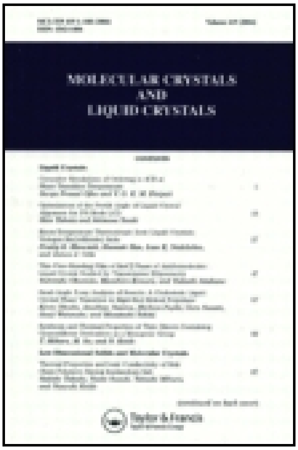

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Pressure Dependence of the Magnetization of M^{II} $(N(CN)_2)2$: Mechanism for the Long Range Magnetic Ordering

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Pressure Dependence of the Magnetization of $M^{II}(N(CN)_2)_2$: Mechanism for the Long Range Magnetic Ordering

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The *ac*-susceptibilities of the isostructural metal-organic magnets, $M^{II}(N(CN)_2)_2$(M = Ni (**1**), Co (**2**) and Fe (**3**)) have been studied as a function of temperature and pressure. Large variation in behaviors has been observed; the transition temperature initially increases in all three compounds and at higher pressures that for (**1**) saturates, for (**2**) decreases and for (**3**) increases continuously. These behaviors are due to the competition between antiferromagnetic ($t_{2g} \leftrightarrow e_g$) and ferromagnetic ($t_{2g} \leftrightarrow t_{2g}$ and $e_g \leftrightarrow e_g$) interactions to the most dominant exchange pathway, M···N≡C-N···M. A mechanism for the magnetic ordering is proposed.

Keywords: Cobalt; Dicyanamide; Iron; Magnetism; Nickel; Pressure

INTRODUCTION

Recently, we[1] and others[2,3] have found that the isostructural family of binary coordination compounds based on the first row transition metal complexes with the dicyanamide anion exhibits long range magnetic

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ordering. These compounds adopt a rutile-like structure with the metal in a distorted octahedral coordination[1,2]. The metals are doubly bridged by the dicyanamide anion into chains and adjacent chains are nearly orthogonal to one another.

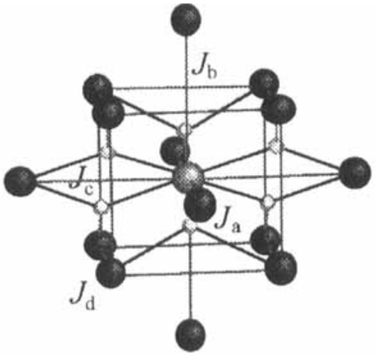

FIGURE 1: Definition of the four exchange interactions within the rutile structure of $M^{II}(N(CN)_2)_2$; only the metals and the amide nitrogen atoms are shown for clarity. J_a, J_b and J_c refer to those along the crystallographic axes and J_d to that along the diagonal of the unit cell.

While $Cu(N(CN)_2)_2$ is a paramagnet, $Ni(N(CN)_2)_2$ and $Co(N(CN)_2)_2$ behave as mean field ferromagnets with Curie temperature of 21 and 9 K, respectively, and $Fe(N(CN)_2)_2$, $Mn(N(CN)_2)_2$ and $Cr(N(CN)_2)_2$ are canted antiferromagnets (T_N = 19, 16 and 47 K, respectively). To understand the mechanism for these contrasting long range magnetic orderings we have undertaken a study of their magnetization under pressure. The simplicity of the crystal structure and the lack of void space, therefore low compressibilities, and the presence of one dominant magnetic exchange interaction (J_d) through M···N≡C-N···M (figure 1), are appealing properties for the pressure studies compared to the organic ferromagnet[4], β-NPNN (*para*- nitrophenyl nitronyl nitroxide). For similar reasons pressure study of the magnetization of perovskites[5] has been very useful in understanding the mechanism of magnetic ordering. Since the crystal system is orthorhombic, we anticipate that isothermal compression will be anisotropic, consequently changing the relative magnitudes of the exchange energies under pressure. Thermal expansion studies on $Ni(N(CN)_2)_2$ and $Co(N(CN)_2)_2$ show a continuous contraction of the volume on cooling; while the a- and b- lattice parameters decrease the c-parameter increases.

