

Phase behavior of the organic superconductors κ -(BEDT-TTF)₂Cu[N(CN)₂]X (X = Br and Cl) studied by ac calorimetry

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Temperature dependence of heat capacities of organic superconductors, κ -(BEDT-TTF)₂Cu[N(CN)₂]X (X = Br and Cl), was measured by chopped-light ac calorimetry between 10 and 300 K. A small anomaly was clearly detected at the superconducting transition in the Br salt. For the Cl salt, a slight anomaly was observed at 45 K where the spin-density wave-like transition was previously suggested to occur, while there was no anomaly at the magnetic phase transition temperature to weak ferromagnetism around 22 K. In both salts, the steplike anomalies were observed around 100 K. The temperature of this anomaly depends on the measurement frequency. The anomalies are attributed to a glass transition caused by freezing of the motion of the ethylene moiety in BEDT-TTF molecule. The glass transition plays no important role in the electrical properties for the Cl salt, but does affect the electronic properties including superconducting properties for the Br salt.

I. INTRODUCTION

BEDT-TTF salts with the κ -type arrangement of the BEDT-TTF molecules have attracted great interest because the salts have not only high T_c [T_c : superconducting (SC) transition temperature] but also highly correlated electronic states with two-dimensional character.^{1,2} Crystals of the κ -type salts consist of alternating stack of electronically two-dimensional conduction layer of BEDT-TTF and insulating anion layer. Even a similarity to the high- T_c oxides has also been suggested for the salts.

The title compounds, κ -(BEDT-TTF)₂Cu[N(CN)₂]Br and κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl, belong to the κ -type salts and are known as superconductors with the highest T_c under ambient pressure (the Br salt)³ and under moderate pressure (the Cl salt),⁴ respectively. The conducting behavior of the Br salt is quite unusual. On cooling, the resistivity increases gradually down to about 100 K, rapidly decreases with a small inflection around 77 K and suddenly drops to zero at 11.6 K, the SC transition.² The SC phase is quite sensitive to pressure. Application of only 5 kbar is enough to fade out the SC phase.⁵ The magnetization curve is also unusual.² The magnetization is roughly constant around room temperature like a metal, decreases gradually with lowering temperature, turns into rapid decrease around 50 K, and then drops suddenly at T_c . The reason for the decrease around 50 K is unknown.

Although κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl is isostructural to the Br salt, the salt is semiconducting under ambient pressure.⁴ The magnetization curve is similar to that of the Br salt. An antiferromagnetic transition was first reported at 45 K.⁶ The resistivity curve also has a small inflection at 42 K.⁴ The existence of the transition was supported by successive experiments.^{7,8} The later NMR however gave a negative result, though it suggested a magnetic transition at 27 K.⁹ At 22 K, a canted antiferromagnetic (AF) transition occurs⁶ with a moment of (0.4–1.0) μ_B /dimer.⁹ The relatively large magnetic moment around 22 K suggests that the AF order

is driven by the strong electron correlation. Nakazawa and Kanoda¹⁰ reported magnetic field dependence of the heat capacity at low temperature. Neither significant anomaly nor field dependence was observed between 20 and 50 K, suggesting a growth of the two-dimensional short-range order at high temperatures far above the three-dimensional long-range order. The electronic properties of the Cl salt are also sensitive to pressure: 0.3 kbar is enough to realize the SC phase.⁴ Nowadays, it is generally accepted that both salts are near the phase boundary between the SC and AF insulating phases. Recently, partially deuterated κ -(BEDT-TTF)₂Cu[N(CN)₂]Br was synthesized. The salt seems to be just on the phase boundary, and the SC-insulator transition occurs.¹¹

Besides the transitions related to the electronic states, structural transitions have been suggested to exist. According to the x-ray structural analysis,¹² one terminal ethylene moiety in the BEDT-TTF molecules (Fig. 1) of both salts shows positional disorder at room temperature while no appreciable disorder is detected at 127 K. Some papers suggested a structural phase transition related to this disordering at low temperature.^{13–16} On the other hand, Nogami *et al.*¹⁷ reported the appearance and growth of superlattice reflections below 200 K for the Br salt and attributed them to a displa-

