concept [13]. For the first order Raman scattering from one quasiharmonic soft mode (Fig. 3), the intensity is described by:

$$I(\omega) = I \frac{\Gamma \omega_0^2}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2}, \quad (1)$$

where ω is the Raman wavenumber shift, ω_0 is the active vibration wavenumber, Γ is the half-width of this vibration, *I* is the scattering amplitude (integral intensity).

When approaching the phase transition point (in our case – of magnetic phase transition) the soft mode wavenumber ω_0 decreases and the side Raman components get closer to each other as it is observed in our experiment (Fig. 3).

Fig. 4 shows the position of the maximum of mode 22 cm^{-1} and its half-width vs. temperature in the range of 5–90 K (sample heating denies determination of the wavenumber of the mode). The heating of the sample decreases the wavenumber of this mode and increases its half-width.

Analogous behavior of low wavenumber Raman scattering was earlier observed in α-MnSe, where the authors interpreted this peak as a single-magnon scattering [14].

The low-frequency mode in the center of the Brillouin zone was theoretically evaluated by the empirical expression:[14]

$$\hbar\omega = S\sqrt{24D(J_1 + J_2)} \quad (2)$$

where *D* is the anisotropy constant, J_1 and J_2 are the constants of the exchange interaction between the first and second neighbors, respectively.

The type of magnetic structure in MnS and constants of exchange interaction and anisotropy were theoretically calculated by spin-polarized relativistic Korringa – Kohn – Rostoker (SPR-KKR) code [15, 16] (the Munich SPRKKR-package), based on multiple scattering theory.[17 18]

Within the framework of this approach energies of different magnetic configurations were calculated; the most energy favorable magnetic ordering is the antiferromagnetically ordered planes parallel to [110] the direction of the cubic cell, corresponding to the experimental neutron diffraction data [19]. Constants of the exchange interaction and anisotropy were calculated for such configuration to yield the following values: J_1 = 0.4 meV, J_2 = 1.6 meV, *D* = 0.03 meV, *S* = 5/2. These values are close to [4]. As a result, the frequency of magnon mode in the α-MnS crystal was theoretically evaluated at 0 K: ω_0 = 24.2 cm^{-1}, this fairly well agrees with experimental ω_0 = 22 cm^{-1} at 5 K.

The wavenumber of the magnon calculated on the basis of simple model [14] and evaluation of the exchange energy also counts in favor of light scattering by magnetic excitations. This forms solid grounds for the prospects to further study inelastic neutron scattering spectra for α-MnS.

4 CONCLUSIONS

A joint experimental and theoretical study of the lattice dynamics of an α-MnS single crystal is reported. The Raman spectra are for the first time investigated in the temperature range of 4.2–300 K. A new peak at 22 cm^{-1} has been found at 5 K. Absence of structural phase transitions in the compound make possible to attribute this peak to the magnon mode at $k = 0$.

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Captions to Figures

Figure 1. α-MnS Raman and IR spectra at 5 K.
Figure 2. Temperature transformation of the low-frequency Stokes and anti-Stokes parts of the MnS spectrum.

Figure 3. Soft mode Raman scattering spectrum: dots are the experimental spectrum at 5 K and the solid red line is the calculation by equation (1).
Figure 4. (a) – Soft mode frequency ω_0 vs. temperature, (b) – half-width Γ of this mode vs. temperature.