EXPERIMENTAL

The synthesis and characterization of the compounds have been described previously[1]. The *ac*-susceptibility measurements were performed in zero applied field by use of a SQUID (Quantum Design MPMS) and a home built susceptometer. For the pressure measurements, powdered samples were introduced into glass capillaries (10 × 1.5 mm) to a height of ~5 mm. Capillaries were then introduced into uniform *ac* pick-up (300 turns each) and field (200 turns) coils, which had been wound from copper wire of 0.05mm diameter on a plastic base of 1.8 mm diameter. The coils together with a manganin pressure gauge were loaded into a Teflon cell and filled with a 1:1 mixture of Fluorinert FC70 and FC77, as the pressure medium. Care was taken to allow the pressure medium to fully soak the samples. A Swenson-type Be-Cu pressure cell was used to apply and maintain pressure on the sample at room temperature, as described[6]. Samples were typically cooled to 4.2 K in a cryostat and the *ac*-susceptibility was measured during controlled warming through the magnetic ordering temperature. The temperature was recorded by means of a Pt-Co thermometer embedded in the cell near the sample. The cell has been calibrated for the pressure drop occurring during cooling a sample for the range of measuring temperatures[7,8]. The estimated error in pressure is of the order of ±0.5 kbar, resulting from both the pressure calibration method and measured small pressure losses (~-0.2 kbar) occurring after a temperature cycle.

RESULTS AND DISCUSSION

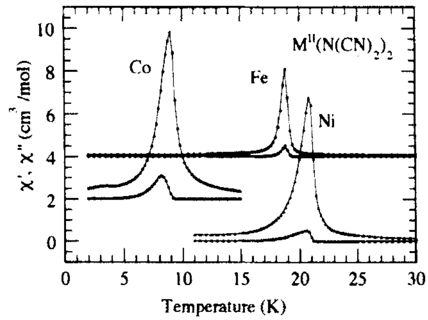

FIGURE 2 Temperature dependence of the *ac*-susceptibilities of (**1**), (**2**) and (**3**). Those of (**2**) and (**3**) are offset by 2 and 4 units, respectively.

The in- and out-of-phase components of the *ac*-susceptibilities, measured by the SQUID, of the three compounds are shown in figure 2. In all cases, an out-of-phase signal is observed due to the long range magnetic ordering. The widths of the peaks are similar for (**1**) and (**2**) while they are narrow for (**3**); this is due to ferromagnetic ordering for (**1**) and (**2**) but to a canted antiferromagnetic ordering for (**3**). Similar results were observed at ambient pressure using the pressure bomb. The temperature dependence of the real part of the susceptibility of (**1**) and (**2**) for several applied pressure are shown in figure 3. The critical temperature was defined at the peak maximum of the in-phase component. Application of pressure has the effect of first displacing the transition temperature and secondly of broadening the width of the peak. This effect increases in the order Ni<Co<Fe; an order consistent with the increase of single ion anisotropy of the metal[9]. At higher pressures the peak also becomes more symmetric. These effects may be a due to pressure induced changes to the magnetic domain structure.

The *ac* peak in the antiferromagnetic iron compound (not displayed) represents the development of ferromagnetic domains resulting from a 'canting' of the moments from exactly anti-parallel. The 'canting' angle has been estimated from bulk magnetometry measurements as 7.2° [1]. Towards higher pressures the peak broadens so that the maximum is only just observable at the highest measured pressure.

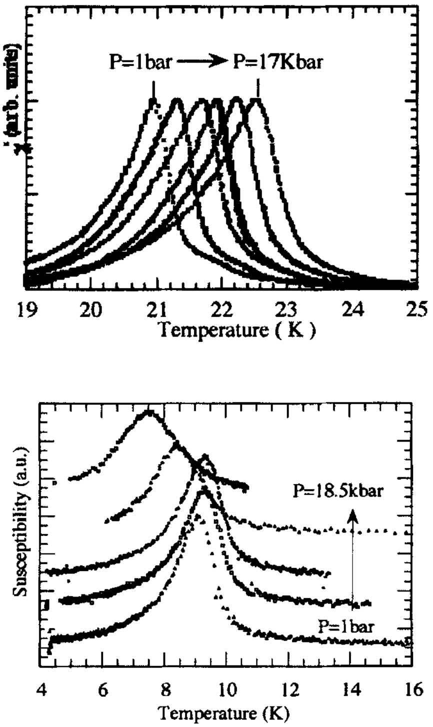

FIGURE 2 Temperature dependence of the *ac*-susceptibility of $Ni(N(CN)_2)_2$ (top) and $Co(N(CN)_2)_2$ (bottom) at various pressures [8].

