

Hall effect and magnetic viscosity phenomena in κ -(BEDT-TTF)₂Cu[N(CN)₂]X (X = Cl, Br)

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(Received 11 October 1996; revised manuscript received 23 December 1996)

Hall effect studies have been performed in the compounds κ -(BEDT-TTF)₂Cu[N(CN)₂]X, where X = Cl and Br and BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene, in the temperature range 100 to 10 K. Hall constant has been found to be temperature independent in the Br salt down to 55 K and equal to $+2 \times 10^{-8}$ m³/C. In the Cl salt the Hall constant is equal to $+1.4 \times 10^{-7}$ m³/C at 100 K and increases on cooling down to 70 K almost parallel to the resistance increase. Below ~ 70 and ~ 55 K in the Cl and Br, respectively, the magnetic field change has been found to produce long-term sample resistance relaxation. The relaxation phenomena change dramatically with temperature, reaching the maximum above magnetic ordering temperature in the Cl salt at 30 K, and then sharply dropping in magnitude in the magnetically ordered state. A similar relaxation is observed in the Br salt. These effects are considered to be due to the magnetic domain structure formation in the antiferromagnetically ordered state. Essential changes of the domain wall dynamics, appearing in the Br salt at 25 K, evidence the presence of the second magnetic transition in the Br salt, quite similar to the Cl salt. By studying the anisotropy of the relaxation phenomena within highly conducting plane in the Cl compound it is shown that domain walls are lying parallel to the *a* direction. A possible origin of the magnetic order in the salts is discussed. [S0163-1829(97)03918-0]

I. INTRODUCTION

κ phases of the bis(ethylenedithio)tetrathiafulvalene (abbreviated BEDT-TTF hereafter) with pseudohalide anions of general formula (BEDT-TTF)₂Cu[N(CN)₂]X, X = Cl and Br (the compounds are denoted as Cl and Br, respectively, in the following) are the subject of intensive studies in recent years. At room temperature the salts possess an orthorhombic crystal lattice, with the characteristic feature of a sequence of alternating layers of BEDT-TTF molecules and polymeric anions. BEDT-TTF molecules within the layer are arranged in the nearly perpendicular dimers. This crystal structure of the materials, according to the band structure calculations,¹ has to lead to essentially the same metallic two-dimensional electronic structure for both salts. The calculated band structure has been experimentally confirmed at high pressures for the both Br² and Cl.^{3,4} Nevertheless, at ambient pressure the Br salt is a superconductor, while the Cl one is an insulator at low temperatures. Discovery of weak ferromagnetism (WF) in the Cl salt at 22 K⁵ at ambient pressure, resulting in the coexistence of magnetism and superconductivity in a definite pressure range and reentrant resistance behavior,^{6,7} made it attractive to relate the lack of superconductivity in the Cl salt with the formation of the spin density wave (SDW).⁸ Very recently, however, the role of the SDW in the formation of the magnetically ordered ground state has been questioned by NMR study results in the Cl salt^{9,10} suggesting the formation of the antiferromagnetically (AF) ordered state due to the presence of strong Mott-Hubbard-type correlations.

Since Hall effect studies could determine the carrier density and its temperature variation and thus could elucidate the properties of the respective phases, we carried out Hall effect measurements in the salts. In the process of the work it has been found that the magnetic order is present in the salts at very high temperatures. Comparing the results of our relaxation and Hall effect studies with those of the thermopower, thermal expansion, NMR, and electron spin resonance (ESR) investigations in the salts, we have come to the conclusion that the AF transitions with magnetic domains formation proceed in the salts at temperatures as high as at least 70 and 55 K in Cl and Br salts, respectively. It is shown, that the magnetic transition at nearly 25 K, known well for the Cl salt,⁵ is present in the Br salt as well.

II. EXPERIMENT

Single crystals of the compounds were grown by electrochemical oxidation of BEDT-TTF molecules.¹¹ Rhombic shaped single crystals were selected for Hall effect studies. Typical sample dimensions were $1.5 \times 2 \times 0.1$ mm³. The longer and shorter rhombus diagonals corresponded to the crystallographic *a*- and *c*-axes, respectively.

Electrical contacts to the sample surface were made with Dotite carbon paint. Contact resistance was in the range of 20 to 50 Ω . The measurements were performed at the dc, with current flow direction reversal. No electrical polarization phenomena were observed. From the time of the com-

plete voltage relaxation during current direction reversal, the setup time constant was found as 3 sec. This resulted in a 13 sec measuring time per point, as an average of the measurements during 5 sec for each current direction was used. A carbon glass resistor was used for the temperature measurements in the magnetic field. As all the measurements were performed without field sweep, the temperature was stabilized with an accuracy of better than 0.01 K, resulting in reproducible sample resistance values within at least 10^{-4} or better, depending on temperature.