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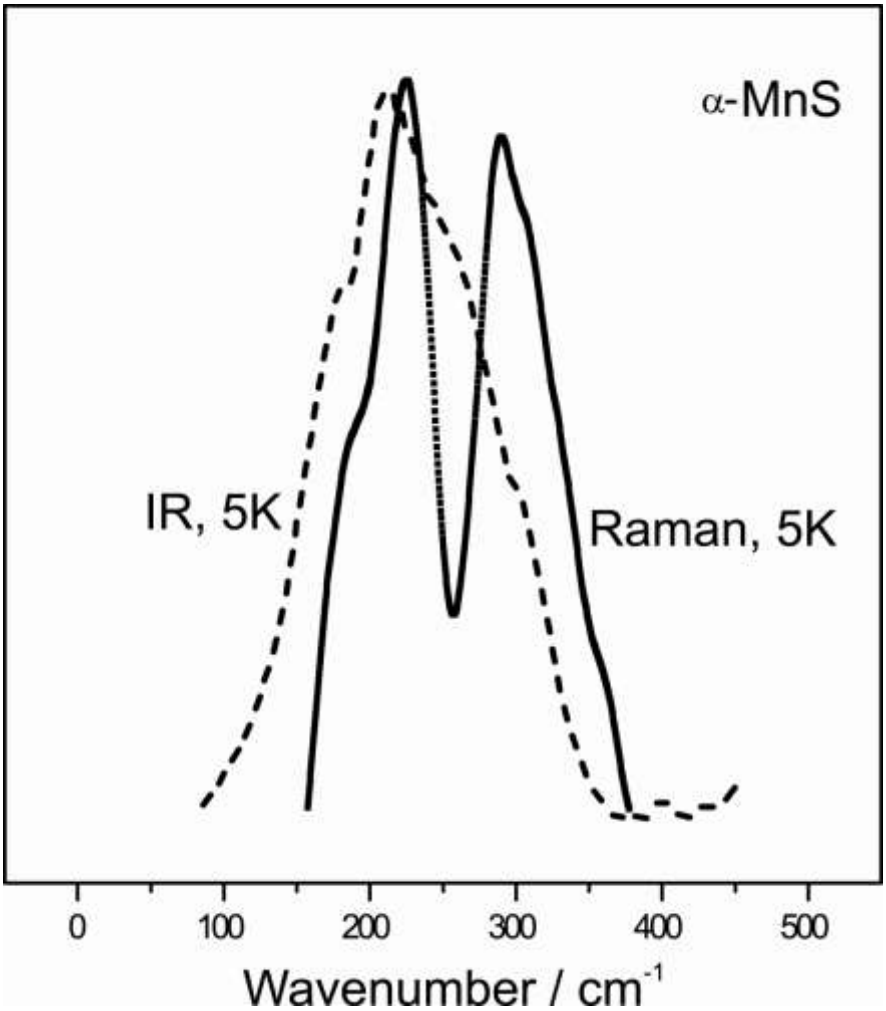
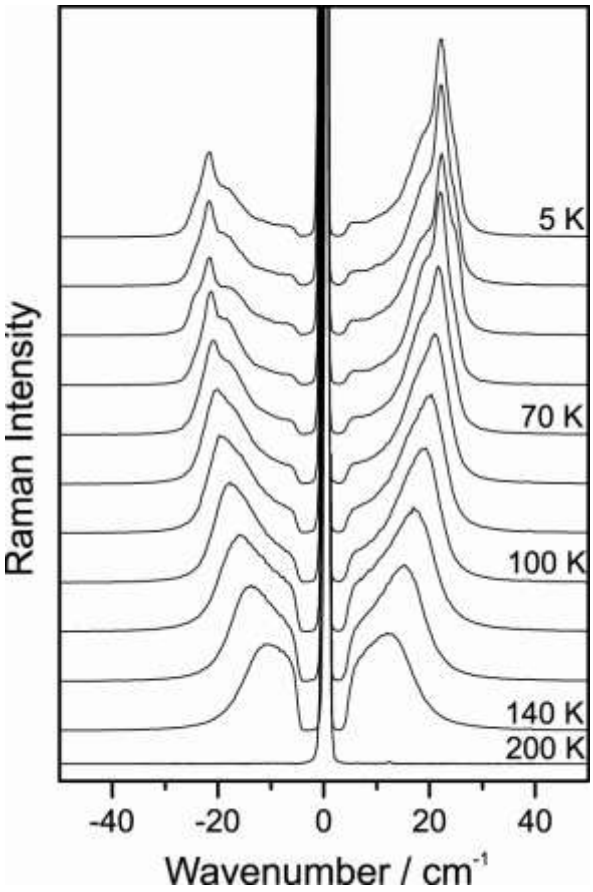


Figure 2. Temperature transformation of the low- wavenumber Stokes and anti-Stokes parts of the MnS spectrum.