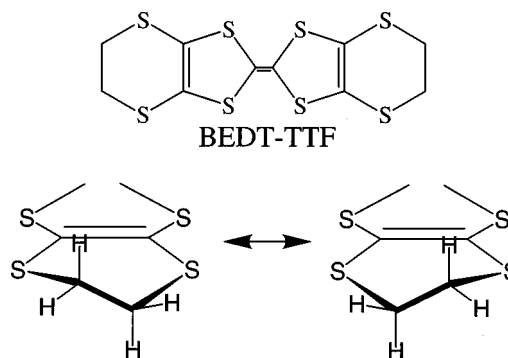


FIG. 1. Molecule of BEDT-TTF and two possible conformations of the ethylene moiety.

cive phase transition mainly related to the anion layer. No paper has been published to report a precise study on the Cl salt around this temperature.

In the last several years, another point has been actively discussed, which seems to have a close connection with an interplay between the electronic system and the structural ordering. The properties of the Br salt depends on its thermal history. It has been reported that the temperature and the magnitude of the inflection on the resistivity curve depend on cooling (or heating) rate and/or annealing.^{13-16,18,19} With increasing cooling rate, the temperature shifts toward the high-temperature side and the magnitude of the anomaly is enhanced. The cooling rate also has a great influence on T_c . The T_c increases with decreasing cooling rate. The thermal expansion measurement shows an anomaly at 77 K,²⁰ where the inflection was reported in the temperature dependence of the resistivity. Su *et al.*¹³ suggested in their first report that this anomaly be due to an order-disorder transition of the ethylene moieties from the cooling rate-dependent electrical resistivity measurements. They claimed, however, in a recent paper that the anomaly around 77 K is due to a structural transition of the anion layer¹⁴ because the onset temperature of the order-disorder transition of ethylene moiety they assumed was as high as 140 K.¹⁵ This contradicts the previous paper by Nogami *et al.*¹⁷ Tanatar *et al.*¹⁶ studied the annealing effect of the resistivity around the inflection at 77 K. The resistivity depended on the annealing temperature and the duration of annealing. The annealing effect was maximum around 66 K. The activation energy, E_a , derived from the Arrhenius plot of the temperature dependence of the relaxation time is quite similar to that of the motion of the terminal ethylene moiety determined by NMR measurement.²¹ From these observations, they claimed that the first-order phase transition related to the ethylene moieties occurs around 60 K. The magnetic susceptibility of κ -(BEDT-TTF- d_8)₂Cu[N(CN)₂]Br,²² whose properties are similar to those of the Cl salt, also depends on the cooling rate. Rapid cooling suppresses the spin canting in this salt. There is no report that studies the thermal history dependence of physical properties of the Cl salt itself.

Although extensive studies have been carried out and their properties compared in detail for κ -(BEDT-TTF)₂Cu[N(CN)₂]Br and κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl, it is surprising that the phase sequences have not been clarified yet. For example, it is unknown whether there is a phase transition around 200 K in the Cl salt or not. Also unclear is the point whether the anomalies in the resistivity and thermal expansivity at 77 K are accompanied by any structural phase transition. Concerning the electronic states, the origin of the decrease in magnetic susceptibility around 50 K is still controversial. The first aim of this paper is to clarify these points based on calorimetric measurement because it seems to provide the most direct evidence.

The second aim is to examine the possibility of a glass transition, i.e., a transition between ergodicity and nonergodicity. Recently, the authors discovered a glass transition in the BEDT-TTF related organic conductors, (DMET)₂BF₄ and (DMET)₂CIO₄, for the first time.²³ The degree of freedom relevant to the glass transition is the conformation of the ethylene moiety of the BEDT-TTF molecule. Since the

glass transition in organic conductors is scarce in this field, the existence of such glass transition throw light unresolved problems such as the thermal history dependence of the property of the Br salt. This is indeed the case as reported preliminarily.²⁴ Full account of the results on the Br salt and the new results on the Cl salt will be described in detail here.

In this paper, the results of the ac calorimetric measurements on κ -(BEDT-TTF)₂Cu[N(CN)₂]Br and κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl are described. Although the ac calorimetry has an intrinsic difficulty in determination of the absolute value of heat capacity, the technique is superior to other calorimetric techniques mainly in three aspects: (1) A sample is very small. Only a small single crystal is enough for measurement. It is appropriate for study of organic conductors because of the difficulty in large scale synthesis. (2) Temperature resolution is very high. It is possible to detect an anomaly even if that is very small. (3) The technique can be regarded as a low-frequency spectroscopy. Very slow dynamics such as glass transitions is clearly detected as frequency-dependent thermal anomaly.