The Hall voltage was measured with the usual five probe technique. For both Cl and Br samples the current flow direction corresponded commonly to the a axis, and the Hall voltage was measured nearly along the c axis. For the Cl samples we have succeeded also in arranging the sample in such a way that current was flowing along the short sample diagonal (c axis) and the Hall voltage was measured along the a axis. (We refer to these configurations hereafter according to the current flow direction as the a - and c -axis cases, respectively.) As the shape of the samples was far from that necessary to obtain a homogeneous current distribution, an essential admixture of the signal from the transverse direction was always present in these measurements. In the process of the Hall effect measurements magnetic field direction reversal was performed by rotating the sample in the magnetic field of the superconducting solenoid of 10 T, if not specified specially. The Hall voltage V_H was obtained as averaged for two contact pairs voltage difference for the positive (n^+) and negative (n^-) directions of the magnetic field. The Hall constant was defined as $R_H = V_H d / I B$, where d is the sample thickness, I is the electrical current through the sample, and B is the magnetic-field induction. However, commonly the Hall resistance was presented as $R_{xy} = V_H / I$. In the process of sample rotation, the magnetic field was normal to the current flow direction and was inclined in the b - c plane in the case of the a -axis, and a - b plane in that of the c -axis. Typically 180° rotation lasted for 10 sec and resulted in the loss of 1 experimental point. This technique gave rather reproducible results at high temperatures, coinciding well with those obtained by the field sweep procedure.

Relaxation was studied by measuring the time dependence of the sample resistance. The first point after rotation completed was defined as $R(t=0)$. The shape of the transient was analyzed by extracting the steady state resistance value R_{rlx} . Two values were obtained and presented—resistance change during steady state establishments after the rotation $R(t, T) - R_{rlx}(T)$ and normalized resistance change $[R(t, T) - R_{rlx}(T)] / R_{rlx}(T)$.

III. EXPERIMENTAL RESULTS

A. Resistance and Hall effect

Figure 1 shows Arrhenius plots of the resistance R_{xx} and Hall effect resistance R_{xy} for the two in-plane directions of the Cl samples below 100 K. Resistance increases on cooling from room temperature down to 70 K with a nearly constant activation temperature of 70 to 80 K. On further cooling the slope increases, reaching a maximum value of 200 to 250 K at about 35 K, and then tending to zero.

The Hall effect signal is positive for both in plane directions and its value at 100 K for the better defined a -axis is

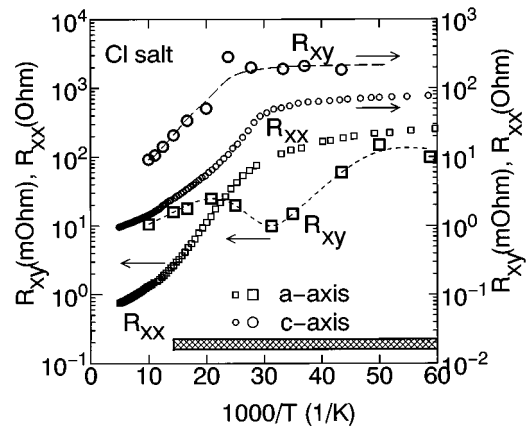


FIG. 1. Temperature dependences of the resistance and stationary and quasistationary Hall effects in the Cl salt for electrical current flowing along the a and c axes. The quasistationary Hall effect temperature interval is marked. Note the right scale shift with respect to the left one. The lines are guides for the eye.

+ $1.4 \times 10^{-7} \text{ m}^3/\text{C}$. The temperature dependence of R_{xy} follows in general that of the resistance in both directions in Cl salt until 70 K.¹² A transient behavior was observed in the resistance below 70 K, when the sample was rotated in the magnetic field, interfering strongly Hall effect signal. In this situation Hall signal becomes time dependent. Therefore, only the signal in the totally relaxed state was measured. We call this signal the quasistationary Hall effect (QSHE). The temperature region of this effect is marked by shadowing in the figures. In the Cl salt for the c -axis QSHE, R_{xy} in general follows R_{xx} , while for the a axis it shows a rather strong dip in the region of 30 K, and then increases again. Contrary to the thermopower results in the same salts,¹³ no sign change was observed neither in the stationary nor in the quasistationary Hall effect.

Temperature dependences of the resistance and Hall effect, both normal and quasistationary below 55 K for the Br salt are shown in Fig. 2. R_{xx} shows a broad peak centered at ~ 80 K, followed by a rapid resistance decrease with a slope

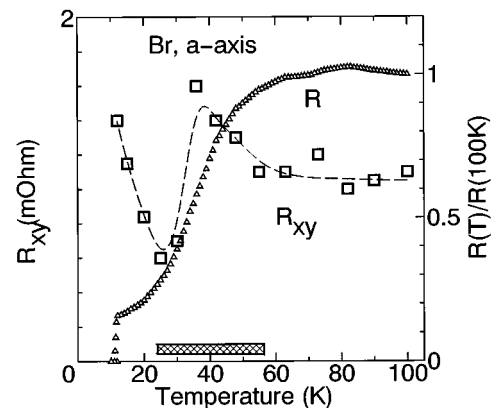


FIG. 2. Temperature dependence of the resistance in the zero magnetic field and stationary and quasistationary Hall effects in the Br salt for electrical current flowing along the a axis. The quasistationary Hall effect temperature interval is marked. The line is a guide for the eye.

