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MAGNETISM AND FERROELECTRICITY

Absorption of Light by Exchange-Coupled Ions in a 2D Antiferromagnet

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Abstract—The optical absorption spectra of $Rb_2Mn_xCd_{1-x}Cl_4$ crystals are experimentally studied in the vicinity of a magnon sideband of the exciton band at a manganese content x ranging from 1.0 to 0.4. Additional absorption bands are observed with an increase in the magnetic structural disorder upon replacement of manganese ions by cadmium ions. An analysis of the evolution of the additional absorption bands in a magnetic field during the spin-flop phase transition and the change in the intensity with variations in the manganese content x demonstrates that these bands are associated with the excitation of the exchange-coupled pairs of manganese ions located in different environments in a plane square lattice. The phase boundary between the antiferromagnetic and spin-flop phases is constructed using the results of optical measurements. The manganese content corresponding to the magnetic percolation point is evaluated. *© 2003 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

As is known, a fine structure observed in the optical absorption spectra of antiferromagnets containing 3*d* ions is caused by interactions of different natures in the crystals. In addition to the bands attributed to the single-ion electron optical transitions, the spectra of magnetic crystals at optical frequencies exhibit bands associated with excitations of different origins (magnons, phonons, etc.). Since the main features of spectral bands of different natures are well known [1, 2], it is possible to identify the absorption bands and then to use available data on the optical spectra in analyzing the specific features of the excitation energy spectra and the magnetic structure of the crystal. Disordering of the crystal, for example, due to an appreciable impurity concentration, violates translational symmetry. In this case, the quasiparticle approach underlying the description of the optical spectra does not hold. If the order in a crystal is disturbed, one can expect qualitative changes in the absorption optical spectra. For example, the introduction of a magnetic impurity into a antiferromagnet can give rise to additional bands in the spectrum due to the occurrence of either the localized states or the resonance states [2, 3]. We succeeded in observing new bands in the spectrum of a two-dimensional (2D) antiferromagnet upon replacement of magnetic ions by nonmagnetic ions in an Rb_2MnCl_4 crystal diluted with Cd^{2+} ions.

Crystals of Rb_2MnCl_4 at room temperature have a tetragonal structure with D_{4h}^{17} symmetry. At the Néel temperature $T_N = 57$ K, the Rb_2MnCl_4 crystal is characterized by an antiferromagnetic order with easy-axis anisotropy parallel to the C_4 symmetry axis of the crystal [4]. The spin-flop transition occurs in the field $H_{SF} = 56$ kOe. The Mn^{2+} ions are located in layers perpendicular to the C_4 symmetry axis at sites of a plane square lattice of the crystal. The interlayer distance considerably exceeds the distance between the Mn^{2+} nearest neighbor ions located in the same layer. As a result, the intralayer exchange interaction between the manganese ions is two orders of magnitude stronger than their interlayer exchange interaction, which is responsible for the two-dimensional behavior of the magnetic system of the crystal.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

Crystals for study were grown using the Bridgman method in a vertical tube furnace. The optical absorption spectra were measured on a spectrometer with a resolution of 3 Å/mm at a temperature of 4.3 K. Magnetic fields with a strength up to 250 kOe were generated in a pulsed solenoid with a pulse duration of 20 ms. The spectra were recorded on photographic film.

3. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of $Rb_2Mn_xCd_{1-x}Cl_4$ for the α polarization at frequencies close to ~26500 cm^{-1} and different manganese contents x. The absorption observed in this range is due to the transition ${}^6A_{1g}({}^6S) \longrightarrow {}^4T_{2g}({}^4D)$ inside the 3*d* shell of

