Two-magnon light scattering in the quasi-two-dimensional antiferromagnetic $(NH_3(CH_2)_2NH_3)MnCl_4$

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Raman spectra of the quasi-two-dimensional antiferromagnet $(NH_3(CH_2)_2NH_3)MnCl_4$, in the magnetically ordered state are studied. Two-magnon scattering is observed. The temperature behavior of the two-magnon band agrees well with theoretical predictions which take into account spin-wave damping processes. The value of the exchange interaction integral ($J = 6.65$ cm^{-1}) is determined from the experimental data.

The compound $(NH_3(CH_2)_2NH_3)MnCl_4$(EDA $\cdot MnCl_4$) belongs to the family of perovskite-like layered crystals with the general chemical formula $(NH_3(CH_2)_n NH_3)MnCl_4$ ($n = 2$–5), which have similar crystal structures and magnetic properties. In all these compounds, magnetic phase transitions (PT) to the quasi-two-dimensional antiferromagnetic order are observed near 45 K (Ref. 1). Peculiarities of the crystal structure of this family allow the distance between their layers to be varied several-fold, practically without any change in the two-dimensional character of the arrangement of the paramagnetic ions by varying the number of CH_2-groups in the $(NH_3(CH_2)_n NH_3)^{2+}$ organic chains. Consequently, it is interesting to study the properties of these compounds to see how the weak interlayer exchange interaction influences the degree of two-dimensionality of the magnetic structure.

Raman scattering (RS) is one of the useful methods to characterize formation of spectra of one- and many-magnon excitations. Recently, many experimental and theoretical papers on two-magnon RS in magnetic systems with different dimensions have been published.[2–9] In the present work, an attempt has been made to study RS in EDA $\cdot MnCl_4$ crystals at the transition into magnetically ordered state. From previous studies on similar metal-organic compounds only one unsuccessful attempt to observe RS spectrum on spin waves in $(NH_3(CH_2)_n NH_3)CuCl_4$ ($n = 2,3,5$) is known.[10]

We chose to study EDA $\cdot MnCl_4$ because it does not undergo structural PT down to T_N ($T_N = 54 \pm 2$ K), the temperature of magnetic ordering.[1,11] The lattice vibration spectra of EDA $\cdot MnCl_4$ in the paramagnetic phase has been studied in detail previously as a function of temperature,[12] and the number and polarization of the observed phonon excitations are well described by theoretical group analysis. Therefore, all expected variations in RS spectra for $T < T_N$ can only be related to the appearance of long-range magnetic order in the crystal.

1. EXPERIMENTAL METHOD

To obtain the RS spectra in EDA $\cdot MnCl_4$, an Ar^+ laser ($\lambda_0 = 488$ nm) with a radiative power of 60 mW was used. Light scattered by the sample at an angle of 90° was analyzed by a "Ramanor U 1000" double monochromator with a linear dispersion of 2.43 Å/mm. To exclude polarization effects of the spectral instrument from the polarization measurements, a depolarization prism of crystalline quartz was placed before the entrance slit of the monochromator. A cooled FEU-136 photomultiplier tube was used as a light detector. Spectra were recorded in the photon-counting mode. Samples were mounted in an optical cryostat for measurements in the temperature range of 4.2 to 300 K. The temperature was measured using a copper-constantan thermocouple placed on the surface of the sample. Since the excitation radiation line falls in an absorption band of the crystal, the real temperature of the sample in the laser beam was determined from the ratio of the intensity of Stokes and anti-Stokes low-frequency phonon lines in the RS spectra. The observed heating was 4–5 K.

The EDA $\cdot MnCl_4$ crystals were grown from an aqueous solution of $MnCl_2 \cdot 4H_2O$ and $(NH_3)_2(CH_2)_2Cl_2$ by the slow evaporation method at a temperature of 40 ± 1 °C; they grew as thin rectangular plates with the growing surface parallel to the perovskite layers.[13] The crystal orientation was determined with the help of a polarization microscope using known data on the orientation of the refractive index ellipsoid relative to the crystallographical axis.[14] The samples used in the study were of rectangular parallelepiped shape with carefully polished faces and typical dimensions $6 \times 3 \times 1$ mm.

