Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

Mol. Cryst. Liq. Cryst., 2000, Vol. 342, pp. 185-192
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Calorimetry of Low-Dimensional Magnets*

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Heat capacity is very sensitive to the change in the long- and short-range order effects, which crucially depend on lattice dimensionality and spin-spin interaction. Dimensional crossover is often encountered in actual molecule-based or metal-assembled magnets and thus phase transitions due to the spin ordering may occur at low temperatures even for low-dimensional magnets. The important factor governing the short-range order effect due to magnetic fluctuation is the number of the nearest neighbor magnetic ions as well as the lattice dimensionality.

Keywords: phase transition; low-dimensional magnet; dimensional crossover; assembled metal complex; heat capacity; short-range order

INTRODUCTION

Since assembled metal complexes contain molecular parts as the building-blocks, their structures are anisotropic and thus physical properties such as magnetic interactions inevitably become anisotropic. This leads to low-dimensional magnets in which one- or two-

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dimensional interaction is dominant. Short- and long-range orders formed by spins crucially depend on the magnetic lattice structure. These features are very sensitively reflected in the heat capacity. For a linear chain structure (one-dimensional lattice: 1D), no phase transition is theoretically expected because fluctuation of the spin orientation is extremely large. For a layer structure (two-dimensional lattice: 2D), a phase transition with remarkable short-range order effect takes place when the interaction is of the Ising type, while no phase transition for the Heisenberg type. Contrary to this, three-dimensional (3D) structure gives rise to a phase transition with minor short-range order effect, indifferently of the type of spin-spin interaction. In actual magnetic materials, interaction paths, through which super-exchange spin-spin interaction takes place, are often much more complicated than being classified into a homogeneous single dimension. As the result, it happens that apparent dimensionality changes with temperature. In other words, dimensional crossover may occur between any pair of 1D, 2D and 3D.[1]

This paper demonstrates important roles played by heat capacity measurements on assessing physicochemical properties of substances, in particular, the magnetic interactions in assembled metal complexes.[2]

ONE-DIMENSIONAL SYSTEMS

In the case of a magnetic system characterized by Ising- or XY-type interaction, heat capacity curves calculated for ferromagnetic and antiferromagnetic interactions are identical. However, this is not the case for the system showing Heisenberg-type interactions: the heat capacity of antiferromagnet is larger than ferromagnetic one. By comparing experimental heat capacity with these theoretical curves one can easily estimate the type of spin-spin interaction in the material.

Figure 1 shows the heat capacity of a pure organic free radical MOTMP (4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl).[3] Its magnetic susceptibility indicates the evidence of ferromagnetic interaction between the neighboring radicals. As shown in Fig. 1, its heat capacity exhibited a λ-type phase transition due to the onset of long-range ordering at 0.14 K. Unexpectedly, a remarkably broad anomaly was observed above the transition temperature. This anomaly was well accounted for in terms of the short-range order in the ferromagnetic Heisenberg chains with the interaction parameter of $J/k_B = 0.45$ K. As

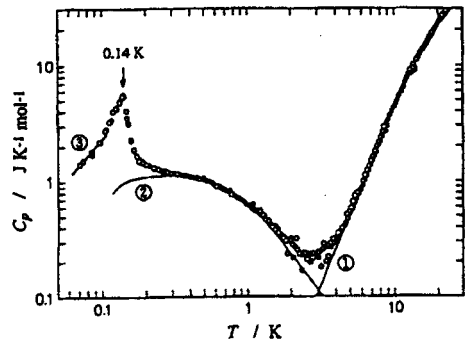

FIGURE 1 Molar heat capacity of MOTMP. (1) Lattice heat capacity; (2) 1D Heisenberg ferromagnet (J/k_B = 0.45 K): (3) Spin-wave contribution.

far as its crystal structure is concerned, there seems to be no indication of favorable 1D exchange paths. This fact evidently indicates how sensitive to dimensionality the heat capacity is. This finding of 1D behavior was confirmed by magnetic susceptibility measurements done below 1 K.[4]

The initial slope of the heat capacity at the lowest temperatures corresponds to the spin-wave excitation. In a simple framework of the spin-wave theory, the heat capacity arising from the excitation of spin wave is represented by $T^{d/n}$, where d stands for dimensionality of the magnetic lattice while n is 1 or 2 for antiferro- or ferromagnetic interaction, respectively. In case of MOTMP, temperature dependence was T to the power of 1.53. This exponent value is well approximated by 3/2, indicating that a dimensional crossover occurred from 1D to 3D on going from high- to low-temperatures, indicating that MOTMP behaves as three dimensional ferromagnet below the transition temperature. The entropy gain due to the cooperative and the non-cooperative anomalies was ΔS = 5.81 JK^{-1} mol^{-1}. Since this value is very close to R ln 2 = 5.76 JK^{-1} mol^{-1} expected for the spin S=1/2 system, it turns out that one mole of the spin is involved in MOTMP crystal.