II. EXPERIMENTAL

Crystals of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br and κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl were prepared by the conventional electrochemical method.²⁵ Black blocklike crystals were obtained. The lattice parameters of the sample crystals were confirmed to be consistent with those reported previously.^{3,4} The crystal sizes used for the heat capacity measurement were $0.2 \times 0.3 \times 0.35$ and $0.5 \times 0.4 \times 0.2$ mm³ for the Br and Cl salts, respectively. Chromel and Constantan wires (13 μ m in diameter) were crossed at the center of the wires on a holder and electrically connected at the crossing point by gold paste. Each sample crystal was fixed by gold paste on the crossing point of the thermocouples. The magnitude of temperature oscillation that is inversely proportional to heat capacity was measured using the one pair of the thermocouples, and another pair was used to determine the temperature difference between the sample and the heat sink. The temperature of the heat sink was measured by a platinum (above 20 K) or germanium (below 40 K) resistance thermometer. The sample was heated periodically by chopped white light from a stabilized halogen lamp. The amplitude of temperature oscillation of the sample was kept less than 0.01 K. The scan rate of the temperature was about 0.05 K min⁻¹ above 30 K, which is by an order of magnitude smaller than that caused by temperature oscillation at the lowest frequency in the present study (0.24 Hz). The details of the ac calorimeter were already described elsewhere.²⁶

III. RESULTS AND DISCUSSION

A. Anomalies due to the electronic and magnetic phase transition

Figure 2 shows the tempered heat capacity of the κ -(BEDT-TTF)₂Cu[N(CN)₂]Br around T_c where “tempered” means “divided by temperature.” An inflection is clearly observed at 12.5 K that is about 1 K higher than the diamagnetic onset.³ The magnitude of the anomaly is very small. The present results agree fairly well with those previously observed by Andranka *et al.*,²⁷ who reported the

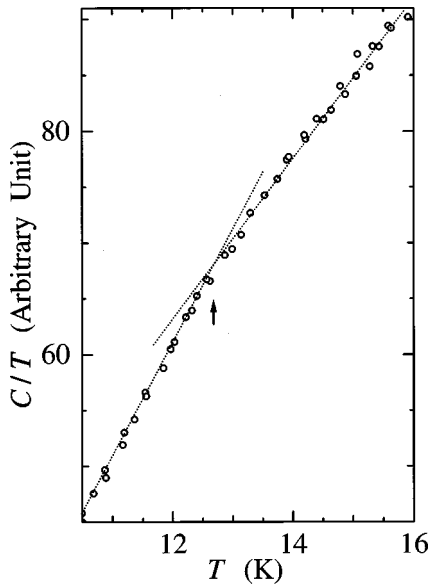


FIG. 2. C/T of κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br plotted against T around the superconducting transition.

anomaly at about 13 K. Both results show that T_c determined by calorimetry is higher than that by magnetic measurements. These T_c , however, agree with the resistivity onset.³ Andraka *et al.*²⁷ suggested that the discrepancy results from not only the intrinsic averaging effect in heat capacity measurement (about 0.4 K) but also the SC fluctuation, which was observed in the oxide superconductor by ac calorimetric measurement.²⁸ Since the temperature interval over which averaging occurs in calorimetric measurements is narrower than the difference in T_c , the effect of the SC fluctuation would work in the Br salt.

The heat capacity result of the Cl salt below 30 K is shown in Fig. 3. Although there is no controversy concerning the presence of the magnetic transition into a weak ferromagnetism, no anomaly is seen around $T_{WF}=22$ K, in accor-

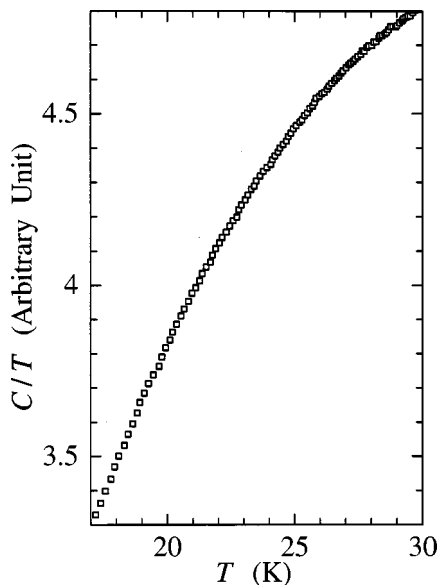


FIG. 3. C/T of κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Cl plotted against T around a magnetic transition into weak ferromagnetism at 22 K.

