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A STUDY OF MAGNETIC PROPERTIES OF LAYERED COPPER HYDROXIDE-BASED MOLECULAR MAGNETS UNDER PRESSURE

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The influence of high hydrostatic pressure on magnetic properties of layered copper compounds $Cu_2(OH)_3(C_nH_{2n+1}CO_2)$ was studied. The temperature dependences of the magnetization under pressure of these compounds) for n = 10 and 12 were measured and spin interactions were calculated. As a result, it was established that the temperature of ferromagnetic ordering and intralayer spin interactions in β-$Cu_2(OH)_3(C_nH_{2n+1}CO_2)$ are decreased linearly with pressure increasing. The decrease of T_c under pressure is determined by decrease of intralayer spin interactions, which can be realised by variation of interaction angles or due to the competition of interactions of different types in the layer.

1. Introduction

The spin interactions in materials with low-dimensional structure have got a considerable attention in the study of condensed matter magnetic properties [1–5]. For this kind of experimental investigations, the layered compounds with general formula $M_2(Cu)_3(X)mH_2O$ (where M = Ni, Cu, Co; and X = NO_3, Cl, CH_3COO) can be considered as model systems, because it is possible to change the interlayer spacing up to 40 Å [6–9]. The magnetic properties of these compounds are very interesting. For example, the $Cu_2(OH)_3(C_nH_{2n+1}CO_2)$ exists in two structural polymorphs α and β. The former is ordered antiferromagnetically and the latter – ferromagnetically. The long-range ferromagnetic order is observed even for very large interlayer spacing (e.g. up to 40 Å for n = 12). The ordering temperature T_c is found to lie between 20 K and 15 K for n ranging from 7 to 12 [8,9].

Thus, it is very interesting to study the effect of high hydrostatic pressure on magnetic properties of these compounds. This interest has arisen from the fact that one observes the gradual variation of the interlayer spacing under pressure. It allows one to study the variation of in-plane and interplane spin interactions and their influence on the character of magnetic order and behavior of the transition temperature.

In the present work the experimental results of high pressure (up to 10 kbar) effect on magnetic properties of layered magnets $Cu_2(OH)_3(C_nH_{2n+1}CO_2)mH_2O$ are analyzed.

2. Experimental

The layered copper(II) compounds $Cu_2(OH)_3(C_nH_{2n+1}CO_2)mH_2O$ have been synthesized according to the procedures reported previously [9–11]. From the structural point of view, these compounds exhibit a 2d triangular array of the Cu(II) ions. The acetate anions are located in the interlayer space. The interlayer distance is determined by expression d(Å) = 2.54$n$cosα +

+ 14.2, where α = 35° is the tilt angle with respect to the normal to the plane.

The temperature dependencies of the magnetization under pressure in the magnetic field 0.6 Oe and 500 Oe for compounds $Cu_2(OH)_3(C_nH_{2n+1}CO_2)$ for n = 10 and 12 were measured by means of a Foner magnetometer PAR-151 in the range 4–150 K. The measurements were performed at the fixed pressures. For pressure generation we used a high-pressure chamber of special construction [12,13].

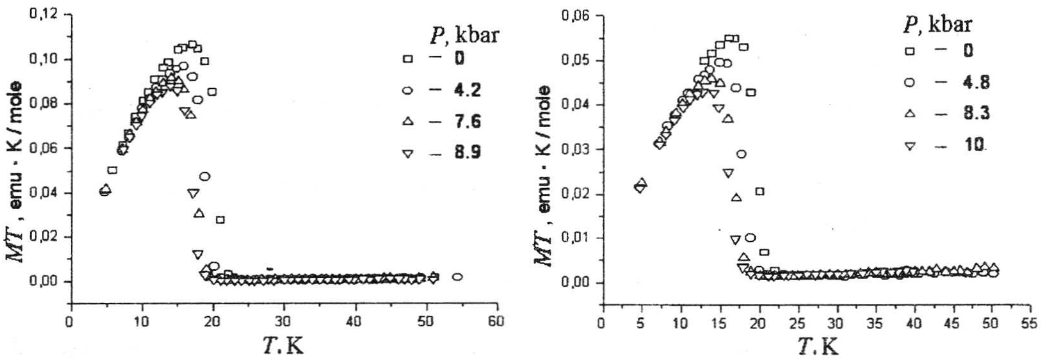

Fig. 1. Temperature dependencies of *MT* for β-$Cu_2(OH)_3(C_{10}H_{21}CO_2)$ (*a*) and for β-$Cu_2(OH)_3(C_{12}H_{25}CO_2)$ (*b*) under different fixed pressures (the applied field H = 0.6 Oe)

The temperature dependencies of the product of magnetization and temperature $MT(T)$ at fixed pressures for β-$Cu_2(OH)_3(C_{10}H_{21}CO_2)$ and β-$Cu_2(OH)_3(C_{12}H_{25}CO_2)$ are illustrated in fig. 1,*a*,*b*, respectively. The temperature of FM order, determined from the maximum of the curve, lowers with pressure increase for the both compounds. The pressure dependencies of transition temperature $T_c(p)$ for both compounds are shown in fig. 2. The linear decrease of the transition temperature with pressure increase is seen.