Kahn and his collaborators[5] reported the ferrimagnetic chain complex MnCu(obbz)·5H_2O. The spins in this complex form a linear chain consisting of alternating array of the 5/2 up-spin of Mn^{3+} ion and the 1/2 down-spin of Cu^{2+} ions (Fig.2a). As shown in Fig.2c,

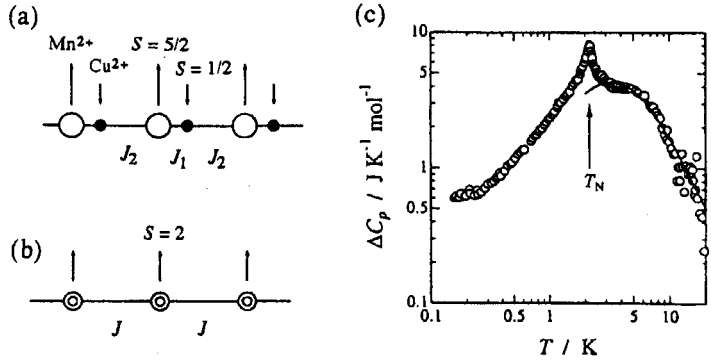

FIGURE 2 (a) Schematic magnetic structure of the 1D ferrimagnetic chain in MnCu(obbz)·5H_2O. Open and filled circles stand for Mn^{2+} and Cu^{2+} ions, respectively; (b) 1D ferromagnetic chain consisting of the resultant S=2 spins; (c) Excess heat capacity of MnCu(obbz)·5H_2O. Solid curve indicates the theoretical heat capacity estimated by the high temperature series expansions for S=2 1D ferromagnetic Heisenberg model with J/k_B=0.75 K.

MnCu(obbz)·5H_2O exhibited a phase transition at 2.18 K and a broad heat-capacity anomaly above the antiferromagnetic phase transition.[6] The super-exchange parameters between these two ions J_1/k_B=–42 K and J_2/k_B=–7.2 K were determined by magnetic susceptibility. This ferrimagnetic system (Fig.2a) can be replaced by an equivalent ferromagnetic linear chain consisting of a resultant spin S=2 with effective exchange parameter of J/k_B = 0.75 K (Fig.2b). As clearly seen in Fig.2c, the heat capacity anomaly detected above the Neél temperature was well reproduced by the 1D ferromagnetic Heisenberg model. This fact indicates the validity of this treatment.

TWO-DIMENSIONAL SYSTEM

As one of the strategies for new design of molecule-based magnets, Ôkawa and his collaborators[7] reported a series of mixed-metal assemblies $\{NBu_4[M^{II}Cr^{III}(ox)_3]\}_n$, where NBu_4 is tetra-*n*-butyl ammonium ion. These complexes exhibit spontaneous magnetization at

low temperatures. On the basis of molecular model considerations it is suggested that these complexes may form either 2D- or 3D-network structure extended by the Cr(III)-ox-M(II) bridges. When the chiralities of the neighboring $[M^{II}(ox)_3]$ and $[Cr^{III}(ox)_3]$ octahedra are a pair of (Δ and Λ), 2D structure is formed (Fig.3a) while the combination of either (Δ and Δ) or (Λ and Λ) brings about a 3D structure (Fig.3b). Unfortunately, however, since these complexes were prepared as fine powder, single crystal X-ray diffraction study had not been successful. As heat capacity is sensitive to lattice dimensionality, we tried to determine the actual dimensionality on the basis of heat capacity measurements for this series of complexes.

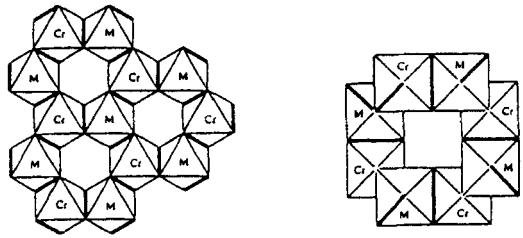

FIGURE 3 Schematic structure of $\{NBu_4[MCr(ox)_3]\}_n$ for (a) 2D and (b) 3D lattices.

As shown in Fig.4, mixed-metal $\{NBu_4[CuCr(ox)_3]\}_n$ complex gave rise to a phase transition at 6.99 K. This phase transition is attributable to the ferromagnetic spin ordering because the entropy gain, ΔS = 17.14 JK^{-1} mol^{-1}, agrees well with the theoretical value, R ln (2×4) = 17.29 JK^{-1} mol^{-1}, expected for the spin system consisting of Cu^{2+} (spin 1/2) and Cr^{3+} (spin 3/2), and also because the transition temperature agrees well with the onset temperature of the spontaneous magnetization.[7] A remarkable feature is the existence of a dominant short-range order manifested by the large tail of the magnetic heat capacity. This type of heat-capacity anomaly is characteristic of low-dimensional magnets. Since 1D magnetic interaction paths cannot be found in this complex, we may conclude that this series of mixed-metal complexes have 2D magnetic structures. A question arises here. Since the spin-spin interaction in this complex is of Heisenberg type, no phase

