Observation of exchange modes of antiferromagnetic resonance in $CuCl_2{\cdot}2H_2O$

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Two weak absorption lines are observed in the submillimeter region of the spectrum of the antiferromagnetic crystal $CuCl_2{\cdot}2H_2O$. Their frequency dependence and the polarization and intensities as a function of the magnetic field are investigated. The lines are uniquely identified as exchange modes of the antiferromagnetic resonance (AFMR).

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Most physical properties of copper chloride dihydride $CuCl_2{\cdot}2H_2O$, which is an orthorhombic antiferromagnet (AF) below the Néel temperature $T_N = 4.3$ K, are satisfactorily described by a two-lattice model. However, according to data obtained from neutron-diffraction studies of the isomorphic compound $CuCl_2{\cdot}2D_2O$,[1] it is usually assumed that this compound also has four magnetic sublattices (Fig. 1) with the magnetic moments of the spins of the Cu^{2+} ions positioned in the ac plane. The ground state of $CuCl_2{\cdot}2H_2O$ is charaterized by the vectors $\mathbf{L} = \mathbf{S}_1 + \mathbf{S}_2 - \mathbf{S}_3 - \mathbf{S}_4$ and $\mathbf{l} = \mathbf{S}_1 - \mathbf{S}_2 - \mathbf{S}_3 + \mathbf{S}_4$ and, in addition, $\mathbf{L} \gg \mathbf{l}$. Then, the vector **L** is the principal antiferromagnetism vector, while **l** can be called the weak antiferromagnetism vector. The number of AFMR modes must equal the number of magnetic sublattices. The two lower modes have now been studied carefully [it should be noted that AFMR was discovered while performing measurements on $CuCl_2{\cdot}2H_2O$ (Ref. 2)], while the observation and investigation of the two higher modes would finally provide proof of the existence of four sublattices in $CuCl_2{\cdot}2H_2O$ and would provide new data on the magnetic properties of the crystal.

It is shown in theoretical work[3,4] concerned with AFMR in $CuCl_2{\cdot}2H_2O$ in the four-sublattice model that the frequencies of the upper modes in the absence of an external field H are proportional to the geometric mean of the antiferromagnetic and

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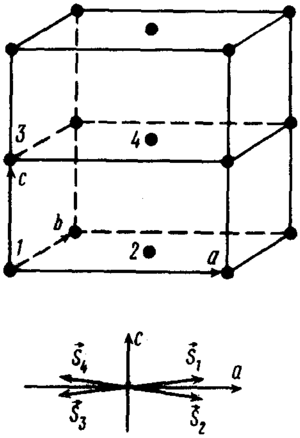

FIG. 1. Magnetic structure of $CuCl_2 \cdot 2H_2O$. The circles indicate Cu^{2+} ions. a, b, and c are the crystallographic axes. The spins of ions 1, 2, 3, and 4 (S_1, S_2, S_3, S_4, respectively,) form a "hedgehog" of spins in the unit cell.

ferromagnetic exchange integrals (for this reason, these modes are called exchange modes). Exchange modes (EM) correspond to uniform precession of spins in the sublattice, while the weak antiferromagnetism vector **l** oscillates with the highest amplitude, while the "hedgehog"of spins in the unit cell does not oscillate as a whole. In this sense, EM are an analog of optical phonons. The lower "acoustical" modes (AM) of AFMR correspond to oscillations of the "hedgehog" of spins as a whole, i.e., small deviations primarily of the principal antiferromagnetism vector **L** from the equilibrium position. It is important to note that for the investigations of EM, we chose a crystal with magnetic ions Cu^{2+} for which the spin $S = 1/2$, since for ions with $S \geqslant 1$ the presence of single-ion anisotropy can lead to the appearance of additional perturbations attributable to transitions in which the projection of the spin, is not conserved whose energy is of the order of the exchange energy. However, these excitations are not the exchange modes, since they are not related to the number of AF sublattices. The observation of excitations at exchange frequencies (for example, by means of Raman scattering of light[5] and inelastic neutron scattering[6]) has heretofore been reported only for AF of crystals with ionic spins $S \geqslant 1$, which leads to the nonunique interpretation.

