Antiferromagnetic Ordering and Spin Structure in the Organic Conductor, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl

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The magnetism of an insulator, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, situated near the 10 K superconducting phase in κ-type BEDT-TTF family, has been studied by ^{1}H NMR for the first time. A commensurate antiferromagnetic ordering with a moment of $(0.4-1.0)\mu_B$/dimer was found below 26–27 K. The features, quite different from the conventional spin density wave, suggest that the magnetic order is driven by strong electron correlation rather than by nesting of the Fermi surface, and that the present salt is a Mott insulator. Magnetization measurements show spin canting parallel to the conducting layer below 23 K at low fields.

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The metal-insulator (M-I) transition has been always a center of interest in the physics of organic conductors [1]. The well known material, TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane), which is the first generation of organic conductors, undergoes a transition into a charge-density-wave (CDW) insulator from a metallic state around 53 K. The second generation, TMTSF (tetramethyltetraselenafulvalene), compounds also show a spin-density-wave (SDW) transition around 10 K. Although the type of insulators is different in these epoch-making compounds, the mechanism of the transition has a common nature; that is, nesting of an open Fermi surface in one-dimensional electronic systems. The third generation, BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene], compounds are novel in that many salts have quasi-two-dimensional nature in the electronic state [2], where the Fermi surface is closed and is against nesting. Thus, the metallic state in many BEDT-TTF salts is kept stabilized down to lower temperatures, being free from the M-I transitions encountered in quasi-one-dimensional systems. Representative of them is the κ-phase family of BEDT-TTF compounds, which include superconductors, κ-(BEDT-TTF)$_2X$ [X = Cu(NCS)$_2$ [3] and Cu[N(CN)$_2$]Br [4]], with transition temperatures in excess of 10 K. In spite of structural similarity, however, the salt with X = Cu[N(CN)$_2$]Cl is an insulator [5]. Considering the two-dimensionality of the electronic state in the κ-phase family, one cannot take for granted the fact that the same scenario as in the above one-dimensional conductors will work for the M-I transition in this case. There is a speculation on the origin of the insulating state based on lattice disorder due to conformational disorder of the ethylene groups of BEDT-TTF [6]. Characterization of the insulating phase is important for an understanding of the origin of the M-I transition in the κ-phase family in terms of two-dimensional systems of correlated electrons.

In the present work, the magnetism of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl at ambient pressure has been investigated by NMR for the first time, along with magnetization measurements. This letter reports on unambiguous evidence for antiferromagnetic ordering at 27 K and spin canting below 23 K. A spin structure different from conventional SDW is also uncovered.

Single crystals of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl were grown by the conventional electrochemical method. The ^{1}H NMR and magnetization measurements presented here were performed for an identical crystal, the size of which is 1.8 × 1.4 × 1.2 mm^3. The ^{1}H NMR spectra and the nuclear spin-lattice relaxation rate were measured in a temperature range between 2 and 300 K at a magnetic field of 37 kOe. The spectra were obtained by the fast Fourier transformation (FFT) of the quadrature-detected echo signal. Pulse sequences of $(\pi/2)_X$-$(\pi/2)_Y$ (so-called solid echo) and $(\pi/2)_X$-$(\pi)_X$ were used above and below a magnetic transition, respectively, where X and Y stand for axes in the rotational frame. The relaxation curves were obtained from the recovery of the echo intensity following saturation comb pulses. The magnetization measurements were made with a SQUID magnetometer.

The ^{1}H nuclear spin-lattice relaxation rate divided by temperature $(T_lT)^{-1}$ is shown in Fig. 1. A sharp increase above 200 K and a peak formation around 280 K is not of electronic origin but a motional contribution due to thermally activated vibration of ethylene groups located at the edges of BEDT-TTF molecules. Since the motional contribution dies away with an exponential function of temperature, the behavior of $(T_lT)^{-1}$ below 160 K is an electronic contribution. From the Bloembergen-Purcell-Pound analysis of motional contribution in T_l^{-1}, which is deduced from a subtraction of the electronic contribution extrapolated from the data in a lower temperature region below 160 K, an activation energy of the vibration is estimated at 2600 ± 100 K.

