Antiferromagnetic resonance of the organic compound κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br with deuterated BEDT-TTF

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In the nonmetallic state of the organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br synthesized with deuterated BEDT-TTF molecule, an angle-dependent electron spin resonance signal below 6–8 K was found. This is interpreted in terms of an antiferromagnetic resonance. The signal was found only when the sample was rapidly cooled, corresponding to the characteristics in that the present salt stays close to the boundary of the metal-nonmetal transition.

The κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X (X=Br, Cl) family of organic compounds [where BEDT-TTF is bis(ethylene-dithio)tetrathiafulvalene] is attracting attention due to the metal-nonmetal transition depending on X. The X=Br salt (Br salt) shows metallic behavior below 80 K exhibiting the superconductivity transition below T_C=11.6 K, while X=Cl salt (Cl salt) shows nonmetallic behavior at ambient pressure. Under a pressure above 30 MPa, the Cl salt becomes metallic and the superconductivity state below T_C=12.5 K appears. In spite of the difference in the electronic state, the two salts are isostructural and belong to the orthorhombic *Pnma* space group.[1] The BEDT-TTF molecules are dimerized and packed into a checkered pattern to form conducting layers (referred to as κ-type structure). The counter anions are polymerized to form insulating layers that separate the conducting layers. The layer stacking direction is assigned as the b axis, and the anion polymer chain direction as the a axis. The c axis lies on the conducting layer perpendicularly to the a axis.

In the nonmetallic state of the Cl salt, antiferromagnetic interaction and relevant fluctuation phenomena have been recognized by the measurements of the NMR line shape and relaxation rate.[2] The relaxation rate $(T_1 T)^{-1}$ increases anomalously with decrease of temperature from room temperature until it diverges near 30 K. The NMR line shape changes so as to represent a long-ranged antiferromagnetic ordering.[2] The easy axis of the antiferromagnetic order has been controversial. Welp *et al.* claimed that the easy axis lies in the conducting a-c plane for the Cl salt, based on the anisotropy of the static magnetic susceptibility found below 45 K,[3] although later reports did not reproduce their findings. While, the spin-flop-like transition was observed for the Cl salt which implied that the easy axis was directed along the b axis, which is out-of-plane direction.[2,4]

Incidentally, Kubota *et al.* reported a novel electron spin resonance (ESR) line arising below 17 K other than the para-magnetic resonance line for the aligned single crystal of the Cl salt.[4] The new line was dependent on temperature and the angle of the magnetic field with respect to the crystallographic axis. Subsequently, the dependence on the micro-wave frequency was measured in the submillimeter wave region indicating that the new resonant line represents antiferromagnetic resonance (AFMR).[5] However, the angle dependence of the resonance field has not been analyzed properly based on the standard AFMR treatment. It is tempting to search for the AFMR in the sister Br salt, implying the antiferromagnetic interaction similar to the Cl salt above 50 K although it is metallic at low temperature.[6] While, by using deuterated BEDT-TTF molecule for the synthesis, the Br salt (hereafter abbreviated as d-Br salt) shows nonmetallic behavior like the Cl salt below 50 K.[7,8] The NMR measurement suggests that the d-Br salt also exhibits antiferromagnetic interaction resulting in a long-ranged antiferromagnetic ordering below 14–15 K.[9] The antiferromagnetism of the d-Br salt is particularly intriguing since the salt stays on the border line of the metal-nonmetal transition in the ambient pressure region.[8–10] In this paper we report the angle-dependent ESR signal, which can be ascribed to the AFMR in the d-Br salt when the sample was cooled rapidly. A brief description of the data has been presented previously.[11]

The single crystals were grown using an electrochemical method described elsewhere.[7] Two crystals with shiny black rhombus shape of size 1 mm×1 mm×0.2 mm were examined giving essentially the same result. The measurements were carried out using a Bruker ESP300E X-band ESR spectrometer equipped with an OXFORD 910 helium gas flow cryostat. The frequency of the microwave cavity was fixed to ~9.41 GHz and the microwave power level was 1 mW. A single crystal was set within a quartz tube of 3 mm inner diameter using a Teflon holder with a slot adjusted to the thickness of the sample. This enables the sample to be accommodated and aligned without any grease, which often gives rise to pressure effect onto the sample. The precision of the alignment of the sample with respect to the external magnetic field was 2°–3°. The cooling rate was controllable from 1 K/min to 150 K/min by adjusting a connection valve between the sample chamber and a helium reservoir. Prior to sample setting, a quartz tube and the sample holder were measured without sample to check that no contamination was present in the tube and the holder. The ESR signals were measured during heating after cooling the sample down to
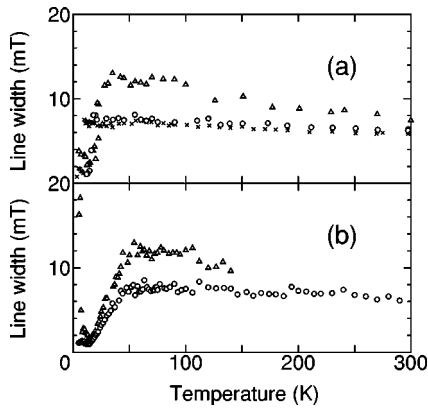
FIG. 1. The temperature dependence of the linewidth of the EPR line under the magnetic field along *a* (circle), *b* (cross), and *c* (triangle) crystallographic axes when the sample was cooled slowly (a) or rapidly (b).