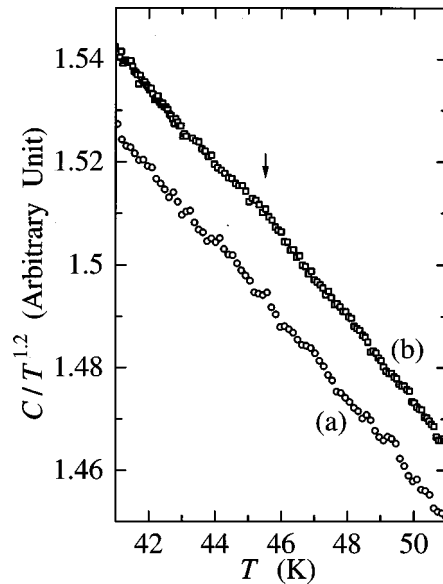


FIG. 4. $C/T^{1.2}$ plotted against T of (a) κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br and (b) κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Cl around 45 K.

dance with the previous report.¹⁰ It is noted that there is also no anomaly at $T_N=27$ K suggested from the NMR experiment.⁹ The absence of thermal anomalies implies that the spins are well ordered even above T_{WF} or T_N . In this respect, it is of interest to clarify the presence (or absence) of a magnetic transition around 45 K, which was suggested from some experiments⁶⁻⁸ but denied on the basis of the NMR results.⁹ Figure 4 shows the results for both salts in this temperature region. Only to see the anomaly clearly, the ordinate of the figure is set as $C/T^{1.2}$. No anomaly appears for the Br salt. On the other hand, a small anomaly can be recognized at 45 K for the Cl salt. Although the ‘‘anomaly’’ was completely reproducible in repeating measurements, it is too small to claim convincingly its existence. The discussion is therefore left for future studies. It is however noteworthy that its location just corresponds to that of the magnetic phase transition previously suggested.⁶⁻⁸ If this correspondence implies the reality, the decreases of the susceptibility around 45 K may be involved in different phenomena between the Br and Cl salts.

B. Anomalies due to the structural transition within the anion layer

The superlattice reflections appear below 200 K for the Br salt, indicating a phase transition.¹⁷ In spite of repeated runs, any anomaly could not be detected around 200 K in the present ac calorimetry as shown in Fig. 5. There seem to exist three possible explanations. The first denies the existence of the phase transition. The second involves strong sample dependence. It is noted that the absence of the anomaly was also confirmed on another sample. The last assumes that the anomaly is very small. Assuming the last possibility, some discussion about the property of the phase transition may be made. The absence of anomalies in transport and magnetic properties at this transition suggests the phase transition be of no electronic/magnetic but structural origin. Since the entropy of transition (usually estimated

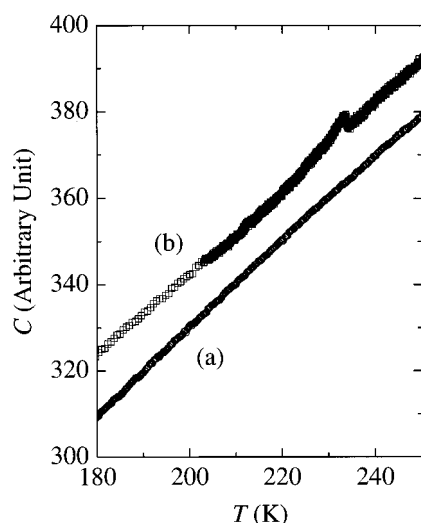


FIG. 5. C plotted against T of (a) κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br and (b) κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Cl around 220 K.