Below 160 K, $(T_lT)^{-1}$ exhibits a moderate increase, which becomes steeper at lower temperatures. It then shows a sharp peak in a divergent manner at 26–27 K. This is an indication of magnetic transition,

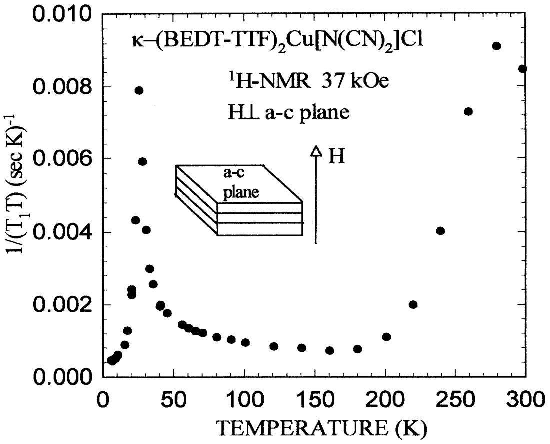

FIG. 1. $(T_l T)^{-1}$ of a single crystal as a function of temperature. A field of 37 kOe was applied perpendicular to the conducting *a-c* plane.

which is confirmed below to be antiferromagnetic. The temperature dependence of $(T_l T)^{-1}$ above the transition reflects antiferromagnetic spin fluctuations. The values of $(T_l T)^{-1}$ is, for example, 0.001 $\mathrm{sec}^{-1}\mathrm{K}^{-1}$ at 100 K. It is mentioned that similar values are obtained even for the superconducting salts, κ-(BEDT-TTF)$_2X$ [X = Cu(NCS)$_2$ [7] and Cu[N(CN)$_2$]Br [8]], which do not show magnetic order. This is consistent with ^{13}C NMR results, which show a sign of antiferromagnetic fluctuation for these superconductors at higher temperatures [9].

Figure 2 displays the evolution of ^{1}H NMR line shape as a function of temperature. A magnetic field of 3.7 T was applied perpendicular to the conducting layer. The line shape does not change when moved from 160 down to 30 K. The width in this temperature range is explained reasonably by the nuclear dipole interaction between the protons in the ethylene groups. Below 27 K, however, the line shape starts to split into three lines. The splitting becomes larger as the temperature is lowered. This indicates a generation of an inhomogeneous local field at the nuclear site and gives unambiguous evidence for antiferromagnetic transition. At the present state, site assignment of the split lines is not attainable because of the complexity coming from more than eight proton sites with magnetic inequivalence, the nonstacking arrangement of molecules, and the uncertainty of in-plane orientation of flopped spins (see below). However, one can extract the two consequences on the ordered state from the observed features of the line splitting.

One consequence is commensurability of the magnetic structure with lattice. When the antiferromagnetic order is incommensurate, distribution of the local field at nuclear sites becomes continuous, giving a broadening of the NMR line. However, when it is commensurate, discrete distribution of the local field leads to a splitting into a finite number of lines. The results shown in Fig. 2 give evidence for the commensurate nature in the present case.

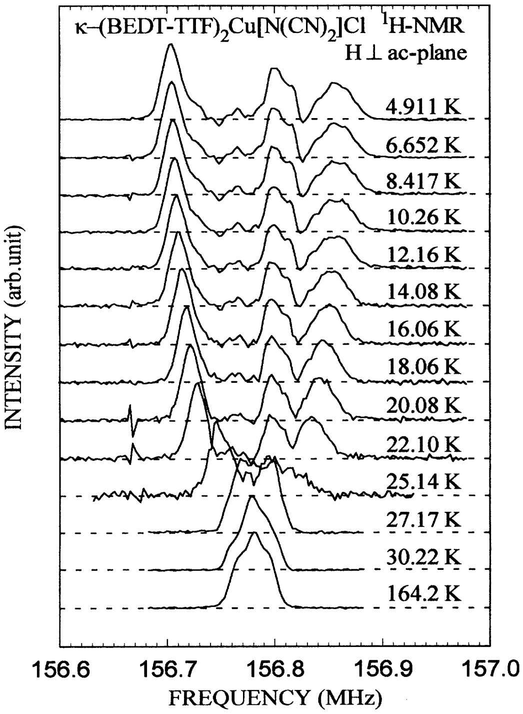

FIG. 2. NMR spectra of a single crystal in a field perpendicular to the conducting *a-c* plane at different temperatures.

