Physics of the Solid State, Vol. 45, No. 3, 2003, pp. 499–502. Translated from Fizika Tverdogo Tela, Vol. 45, No. 3, 2003, pp. 472–475.

MAGNETISM AND FERROELECTRICITY

Magnetic Properties of the Quasi-Two-Dimensional Crystal $(CH_3NH_3)_2CuBr_4$

N. V. Fedoseeva*†, N. V. Volkov*, and G. S. Patrin**

** Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*

*** Krasnoyarsk State University, pr. Svobodnyĭ 79, Krasnoyarsk, 660041 Russia*

e-mail: pat@iph.krasnoyarsk.su

Received May 29, 2002

Abstract—The magnetic properties of $(CH_3NH_3)_2CuBr_4$ quasi-two-dimensional crystals were studied experimentally. The magnetic-field and temperature dependences of magnetization were measured for various magnetic field orientations relative to the crystallographic axes. Possible reasons for features in the behavior of the magnetization are discussed. © *2003 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

Crystals of the family $(C_nH_{2n+1}NH_3)_2BX_4$ (where $n = 1, 2, \ldots$; B is a transition metal; and X stands for a halogen) exhibit a rich variety of physical properties [1]. Ions of the transition metal B in the crystal structure are located in the octahedra formed by ions of halogen X and lie in the planes bridged by the $(C_nH_{2n+1}NH_3)_2$ groups. These crystals have a layered structure and exhibit quasi-two-dimensional magnetic properties. By properly varying the ion-B and halogen-X species or the length of the bridge between the planes (by varying n), one can purposefully control the type of magnetic order, the anisotropic properties, and magnetic-ordering temperature of the crystal. We shall restrict our consideration to the $n = 1$ case (the methyl ammonium group $(CH_3NH_3) \equiv$ MA). The crystals whose magnetic properties have been best studied are MA_2BCl_4, where B is either Mn or Cu. The MA_2MnCl_4 crystals are easy-axis antiferromagnets with $T_N = 45$ K. Their magnetic properties are described satisfactorily in terms of the isotropic quasi-two-dimensional Heisenberg interaction [2]. Replacement of Mn by Cu results in the MA_2CuCl_4 crystals being easy-plane ferromagnets with $T_c = 9$ K.

Substituting bromine for chlorine substantially changes the exchange interaction in crystals of this family, with the type of magnetic order and the ordering temperature changing accordingly. This communication reports on a study of the magnetic properties and the interactions responsible for the experimentally observed features in the MA_2CuBr_4 crystals.

† Deceased.

2. EXPERIMENTAL TECHNIQUE

MA_2CuBr_4 crystals were grown from a solution. The composition was verified using x-ray diffraction. The crystals have orthorhombic symmetry and space group *Pabc*. The unit-cell parameters at room temperature are $a = 7.814$ Å, $b = 7.639$ Å, and $c = 19.167$ Å. The unit cell contains four formula units and, hence, four magnetic ions. Quasi-static magnetic measurements were carried out with a self-compensating superconducting-coil magnetometer [3]. The measurements were performed within the temperature range $T = 4.2$–300 K, with the temperature maintained to within ±0.1 K.

3. EXPERIMENTAL RESULTS

MA_2CuBr_4 is a poorly studied member of the $MA_2Cu(Cl,Br)_4$ family; relevant information on this member in the literature is very scarce. Data on the magnetic susceptibility $\chi(H)$ measured in fields $H \leq 8$ kOe and on the specific heat C_v studied in the interval $T = 4$–20 K were first published in [4]. It was found that this crystal is antiferromagnetic with $T_N \approx 15.8$ K and that the antiferromagnetism vector is aligned with the **c** axis. The $\chi(H)$ relation measured in the **H** ∥ **c** geometry exhibits an anomaly at $H = 5.2$ kOe, which is assigned to a spin-flop transition.

A Br NMR study is described in [5]. The main result achieved in [5] reduces to a refinement of the data on the magnetic structure below T_N. The NMR data are interpreted and are found to agree satisfactorily with quasi-static data [4] when considered in terms of the four-sublattice antiferromagnet model, provided one assumes the sublattice magnetic moments to lie in the (**c**, **b**) plane and to be canted from the **c** axis at an angle $\beta = \pi m \pm 27°$ ($m = 0.1$).