the lowest temperature of 3 K. In the ESR measurement, an external dc magnetic field less than 1 T must be applied. Presence of such magnetic field does not alter the electronic state in the vicinity of the metal-nonmetal transition as evidenced by the recent specific heat measurements.[12] The magnetoresistance in the normal state is small and no effect is observed especially at temperature region at least below 20 K.[13,14]

The ordinary electron paramagnetic resonance (EPR) signal was observed in the whole measured temperature range from room temperature down to 3 K, at any cooling rate. The temperature dependence of the EPR linewidth in the case of the magnetic field applied along the *a*, *b*, and *c* axes are shown in Figs. 1(a) and 1(b), for rapid cooling ($\sim$100 K/min) (a) and slow cooling ($\sim$1 K/min) (b), respectively. The linewidth decreased below 60 K (rapid cooling case) or 40 K (slow cooling case), in qualitative agreement with the former report.[15] The cooling rate dependence is smaller than that of the resistivity, which shows huge effect below 80 K.[8] This finding, together with the different temperature dependence from that of the resistivity, eliminate the possibility of Elliott mechanism to explain the temperature dependence of the linewidth. The linewidth decrease should be interpreted as an appearance of the antiferromagnetic fluctuation like the case for the Cl salt.[16] In both rapid and slow cooling cases, sudden upturn of the linewidth was observed below 15 K, similar to the Cl salt found below 25 K.[4,16] At 15 K, the intensity of the EPR signal dropped sharply. The critical behavior was observed more sharply in the rapid-cooled case. The critical behavior of the linewidth and the intensity implies the change in local field distribution due to the appearance of a long-range antiferromagnetic order, in a similar way for the Bechgaard salts found at the spin density wave (SDW) transition.[17] However, in the present case, the intensity of the signal did not disappear down to 3 K, implying that not all of the spins are ordered. The magnitude of the remanent EPR signal at 3 K differed among each measurement, with no significant correlation to the cooling rate being found.

Below 6–8 K a new line appeared other than the EPR line, only when the sample was cooled rapidly with a cooling rate faster than 100 K/min. In Fig. 2, we show the temperature dependence of the resonance field in the case of the
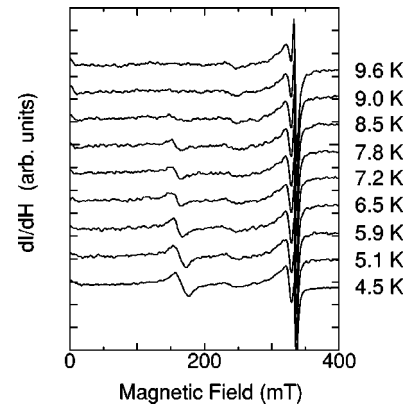

FIG. 2. Temperature dependence of the derivative intensity of the ESR signal. Signals at 0.336 T are the EPR signals. New signals appear below 8 K at 0.17 T. The vertical axis of the signals at each temperature are shifted for clarity.

magnetic field applied along the *c* axis. The new signal appeared well separated from the $g \sim 2$ EPR line appearing at $\mu_0 H_p = 0.336$ T. The new line cannot be ascribed to the paramagnetic spins. This signal did not appear when the sample was cooled down with a cooling rate slower than 100 K/min. The resonance field is almost temperature-independent below 6–8 K. The resonance field of the new line is dependent on the direction of the magnetic field, implying that the new line represents the AFMR. In Fig. 3(a), we show the angle dependence of the resonance field (defined as the field of zero crossing of the derivative intensity dI/dH) when the magnetic field H is rotated within the *a-b* plane of the sample. The angle represents the direction of the magnetic field with respect to the *a* axis. The signal intensity was small at 0° and showed maximum around $\pm 20°$ and diminished at $\sim \pm 30°$. The angle dependence of the resonance field when the *H* was rotated within *c-b* and *a-c* plane are shown in Figs. 3(b) and 3(c), respectively. In this case, the angle represents that of the magnetic field with respect to the *c* axis. The signal intensity was maximum at 0° and decreased gradually with the increase of the angle.
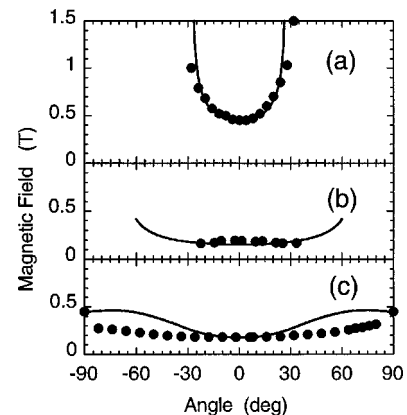