The other is the moment of the antiferromagnetic order. A splitting width from the center is ±80 kHz, which corresponds to the generation of a local field of ±20 G at the ^{1}H sites. In the present value and direction of the magnetic field, the ordered spins flop in a direction perpendicular to the applied field as is evidenced by the magnetization measurements described below. Since the line splitting reflects the local field component parallel to the external field, the isotropic term, possibly due to Fermi contact or core polarization of the 1*s* orbital, should make no contribution to the splitting. Therefore, the local field that we should consider is the dipole field from the electron spin at other sites. Using the highest occupied molecular orbital (HOMO) coefficients of an extended Huckel calculation [10] for spin densities at other atomic sites in the BEDT-TTF molecule, one can calculate a parallel component of the local field at each ^{1}H site for an arbitrary direction of one electron spin per molecule. Based on this calculation and the experimental value of 20 G, the moment of the antiferromagnetic order is estimated at $(0.4-1.0)\mu_B$/dimer. The value of $0.4\mu_B$/dimer, which is a lower limit set by arbitrary choice of spin direction in the conducting layer, is likely to lift in reality.

These features of the ordered state are in contrast to the conventional SDW in (TMTSF)$_2$PF$_6$. There was an argument on whether nesting of the open Fermi surface or electron-electron correlation is dominant as a driving force of the SDW transition [11]. The incommensurate structure found by ^{1}H NMR analysis of (TMTSF)$_2$PF$_6$

favored the former picture of the SDW transition [12]. The commensurate nature observed here seems to support the latter mechanism for the Cu[N(CN)$_2$]Cl salt. The two-dimensional structure in κ-type compounds makes nesting of the Fermi surface less favorable; a pair of open Fermi surfaces predicted in the band calculation has a form unsuitable for nesting. Temperature dependence of resistivity implies a finite energy gap in the charge degree of freedom, also making the Fermi surface less important for magnetic transition. In addition, the moment of the ordered state in the present salt is far larger than the value of $0.08\mu_B$/molecule in (TNTSF)$_2$PF$_6$ [12], implying that ordering of local spins, rather than condensation of the spin density wave, is an appropriate picture of the magnetic order in our salt. These arguments again support that the magnetic ordering in our salt is driven mainly by electron-electron correlation, rather than nesting.

In order to inquire further into the spin structure, magnetization measurements were performed as functions of temperature and field. The first report of magnetization was by Welp *et al.* [13], who pointed out an antiferromagnetic transition around 45 K and a weak ferromagnetic behavior below 22 K. As was seen in the above NMR results, their former conclusion is controversial. Moreover, our results of magnetization measurements show distinguished anisotropy, different from their results, and give additional information on the spin structure deduced from the NMR results as follows: Figure 3 displays temperature dependence of the susceptibility of a single crystal at different magnitudes and configurations of the external field. The susceptibility above the transition temperature (~27 K) has a weakly positive temperature dependence and is similar to those of the κ-type superconductors, the Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br salts, both in magnitude and in temperature dependence, except for the steeper decrease below ~50 K in the present salt. There are two types of antiferromagnetic ordering in layered materials; one is intralayer antiferromagnetic order and the other is intralayer ferromagnetic order with interlayer antiferromagnetic coupling. If the latter were the case, the susceptibility would behave in a Curie-Weiss manner, because the susceptibility above the transition is governed by the strongest coupling, that is, intralayer coupling. The present results indicate the former type of ordering in the Cu[N(CN)$_2$]Cl salt.