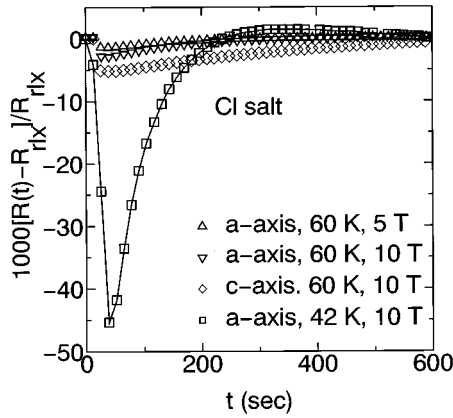


FIG. 3. Resistance transient curves for the Cl salt.

change at ~ 50 K and a superconducting transition without field. The Hall constant is positive and its value ($+2 \times 10^{-8} \text{ m}^3/\text{C}$ at 100 K) remains practically unchanged down to 55 K. On entering the QSHE region, marked with shadowing in Fig. 2, the Hall constant starts to increase, showing a rapid drop at 35 K and an increases on cooling below 25 K.

B. Magnetic relaxation phenomena

As already mentioned, on cooling below 70 and 55 K in Cl and Br salts, respectively, sample resistance shows long term relaxation. Some characteristic transient behaviors for the a - and c -axis cases of the Cl samples and their dependence of temperature and magnetic field are shown in Fig. 3. For the Br samples the curves are basically the same. It is very hard to state definitely the temperature where the relaxation phenomena start, since they appear as rather small resistance transients. Therefore the onset temperatures of 70 and 55 K may be considered as lower bound.

The characteristic features of the relaxation phenomena are summarized as follows.

(1) The relaxation is more evident in the Hall configuration, though its magnitude in the signal from potential probes can amount up to 50% of the Hall one.

(2) The relaxation phenomena are the same for both dc current directions.

(3) The appearance of the transient in the sample is accompanied commonly by the changes of the voltage distribution. Namely, upon cooling through temperatures of 70 and 55 K in the Cl and Br samples, the ratio of the voltages between Hall probe and two potential probes changes in an irregular way, evidencing current distribution change. Therefore we discuss hereafter the transient behavior only for R_{xx} , not R_{xy} .

(4) Voltage redistribution is observed without magnetic field as well.

(5) The relaxation appears irrespective of the field cycling procedure, both when the field is changed from the direction of n^+ to n^- through the field-in-plane (0) position, and from n^+ to 0 and then back to n^+ . In the case of the magnetic field change from either n^+ or n^- to 0, the magnitude of the transient is approximately a half of that for the full cycle, though more exact estimation was difficult due to a different magnetoresistance in two field orientations.

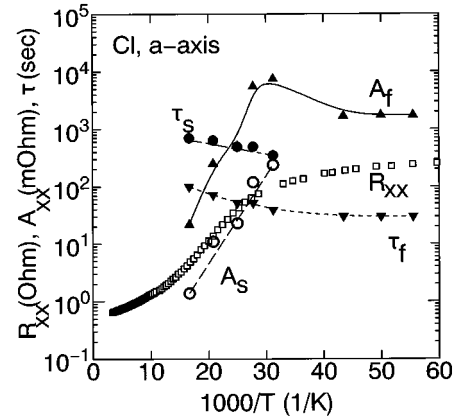


FIG. 4. The temperature dependences of the resistance transient parameters A_f, τ_f, A_s, τ_s in the Cl salt, for electrical current flowing along the a axis. The resistance temperature dependence is shown for reference. The lines are guides for the eye.

(6) There is an accumulation of the effect, that is, by performing the cycle quickly several times, a larger resistivity change has been found, though the relaxation from this heavily distorted state comes in a more complex way and does not follow exponential decay, typical for the phenomenon at high temperatures. After several cycling procedures the R_{xx} decrease was as large as 30% in the Cl salt at 36 K.

(7) There is an essential difference of the relaxation phenomena in the samples having metallic resistance temperature dependences and those with activation temperature dependence. For the Br salt, the resistance after the cycle first increases and then decreases during relaxation, while for the Cl salt it decreases just after field cycle and then increases to the steady state value, coming sometimes through the maximum.

