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1997 J. Phys.: Condens. Matter 9 L83

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LETTER TO THE EDITOR

Inducing a magnetic ordering in the Haldane material $\text{Ni}(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{N}_3(\text{ClO}_4)$ by magnetic field

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Received 2 December 1996

Abstract. From a heat capacity measurement in high magnetic fields and at low temperatures, we have obtained evidence for a magnetic ordering in the $S = 1$ quasi-one dimensional Heisenberg antiferromagnet $\text{Ni}(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{N}_3(\text{ClO}_4)$. The transition temperature is ~ 0.6 K at 12 T parallel to the chain axis.

Quasi-one-dimensional (1D) magnets, in which magnetic interaction dominates in one direction with much weaker interactions in other directions, were extensively studied in the 1970s [1] because they often became prototypical model compounds in statistical physics. Quasi-1D magnets exhibit a short-range ordering over a wide temperature range and usually show a long-range ordering at finite temperature due to the inter-chain coupling.

Recently, a great deal of interest has been paid to 1D Heisenberg antiferromagnets (HAFs) with integer spin quantum number (S) since Haldane [2] conjectured that the excitation spectrum of a 1D HAF changes radically depending on whether S is integer or half odd integer. In the former case, there is an energy gap (Haldane gap) between the singlet ground state and first excited triplet. The effects of inter-chain coupling on the Haldane gap have been studied theoretically [3] and the results show that the Haldane gap survives even at $T = 0$ K if the inter-chain coupling is small ($zJ'/J < 0.05$). In fact, the well-documented $S = 1$ quasi-1D HAF compound $\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NO}_2\text{ClO}_4$ (NENP) exhibits no long-range ordering down to 0.5 K [4]. On the other hand, strong magnetic fields destroy the Haldane gap and the system recovers magnetism [5]. Then, we expect a magnetic ordering to occur in a quasi-1D $S = 1$ HAF under high fields and at low temperatures. There has been no report on this subject. One of the reasons for this is that an external magnetic field applied along the chain axis of NENP induces a staggered field on the Ni sites because of the presence of two crystallographically inequivalent sites for Ni^{2+} [6]. This staggered field causes a small energy gap near the transition field [7–12] and thus prevents the occurrence of long-range ordering at low temperatures. In this Letter we report the first observation of field-induced magnetic ordering in the $S = 1$ quasi-1D HAF compound $\text{Ni}(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{N}_3(\text{ClO}_4)$, abbreviated NDMAZ.

First, we summarize the crystal and magnetic properties of NDMAZ. Figure 1 shows the crystal structure of NDMAZ. This compound belongs to the monoclinic system [13]. The lattice constants at room temperature are $a = 18.860$ Å, $b = 8.152$ Å, $c = 6.098$ Å and $\beta = 98.27^\circ$. The structure consists of $\text{Ni}(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{N}_3$ chains along the c -axis. These

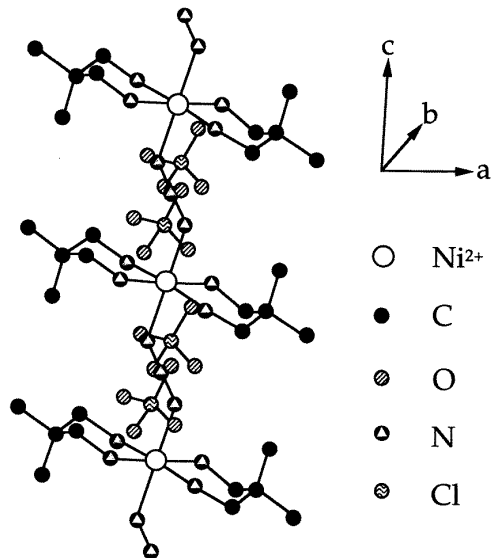


Figure 1. The crystal structure of $\text{Ni}(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{N}_3(\text{ClO}_4)$, abbreviated NDMAZ.