1063-7834/03/4503-0499$24.00 © 2003 MAIK "Nauka/Interperiodica"

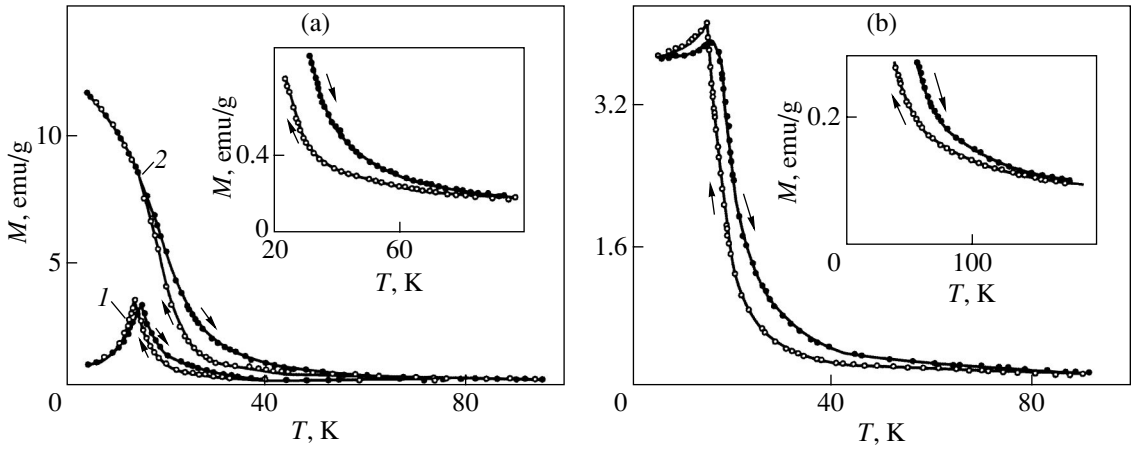

Fig. 1. Temperature dependences of magnetization of the $(CH_3NH_3)_2CuBr_4$ crystal. (a) **H** ∥ **c**, magnetic field is equal to: (*1*) H_1 = 2.16 kOe and (*2*) H_2 = 11 kOe; (b) **H** ⊥ **c**, magnetic field is H_1 = 3.76 kOe. The insets show high-temperature parts of these relations measured in the field H_1. Arrows specify the direction of temperature variation.

We performed a comprehensive investigation of the magnetization of MA_2CuBr_4 crystals in magnetic fields $H \leq 60$ kOe. The main experimental results obtained can be summarized as follows.

3.1. Magnetically Ordered State

Figure 1 presents temperature dependences of the magnetization $M(T, H)$ measured in the geometries **H** ∥ **c** (Fig. 1a) and **H** ⊥ **c** (Fig. 1b). In the first case, the measurements were performed both below and above the saturation field, while in the second, the experiment was performed below the saturation field. One readily sees a nonzero magnetic moment to exist at low temperatures in fields considerably lower than the spin-flop field. The curves obtained in a field $H \cong 11$ kOe are typical of a ferromagnet (curve *2* in Fig. 1a). The temperature behavior of $M(T)$ exhibits a hysteresis for both magnetic-field directions. In the **H** ∥ **c** case, hysteresis starts near $T \cong 100$ K (inset to Fig. 1a), while in the **H** ⊥ **c** geometry, it becomes evident in the region of $T \cong 150$ K (inset to Fig. 1b). The temperatures of the maxima in magnetization, which are identified with the temperatures T_N of phase transitions to the antiferromagnetic state, are also different for the heating and cooling runs. For instance, for **H** ∥ **c** and H = 3.76 kOe, the maximum in $M(T)$ obtained in a cooling run lies approximately 1.8 K lower than that measured in a heating run. As the field H increases, the temperature corresponding to the maximum in $M(T)$ decreases for both magnetic field directions, irrespective of the direction of temperature variation. Note also a strong dependence of the magnetization tails on magnetic field.

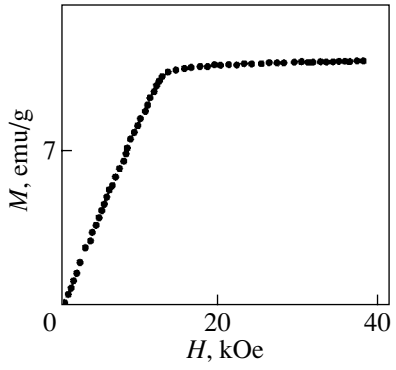

Fig. 2. Field dependence of magnetization measured in the **H** ⊥ **c** geometry. T = 4.2 K.