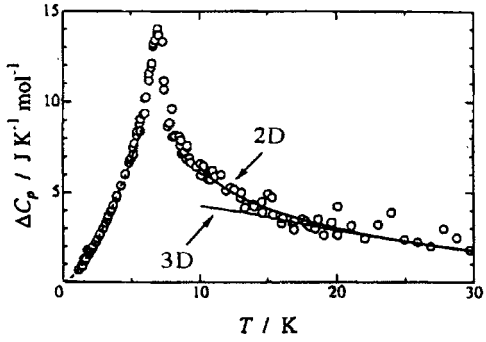

FIGURE 4 Excess heat capacity for $\{NBu_4[CuCr(ox)_3]\}_n$. The thick curve represents 2D, while the thin curve corresponds to 3D structure.

transition is theoretically expected for 2D systems. However, the occurrence of the magnetic phase transition does not necessarily imply that this complex should be of 3D Heisenberg ferromagnet. When 3D interaction, even though weak, exists at low temperatures, dimensional crossover between 2D and 3D nay happen and bring about a phase transition. In fact, the heat capacities of $\{NBu_4[CuCr(ox)_3]\}_n$ in the spin-wave excitation region are well reproduced by $T^{1.51}$, whose exponent is approximated by $d/n = 3/2$, implying that the ordered state at low temperatures is actually of 3D ferromagnet.

On the basis of this fact, we concluded that the dominant magnetic interaction may be of two-dimensional. However, we should be very careful to draw a conclusion about the dimensionality when the number of the nearest neighbor paramagnetic ions is extremely small. In case of the present complex, it is only three. This number is extremely small in comparison with 6 (s.c.), 8 (b.c.c.), and 12 (f.c.c.) of 3D lattices or 4 (square and Kagomé), and 6 (triangle) of 2D lattices. Even if the present complex were crystallized into 3D lattice, such a small number of the nearest neighbors would bring about a dominant short-range order effect resulting form the magnetic fluctuation.

In order to examine quantitatively the dimensionality of the magnetic structure of the present complex, we formulated the magnetic heat capacities for possible 2D and 3D structures by the high-temperature series expansion with the Padé approximation and fitted to the excess heat capacities above the transition temperature. Since the number of the nearest neighbors is extremely small, two formulae for 2D and 3D

structures closely resemble each other. As the results, the short-range order effect was extremely large for both 2D and 3D structures. However, as can be seen in Fig.4, good agreement is obtained for 2D structure, where the super-exchange interaction parameter is J/k_B = 5.0 K. Therefore, from a thermodynamic viewpoint, we may conclude that the magnetic lattice structure might be two-dimensional.

It is of great interest, however, that the short-range order effect estimated for 3D structure is also unusually large compared with those for s.c., b.c.c., or f.c.c. lattices. This fact clearly implies that in addition to the dimensionality the important factor governing the short-range order effect due to magnetic fluctuation is the number of the nearest neighbors.

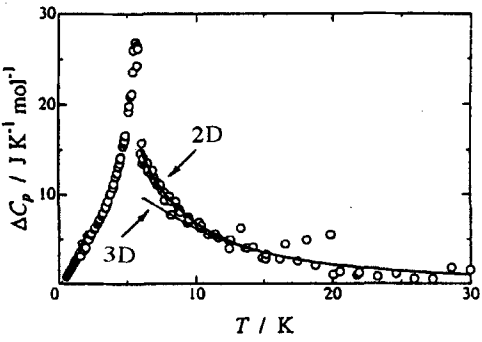

FIGURE 5 Excess heat capacity for $\{P(Ph)_4[MnCr(ox)_3]\}_n$. The thick curve represents 2D, while the thin curve corresponds to 3D structure.

It should be remarked here that Decurtins *et al.*[8] reported the single crystal X-ray study of an analogous complex $\{P(Ph)_4[MnCr(ox)_3]\}_n$ and concluded a 2D network structure, where $P(Ph)_4$ is tetraphenyl-phosphate. We measured heat capacity of this complex and found a magnetic phase transition at 5.59 K. As compared in Fig.5, the analysis of heat capacity of this complex based on the high-temperature series expansion clearly supports the 2D magnetic structure with the spin-spin interaction of J/k_B = 1.1 K. The coincidence of the dimensionality derived from X-ray structural analysis and the present calorimetric study would guarantee the validity of the present treatment. In other words, we may safely conclude that the magnetic dimensionality of the present series of mixed-metal complexes is two-dimensional.

ACKNOWLEDGEMENT

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas "Metal-assembled Complexes" (Area No.401/11136226) from the Ministry of Education, Science, Sports and Culture, Japan.

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