

High-pressure effects on a manganese hexacyanomanganate ferrimagnet with $T_N = 29$ K

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Abstract

The effects of high pressure, up to 1 GPa, on a Mn-based Prussian blue ferrimagnet, $\text{Mn}_3^{\text{II}}[\text{Mn}^{\text{III}}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O} \cdot 1.7(\text{CH}_3\text{OH})$ with $T_N = 29$ K, were studied. The transition temperature gradually increases with an increase in pressure and becomes ~ 40 K at 1 GPa. The pressure dependence of T_N can be semi-quantitatively interpreted in terms of the shrinkage of the Mn–CN–Mn superexchange pathway. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The magnetic properties of inorganic coordination compounds have been studied extensively, and the search for molecular magnets has been intensified in recent years [1,2]. In this field, Prussian blue analogs of the type $A_n\text{M}[\text{M}'(\text{CN})_6]_m$ (A is a counter cation), which have face-centered cubic structures with linear M–NC–M' bridges, are of interest to researchers because some of these compounds have magnetic ordering near (and in some cases exceeding) room temperature [3–5]. These properties are obtained in Prussian blue ferrimagnets, which consist of an anti-ferromagnetic superexchange interaction between the M and M' ions that is enhanced by π -back bonding into cyanide π^* orbitals. In addition, Hashimoto and co-workers have demonstrated that the magnetic

properties of some Prussian blue materials can be controlled by electrochemical and optical stimuli [6–8].

Magnetic measurements under high pressure might be useful and important in the study of molecular magnetism. The pressure dependence of the ferromagnetic behavior may provide microscopic data about magnetic interactions and, in some examples, about magnetic ordering. This study describes the effect of pressures up to 1 GPa on a Prussian blue ferrimagnet, $\text{Mn}_3^{\text{II}}[\text{Mn}^{\text{III}}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O} \cdot 1.7(\text{CH}_3\text{OH})$ (**1**), with $T_N = 29$ K.

2. Experimental

Material **1** was prepared by the method reported in Ref. [9]. Hydrostatic pressure was applied to 4.29 mg of **1** with the pressure fluid, Lipolube 40 oil

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(Lion, Tokyo) and was maintained by using a miniature Be–Cu pressure clamp cell [10]. The temperature and field dependences of the magnetization of the Be–Cu cell that contained the sample were measured with a Faraday susceptometer [10] at ambient and high pressures under the same conditions. The pressure-induced difference in magnetization ΔM , was obtained by subtracting the contributions of the pressure cell and pressure fluid. The pressure dependence of the magnetization of the blank was negligible as compared to the observed ΔM . The dependence of the diamagnetism of **1** on the pressure was also negligible, because the diamagnetic contribution itself is of an order of 10^1 emu mol⁻¹ at 10^4 Oe. The magnetization at ambient pressure $M(0)$ was separately measured by using a standard quartz cell and the high-pressure magnetization $M(P)$ was calculated from the equation, $M(P) = M(0) + \Delta M$.

The ac susceptibility at ambient pressure was measured on an ac magnetosusceptometer (Lake Shore ACS 7221) in a field of 5 Oe (125 Hz) below 50 K.

3. Results and discussion

The temperature dependence of the ac magnetic susceptibility of **1** was examined in order to obtain the transition temperature T_N at ambient pressure.

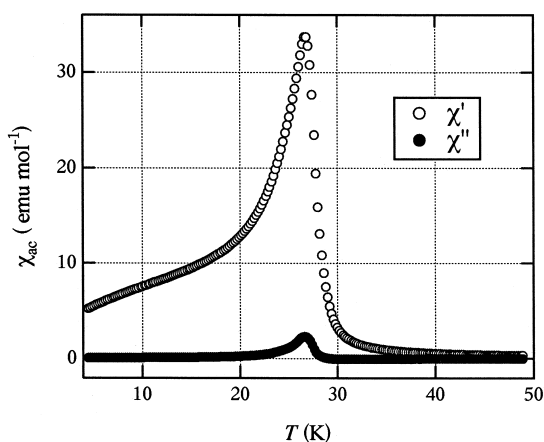


Fig. 1. Temperature dependence of the ac susceptibility for **1**; real (○) and imaginary (●) components.

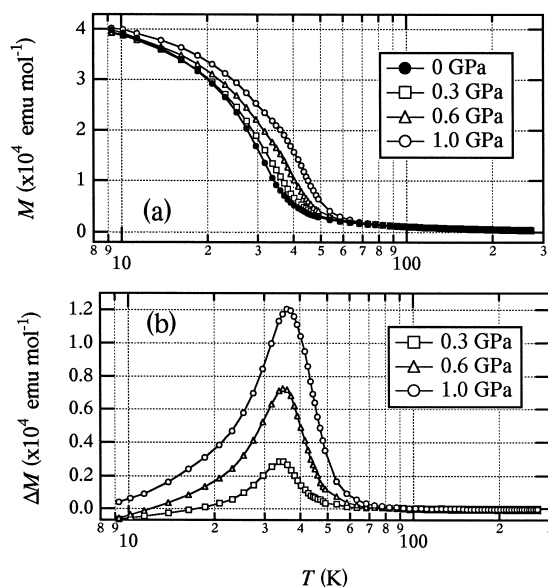


Fig. 2. (a) Temperature dependence of the magnetization for **1**. (b) Temperature dependence of the difference between the magnetizations at high pressure and at ambient pressure.