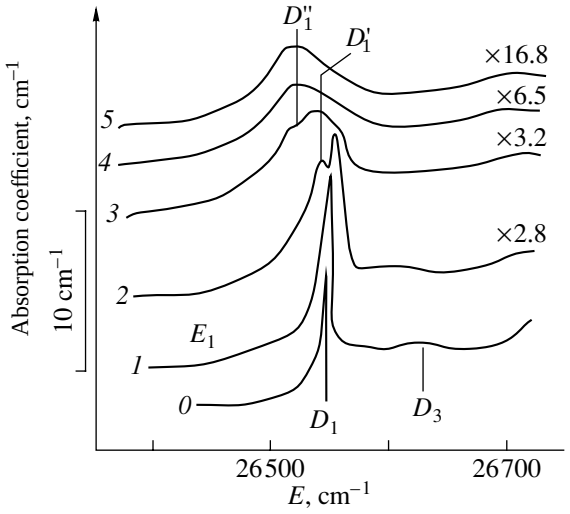

Fig. 1. Absorption spectra of $Rb_2Mn_xCd_{1-x}Cl_4$ crystals in the vicinity of the exciton–magnon absorption band D_1 for the α polarization with the wave vector $\mathbf{k} \parallel C_4$, the electric-field vector $\mathbf{E} \perp C_4$, T = 4.3 K, and different magnesium contents x: (*0*) 1.0 (calculated shape of the exciton–magnon band), (*1*) 1.0, (*2*) 0.9, (*3*) 0.8, (*4*) 0.7, and (*5*) 0.4.

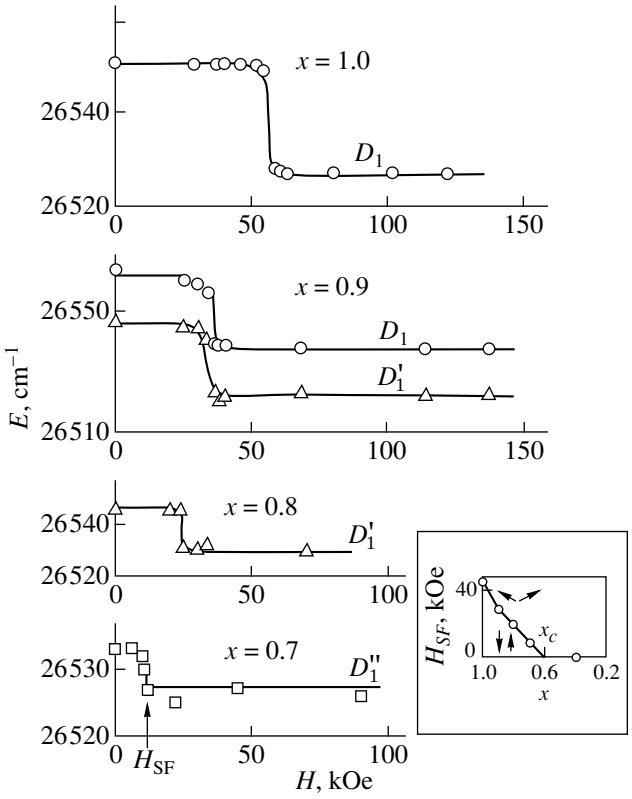

Fig. 2. Dependences of the energies of the bands D_1, D_1', and D_1'' on the magnetic field $\mathbf{H} \parallel C_4$ at different magnesium contents x. T = 4.3 K. The inset shows a fragment of the phase diagram plotted in the x–**H** coordinates at T = 4.3 K according to the results of spectral measurements.

Mn^{2+} ions. This figure represents a group of bands attributed to this transition in the long-wavelength range. It can be seen that the absorption spectra of the crystal at x = 1.0 contain a narrow electrodipole band D_1. The polarization of the D_1 band corresponds to selection rules for a single-magnon sideband of the exciton band. The intralayer exchange interaction between Mn^{2+} ions was estimated as J/k = –5.6 K from the results of magnetic [5] and magneto-optical [6] measurements. The energy of magnons with wave vectors at the boundary of the Brillouin zone, which, as a rule, make the main contribution to the exciton–magnon absorption in a collinear antiferromagnet, was estimated at 80 cm^{-1}. The magnetodipole exciton band at an energy of ~80 cm^{-1} below the energy corresponding to the D_1 band was revealed in the spectrum of magnetic circular dichroism [7]. Although this band was not observed in the absorption spectrum due to the low intensity, its energy location is indicated in Fig. 1 and the band itself is designated as E_1. Kojima *et al.* [8] calculated the line shape for exciton–magnon absorption of a 2D antiferromagnet with a square lattice. The line shape depends on many parameters and can be different. However, in the case when the interaction between the exciton and the magnon can be disregarded and the parameters of the resonance transmission of optical excitation from ion to ion are small (and, as a consequence, the dispersion of the exciton band is small), the band under consideration becomes narrow and strongly asymmetric. The line shape calculated for a square antiferromagnetic lattice under the above assumptions with the relationships described in [8] is presented in Fig. 1 (curve *0*). In these calculations, the exchange integral and the anisotropy field were taken from [6] and [5], respectively. The anisotropy field virtually does not affect the exciton–magnon band but eliminates the divergence in the expression for the line shape at the center of the Brillouin zone.