FIG. 3. Angle dependence of the AFMR signal under the magnetic field rotated within (a) *a-b*, (b) *c-b*, and (c) *a-c* planes at 4.2 K. The angle 0° corresponds to the *a*-axis, *c*-axis, and *c*-axis direction, respectively. The solid lines fit the standard theory assuming that *a*, *b*, and *c* axes are easy, hard, and intermediate axes, respectively.

We try to apply the standard AFMR theory[18] to the data shown in Figs. 3(a)–3(c). We assume that the easy, hard, and intermediate axes of the antiferromagnetic ordering lie perpendicularly with each other. When the magnetic field applied within the plane made of easy and hard axes of the ordering, the resonance field is explicitly written as,

$$H = \sqrt{\dfrac{1}{\dfrac{\cos\theta^2}{C_1 + H_p^2} - \dfrac{\sin\theta^2}{(C_2 - C_1) - H_p^2}}}. \qquad (1)$$

Here, the angle θ represents the direction of H with respect to the easy axis. The parameters C_1 and C_2 represents the anisotropy of the interaction energy. Similarly, if the magnetic field is applied within the plane made of intermediate and hard axes, the resonance field is explicitly written as,

$$H = \sqrt{\dfrac{1}{\dfrac{\cos\theta^2}{H_p^2 - C_1} + \dfrac{\sin\theta^2}{H_p^2 - C_2}}}, \qquad (2)$$

where angle θ represents the direction of H with respect to the intermediate axis. When the magnetic field is applied within the plane made of easy and intermediate axes, the resonance field cannot be written explicitly, but is obtained by solving numerically the equations written as,

$$(H_p)^4 - (H_p^2)\{H^2(\alpha^2\cos\psi^2 + 1) + C_2$$
$$+ C_1[\cos(\psi - \phi)^2 - 2\sin(\psi - \phi)]\}$$
$$+ H^4\alpha^2\cos\psi^2 - H^2\{C_1[\alpha\cos\psi^2\cos 2(\psi - \phi)$$
$$+ \alpha\sin\phi\cos\psi\sin(\psi - \phi) + \cos\phi\sin\psi\sin(\psi - \phi)]$$
$$+ C_2(\alpha\cos\psi^2 - \sin\psi^2)\}$$
$$+ C_1\cos 2(\psi - \phi)[C_2 - C_1\sin(\psi - \phi)] = 0,$$

$$\tan 2\psi = \dfrac{\sin 2\phi}{\cos 2\phi - H^2\alpha/C_2}, \qquad (3)$$

where ϕ is the direction of the magnetic field with respect to the easy axis. The angle ψ represents the direction of the spins at the resonance. The parameter α is written as $\alpha = 1 - \chi_\parallel/\chi_\perp$, where $\chi_\parallel$ and $\chi_\perp$ are static magnetic susceptibility along the easy and hard axis, respectively. The calculated result does not depend much on the value of α if it is larger than 0.9, which is a good assumption at temperatures well below the Néel temperature.

By assuming that the a axis is the easy axis, the b axis is the hard axis of antiferromagnetic ordering, the angle dependence is well fitted to Eq. (1) as shown by the solid line in Fig. 3(a) with parameters of $\sqrt{C_1} = 0.30$ T and $\sqrt{C_2} = 0.51$ T. For the data shown in Fig. 3(b), Eq. (2) can be applied, although it does not fit near the 0° region. The intermediate axis may not be exactly parallel to the c axis, but it is noteworthy that the angle dependence given by Eq. (2) is sensitive to small misalignment near the c axis. With regard to the data displayed in Fig. 3(c), it was attempted to apply Eq. (3) by setting α to be 0.9, because the measured temperature of 4.2 K was considered to be well below the Néel temperature