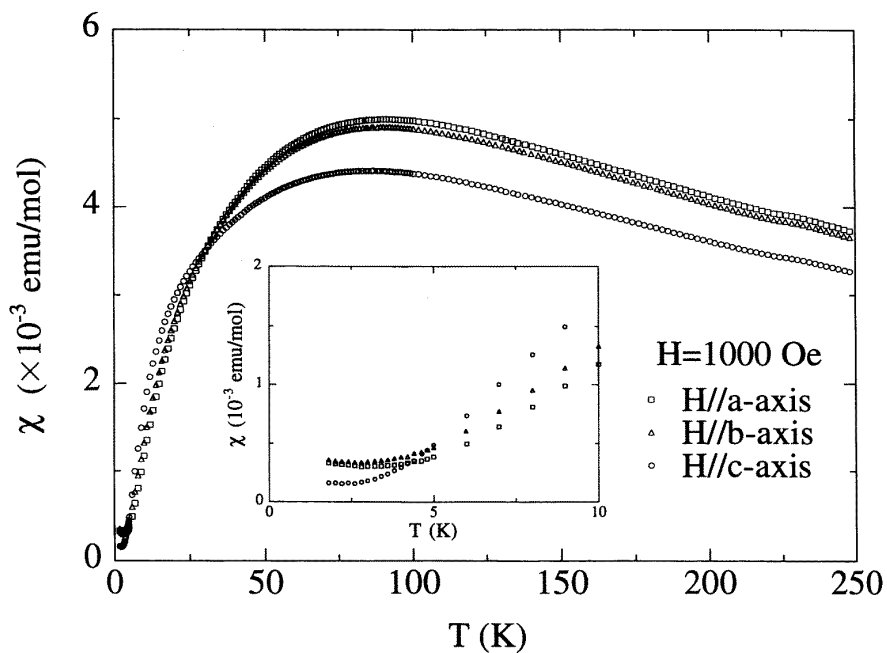


Figure 2. Temperature dependence of susceptibility along the crystallographic a , b and c axes of a single-crystal sample of NDMAZ. The inset shows the low-temperature part.

chains are well separated from each other by ClO_4 molecules. All the Ni^{2+} sites in the crystal are equivalent, i.e., only one site exists for Ni^{2+} . Therefore, we expect that the staggered field will be absent in this compound. From the analysis of the magnetic susceptibility made

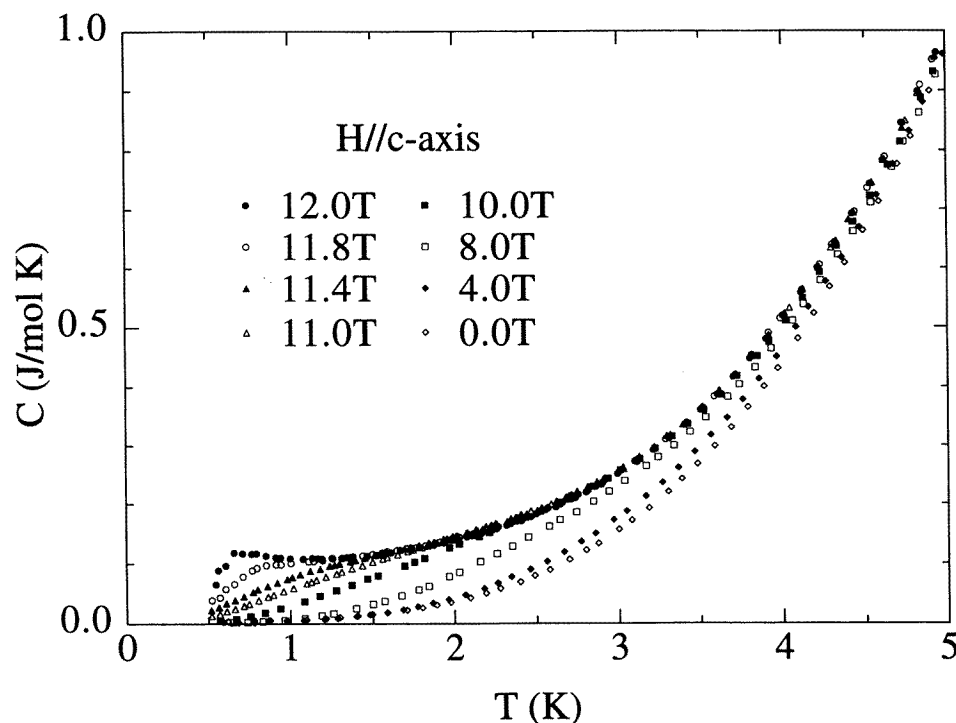


Figure 3. Temperature dependence of heat capacity of a single crystal of NDMAZ measured in magnetic fields parallel to the c -axis.

on a polycrystalline sample, the intra-chain exchange interaction constant was determined to be $J/k_B = -70.6$ K [13]. The magnetization measurement on a polycrystalline sample shows that the magnetization is almost zero below about 8 T and begins to increase around 14 T [13].