As the content of Mn^{2+} ions decreases, additional bands (D_1' and D_1'') appear in the range of the D_1 exciton–magnon band, whereas the D_1 band itself becomes less intense and almost disappears at x = 0.7 (curve *4* in Fig. 1).

Figure 2 depicts the dependences of the energy location of the bands D_1, D_1', and D_1'' on the magnetic field aligned parallel to the C_4 axis of the crystals. In the antiferromagnetic phase, the spin-flop transition leads to a jumplike shift of all the bands revealed in the α-polarized absorption spectrum (including the bands observed upon dilution of the magnetic crystal) by the same value. This suggests that all these bands are associated with the same exciton.

The magnitude of the jump in the energy of the absorption bands upon the spin-flop transition decreases almost linearly as the manganese content x

decreases, which reflects the decrease in the mean exchange field due to the dilution of the Rb_2MnCl_4 crystal, and vanishes at $x \approx 0.6$. The inset in Fig. 2 shows the dependence of the field of the spin-flop transition on the manganese content at $T = 4.3$ K, which was obtained from observations of the D_1, D_1', and D_1'' bands in a magnetic field. The estimate of the critical manganese content ($x_c = 0.6$) corresponding to a transition from the antiferromagnetic state to a disordered state of the crystal agrees well with the theoretical value (0.59) for the point of magnetic percolation in a plane square lattice.

For the Rb_2MnCl_4 crystal, the D_1 exciton–magnon band is unique with respect to its parameters owing to the small dispersion of the exciton band. The replacement of manganese ions by cadmium ions in the magnetic lattice disturbs both translational symmetry and the initial magnetic order. In this case, the contribution of the short-wavelength magnons (short-range magnetic order) to the exciton–magnon absorption increases and the band should become more symmetric and less intense with a decrease in the manganese content x. This behavior is observed for the D_1 band.

The energy location of the D_1' and D_1'' bands in the spectra of diluted crystals indicates that these bands are associated with the same process of excitation as in the case of the D_1 band. The energies at their maxima are $\sim E_m/4$ and $\sim E_m/2$ less than the energy at the maximum of the D_1 band. Here, E_m is the magnon energy at the boundary of the Brillouin zone. The energy separation between the states split along the projection of the spin in a local magnetic field decreases by the same value, provided the nearest environment of the Mn^{2+}–Mn^{2+} pair is considered a field source and, in the nearest environment itself, one or two Mn^{2+} ions are replaced by Cd^{2+} ions. The total absorption by an exchange-coupled pair of magnetic ions is proportional to the number of pairs. The probabilities of finding no Cd^{2+} ions, one Cd^{2+} ion, or two Cd^{2+} ions in the nearest environment of the Mn^{2+}–Mn^{2+} pair depend on the manganese content x. Figure 3 presents the statistical estimates of these probabilities obtained by statistical modeling. The analytical dependences of the probabilities on the manganese content x for these three cases obey the laws x^8, $6x^7(1-x)$, and $15x^6(1-x)^2$, respectively, and coincide with the curves depicted in Fig. 3. In the case when the D_1 exciton–magnon band shape remains unchanged upon dilution of the crystal and the D_1' and D_1'' bands have a Gaussian shape, the concentration dependences of the integrated intensities of these three bands after their separation approximately coincide with the curves shown in Fig. 3. The vertical lines in Fig. 3 indicate the ratios of the numbers of ion pairs for manganese contents at which the measurements were carried out. These ratios correlate well with the intensity ratios of the D_1, D_1', and D_1'' bands. Therefore, the D_1' and D_1'' bands appear in the absorption spectra of $Rb_2Mn_xCd_{1-x}Cl_4$ crystals as a result of the excitation of exchange-coupled pairs of Mn^{2+} ions in a spatially disordered magnetic structure, provided the nearest environment of the Mn^{2+} ions contains Cd^{2+} ions.