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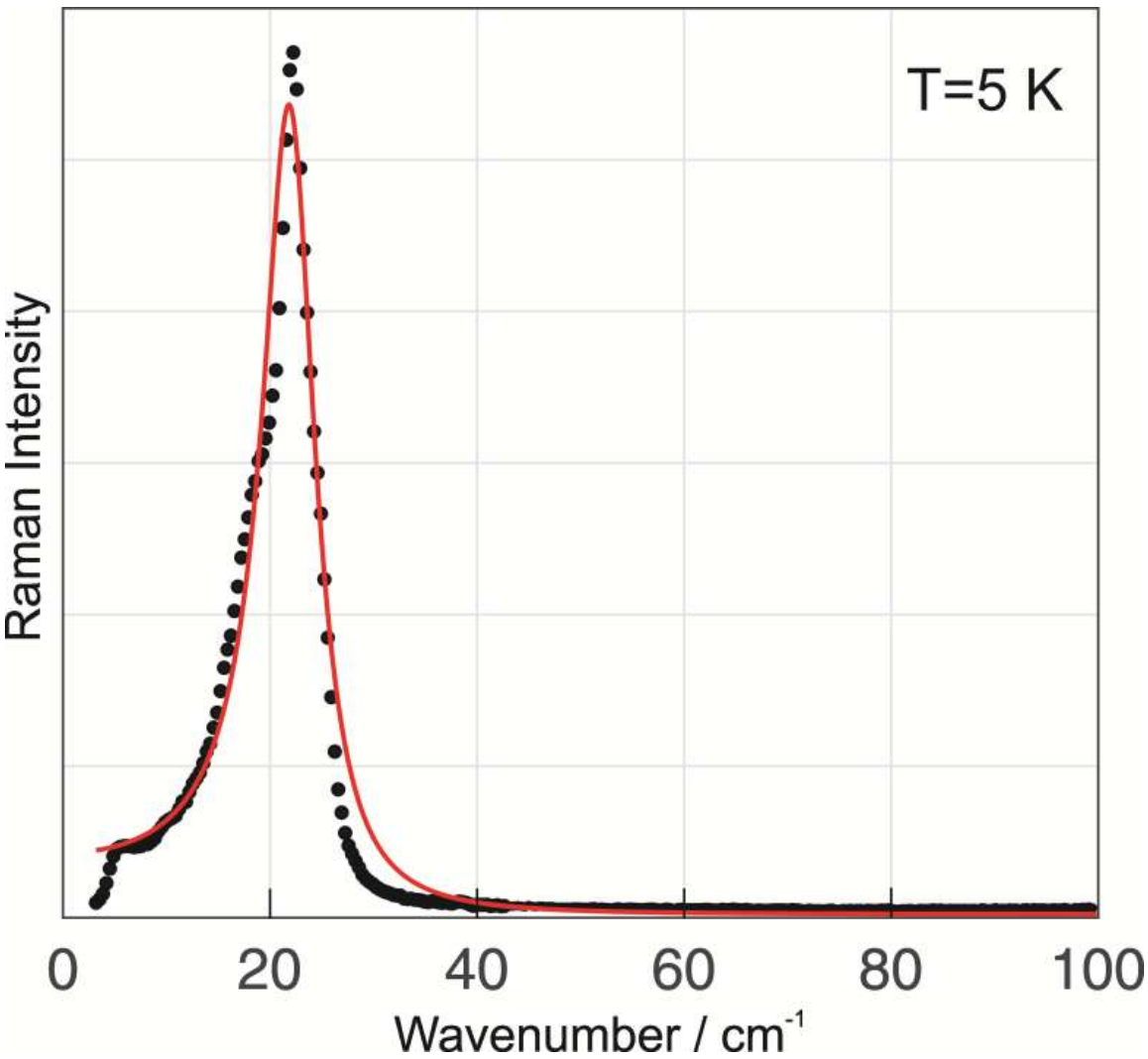

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