The open and closed circles in Fig. 1 show the real and imaginary components χ' and χ'' , respectively. The plots of χ' and χ'' exhibit large anomalies at a transition temperature of $T_N(0 \text{ GPa}) = 29 \text{ K}$, where the slope of the χ' curve is at a maximum. In comparison, the transition temperature for $\text{Mn}_3[\text{Mn}^{\text{III}}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ was reported to be 37 K [9]. The ordering temperature for Prussian blue analogues with a 3:2 stoichiometry is known to be especially dependent on the sample history. Factors such as the extent of linkage isomerism, the distribution of the hexacyanometalate vacancies and the water content can critically depend on the method of sample preparation and storage.

The closed circles in Fig. 2a show the temperature dependence of M for **1** at an ambient pressure at 9880 Oe, as recorded on the Faraday balance. The Curie and Weiss constants were obtained to be $13.6 \text{ emu K mol}^{-1}$ and -33 K , respectively, by fitting the data above 40 K to the hyperbolic equation [9,11]. The value of M increases rapidly below 40 K, which signals the onset of long-range magnetic ordering. Fig. 2b shows the difference, ΔM , between the

magnetization at high pressure and at ambient pressure. An increase in the pressure increases the magnetization in the entire temperature range and the maximum value of ΔM occurs at ~ 34 K. The magnetization at high pressure, $M(P)$, was calculated by the procedure described in Section 2. The results are shown in Fig. 2a. The ferrimagnetic ordering shifts to a higher temperature with increasing pressure.

The field dependence of the magnetization was examined up to 50 kOe at 34, 36, 39 and 44 K under pressures of 0, 0.3, 0.6 and 1.0 GPa, in order to estimate the pressure dependence of T_N more precisely. The results are shown in Fig. 3a–d. As the temperature is decreased and the pressure is increased, the magnetization tends to become saturated

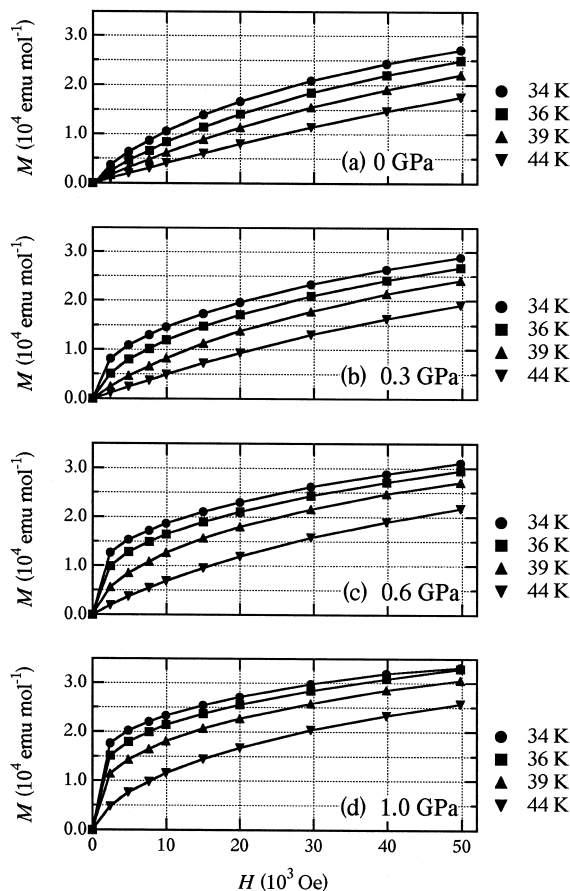


Fig. 3. Temperature dependence of the magnetization curve for **1**.

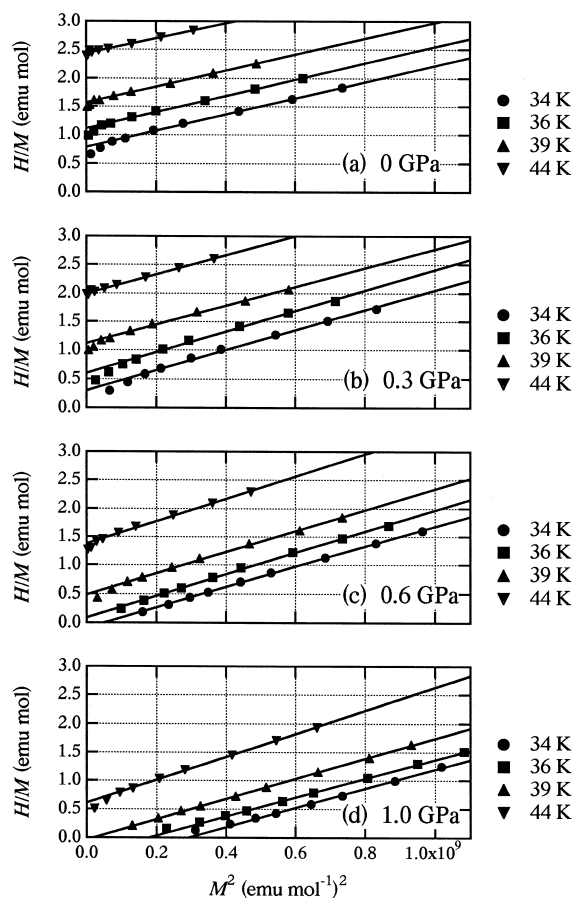


Fig. 4. Arrott plots for **1**.