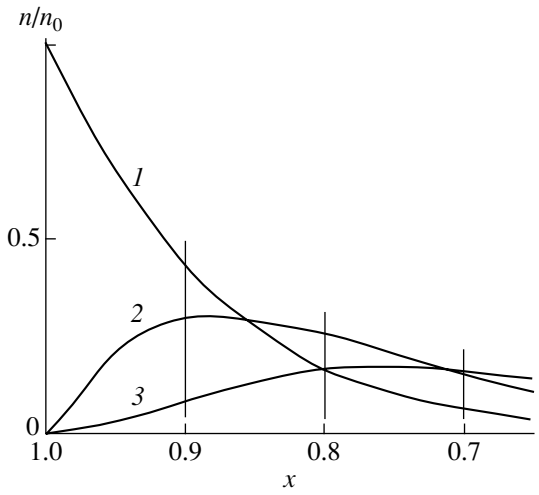

Fig. 3. Dependences of the relative number of nearest neighbor manganese ion pairs in a square lattice on the manganese content x when the nearest environment of manganese ions contains (*1*) no cadmium ions, (*2*) one cadmium ion, and (*3*) two cadmium ions.

In addition to the D_1 band, the spectra of the Rb_2MnCl_4 crystal exhibit magnon sidebands in the vicinity of the transitions ${}^6A_{1g}({}^6S) \longrightarrow {}^4T_{2g}({}^4D)$ [9] and ${}^6A_{1g}({}^6S) \longrightarrow {}^4A_{1g}{}^4E_g({}^4G)$. However, the line shape of these satellites does not allow one to observe additional bands similar to the bands D_1' and D_1''.

4. CONCLUSIONS

Thus, we studied the dependences of the optical absorption of a 2D magnet on the content of magnetic ions and on the magnetic field in the range of the exciton–magnon absorption. Owing to the unique parameters of the D_1 exciton–magnon band, the additional absorption bands associated with the optical excitation of exchange-coupled pairs of Mn^{2+} ions were observed for the first time in the spectrum of an antiferromagnetic crystal upon its dilution with a nonmagnetic impurity. The phase boundary between the antiferromagnetic and spin-flop phases was constructed using the results of optical measurements.

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REFERENCES

1. É. G. Petrov, *Theory of Magnetic Excitons* (Naukova Dumka, Kiev, 1976).
2. V. V. Eremenko, N. F. Kharchenko, Yu. G. Litvinenko, and V. M. Naumenko, *Magneto-Optics and Spectroscopy of Antiferromagnets* (Naukova Dumka, Kiev, 1989).
3. O. Cador, C. Mathoniere, and O. Kahn, Inorg. Chem. **39** (17), 3799 (2000).
4. H. T. Witteveen, J. Solid. State Chem. **11** (3), 245 (1974).
5. N. V. Fedoseeva, I. P. Spevakova, A. N. Bazhan, and B. V. Beznosikov, Fiz. Tverd. Tela (Leningrad) **20** (9), 2776 (1978) [Sov. Phys. Solid State **20**, 1600 (1978)].
6. E. A. Popov and M. M. Kotlyarskiĭ, Fiz. Tverd. Tela (Leningrad) **22** (10), 3019 (1980) [Sov. Phys. Solid State **22**, 1763 (1980)].
7. A. Vervoitte, J. C. Canit, B. Briat, and U. Cambli, Phys. Status Solidi B **124** (1), 87 (1984).
8. N. Kojima, T. Ban, and I. Tsujikawa, J. Phys. Soc. Jpn. **44** (3), 923 (1978).
9. E. A. Popov and M. M. Kotlyrskii, Phys. Status Solidi **96** (1), 163 (1979).

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