2. STRUCTURE OF EDA·$MnCl_4$

The unit cell of EDA $\cdot MnCl_4$ belongs to the space-group C_{2h}^5 ($P2_1/c$) and contains two formula units. In a crystal, the $MnCl_4^{2-}$ anions form infinite perovskite plane layers, consisting of four equatorial vertices of $MnCl_6$ octa-

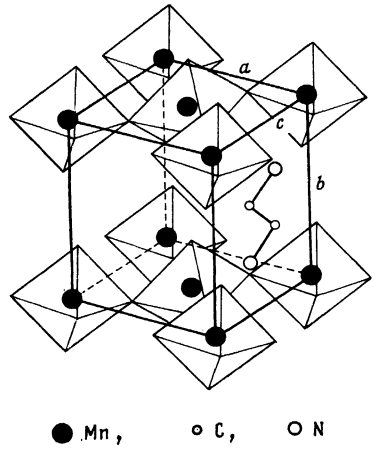

FIG. 1. $(NH_3(CH_2)_2NH_3)MnCl_4$ unit cell. For clarity, only one organic N–C–C–N chain is shown (hydrogen atoms are not shown).

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hedrons which are bonded between them. Organic cations $NH_3(CH_2)_2NH_3^{2+}$ are oriented almost perpendicularly to these layers and form with them hydrogen bonds: N–H···Cl (Ref. 13). The arrangement of paramagnetic ions Mn^{2+} in adjacent layers is shown in Fig. 1. Each Mn^{++} ion is surrounded by an octahedron of Cl atoms. Although the unit cell is monoclinic, one can regard the magnetic structure of one layer as quasitetragonal since the values of a (7.130 Å) and c (7.192 Å) are close.[13] In the following treatment, a Cartesian system of coordinates x',y',z' (with x' parallel to a, and y' parallel to c), as well as a coordinate system related to the magnetic structure of the crystal will be used. The x and y axis of the latter determine the directions to the nearest magnetic neighbor and, consequently, are rotated in the ac plane by an angle $\approx 45°$ relative to the crystallographic axes.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The phonon lines observed in the low-frequency spectra (0–240 cm^{-1}) of EDA·$MnCl_4$ in the antiferromagnetic phase do not show noticeable anomalies except that, as usual, the spectral line half-width decreases with temperature in comparison with that observed in the paramagnetic phase. The difference in the spectra consists only in the presence of an additional weak diffusive asymmetrical band with peak frequency ≈ 125 cm^{-1}. Polarization studies of this feature showed that the strongest intensity of RS is observed when the electric field vectors of the incident and scattered light are parallel to the plane of perovskite layers and are directed along the crystallographic axis a and c, respectively (or conversely). With increasing temperature the band broadens quickly and its intensity decreases while its maximum shifts towards the low-frequency region of the spectrum (Fig. 2). The narrow lines at 128 and 110 cm^{-1} correspond to lattice vibration excitations.[12]

The temperature behavior of the band described above, observed in low-temperature spectra of RS, implies that it is produced by scattering of light by two-magnon excitations in EDA·$MnCl_4$.

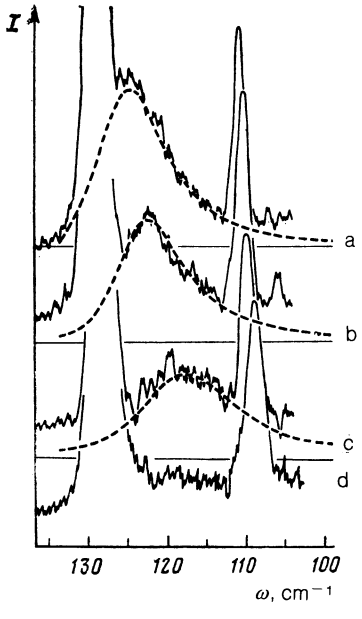

FIG. 2. The RS spectra of $(NH_3(CH_2)_2NH_3)MnCl_4$ for $x'y'$ polarization at the following temperatures: a — 10 K, b — 27 K, C — 35 K, and d — 90 K. The theoretical line shape of the two-magnon RS is shown by the dashed lines. I is the scattering intensity.