The shape of the relaxation curve $\Delta R(t) = R(t) - R_{rlx}$ depends on temperature. At high temperatures, close to the transient appearance, the curves are well approximated by the exponential decay, both for the Cl (especially for the a -axis case) and the Br salts, and can be described by the formula $\Delta R(t) = A_f \exp(-t/\tau_f)$. However, deviations from the exponential decrease are seen upon cooling, and the shape of the curve cannot be described neither by the sum of these two exponents, nor by a sum of common and expanded exponent.¹⁴ In this case we approximated the initial decay with an exponent, subtracted this exponent from the signal, and presented the magnitude and characteristic decrease time of the residue. So the transient was presented as $\Delta R(t) = A_f \exp(-t/\tau_f) + A_s f(-t/\tau_s)$, and τ_s corresponds to the e -times decrease of the residue function $f(-t/\tau_s)$. The temperature dependences of the respective signals, namely, A_f and t_f of the exponential part and those (A_s and t_s) of the residue, are presented in Figs. 4–6 for the a -axis and c -axis cases in the Cl and the a -axis case in the Br salts. It is worth noting that the transient shape is principally different for the a - and c -axis cases in the Cl salt. For the a -axis case the magnitude of the slow component is essentially smaller than that for the fast, and it vanishes at temperatures below 30 K. For the c -axis case the magnitudes of the fast and slow components are nearly the same. As long as there exists

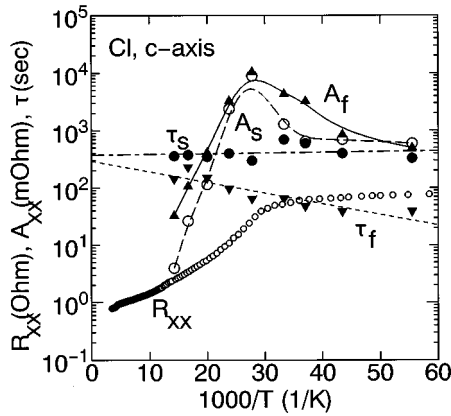


FIG. 5. The temperature dependences of the resistance transient parameters A_f, τ_f, A_s, τ_s in the Cl salt, for electrical current flowing along the c axis. The resistance temperature dependence is shown for reference. The lines are guides for the eye.

strong mixing for both directions, it can be, in principle, thought that the slow component is absent in the a -direction.

Magnetic field dependences of the transient parameters for the Br salt are depicted in Fig. 7. For the Cl salt the dependences are basically the same, and are shown only for the c -axis case (Fig. 8). Magnetoresistance is positive in all the salts and is not very large. The magnitude of the fast resistance transients increases nearly linearly with the magnetic field, while that for the slow transient is nearly proportional to the second power of the field. The relaxation time decreases slightly with the magnetic field. Quasistationary Hall resistance is nearly proportional to the field.

IV. DISCUSSION

A. The Hall effect and magnetic viscosity phenomena

The Hall effect data for the Cl salt, with R_{xy} going in parallel to R_{xx} , show the presence of the real gap in the compound's electronic spectrum. It is interesting, however, that the signs of the Hall effect and thermopower are different: below 70 K the thermopower is negative for both in-

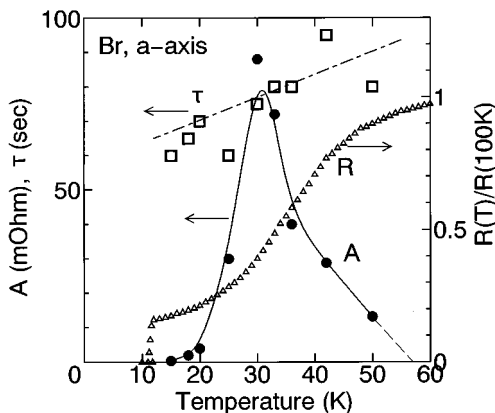


FIG. 6. Temperature dependences of the resistance transient parameters A and τ in the Br salt. The resistance temperature dependence is shown for reference. The lines are guides for the eye.

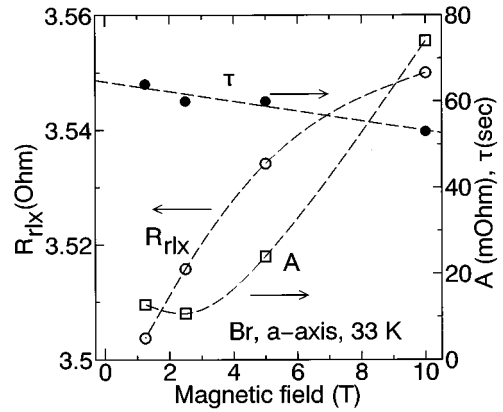


FIG. 7. Magnetic field dependences of the resistance transient parameters A and τ and R_{rlx} in the Br salt.

