Specific heat of $S = 1$ quasi-1D antiferromagnet NDMAP in magnetic fields

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Abstract

NDMAP, $Ni(C_5H_{14}N_2)_2N_3(PF_6)$, is a quasi-one-dimensional $S = 1$ Heisenberg antiferromagnet with Haldane-gap energies of 22 K and 5.5 K for excitations polarized parallel and perpendicular to the chain c axis, respectively. We have extended the specific-heat measurements by Honda *et al*. in this compound to 150 mK in temperature and 18 T in magnetic field, employing a novel relaxation calorimeter. The experiment provides an accurate determination of the exponent for the transition line for the field-assisted ordered phase. In addition, a new feature has been found in the phase diagram at around 14 T.

Key words: Haldane gap; low-dimensional magnetism; magnetic ordering

The ground state of one-dimensional integer-spin Heisenberg antiferromagnets is a spin singlet with only short-range correlations and is often referred to as a quantum spin liquid. As has been predicted by Haldane [1], there is an energy gap between the ground state and the first excited triplet. This prohibits three-dimensional ordering in one-dimensional antiferomagnets with a weak inter-chain coupling. However, a magnetic field destroys the gap and allows phase transition to an antiferromagnetically ordered state to appear. Such 3D ordering has been observed in spin-1 antiferromagnetic chain materials $Ni(C_5H_{14}N_2)_2N_3(PF_6)$ (NDMAP) [2,3] and $Ni(C_5H_{14}N_2)_2N_3(ClO_4)$ (NDMAZ) [4,5].

NDMAP has an orthorhombic structure with the lattice parameters $a = 18.046$ Å, $b = 8.7050$ Å, and $c = 6.139$ Å. The antiferromagnetic spin chains run along the c axis. The structure of NDMAZ is similar, with somewhat different lattice parameters. The in-chain exchange constant J, the anisotropy constant D, and the Haldane gap energies of NDMAP have been determined from the magnetic susceptibility by Honda *et al.* [2]. The magnetic phase diagram has been determined by specific heat measurements up to 12 T [2]. Depending on the direction of the applied field, the field-assisted ordered phase has either three-dimensional long range order or quasi-two-dimensional short range order [6].

To extend the specific-heat measurements to 18 T and to mK temperatures, we have grown fully deuterated single crystals of NDMAP to reduce the nuclear heat capacity of protons. Neutron scattering and magnetic susceptibility measurements [2,3,7] indicate that there is no difference between hydrogenated samples and deuterated samples in their magnetic properties.

The magnetic-field dependence of the specific heat at constant temperatures in the field applied along the c axis is shown in Fig. 1. The peaks in the specific heat clearly show phase transition. The phase boundary obtained from these data, as well as from data taken as a function of temperature at constant magnetic fields, is given in Fig. 2. There is a small difference between the present phase diagram and the earlier one [2], which is shown with open symbols. This difference probably

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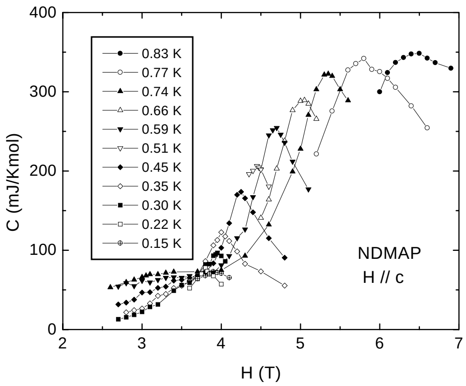

Fig. 1. Magnetic field dependence of the specific heat of NDMAP measured at constant temperatures. The external magnetic field is applied along the c axis. The lines are guides to the eye.

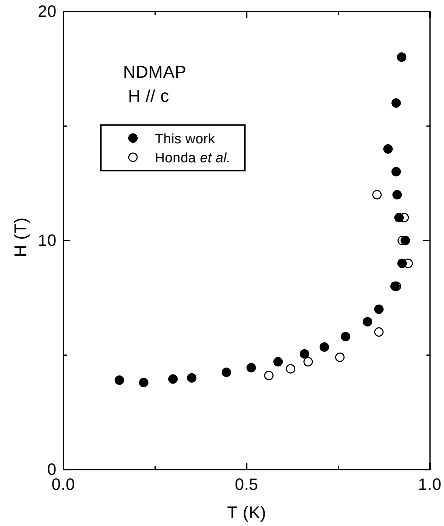

Fig. 2. Temperature vs magnetic field diagram of NDMAP for the field applied parallel to the c axis.

arises from a small misalignment of the samples with respect to the field, rather than an intrinsic difference between a hydrogenated NDMAP and a deuterated NDMAP.

An important feature of the new phase diagram is a shallow local minimum in the transition temperature at around 14 T, as can be seen in Fig. 2. We have searched for a possible second phase boundary originating from this minimum by making a field scan from 12 T to 15 T at 0.7 K, but no feature indicative of a phase boundary has appeared in the specific heat. Since the derivative of specific heat with respect to the magnetic field is given by

$$\left(\frac{\partial C_H}{\partial H}\right)_T = T\left(\frac{\partial^2 M}{\partial T^2}\right)_H, \tag{1}$$

and the magnetization is exactly the same in two phases separated by second-order transition, a perfectly horizontal second-order line produces no discontinuity in $(\partial C_H/\partial H)_T$ at the transition. For this reason, the present result does not rule out an existence of a horizontal phase boundary at 14 T. Further study using techniques other than specific heat is needed.

Recently, field-assisted magnetic ordering in the $S = 1/2$ spin-dimer material $TlCuCl_3$ has been interpreted in terms of the Bose-Einstein condensation of magnons [8]. According to the magnon Bose-Einstein condensation theory, the phase boundary in the temperature vs field plot obeys a power law $T_c \propto (H - H_c)^\alpha$. However, the exponent α of 0.50 measured in $TlCuCl_3$ is smaller than the theoretical value of 2/3. The exponent for NDMAZ has been reported to be 0.45 [5], which is also less than the theoretical value.

We find from our data that the exponent α for NDMAP is 0.35 for magnetic fields oriented in the direction of the c axis. This is substantially smaller than $\alpha = 2/3$ predicted by the theory and the experimental values for $TlCuCl_3$ and NDMAZ. The failure of the theory is probably due to a limitation of the Hartree-Fock approximation employed or some feature in real systems that has been ignored by the theory.

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