of 14–15 K. However, the equation failed to reproduce the rapid change of the resonance field near the a axis direction ($\pm 90°$) with any set of parameters. The discrepancy, which was too large to be ascribed to misorientation, could originate from some additional magnetic interaction between antiferromagnetically ordered spins within the a-c plane, such as the Dzyaloshinskii-Moriya (DM) interaction which is considered to be responsible for the weak ferromagnetism observed in this material.[9] The DM interaction is absent in the orthorhombic space group system with inversion symmetry, but it is possible that the inversion symmetry is broken at low temperature in the present material, like the case for the Cl salt.[19] If the DM interaction exists, the angle dependence of the resonant field is notably modified as is known in the case of α-Fe$_2$O$_3$,[20] Cu(HCOO)$_2 \cdot 4$H$_2$O,[21] etc. Although the angle dependence of the signal with respect to the magnetic field direction in the c-b and a-c planes shows a quantitative discrepancy, the spin structure with the easy, hard, and intermediate axes corresponding to the a, b, c, axes is the best combination in order to explain the angle dependence of the measured resonance signal in terms of the standard AFMR theory.

The antiferromagnetic order with easy axis along the a axis is consistent to the models for the origin of the antiferromagnetic interaction of the family of the salts. One of the models is following. The dimerization of BEDT-TTF molecules in the conducting plane makes the conduction band half-filled in the case of κ-type structure. The half-filled band gives rise to the Mott insulating phase in the case that the electron correlation is strong enough. Kino and Fukuyama calculated the ground state of the κ-type BEDT-TTF salt within the Hartree-Fock approximation and found that the antiferromagnetic ordered state within the conducting plane in case the intradimer interaction energy is larger than 0.26 eV.[22] The spin structure with the easy axis along the a axis agrees with their prediction. The other model for the origin of the antiferromagnetic interaction in the present system is that the nesting instability of the planar parts of the Fermi surface induces the SDW state.[6,23] In the case of TMTTF salts, (TMTTF)$_2$SCN, (TMTTF)$_2$SbF$_6$, nesting instability of the planar Fermi surface induces an SDW state with antiferromagnetic order below 8.8 K and 6 K, respectively.[24] The easy axis found by AFMR measurements lies along the b' axis, which corresponds to the direction of the open Fermi surface causing the SDW state.[24] In the d-Br salt, the open Fermi surface with possible nesting instability lies along the a axis. It is plausible that the easy axis of the antiferromagnetic order results in the same a axis like the TMTTF salts. On the other hand, it has been considered that the easy axis lies in the b axis for the sister material Cl salt.[2,4] For the Cl salt, Ohta et al. recently found that the intensity of the AFMR signal was strongly enhanced when the magnetic field is applied in the direction with angle 35° from the a-c plane.[25] The peculiar angle dependence suggests that the spin structure of the antiferromagnetic state of the Cl salt may be more complicated than supposed formerly[2,3] and may depend on the experimental condition, such as the cooling rate. The difference in the antiferromagnetic order between the Br and Cl salt may be ascribed to the difference in the dynamics of the terminal ethylene motion,[14] which induces the super-

structure in the case of the Br salt.[26]

The AFMR signals appeared dependent on the cooling rate. It is explained in relation to the electronic state close to the boundary of the metal-nonmetal transition in the present material. Rapid cooling tends to push the electronic state into the nonmetallic phase.[8,14] At ambient pressure, a small fraction of two-dimensional superconductivity phase appears when the sample is cooled slowly at a rate of 0.7 K/min.[27] The presence of the superconductivity can violate the magnetic field homogeneity needed for the clear electron spin resonance. While, in the quenched condition the nonmetallic phase prevails in the crystal and the superconductivity is suppressed and the electronic state becomes more homogeneous.

The presence of the reentrant superconductivity transition of the d-Br salt[27] explains the temperature-independence of the resonance field, in contrast to the case for the Cl salt.[4] The critical temperature of 6–8 K agrees with the lower critical temperature for the reentrant superconductivity transition below T_{C2}, found by the resistivity measurement under a pressure of 2–6 MPa.[11,27] The reentrant transition may occur at ambient pressure when the sample is cooled rapidly, since the electronic state is sensitive to the cooling condition.[8,14] Since the AFMR is suppressed if the superconductivity fraction is present, the signal appears only below T_{C2}, where the superconductivity is suppressed. The antiferromagnetic order amplitude is well developed when the AFMR appears at 6–8 K, which is much lower than the Néel temperature, so that the resonance field is temperature-independent. On the other hand, in the case of the Cl salt the reentrant superconductivity transition does not occur at ambient pressure. In this case, the antiferromagnetic signal is observed in all temperature ranges below 17 K and the resonance field is temperature-dependent in accordance with the growth of the antiferromagnetic order amplitude.

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