plane directions. Then the negative sign of the thermopower may be magnetic in origin, that explains well its large sensitivity to the magnetic field.¹⁵ It is worth noting, that the Hall constant value for the Br salt is temperature independent, with a rather large value, which may be evidence of a low hole density ($3 \times 10^{20} \text{ cm}^{-3}$) even in the metallic state. At temperatures below 25 K the behavior of the Hall constant resembles strongly that of α -(BEDT-TTE)₂MHg(SCN)₄ below the SDW phase transition.^{16,17}

It is evident that the relaxation of the resistance is due to the magnetic relaxation in the salts. Since the emergence of the relaxation is accompanied by an essential redistribution of the voltage along the sample lengths (3) and (4), it may be concluded that the sample becomes inhomogeneous even in the absence of magnetic field. Then the effect of the magnetic field is to change this inhomogeneity. This situation clearly evidences the formation of magnetic domains in the sample. The accumulation of the effect (6) and the lack of its dependence on the magnetic field cycle (5) allow us to state that essential sample resistance changes take place in the domain wall region, and there is some aftereffect of the excitation. Interrelation of the relaxation phenomena of the

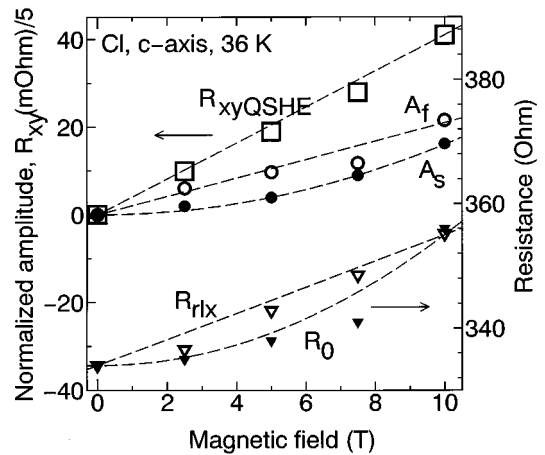


FIG. 8. Magnetic field dependences of the resistance transient amplitudes (A_f, A_s), resistance in the position when the magnetic field is lying in the highly conducting plane (R_0), R_{rlx} , and the quasistationary Hall resistance R_{xyQSHE} in the Cl salt's c axis.

type of the sample resistance temperature dependence (7) shows that some defects are formed in the domain wall region, resulting in a resistance decrease for insulating compounds and a resistance increase for metallic compounds.

It is commonly accepted that magnetic viscosity phenomena are due to some slow processes in the lattice. For the ferromagnetic compounds, these are known to be the diffusion of the atomic species and the nucleation of new phases in the boundary region, and for the ferrites recharging of the ions.¹⁸ If the first and third processes are unlikely to be the case in the compounds under consideration, nucleation of the new phases seems very plausible in view of the numerous evidences for the presence of the metastable phases in the salts, resulting in thermal history phenomena.^{19,20} The relaxation times also have rather common values for these slow processes. Evidently, however, that relaxation of the magnetization commonly does not follow an exponential curve. The presence of exponential decay in the resistance may be recognized then as a result of a small deviation of the resistance in the domain wall area compared to that of domain volume.

It should be noted, that magnetic hysteresis phenomena, evidencing formation of the magnetic domains, were observed earlier in some α -(BEDT-TTE)₂MHg(SCN)₄ salts in the magnetic field above nearly 8 T.^{21–24} The established appearance of the phase inhomogeneity in this case²¹ may correspond to the prediction of the theory for the inhomogeneous phase formation in the fields, close to the spin-flip transition.^{25,26} Observation of the magnetic viscosity phenomena with possible second phase formation in the compounds under study at essentially lower fields can then imply that the magnetic state is much less stable in the κ phases with respect to the α phases.

The pronounced anisotropy of the effect within the conducting plane is noteworthy. As is evident, the transient behavior is essentially different for the a and c directions in the Cl salt. Since the resistance change is related to defects formed in the vicinity of domain wall, it may be concluded that electrical current, when flowing in the c direction, has to cross defected areas much more frequently. This means that the domain walls run preferably along the a direction. Namely the anisotropy of the domain walls can be responsible for an essential QSHE voltage drop in the a -axis case, due to the formation of the current lines that do not reach the contacts.