Figure 2 shows the temperature dependence of susceptibility of a single crystal of NDMAZ measured with a SQUID magnetometer (Quantum Design MPMS2). We see that a broad peak appears around 80 K and that the susceptibility decreases steeply for all of the crystal axes when the temperature is decreased further. The difference between the susceptibilities parallel and perpendicular to the c -axis suggests the presence of single-ion anisotropy term DS_z^2 . As is seen from the inset of figure 2 we have no indication of paramagnetic behaviour down to 1.8 K. All these behaviours of the susceptibility in NDMAZ are qualitatively the same as those observed in NENP [14].

We have measured the heat capacity of a single crystal sample of NDMAZ using a MagLab^{HC} microcalorimeter (Oxford Instruments). This calorimeter employs the relaxation method using an integrated sapphire chip. A single crystal with the dimensions $4 \times 3 \times 1$ mm³ was used for the measurements. Figure 3 shows the temperature dependence of the total heat capacity including the contribution of the lattice measured in applied magnetic field (H) parallel to the c -axis. We see that heat capacity increases with increasing field strength at low temperatures. This is consistent with the results of heat capacity measurement on NENP [8]. A new finding in this experiment is that a broad shoulder appears around 1 K when $H > 11$ T, which becomes sharper with increasing H . We show in figure 4 the results when H is applied to the b -axis perpendicular to the chain. We see no peak at low

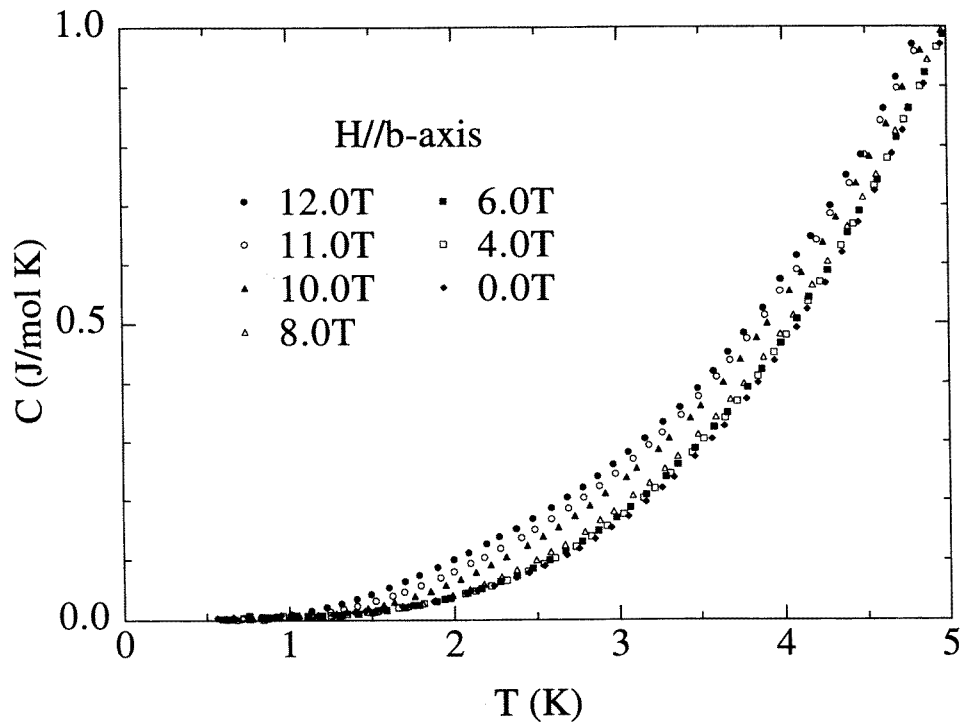


Figure 4. Temperature versus heat capacity of a single crystal sample of NDMAZ. The external magnetic field is applied to the b -axis.

temperatures up to 12 T.