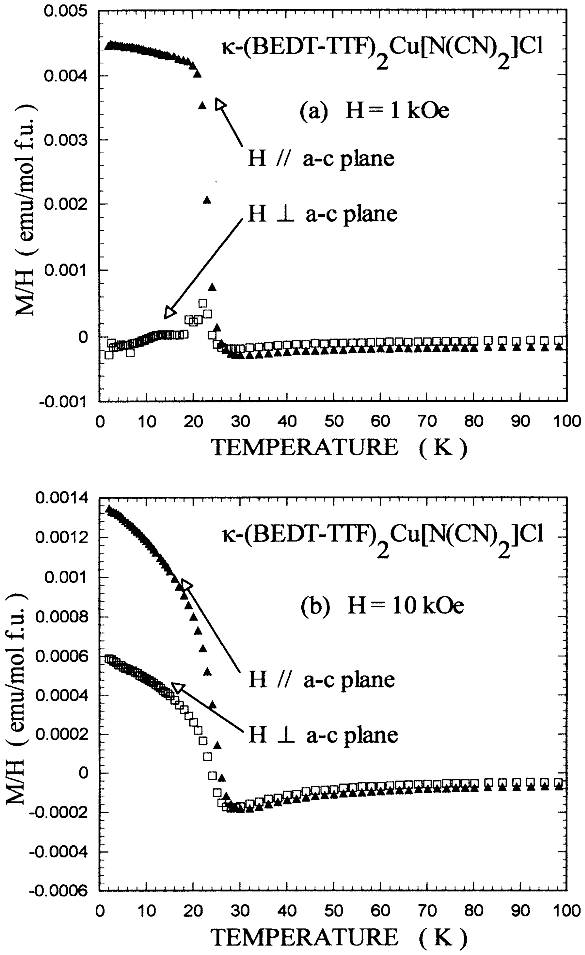

FIG. 3. Magnetic susceptibility of a single crystal at magnetic fields of (a) 1 kOe and (b) 10 kOe.

At a field of 1 kOe, the susceptibility shows a prominent anisotropy below ~25 K, as is seen in Fig. 3(a). The susceptibility is enhanced at a field parallel to the layers, while it is suppressed at a perpendicular field. This fact suggests that the weak ferromagnetic moment is oriented parallel to the conducting layers. Application of a field of 10 kOe induces enhancement of the susceptibility that is also in the perpendicular geometry, as shown in Fig. 3(b), but significant anisotropy still remains. Figure 4 shows magnetization in different orientations of the magnetic field against the crystal. In the field parallel to the layers [Fig. 4(a)], the field dependence of magnetization is linear up to 27 K, where the antiferromagnetic transition occurs. At lower temperatures, magnetization becomes nonlinear with enhancement of the magnitude. Then, below 23 K, hysteresis appears at low field as is seen in the inset of the figure. Since we know from the NMR results that the ordered state is antiferromagnetic with the localized nature of spins, it is reasonable to conclude that the origin of the weak ferromagnetic moment is the spontaneous canting of the ordered spins. Considering that the canting is parallel to the conducting layers, the easy axis of the ordered spin is found to be perpendicular to the layers. This was confirmed by the magnetization measurements in a perpendicular field. As shown in Fig. 4(b), there was no observation of anomalous behavior at low fields down to the lowest temperature available, corresponding to the absence of enhancement in susceptibility in Fig. 3(a). At a certain field depending on temperature below 23 K, however, magnetization exhibits an abrupt jump. This is indicative of a spin flop and again supports the fact that the easy axis is parallel to the field, namely, perpendicular to the layer. Even above 23 K, one can see enhancement and nonlinearity of the magnetization without spontaneous