Figure 2 shows a field dependence of magnetization obtained in the **H** ⊥ **c** geometry at T = 4.2 K. Its pattern is typical of a Heisenberg uniaxial antiferromagnet placed in a magnetic field perpendicular to the principal axis and does not change with temperature for $T < T_N$ [6]. Only the saturation magnetization depends on temperature. The field dependence of magnetization in the **H** ∥ **c** geometry has a more complicated pattern (Fig. 3). Curve *1*, measured at T = 4.2 K, illustrates the main relevant features. The magnetization passes through an inflection point at $H_{c1} \cong 5$ kOe associated with a spin-flop transition, then the slope of the magnetization curve changes in the field H_c, the sublattices collapse at H_{c2}, and saturation sets in. In contrast to a uniaxial two-sublattice antiferromagnet, one clearly observes the fields H_{c1} and H_c to be separated. Note that the break at the field H_c practically disappears at $T \geq 10$ K. As seen from Fig. 3, the values of all critical fields plotted vs. temperature fall on straight lines to within experimental error.

3.2. Paramagnetic Region

Figure 4 gives an idea of the behavior of magnetization in the paramagnetic region. It appears unusual that

the $M(H)$ curve deviates widely from a linear course in such weak fields and that this deviation is seen to persist up to high temperatures despite the fact that $T_N \approx 15$ K. In addition to the temperature hysteresis, one clearly sees the existence of a field hysteresis up to $T \cong 30$ K. As follows from the high-temperature asymptotic behavior of the experimental data treated in terms of standard molecular-field theory under the assumption of Heisenberg interaction, the magnetization obeys the Curie–Weiss law at temperatures $T \geq 200$ K, with $\Theta_c^{\parallel} = -80$ K and $\Theta_c^{\perp} = -190$ K. In this approach, the relation between Θ_c and the exchange parameters is given by $\Theta_c^{\alpha} = 2\mu^{\alpha}\sum_m Z_m J_m/[3k_B(g^{\alpha}\mu_B)^2]$ [7], where α stands for "$\parallel$" or "$\perp$" (the rest is a matter of traditional notation). Therefore, the first explanation that comes to mind is that the magnetic moment per copper ion and/or the exchange constants are anisotropic; this conclusion does not agree with the Heisenberg interaction between the copper ions (electron configuration d^9, $S = 1/2$).

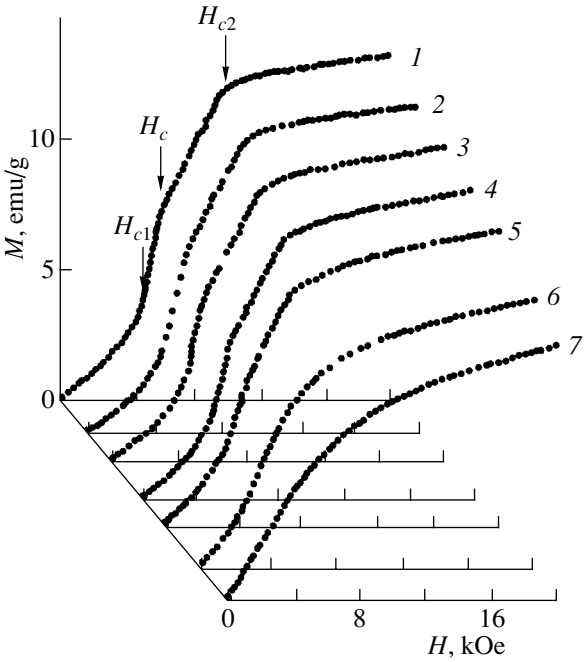

Fig. 3. Field dependences of magnetization measured in the **H** || **c** geometry. T (K): (*1*) 4.2, (*2*) 6, (*3*) 8, (*4*) 10.5, (*5*) 12.5, (*6*) 15, and (*7*) 17.