We subtracted the lattice heat capacity from the total to obtain the magnetic heat capacity (C_m). Here, we assumed that the lattice heat capacity varied as T^3 and was independent of magnetic fields. The result for $H \parallel c$ -axis is shown in figure 5. Below 8 T C_m decreases steeply with decreasing temperature. This means that the broad peak in C_m expected for an $S = 1$ 1D HAF [15] is located at much higher temperature and we are observing the low-temperature tail. When H is increased further a broad shoulder appears the position of which moves to the low-temperature side with increasing field strength. Similar behaviour has been observed in NENP and has been explained as due to the decrease of Haldane gap with H [8]. Above 11.6 T the shoulder becomes sharper and finally we have an anomaly in C_m at about 0.6 K under the highest magnetic field of 12 T available in this calorimeter. We interpret this anomaly in C_m as the field-induced magnetic ordering in an $S = 1$ quasi-1D HAF compound.

Now we consider the possible contribution of protons to the heat capacity. Protons have a nuclear moment and thus contribute the heat capacity in magnetic fields due to the Zeeman split levels. We plot in figure 5 the theoretical heat capacity from protons in NDMAZ at 12 T. If the thermal equilibrium condition is fulfilled, we could observe the heat capacity expected from this curve. The nuclear spin-lattice relaxation time (T_1) of the protons in the Haldane material such as NENP show complex behaviour [16]. With decreasing temperature T_1 becomes longer under a given magnetic field. On the other hand, T_1 becomes shorter when H approaches the transition field under a given temperature. When T_1 is comparable to the measuring time of calorimeter, one observes a peak in the temperature dependence of

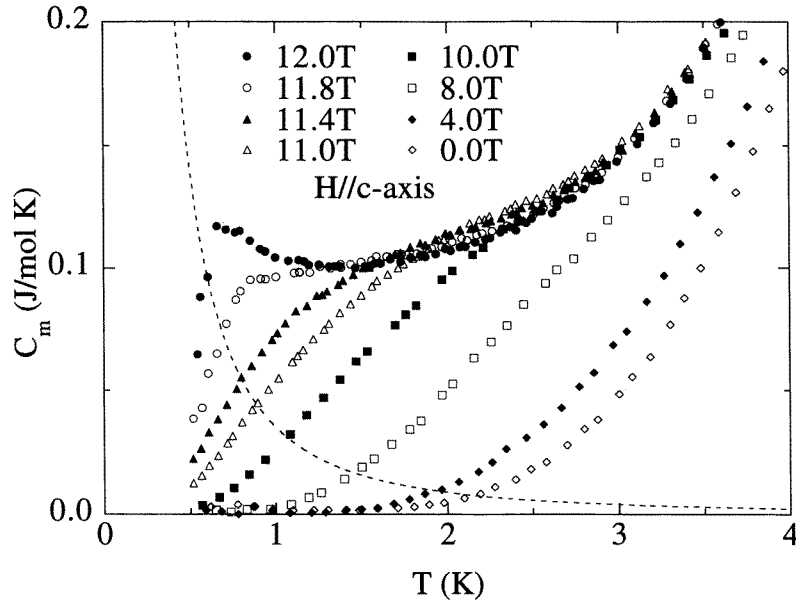


Figure 5. Temperature dependence of the magnetic part of heat capacity in NDMAZ for magnetic fields parallel to the c -axis. The dotted line shows the theoretical heat capacity from proton nuclear spins in NDMAZ at 12 T.

proton heat capacity, as reported by Kobayashi and coworkers [8]. From a detailed analysis of the relaxation curve obtained from our heat capacity system, we find that the curve can be fitted with a sum of two relaxation functions with different relaxation times at $T = 0.5$ K and $10 \text{ T} \leq H \leq 12 \text{ T}$. The result shows that one of the relaxation times does not depend much on H , while the other one *increases* with increasing H from 10 T to 12 T. Since the relaxation times are related to T_1 if we were measuring the heat capacity of protons, the above fact means that we have measured essentially the heat capacity of electron spins. Moreover, the large change in C_m from 11.8 T to 12.0 T can hardly be explained as the effects of proton nuclear spins.

In conclusion, we have observed a long-range ordering in the $S = 1$ quasi-1D HAF compound NDMAZ at ~ 0.6 K and at 12 T from a heat capacity measurement.

We would like to thank Dr Nestor Patrikios of Oxford Instruments, UK, for his effort in starting up the heat capacity measuring system. This work was supported in part by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science, Sports and Culture.

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