B. Temperature dependence of magnetic viscosity phenomena

With regard to the temperature dependence of the magnetic viscosity phenomena, two special points are evident in the temperature interval studied for each compound: 70 and 25 K in the Cl, and 55 and 25 K in the Br salts. In regards to the higher temperature points, we have mentioned above that they correspond to the domain structure formation at the magnetic phase transition, most probably the AF one. We will check whether this statement finds some support in the results obtained with other techniques. In the Cl salt a very strong anomaly is observed in the temperature dependence of the lattice expansion just at 70 K, evidencing second order phase transition in the salt.¹⁸ This transition is reflected in the electronic properties of the salts as the thermopower sign

changes from positive to negative, and the thermopower slope changes.^{12,13} At nearly the same temperature a rather strong ESR spin susceptibility decrease is observed;^{11,27} assigned to the one-dimensional magnetic fluctuations,²⁷ and on further cooling the magnetic field dependence of the thermopower appears¹⁵ at nearly 55 K. Both the NMR line width and the static magnetic susceptibility show decreases starting from this temperature as well.^{9,10} All these anomalies were assigned to the magnetic fluctuations, not the magnetic transition, though it has been supposed that magnetic order can be induced by the field, at least for the pressure of 1 kbar.²⁸ Clearly, however, that magnetic domain formation can not be typical for the magnetic fluctuation region, as the domains are formed only at the Néel temperature for the AF transition or the Curie temperature for the ferromagnetic one.²⁹ Thus, it may be stated that the real AF phase transition takes place in the Cl salt at nearly 70 K.

In the Br salt, numerous anomalies are observed at around 50 K as well. There exists an essential decrease of the ESR magnetic susceptibility,³⁰ NMR line shift, and width change^{31–33} and the thermopower and resistance anisotropy temperature dependences show some anomalies,^{34,35} though not so definite as in the Cl salt.^{12,13} However, static magnetic susceptibility starts to decrease at nearly 70 K,¹⁰ and there are some problems with the relation of this transition with lattice anomalies. The lattice expansion anomaly in the Br salt, similar to the 70 K anomaly in the Cl salt we have just related with the AF phase transition, is shifted to 80 K, though the magnetic anomalies are shifted down to nearly 50 K. We would like to note, however, that the anomalies in different crystallographic directions at 80 K cancel each other, and that the volume expansion anomaly is indeed observed at 50 K.³⁶ This allows us to support our conclusion about real AF ordering in the Br salt as well.

The magnitude of the transient reaches a maximum at the temperature of 30 K both in Cl and Br, and drops on further cooling. The magnetic properties of the Cl salt are well established, so it is easy to ascribe essential changes in the character of magnetic relaxation phenomena to the well documented magnetic phase transition to the three-dimensionally ordered AF state with WF.^{5,9} The increase of the relaxation rate in this case should be due to the appearance of an uncompensated moment in the magnetic lattice upon WF transition, leading to an essential acceleration of the domain wall movement in the magnetic field.²⁹ It is most interesting, however, that the transient magnitude drop is observed in the Br salt at the same temperature. This clearly shows that the underlying magnetically ordered state is present in the Br salt. The conclusion about the phase transition in this temperature range was made previously in the course of thermal expansion studies,³⁶ and its magnetic origin finds support in the NMR results³³ and our observation of the Hall constant behavior.

Thus, summarizing the experimental observations of magnetic viscosity phenomena for the Cl salt, we can state that:

(1) The phase transition to the AF ordered state takes place at nearly 70 K.

(2) The transformation of the magnetic structure at 25 K transition to three-dimensional AF state with WF is revealed as a sharp relaxation magnitude drop. It is not clear, whether the beginning of this drop at nearly 30 K can be related to the

fluctuations above the transition itself, or whether they are the manifestation of one more phase transition, as was supposed.^{6,37}

(3) No special features are found that accompany the 45 K metal to insulator transition.

(4) Magnetic (AF) domains are formed at the AF transition at 70 K, and their walls are running along the a direction.

In regards to the Br salt, we observe that (1) AF ordering takes place at nearly 50 K and (2) the magnetic phase transition proceeds at 25 K, just as in the Cl salt, confirming the results of the lattice thermal expansion studies³⁶ and implications from the NMR³³ and specific-heat³⁸ studies, and probably to the three-dimensionally AF ordered state.

Some of these findings are worthy of special attention. The results regarding the Br salt show that the AF state is compatible with the metallic state. Besides, it was previously shown from the anisotropy of the magnetic susceptibility in the Cl compound, that the easy axis corresponds to the direction of the normal to the conducting plane.^{9,27} The direction of the domain wall within the conducting plane then is determined by the higher order magnetic anisotropy constants (K_4 or K_6).²⁹ As these constants are not as large as K_2 and the spin-flop transition, determined mainly by the K_2 value, at low temperature proceeds in the field of 0.4 T,^{9,27} it is believed that the direction of the magnetic domain walls within the conducting plane should not be very strongly fixed. Rather strong anisotropy of the relaxation phenomena may then evidence that the anisotropy of defects in the crystal is responsible for the preferential stabilization of the domain wall, running along the a axis. Based on the direction of the normal to the domain wall that corresponds to the direction of the normal to the open sheets of the compounds Fermi surface (FS), an essential contribution from the electronic energy to the stabilization of this structure can be thought of, just as is the case for (BEDT-TTF)₂Cu(SCN)₂ at high temperatures.³⁹