The observation of AFMR exchange modes in absorption experiments presents considerable difficulties, since the intensity of the corresponding lines is low and is proportional to the magnitude of the noncollinearity of the sublattices. The noncollinearity is determined by the ratio of the Dzyaloshinskiĭ constant (in invariants of the free energy of the form DLl) to the exchange constant. At $D = 0$ EM are not excited at all.

The experiment was performed on a pulsed straight-through submillimeter spectrometer.[7] A Helmholtz solenoid was used to satisfy the conditions for exciting EM[3,4] (polarization of the magnetic vector of microwave radiation $h_\omega \| H \| a$, where a is the easy axis). The specimen had the shape of a cube with an edge of 3 mm and faces along the crystalline axes. The microwave radiation propagated along the b axis.

We observed two weak absorption lines near the frequency 8.4 cm^{-1} with polarization $h_\omega \| H \| L$. At $H = 0.27$ T, the intensity at the peak (to within $\pm 20\%$), the integrated intensity ($\pm 50\%$), and the linewidth at half-maximum ($\pm 20\%$) constituted respectively, 0.08 cm^{-1}, 3×10^{-3} cm^{-2}, and 0.07 cm^{-1}, for the high-frequency line and 0.12 cm^{-1}, 4.5×10^{-3} cm^{-2}, and 0.07 cm^{-1} for the low-frequency line. The intensity of the EM absorption lines in this crystal turned out to be 2–3 orders of magnitude higher. As H increases (at $H < H_{sf}$, the field for the spin-flop transition), the intensity of the lower mode decreases, while the intensity of the higher mode increases, so that near H_{sf} their intensities become equal. As the temperature approaches T_N, the frequencies of the lines decrease, while the lines themselves wash out. The polarization of the lines and the behavior of their intensities in a magnetic field correspond to the behavior of OM, described in Ref. 4. The measured magnetic-field dependence of the frequencies of the observed lines is shown in Fig. 2. The inset in this figure illustrates schematically the theoretical frequency–field dependence of AFMR of the four-sublattice orthorhombic $CuCl_2{\cdot}2H_2O$ AF with H parallel to the easy axis. The convergence of the frequencies of the absorption lines, characteristic for EM, is observed in fields $H \gtrsim H_{sf} = 0.7$ T The presence of absorption lines in the region of convergence for fields ranging from 0.7 to 1.0 T, instead of discontinuities at $H = H_{sf}$ for EM, illustrated in the inset, is apparently due to the tilting of the field in the experiment away from the easy axis. As an illustration, spectrograms of absorption lines at the frequency 8.8 cm^{-1} are shown in Fig. 3.

All of the facts enumerated above taken together permit identifying uniquely the observed absorption lines as AFMR exchange modes in $CuCl_2{\cdot}2H_2O$.

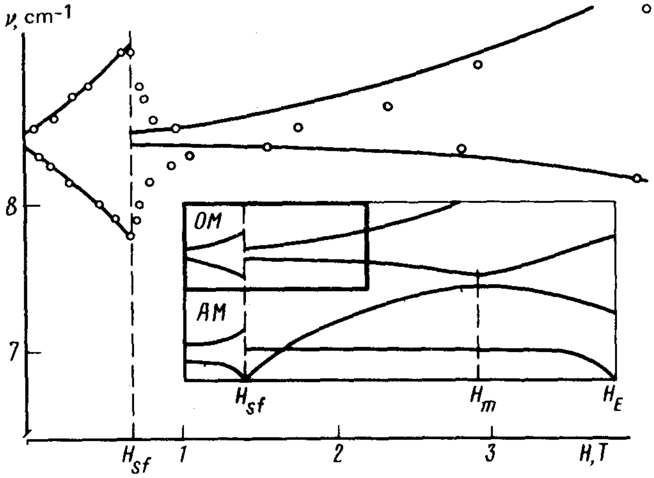

FIG. 2. Magnetic field dependence of the frequencies of the exchange modes in $CuCl_2{\cdot}2H_2O$. $T = 2$ K, $h_\omega \| H \| a$, H is tilted away from the a axis by about 5°. The solid curves represent the calculation. The region investigated is singled out in the inset.