more rapidly. Fig. 4a–d shows the Arrott plots of H/M vs. M^2 [12]. At each temperature, the Arrott plot is approximately linear and T_N can be estimated as the temperature at which the line passes through the origin [12]. Therefore, T_N at 0.6 GPa can be estimated to be in the range of 34–36 K. Fig. 5 shows the phase diagram for **1**, as determined by the Arrott plots in Fig. 4. In Fig. 5, the closed circles indicate the conditions under which compound **1** is in the ordered state and the open circles indicate the conditions under which it is in the paramagnetic state. A phase boundary can be placed between the open and closed circles.

Prussian blue analogs are three-dimensional magnetic materials, therefore T_N must be proportional to

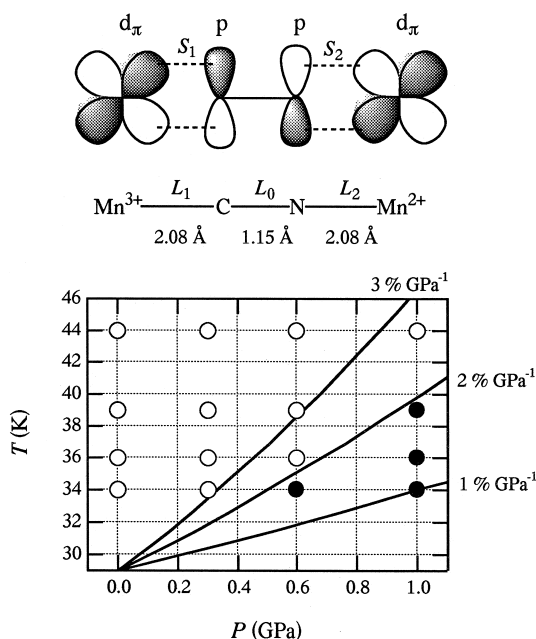


Fig. 5. Phase diagram for **1**. The open and closed circles indicate the paramagnetic and ordered states, respectively. The three curves exhibit pressure dependence, $T_N(0)S_1(P)^2S_2(P)^2/S_1(0)^2S_2(0)^2$, assuming three constant compressibilities. The geometry of the Mn–CN–Mn superexchange pathway as adopted for the calculation of S_1 and S_2 is also shown.

the nearest-neighbor exchange interaction J . The increase in T_N indicates an enhancement of the antiferromagnetic coupling. The spin interactions in Mn-based Prussian blue analogs were discussed in Refs. [4] and [13]; it was concluded that they were responsible for the superexchange interactions between the d_π electrons on the neighboring Mn ions through the π^* orbitals on the CN^- anion. In this mechanism, the coupling constant J is governed by the overlap integrals between $d_\pi(\text{Mn}^{3+})$ and $\pi^*(\text{CN}^-)$ and between $d_\pi(\text{Mn}^{2+})$ and $\pi^*(\text{CN}^-)$. We calculated two kinds of overlap integrals between the d and p orbitals, S_1 and S_2 , in the geometry shown in Fig. 5, letting the values of L_0 , L_1 and L_2 at 0 GPa equal to 1.15, 2.08 and 2.08 Å, respectively. We estimated the pressure dependence of S_1 and S_2 , by assuming that L_0 is constant and that there is a linear relation between the applied pressure and the compressive axial strain for L_1 and L_2 . The solid curves in Fig. 5 show the $T_N(0)(S_1(P))^2$ -

$S_2(P)^2)/(S_1(0)^2S_2(0)^2)$ vs. P plots for constant compressibilities. The phase boundary obtained from the Arrott plots can be explained by the theoretical curve for 2% GPa^{-1} , which is a reasonable value as judged from the compressibilities of ionic crystals [14]. Thus, the high-pressure effect on **1** can be explained semiquantitatively in terms of a three-dimensional shrinkage of the lattice.

The present results show that high-pressure effects are useful for the microscopic characterization of molecular magnets. The Prussian blue ferrimagnet **1** exhibits an understandable response to pressure, which is almost certainly caused by a predictable decrease in the length of the d– π –d superexchange pathway. High- T_N Prussian blue analogs have formerly been obtained by the replacement of the Mn ions in **1** with earlier transition elements, whose d electrons levels are close to those of the π^* orbitals on CN^- . Similar effects of high pressure on the high- T_N Prussian blue ferrimagnets are expected, so that it will become ~ 400 K at 1 GPa if $T_N(0) = 300$ K at the ambient pressure. Pressure might be a useful tool for controlling their magnetic properties.

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