C. Possible origin of the magnetic state in the salts

As possible origins of the magnetism in the salts, the following three can be considered: (1) the presence of the strong Mott-Hubbard correlations, (2) the existence and magnetic ordering of some magnetic moments that are extrinsic to the highly conducting BEDT-TTF layers, namely, Cu²⁺ ions in the anion layer, and (3) the formation of the SDW. There is a general belief, that Mott-Hubbard-type correlations are responsible for the magnetic properties of these compounds.^{9,40} Finding that the metallic phase shows AF order in the Br salt seems to support this idea. We would like to note, however, the striking similarity of the 25 K transition temperature in the metallic Br and insulating Cl salts, despite the fact that, according to the calculation,⁴⁰ in order to obtain insulating and metallic states rather different values of the transfer integrals are necessary, so different temperatures of the phase transitions could be anticipated. The other point, that is hard to explain in this model, is the direction of the domain walls, appearing in the compounds.

As far as the phase transitions looking as something independent of the compound's electrical conductivity, it is attractive to relate them with some process that is not related to

the conducting layer; say, the ordering of copper Cu²⁺ magnetic moments within the anion layer. A close relation between the temperatures of transport property anomalies and those of the distances within the anion layer was revealed by Doi *et al.*⁴¹ In this picture the slow dynamics of the domain walls could find an explanation in slow Cu⁺ to Cu²⁺ recharging processes. However, according to the band structure calculation,¹ the Cu level lies rather far from the Fermi energy to take part in the charge transfer in the salt. Success of the Fermi surface reconstruction showing the FS volume close to that calculated also makes Cu²⁺ formation unlikely.

SDW is an established mechanism for magnetic state formation in the low-dimensional compounds. However, its role in the formation of the magnetically ordered state in the salts under study has been questioned on the basis of two experimental observations.⁹ (1) The commensurability of the magnetic distortion with the lattice is unlikely to meet the best nesting vector for the calculated FS; besides, it was argued that the curvature of the FS is rather large to lead to a large electronic energy decrease upon transition. (2) Rather large magnetic moments of 0.4 to $1\mu_B$, compared with the conventional SDW conductor (TMTSeF)₂PF₆.⁴²

We show, now, that at least (1) is not strictly controversial with the SDW picture in the salts. First of all, it is well established, that the incommensurate structural modulation in the one-dimensional conductors can be transformed into a commensurate one according to the McMillan mechanism.⁴³ The basic idea of the latter is the following. If the best nesting vector in the k space $Q_{ss} = 2k_f$, where k_f is the Fermi wave vector, is incommensurate with the lattice, nesting conditions can be fulfilled by transforming the incommensurate distortion into a periodic domain structure, so that the superstructure becomes commensurate within each domain. In this case the wave vectors of the incommensurate and commensurate density waves Q_{ss} and Q_{dw} , respectively, and that of the periodic domain structure Q_{domain} , fulfill the relation $Q_{ss} = Q_{dw} \pm Q_{domain}$. As a result, some charge within the lattice is redistributed, and it is either the enriching the domain wall ($Q_{dw} < Q_{ss}$), or exhausting it ($Q_{dw} > Q_{ss}$), and thus a charged domain wall (soliton) is formed. In the system under consideration, this can lead to the periodic domain structure with the wave vector normal to the FS open sheets, that is along the c axis, with the walls running along the a axis, in accordance with our finding.

We would like to note, besides, that other possibilities exist in the systems under study to adopt the commensurate structure. These come from the mixed-dimensional topology of the compound's FS, comprising open FS sheets, resembling those of the one-dimensional (1D) conductors and closed cylinders, representing the two-dimensional (2D) part and formed due to the appearance of the gaps in the dispersion curves at the Brillouin zone (BZ) boundaries.

The presence of the 2D cylinder can modify the standard charge or SDW transition picture. First of all, the presence of large amounts of free carriers that are not subjected to the metal-insulator transition screens effectively all the charges in the lattice, thus making the situation favor the SDW with respect to the charge density wave formation. Secondly, according to the theory of magnetic polarons,⁴⁴ in the AF ordered background (typical of the SDW) it is energetically favorable to form quasiparticles, imbedded in the regions of

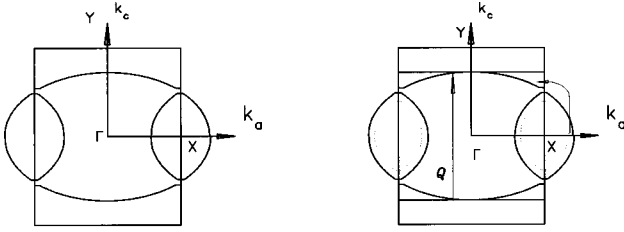


FIG. 9. Fermi surface of the compounds (a) and the proposed Fermi surface transformation upon superstructure formation at wave vector Q (b). Because the gap at the Brillouin zone boundary Δ_{BZ} is very small, much less than the superstructure gap Δ_{SDW} , an essential redistribution of the carriers is expected between the two Fermi surface sheets.