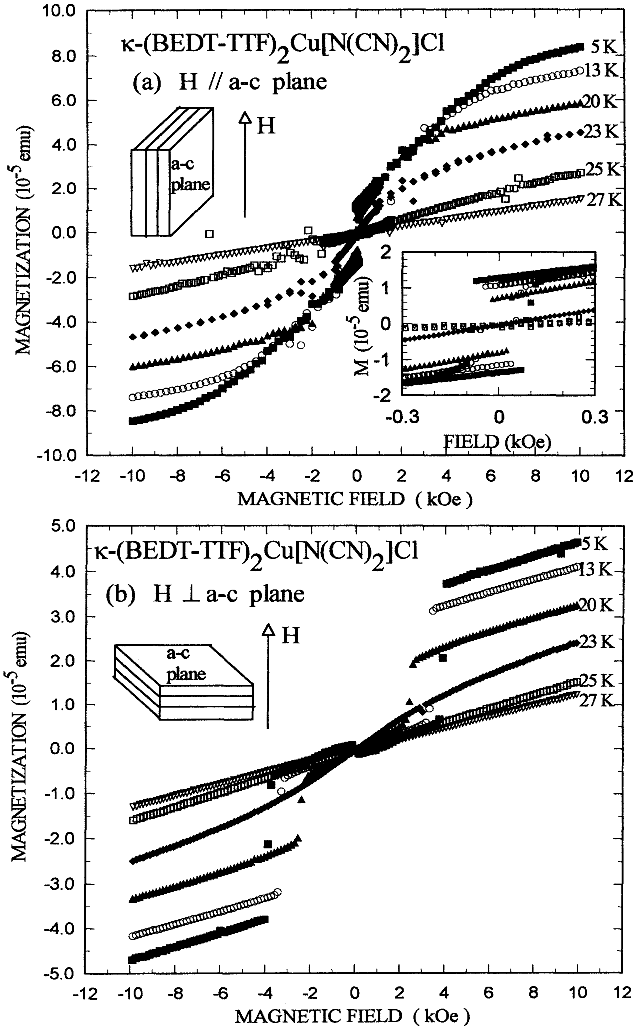

FIG. 4. Magnetization of a single crystal at different temperatures under the field (a) parallel and (b) perpendicular to the conducting *a*-*c* plane. Hysteretic behavior at low fields is expanded in the inset.

canting in both directions, up to 27 K. This is considered as field-induced canting or as ferromagnetic fluctuations as a precursor of spontaneous canting.

From these results, we can summarize the profile of the magnetic transition and structure in the CU[N(CN)$_2$]Cl salt as follows: Below 26–27 K, the system undergoes an antiferromagnetic transition and starts to show weak ferromagnetism due to canting of spins. The spontaneous canting at low fields occurs in a direction parallel to the conducting layers below 23 K. Judging from the magnitude of the ferromagnetic component, the canting is very small and the spins are nearly antiparallel with an easy axis perpendicular to the layers. This is the first characterization of the magnetic order in the BEDT-TTF compounds.

The present study uncovered the magnetic properties in the insulating phase of the κ-type compounds. Most important among them, when attempting to get a comprehensive understanding of the metallic (superconducting) and insulating states in the κ-type compounds, is evidence for strong electron-electron correlation instead of nesting as an origin of the magnetic order. The Cu[N(CN)$_2$]Cl salt is an insulator closely situated in the metallic or superconducting states, because application of pressure leads this insulator to a 13 K superconductor [14]. Taking into account the similar ^{1}H NMR relaxation rate in the paramagnetic state for the three salts and the consequences of our previous ^{13}C NMR studies for the superconducting salts [9], we consider that the metallic (superconducting) phases are also strongly correlated electronic systems. It should be noted that the band-filling is half; the dispersions in the bondinglike and antibondinglike bands are well separated due to the strongly dimeric structure [15], resulting in half-filling of the holes in the upper band. Therefore, it is reasonable to consider that the metal-insulator transition in the κ-type compounds is driven by electron correlation; that is, a Mott transition, rather than disorder-induced localization [6]. The M-I transition in the κ-type quasi-two-dimensional electronic systems has different aspects from that in the conventional quasi-one-dimensional systems.

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[1] D. Jerome and H. J. Schulz, Adv. Phys. **31**, 299 (1982).
[2] J. M. Williams *et al.*, Science **252**, 1510 (1991).
[3] H. Urayama *et al.*, Chem. Lett. **1988**, 55 (1988).
[4] A. M. Kini *et al.*, Inorg. Chem. **29**, 2555 (1990).
[5] J. M. Williams *et al.*, Inorg. Chem. **29**, 3272 (1990).
[6] H. Posselt *et al.*, Phys. Rev. B **49**, 15 849 (1994); Solid State Commun. **92**, 613 (1994).
[7] T. Takahashi *et al.*, Synth. Met. **27**, 319 (1988); A. V. Skripov and A. P. Stepanov, Physica (Amsterdam) **197C**, 89 (1992).
[8] S. M. De Soto *et al.*, Phys. Rev. Lett. **70**, 2956 (1993); K. Kanoda *et al.*, Physica (Amsterdam) **185-189C**, 2667 (1991).
[9] A. Kawamoto, K. Miyagawa, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **74**, 3455 (1995).
[10] T. Mori (private communications).
[11] J. B. Torrance, J. Phys. (Paris) Colloq. **C3**, 799 (1983).
[12] T. Takahashi, Y. Maniwa, H. Kawamura, and G. Saito, J. Phys. Soc. Jpn. **55**, 1364 (1986); J. M. Delrieu *et al.*, J. Phys. (Paris) **47**, 839 (1986).
[13] U. Welp *et al.*, Phys. Rev. Lett. **69**, 840 (1992).
[14] J. E. Schirber *et al.*, Phys. Rev. B **44**, 4666 (1991).
[15] K. Oshima *et al.*, Phys. Rev. B **38**, 938 (1988).