Theoretical aspects of two-magnon RS in magnetic systems with different dimensionalities have been developed in a series of publications.[4–7] Calculations of the temperature dependence of the magnon energy and of its disintegration processes[7] permit an adequate description of the experimental results.[2,3] The extinction coefficient of two-magnon RS, based on the exchange scattering mechanism for two-sublattice tetragonal antiferromagnets, is given by[7]:

$$K(\omega) \propto \frac{\alpha(T)^2}{1-\exp(-\omega/T)} \operatorname{Im} \frac{L_0(\omega)}{1-JL_0(\omega)}, \tag{1}$$

where α (T) is a renormalization factor for the energy of Hartree-Fock magnons, ω is the RS frequency, J is the exchange interaction integral, and $L_0(\omega)$ is the Green's function for two-magnon RS neglecting magnon interactions.[4]

Calculations in the nearest-neighbor approximation neglecting the anisotropy field yield

$$\Omega_{\mathbf{k}}=JSz(1-\gamma_{\mathbf{k}}^2)^{1/2}, \tag{2}$$

for magnon dispersion, where $\Omega_{\mathbf{k}}$ is the energy of a magnon with wavevector $\mathbf{k}$, S is the paramagnetic ion spin, z is the number of nearest neighbors; $\gamma_{\mathbf{k}}$ depends on the spatial dimensionality of the system and is given in general by

$$\gamma_{\mathbf{k}}=(1/z)\sum_{\mathbf{d}} e^{i\mathbf{k}\mathbf{d}}, \tag{3}$$

where $\mathbf{d}$ is the vector between nearest magnetic ions from neighboring sublattices. For two-dimensional systems we have $z=4$ and $\gamma_{\mathbf{k}}=\frac{1}{2}[\cos(k_x d)+\cos(k_y d)]$.

The variation of the magnon energy with temperature is determined by the factor $\alpha(T)$:

$$\bar{\Omega}_{\mathbf{k}}(T)=\Omega_{\mathbf{k}}\alpha(T). \tag{4}$$

In turn, the renormalization factor may be determined from the system of equations

$$\begin{aligned} \alpha(T)&=1-\frac{1}{NJS^2z}\sum_{\mathbf{k}}\Omega_{\mathbf{k}}n_{\mathbf{k}}(T), \\ n_{\mathbf{k}}(T)&=\{\exp[\alpha(T)\Omega_{\mathbf{k}}/T]-1\}^{-1}, \end{aligned} \tag{5}$$

where N is the number of unit cells, $n_{\mathbf{k}}$ (T) is the Bose factor, and the summation is carried out over all unit cells.

The Green's function $L_0(\omega)$ in Eq. (1), which takes into account spin wave damping, has the form[2,7]:

$$L_0(\omega)=-(1/N)\sum_{\mathbf{k}}(\cos k_x d-\cos k_y d)^2\frac{2n_{\mathbf{k}}+1}{\omega-2\bar{\Omega}_{\mathbf{k}}+2i\Gamma_{\mathbf{k}}}, \tag{6}$$

where

$$\Gamma_{\mathbf{k}}=Jz\frac{\pi}{S}\frac{n_{\mathbf{k}}(n_{\mathbf{k}}+1)}{\alpha(T)}(1/N^2)\sum_{\mathbf{r}}\gamma_{\mathbf{r}}^2\sum_{\mathbf{p}}\delta(\Omega_{\mathbf{k}}+\Omega_{\mathbf{p}}-\Omega_{\mathbf{k}-\mathbf{r}}-\Omega_{\mathbf{p}-\mathbf{r}}) \tag{7}$$

determines the magnon decay process.