the ferromagnetic order as their energy is reduced. When the number of these quasiparticles exceeds some threshold, phase separation can occur in the material, resulting in the formation of an insulating AF phase and a conducting ferromagnetic phase. Thus, the presence of the carriers on the FS cylinders can lead to phase separation in the materials and preferential accumulation of the carriers in the domain wall region. There is, however, one more essential difference of the SDW in mixed-dimensional systems. In the 1D system the only condition for the SDW formation is that nesting must occur in a large enough part of the FS. In the systems under study, if SDW leads to the opening of the rather large gap compared to the very small gap at the BZ boundary,^{3,4} essential Fermi surface shape changes may result, as there may be redistribution of the carriers between the two sheets. Say, if we take the temperature of the SDW formation of 50 K and, as is common, assume a BCS-like relation between the critical temperature and the gap $\Delta_{\text{SDW}}/T_c \sim 3.5$, we come to a superstructure gap value of the order of 180 K that is, essentially larger than the energy gap at the BZ, of the order of 16 K from magnetic breakdown field in the Shubnikov-de Haas effect studies.⁴ Thus, the formation of the superstructure at the wave vector Q (Fig. 9) reduces the energy of the states, lying between the initial FS and the new BZ boundary, essentially larger than the gap at the initial BZ boundary. This makes it energetically favorable for the carriers from the hole pockets to occupy the states in the first BZ, leading to the decrease of the volume of the hole part of the FS. It is most interesting, however, that the largest reduction of the total electron energy can result from the superstructure, which does not fulfill the criterion of best nesting $2k_F$ wave number, but its wave number can be defined from the condition of the total electronic energy minimum for this new state. Then the system may first adopt distortion, defined by the initial FS nesting conditions, and then suffer a sequence of transitions to the states with lower electron energy.

In this picture it may be clear why the Br salt does not suffer transition to the insulating state: its Fermi surface is already strongly reconstructed by the superstructure, formed at 200 K,⁴⁵ making this essential energy gain impossible due to the redistribution effect.

The value of the magnetic moment within the WF magnetically ordered state is, however, the principal difficulty for the SDW picture. It can be thought that the redistribution effect, mentioned above, could result in the charge separa-

tion between inequivalent dimers, and thus could lead to larger moments in the magnetically ordered state, though this statements needs further verification.

Of course, at present it is simply impossible to decide, which of the magnetic ordering schemes works as there are no direct determinations of the compound's magnetic structure. However, we would like to note that the situation with the SDW is too far from being clear to consider it totally unapplicable. It explains naturally the phase separation in the salts, the evidence for which can be supposed from both the pronounced magnetic field induced aging effects revealed by Sushko *et al.*⁴⁶ and these experiments. The direction of the domain walls finds a quite natural explanation in the SDW picture, as well as strongly different properties of the domain wall with respect to the domain volume.

It is noteworthy that as a lot of the anomalies are observed at nearly the same temperatures in other κ -phase salts of BEDT-TTF, it is tentative to suppose the presence of the real magnetic transitions in the other salts too. Very recently we observed magnetic viscosity phenomena in the $(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2]\text{I}$ and some $(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2]\text{ClBr}$ alloy samples as well.⁴⁷

V. CONCLUSION

Hall effect studies in κ - $(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ have shown the presence of a real gap in the electronic spectra of the compounds. The Hall constant was found to be temperature independent in the Br salt with a value of $+2 \times 10^{-8} \text{ m}^3/\text{C}$ down to 55 K.

The phase transition to the AF ordered state was found to proceed at temperatures as high as 70 and 55 K in Cl and Br salts, respectively. This transition was shown to lead to magnetic viscosity phenomena in the samples. From the anisotropy of these phenomena in the highly conducting plane of the Cl crystals, the domain wall direction was found to coincide with the a axis.

Temperature dependences of the magnetic relaxation parameters indicate that the magnetic structures of metallic Br and insulating Cl salts are similar. In particular, the appearance of the magnetically ordered state is observed in the Br salt at nearly 25 K, being consistent with earlier observations of the phase transition in the compound.

Based on the direction of the domain wall periodicity corresponding to the direction of the open sheets of the compounds Fermi surface, the SDW mechanism of the magnetic state formation is reexamined. It is shown that the commensurability of the magnetic structure with the lattice does not contradict the SDW picture.

ACKNOWLEDGMENTS

The authors would like to acknowledge support from NEDO in the form of a Proposal-Based Advanced Industrial Technology R&D Program. Support from the International Science Foundation (Grant No. U51200) is also acknowledged. The authors would like to thank Y. Yamauchi for his help in computer software development. One of the authors (M.T.) would like to thank Yu. V. Sushko for stimulating discussions.

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