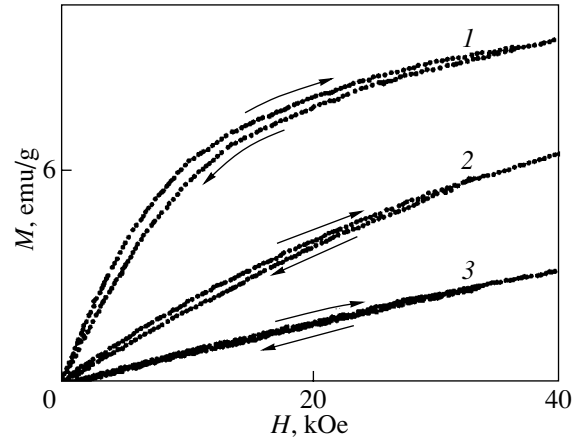

Fig. 4. Field dependences of magnetization in the paramagnetic region measured in the **H** || **c** geometry. T (K): (*1*) 18, (*2*) 25, and (*3*) 39.

4. DISCUSSION

The most interesting results of our study that require interpretation are the high paramagnetic temperatures $|\Theta_c|$ observed at a low transition temperature to long-range order and the reasons for the formation of a crossed magnetic structure in the magnetically ordered region. Clearly, these observations should find explanation within a common approach. We assume, as a working hypothesis, that the Jahn–Teller character of copper ion interaction and the quasi-two-dimensional structure of the crystal play a major role here.

At low temperatures, an MA_2CuBr_4 crystal resides in the monoclinic phase with a very small distortion angle, so that one may assume, as a zero approximation, that the crystal is orthorhombic. The layers containing the magnetic copper ions in the octahedral environment of the halogens have perovskite structure in these crystals, with the layers being bound by weak van der Waals forces [8]. In these conditions, the copper ions in a layer are coupled through indirect exchange interaction, which should be considered with due account of its Jahn–Teller character [9]. Each layer exhibits ferromagnetic orbital ordering (with the local quantization axis canted away from the principal axis at an angle β) and antiferromagnetic spin ordering. It is the magnitude of the spin exchange interaction that determines the value of T_N. Although no long-range order can appear in the two-dimensional case [10], the situation becomes different in the presence of any long-range interaction. It may be conjectured that ions located in different layers are coupled by an interaction which results in antiferromagnetic orbital ordering mediated by the phonon field, so that the quantization axes in the adjoining layers are canted at angles $\pm\beta$. It is known [9] that this interaction can be strongly anisotropic and, as a consequence, can give rise to the effective exchange parameter becoming dependent on both the temperature and magnetic field. Thus, under certain conditions, a crossed antiferromagnetic spin configuration may form.

A more detailed theoretical description of magnetic ordering in MA_2CuX_4 crystals will be given in a later publication.

ACKNOWLEDGMENTS

The authors are indebted to A.P. Perepelitsa for providing the single crystals and to A.D. Balaev for the high-temperature measurements of the magnetic susceptibility.

This study was supported by the federal program "Universities of Russia: Basic research."

REFERENCES

1. K. S. Aleksandrov, N. V. Fedoseeva, and I. P. Spevakova, *Magnetic Phase Transitions in Halide Crystals* (Nauka, Novosibirsk, 1983).
2. N. V. Fedoseeva, V. K. Korolev, A. F. Bovina, and A. P. Perepelitsa, in *Physical Properties of Magnets* (Inst. Fiz. Sib. Otd. Akad. Nauk SSSR, Krasnoyarsk, 1990), p. 61.
3. A. D. Balaev, Yu. V. Boyarshinov, M. M. Karpenko, and B. P. Khrustalev, Prib. Tekh. Éksp., No. 3, 167 (1985).
4. Y. Kimishima, J. Phys. Soc. Jpn. **49**, 62 (1980).
5. Y. Suzuki, K. Tsuru, Y. Kimishima, and H. Kubo, J. Phys. Soc. Jpn. **50**, 1479 (1981).
6. E. A. Turov, A. V. Kolchanov, V. V. Men'shinin, I. F. Mirzoev, and V. V. Nikolaev, *Symmetry and Physical Properties of Antiferromagnets* (Fizmatlit, Moscow, 2001).
7. J. S. Smart, *Effective Field Theories of Magnetism* (Saunders, London, 1966; Mir, Moscow, 1968).
8. K. S. Aleksandrov and B. V. Beznosikov, *Perovskite-like Crystals* (Nauka, Novosibirsk, 1997).
9. K. I. Kugel' and D. I. Khomskiĭ, Usp. Fiz. Nauk **136**, 621 (1982) [Sov. Phys.–Usp. **25**, 231 (1982)].
10. M. E. Lines, J. Phys. Chem. Solids **31**, 101 (1970).

Translated by G. Skrebtsov