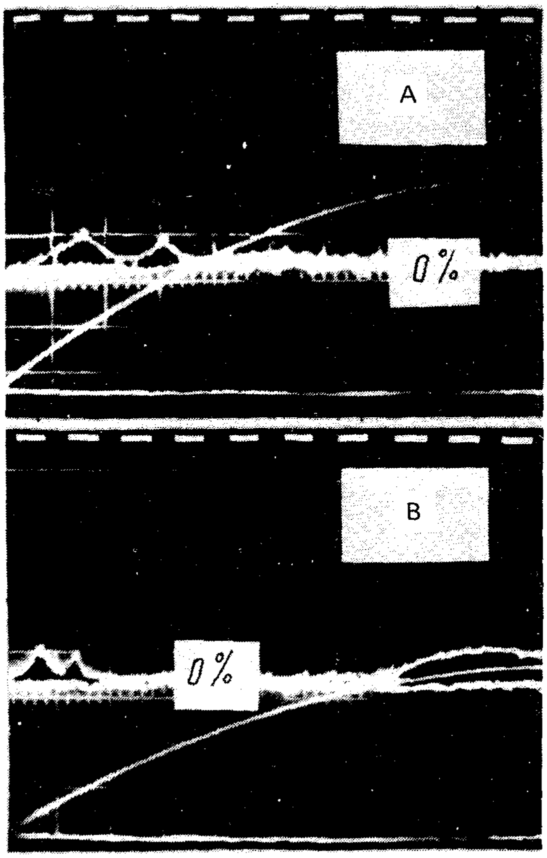

FIG. 3. Spectrograms of absorption lines at the frequency 8.8 cm^{-1}. The calibration level of the absorption signal is 0%.[7] The gain in the signal channel is 2.5 times greater than in Ref. 7– the dashed line denotes the 40% absorption level. The maximum field is a) 1.45 T; b) 2.8 T.

If the interaction options 1 and 4 is ignored in the equations in Ref. 4 (since these ions are next ones beyond the nearest neighbors), then, from the values of the EM frequencies at $H = 0$, $\nu_1 = 8.48\ \text{cm}^{-1}$ and $\nu_2 = 8.38\ \text{cm}^{-1}$, it is possible to determine the characteristic field $H_{E_3} = (3.53 \pm 0.03)$ T (using the notation in Ref. 4), which is directly proportional to the ferromagnetic exchange integral. Here we use the value of the field corresponding to collapse of the sublattices (directly proportional to the antiferromagnetic exchange integral) $H_E = 15.8$ T shown in Ref. 8. Using these values, we calculated the dependences $\nu(H)$, using the equations in Ref. 4, shown in Fig. 2 by the solid curves. The deviation of the computed values from the measured values is due to the inaccurate orientation of H relative to the a axis. The quantity D can be determined from the relation[4] $l/L = D/H_{E_3}$. From neutron diffraction data,[1] we find $l/L = 0.1$ so that $D = 0.353$ T.

In a field $H_m = 7.8$ T (see inset in Fig. 2), the exchange and acoustical modes should not intersect even with strict orientation of H along a, since these modes, according to Ref. 4, have identical symmetry. It can be shown that the minimum distance between these frequencies is directly proportional to D. According to our calculations, it is equal to 0.52 cm^{-1} at $D = 0.353$ T.

In the near future, we will perform experiments in weaker fields, which will permit determining D, H_{E_3} and the magnitude of the interaction of ions 1 and 4 exactly, using only the data from the AFMR experiment, which is especially important for this particular crystal, for which it is very difficult to perform neutron-diffraction studies.

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