In the present work the temperature dependence of the two-magnon RS band shape for two-dimensional tetragonal antiferromagnets ($S=5/2$) was calculated using the scheme just described. The results are shown in Fig. 3.

The frequency at the peak of two-magnon RS band

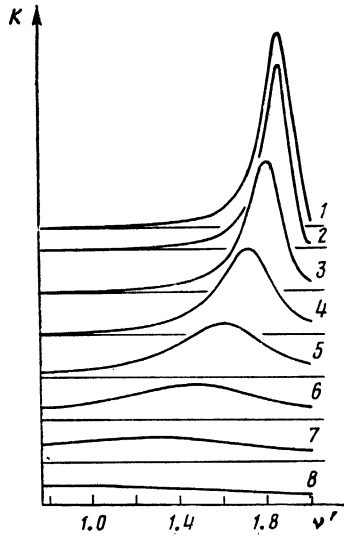

FIG. 3. Theoretical line shape of the two-magnon RS for various temperatures; $t' = T/JSz$ is a reduced temperature, $\nu' = \omega/JSz$ is a reduced frequency ($z = 4$, $S = 5/2$); (1) $t' \leqslant 0.15$, (2) $t' = 0.21$, (3) $t' = 0.32$, (4) $t' = 0.43$, (5) $t' = 0.53$, (6) $t' = 0.64$, (7) $t' = 0.75$, and (8) $t' = 0.85$.

roughly corresponds to twice the energy of a magnon at the Brillouin-zone (BZ) boundary. The magnon energy $E_0 = 3.28\ \text{cm}^{-1}$ at the center of the BZ in EDA·$MnCl_4$, is known from antiferromagnetic resonance measurements.[15] Since the value of E_0 (the anisotropic field) is small, it may be disregarded and the experimental results can be described by the above theory.

The comparison between theoretical calculations and experimental results is shown in Fig. 2. To fit our calculation we varied the value of the exchange interaction integral J and of the peak intensity for the lowest temperature. A good fit is obtained for $J = 6.65\ \text{cm}^{-1}$ (this value corresponds to a magnon energy $E_m = 66.5\ \text{cm}^{-1}$ at the BZ boundary). The latter value agrees well with the value $E_m = 66\ \text{cm}^{-1}$ obtained from inelastic neutron scattering in a crystal $(CH_3NH_3)_2MnCl_4$ (Ref. 16), which has similar $MnCl_4^{2-}$ perovskite layers and differs only in the shape of the organic chains.

The polarization dependence of the extinction coefficient of a two dimensional tetragonal antiferromagnet is given by[12]

$$g(\mathbf{E}_1, \mathbf{E}_2) = (E_1^x E_2^x)^2 + (E_1^y E_2^y)^2 - 2E_1^x E_2^x E_1^y E_2^y, \qquad (8)$$

where $\mathbf{E}_1$ and $\mathbf{E}_2$ are the electric field vectors of the incident and scattered light, respectively. Their projections are given in the xy coordinate system, described above. Polarization measurements of EDA·$MnCl_4$ yield spectra which exhibit two-magnon bands with nonvanishing RS intensity for the following polarizations: xx, xy, $x'y'$, and $z'y'$ (weak), although only $x'y'$ and xx are allowed. This fact may be due either to double refraction of light in the sample, which would lead to mixing of polarizations, or to a change in the selections rules because of the monoclinic character of the structure.

It should be mentioned that the RS band intensity is weak — practically an order of magnitude smaller than that of phonon lines. In other perovskite-like quasi-two-dimensional antiferromagnets containing Mn, the two-magnon RS intensity is comparable with that of phonon lines.[2,8]

In further experimental and theoretical work, the anomalies of two-magnon RS spectra of the low-symmetry quasi-two-dimensional antiferromagnet EDA·$MnCl_4$ and other crystals from this family should be studied.

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