PERGAMON

A pressure study of the antiferromagnetic phase of $FePM_2Cl_2$ (PM = pyrimidine)

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Abstract

We present pressure experiments on $FePM_2Cl_2$ (PM = pyrimidine). This material undergoes a transition into a canted antiferromagnetic state below $T_N = 6.3$ K at ambient pressure. We establish the bulk modulus, the anisotropy of the compression and the pressure dependence of the antiferromagnetic transition temperature. Our experiments demonstrate the usefulness of pressure experiments to investigate the properties of molecular magnetic compounds.
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1. Introduction

Molecular magnets, with their structure consisting of magnetic units assembled within a supermolecular aggregate consisting of organic components, tend to be soft materials. Therefore, they are fairly sensitive to the application of external pressure, as has been demonstrated, for instance, for purely organic magnets [1–3]. Unusual pressure dependencies have been observed, like periodic up/down variations of ferromagnetic transition temperatures or pressure induced ferro- to antiferromagnetic transitions. This reflects that applying pressure to a molecular magnet affects its properties by variation of two structural entities: (i) the distance between the magnetic ions and (ii) the geometry of the exchange path.

Both the variation of the distance between magnetic ions and the geometry of the exchange path, because of the softness of molecular magnets, are extraordinarily large, and in that sense special, distinguishing these

materials from conventional magnets. In consequence, to understand the interplay of structural and magnetic properties in molecular magnets it is necessary to determine the pressure dependence of both structural and magnetic parameters. In a first step towards this goal, here we present a combined structural and magnetic study of the properties of a molecular magnet under externally applied pressure.

For our study we have chosen $FePM_2Cl_2$ (PM = pyrimidine = $C_4N_2H_4$). This material belongs to a series of magnetically ordered transition metal complexes of general formula $TX_2(PM)_2$, whereby T = Fe, Co, Ni and X = Cl or Br [4,5]. These materials crystallize in a tetragonal lattice of space group $I4_122$. The lattice parameters of Fe system have been determined to be $a = 7.4292$ Å and $c = 20.364$ Å. The transition metal ions are connected via pyrimidine rings, thus forming a three-dimensional network of transition metal–pyrimidine complexes. In consequence, a pyrimidine mediated superexchange yields magnetic coupling between the metal ions, causing transitions into long-range magnetically ordered states at low temperatures [6]. In case of $FePM_2Cl_2$, the transition into a canted antiferromagnetic state is reported to occur at $T_N = 6.1$ K. For Fe and Co compounds, it has been possible to directly

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observe the magnetically ordered state by powder neutron diffraction of non-deuterated samples, yielding for $FePM_2Cl_2$ an ordered moment $\mu_{ord} = 3.8\mu_B$ [7].

2. Experimental

We have performed neutron powder diffraction and magnetization experiments under applied hydrostatic pressure. The neutron diffraction experiments have been carried out on a non-deuterated material $FePM_2Cl_2$ at the Berlin Neutron Scattering Center (BENSC) of the Hahn–Meitner Institut, utilizing the focusing diffractometer E6 with a neutron wavelength $\lambda = 2.448$ Å at temperatures ranging from 1.5 K to room temperature. Pressure has been generated by means of a clamped pressure cell. The applied pressure has been determined from the lattice parameter of NaCl, of which a piece was included in the sample space.

The magnetization experiments have been performed in a commercial SQUID at temperatures ranging from 2 to 300 K. Here, for the pressure experiments a clamped pressure cell, fitting into the sample space of the SQUID and as described previously [8,9], has been employed. Only, rather than using the sealing system described in Refs. [8,9], we have used a Teflon cylinder to contain pressure medium, sample and pressure sensor. This cell allows the determination of the absolute value of the magnetization at pressures up to ~ 10 kbar.

3. Results and discussion

In Fig. 1, we plot the neutron diffraction spectra of $FePM_2Cl_2$ taken at 10 K at ambient pressure and 2.2 kbar, respectively. In the plot, in addition to the Bragg peaks from $FePM_2Cl_2$, those from the pressure standard

NaCl can be observed as indicated. From our data, we find no indication for a change of the crystallographic symmetry of the overall lattice or of sub-units of the lattice. We note, however, that because of the non-deuterated sample the level of incoherent background scattering is fairly large, thus reducing the signal-to-noise ratio. This might hinder the observation of small modifications of the structural properties under pressure. The Bragg peak positions shift with pressure, from which we obtain a reduction of the lattice parameters a by 0.56(10)% and c by 0.35(10)%. The experimental resolution is insufficient to detect additional scattering contributions in the antiferromagnetically ordered state below T_N.

From the reduction of the lattice parameters, we derive the bulk modulus $B = V(\Delta p/\Delta V)$, which we evaluate to 15 GPa. This is a very small value, reflecting the softness of this material. Typical intermetallic compounds, for instance, generally have bulk moduli of the order of 100 GPa (for comparison, see for instance Refs. [10,11], citing bulk moduli for intermetallic tetragonal compounds $CeRu_2T_2$, T = Si, Ge).

Interestingly, the anisotropy of the compression is strongly temperature-dependent. An analogous scattering experiment carried out at room temperature yields a reduction of the lattice parameters a by 0.9(1)% and c by 0.0(1)% under an externally applied pressure of 3 kbar. Then, the bulk modulus is evaluated to 17 GPa, closely resembling the low-temperature value. However, at this temperature the compression is highly uniaxial, in contrast to the fairly isotropic compression at low temperatures. These observations highlight the relevance of a detailed structural analysis as function of temperature for the interpretation of pressure experiments.