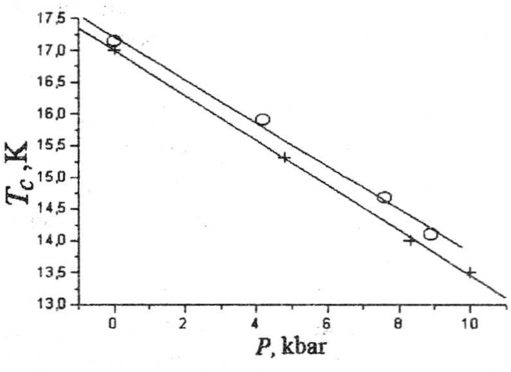

Fig. 2. The pressure dependencies of ordering temperature for β-$Cu_2(OH)_3(C_{10}H_{21}CO_2)$ (o) and β-$Cu_2(OH)_3(C_{12}H_{25}CO_2)$ (+)

3. Analysis and discussion

From previous [7,9] and present investigations we can conclude that the magnetic properties of $Cu_2(OH)_3(C_nH_{2n+1}CO_2)$ have some peculiarities: there are two polymorphs α and β, the β-polymorph is ferromagnetically ordered and the α-polymorph is an antiferromagnetic one [8]; the magnetic ordering is observed at very large distances between the magnetic layers (up to 40 Å) [8]; the chemical modification of distance between the layers in one polymorph doesn't change the type of magnetic order [8]; the temperature of magnetic order is decreased at pressure increase.

To clarify the role of intra- and interlayer interactions we have determined them for

β-$Cu_2(OH)_3(C_{10}H_{21}CO_2)$ using measurements of the magnetization in the range of paramagnetic temperatures. As the magnetic ordering is observed at distances between magnetic layers up to 40 Å we can assume that the intralayer interactions are of the Ising type and between layers the dipole interactions prevail. The Hamiltonian of such a system is:

$$H = -J\sum_{k}\sum_{i,j} S_{ik}^{z} S_{jk}^{z} + \sum_{i,m} \frac{(\mu_0 g)^2}{r_{lm}^3}\left(1 - 3\frac{(\mathbf{r}_{lm}\mathbf{s}_l)(\mathbf{r}_{lm}\mathbf{s}_m)}{r_{lm}^2}\right), \quad (1)$$

where J – an exchange parameter for the Ising model in layer, g – Lander factor, μ_B – Bohr magneton, $\mathbf{r}_{lm}$ – vector connecting l and m ions, s_i^z – z component of i-th spin, the summation i, j runs over all the ions in the plane, summation k runs over all the layers and summation l, m runs over all ions in the system.

At the first stage we derived the intralayer susceptibility by using a high-temperature series (HTS) expansion for the Ising model

$$\chi_0 = \beta\mu\left(1 + \sum a_n w^n\right), \quad (2)$$

where $\beta = 1/kT$, k – Boltzmann constant, μ – magnetic moment of ion, $w = \tanh(J/kT)$.

At the second stage, we introduced the influence of the interlayer interaction within the molecular field approximation. Then the expression for susceptibility can be written as [14]:

$$\chi = \chi_0\left(1 - \frac{zj}{N_a^2\mu_b^2\chi_0}\right)^{-1}, \quad (3)$$

where z – number of nearest neighbours, N_a – Avogadro's number, j – interlayer interaction. The experimental data for β-$Cu_2(OH)_3C_{10}H_{21}CO_2mH_2O$ at the paramagnetic temperatures were fit by expression (4) and the parameters g, J and j were determined for three fixed pressures. These parameters are listed in Table.

Table

Values of the parameters T_c, g, J and j obtained from the best fits of the experimental magnetic susceptibility data for β-$Cu_2(OH)_3(C_{10}H_{21}CO_2)$ using HTS expansion and expression (4)

P, kbar	T_c, K	g	J, K	j, K
0	17.5	2,0	20,0	0,36
5	16.0	2,1	17,6	0,5
9	14.3	2,1	16,4	0,5

From the above results it is seen that for all three pressures the intralayer exchange interactions are a little higher than the ferromagnetic critical temperature, but are of the same order. The interlayer interactions are very small. With pressure increase the intralayer interactions are decreased in the same way as the transition temperature and the interlayer ones are practically unchanged. The fact that the transition temperature is decreased under pressure is not an ordinary phenomenon. Under pressure the distances between magnetic ions are decreased and we should expect the increase of the transition temperature. As is seen from Table, the transition temperature decrease is caused by a decrease of the in-plane interactions. This is possible either due to the exchange angles variation or the competition effects of interactions of different signs in the layer. The fact that they compete is seen from the temperature dependence of (MT) too (Fig. 1), where this product is decreased at $T \geq 50$ K, showing the prevalence of AFM interactions, and increased at $T < 50$ K, showing the prevalence of FM interactions. The nature of this competition is not clear, but it is not associated only with the fact that the interaction distances become more short. Under pressure we have the decrease of FM interactions with distances, and at lower temperatures we have the increase of FM interactions at decrease of the distances. Very likely, the decrease of interactions under pressure is caused by the exchange angles variation, but to confirm this fact the additional investigations are needed.

4. Conclusion

We have performed the experimental investigations of the high pressure influence on magnetic properties of layered compounds $Cu_2(OH)_3C_nH_{2n+1}CO_2mH_2O$. The results of this investigations are:

– the temperature of FM ordering and intralayer spin interactions in β-$Cu_2(OH)_3C_nH_{2n+1}CO_2mH_2O$ linearly decrease with pressure increase. The interlayer dipole interactions are not changed essentially under pressure;

– the decrease of T_c under pressure is determined by decrease of intralayer spin interactions, which can be realised by variation of interaction angles or due to the competition of interactions of different types in the layer.

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