One of the striking result is the diversity of behaviors for the pressure dependence of the Curie and Néel temperatures; for $Ni(N(CN)_2)_2$ T_C increases monotonically by 6%, for $Co(N(CN)_2)_2$ it is depressed after an initial small increase by 16% and for $Fe(N(CN)_2)_2$ it increases continuously by 26% upon application of a pressure of ~17 kbar.

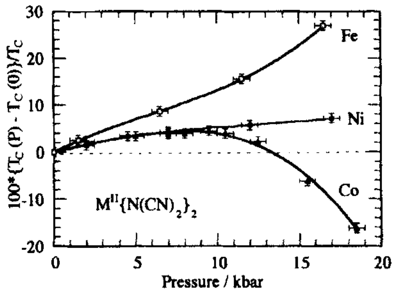

FIGURE 3 Pressure[8] dependence of the relative Curie and Néel temperature.

TABLE 1 Summary of Data on $M^{II}(N(CN)_2)_2$ Compounds:

M	Electronic Configuration	Magnetic Ground State	Curie or Néel Temperature
Cu	d^9 $t_{2g}{}^6 e_g{}^3$	P	
Ni	d^8 $t_{2g}{}^6 e_g{}^2$	F	21K
Co	d^7 $t_{2g}{}^5 e_g{}^2$	F	9 K
Fe	d^6 $t_{2g}{}^4 e_g{}^2$	AF canted	19 K
Mn	d^5 $t_{2g}{}^3 e_g{}^2$	AF canted	16 K
Cr	d^4 $t_{2g}{}^3 e_g{}^1$	AF canted	47 K
V	d^3 $t_{2g}{}^3 e_g{}^0$	***	***

P = paramagnetic, F = ferromagnetic, AF = antiferromagnetic,

*** Predicted to be a ferromagnet with a low Curie temperature

How can we rationalize these observations? The compounds are isostructural and the only difference is the electronic configurations (Table 1). For this structural type one can define four different nearest-neighbor super-exchange pathways, three along the principal axes, labeled J_l for which there are two of each, and one diagonal, J_d for which there are eight for each metal center (Figure 1). The first three involves Mn···N≡C-N-C≡N···Mn bridges and the latter involves Mn···N≡C-N···Mn bridges. Goodenough[10] has proposed several ground states depending on the relative magnitude of these exchanges within the rutile structure. In the present case, the magnitude of J_i is expected to be small compared to J_d and therefore, we can consider J_d as the most dominant. Furthermore, the contributions to J_d come from a number of overlap of the magnetic orbitals. We note that increasing the number of holes in the t_{2g} orbital results in an increase of the antiferromagnetic character (Table 1). From a comparison of the experimental results we may conclude that $t_{2g} \leftrightarrow e_g$ is AF, $t_{2g} \leftrightarrow t_{2g}$ is F and $e_g \leftrightarrow e_g$ is F. One can therefore predict that $V^{II}(N(CN)_2)_2$, with a t_{2g}^3 configuration, will be a ferromagnet, probably with a lower T_C than that of $Ni(N(CN)_2)_2$. In addition, the lack of magnetic anisotropy for $V^{II}(N(CN)_2)_2$ (half filled t_{2g}) would result in a soft magnet. Within the mean field approach, the critical temperature should increase with increasing pressure, as observed for (**1**) and (**3**) in contrast to that of (**2**). Furthermore, T_C is also expected to increase with the spin quantum number; therefore T_C for (**2**) should be higher than for (**1**). Since there is an AF contribution for (**2**) which is absent for (**1**), T_C for the nickel is higher than for the cobalt compound. Our result is consistent with an increase of antiferromagnetic contribution to J_d on application of pressure.

CONCLUSION

Large pressure dependence of the Curie and Néel temperatures has been observed for the metal-organic magnets, $M^{II}(N(CN)_2)_2$. Due to different contributions (F and AF) contrasting ground states are observed for the different transition metals. A mechanism for the long range magnetic ordering has been proposed which accounts for the observed ground states and the critical temperatures. Pressure induces a transformation from a ferromagnetic to an antiferromagnetic exchange interaction in the cobalt compound.

ACKNOWLEDGEMENTS

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