In Fig. 2, we plot the temperature dependence of the magnetization of $FePM_2Cl_2$ in a field of 0.1 T at various pressure values $P \leq 6.9$ kbar. At zero pressure, the
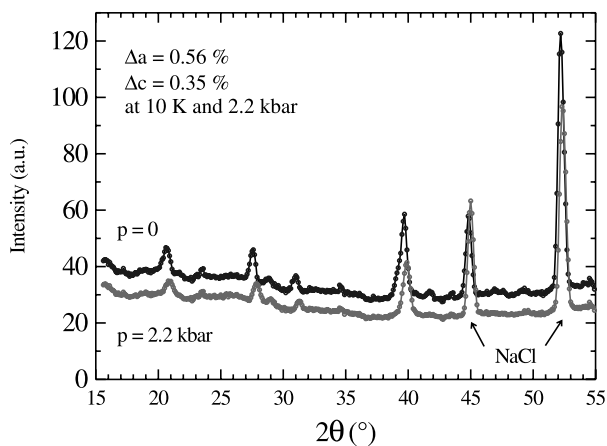

Fig. 1. The neutron diffraction spectra of $FePM_2Cl_2$ taken at 10 K at ambient pressure and 2.2 kbar, respectively. Bragg peaks from the pressure standard NaCl are indicated.
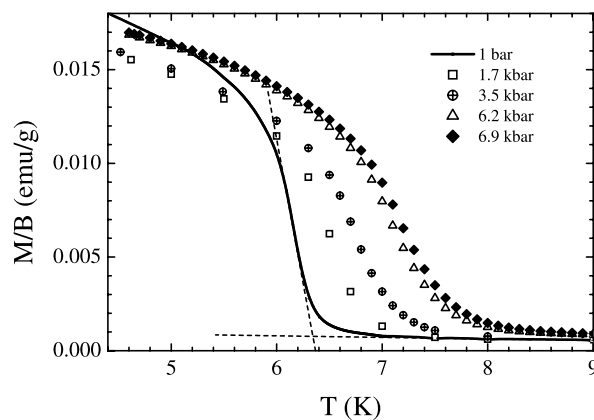

Fig. 2. The temperature dependence of the magnetization of $FePM_2Cl_2$ in a field of 0.1 T under ambient and externally applied pressure.

reported behavior [6] from the transition into the canted antiferromagnetic state, giving rise to weak ferromagnetism with a steep increase of the magnetization and a saturation in the domain state at low temperatures is reproduced. From a linear extrapolation, we obtain $T_N = 6.3$ K (crossing point of the two dashed lines).

Applying pressure does not change the overall behavior of the magnetization, indicating a persistence of the canted antiferromagnetic state. Moreover, it triggers a fairly strong increase of T_N. From analogous constructions as for the ambient pressure case, we obtain the transition temperatures T_N as function of pressure, which are depicted in Fig. 3. At the highest pressure, T_N has been shifted to 7.7 K, corresponding to an increase of T_N by more than 20%. The increase is sublinear, with a slightly negative curvature at all pressures.

To assess the relative strength of the pressure response, it is common to determine the magnetic Grüneisen parameter defined as $\Gamma_m = -\mathrm{d}(\ln(T^*/T_0))/\mathrm{d}(\ln(V^*/V_0))$. Here, T^* denotes the transition temperature under applied pressure with a unit cell volume V^*, while T_0 and V_0 represent the ambient pressure values. Assuming that the volume compression at low temperatures is linear with pressure up to 6.9 kbar, we evaluate Γ_m, ranging from 7 to 4 between ambient and highest pressure. The range of values is fairly typical for common magnets, this in contrast to, for instance, strongly correlated materials with Grüneisen parameters being an order of magnitude larger [12–14]. Hence, the fairly large increase of the antiferromagnetic transition temperature in $FePM_2Cl_2$ mainly reflects the softness of the material, as evidenced by a very small bulk modulus. In consequence, it triggers a stronger orbital overlap giving rise to an enhanced superexchange.
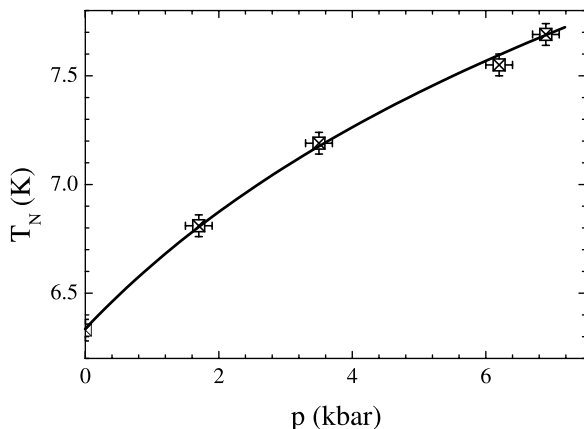
4. Conclusions

In conclusion, we have performed high-pressure experiments on the crystallographic structure and antiferromagnetically ordered phase of the transition metal complex $FePM_2Cl_2$. We obtain the bulk modulus at low and high temperatures, establishing the softness of the material. Moreover, we observe a strong temperature dependence of the anisotropy of the compression, being highly uniaxial at high temperatures, in contrast to an almost isotropic response at cryogenic T. We determine the pressure response of the antiferromagnetic transition temperature T_N, which increases by more than 20% in about 7 kbar. This large response reflects the softness of the lattice, with an enhanced superexchange under high pressure. Our findings demonstrate that in pressure experiments on molecular magnets, it is very important to establish at the same time the structural and magnetic properties as function of pressure.

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Fig. 3. The pressure dependence of the antiferromagnetic transition temperatures of $FePM_2Cl_2$, as determined from the experiments depicted in Fig. 2.