from excess heat capacity) is comparable to or larger than $R \ln 2$ for order-disorder transitions, the phase transition at 200 K is of displacive type. Seeming conformational disorder of the ethylene moieties contradicts the displacive nature of the phase transition. The cause is therefore thought to originate in the anion layers. These are compatible with the conclusion by Nogami *et al.*¹⁷ but in contradiction with that by Su *et al.*¹⁵

In Fig. 5, an anomaly is clearly seen around 233 K for the Cl salt. The shape of the anomaly suggests a higher-order nature. Although the anomaly is much larger than that due to the electronic or magnetic phase transition in low temperature regions, the entropy of transition roughly estimated, $(0.5-1.0) \text{ JK}^{-1} \text{ mol}^{-1}$, is much smaller than $R \ln 2$, suggesting a displacive nature of the phase transition. This phase transition bears some resemblance to the “phase transition at 200 K” of the Br salt assuming its presence, in the ways such as the displacive nature, the absence of anomaly in transport and magnetic properties, and the transition temperature. This resemblance may imply that the common mechanism governs the phase transitions for the Br and Cl salts. Search for the superlattice reflections in the Cl salt will be necessary to clarify this issue.

C. Glass transition due to conformational freezing of the terminal ethylene groups

There are some reports indicating an inflection point around 77 K in the resistivity curve of the Br salt,¹³ and an anomaly in the thermal expansivity around this temperature.²⁰ Figure 6 shows the heat capacity curves of both salts around 77 K. No anomaly could be detected in the repeated runs. In contrast, steplike anomalies were observed around 100 and 90 K for the Br and Cl salts as shown in Fig. 7. The anomalies depend on the frequency of the temperature modulation for both salts. The anomaly shifts toward the high-temperature side with increasing frequency. The authors have briefly reported this result for the Br salt.²⁴ The steplike shape of the anomaly and the frequency dependence of its location are characteristic of glass transition. Since the

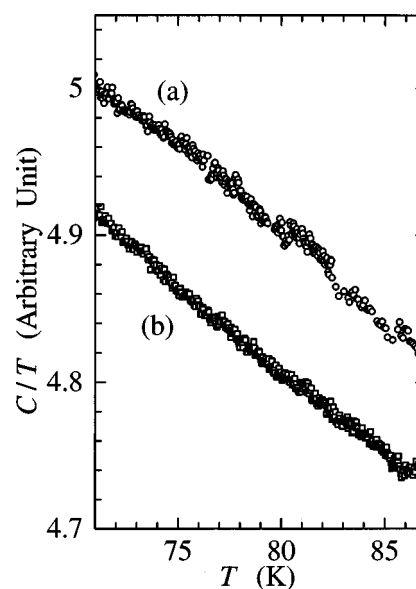


FIG. 6. C/T plotted against T of (a) κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br and (b) κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Cl around 77 K.

conformational disorder of the terminal ethylene moiety has been detected by structure analysis,¹² it is natural to attribute these glass transitions to the conformational freezing of the ethylene moieties. This type of glass transition in organic conductors was first found for (DMET) $_2$ BF $_4$ and (DMET) $_2$ ClO $_4$ by the present authors.²³ The ethylene moiety in the six-membered ring has two possible conformations as shown in Fig. 1. Two conformations are equivalent in the isolated state of the molecule but nonequivalent in the crystal lattice because of the intermolecular interaction. That is, one conformation is more stable than the other. Above the glass transition, the motion of the ethylene moieties is thermally activated, establishing the equilibrium between two nonequivalent conformations. The rate of the motion characterized by the inverse of a conformational correlation time or relaxation time, τ , however, decreases with decreasing temperature. If τ exceeds the time scale of the measurement, the population of two conformations is effectively frozen in and the motion no longer contributes to the heat capacity. For instance, τ is much longer than 1 s, the motion does not contribute to the heat capacity measured at 1 Hz by ac calorimetry. This results in a steplike anomaly in heat capacity.

The assignment of the glass transition to the conformational freezing of the ethylene group is supported by the magnitude of the activation energy (E_a) for the motion. This quantity is derived from the so-called Arrhenius plot of the present results shown in Fig. 8. The resulting magnitudes are 2400 K for the Br salt and 2700 K for the Cl salt, respectively. These are favorably compared with the previously reported values, 2200 K by the resistivity measurement,¹⁶ 2650 K by the $^1\text{H-NMR}$ measurement²¹ both for the Br salt, and (2600 ± 100) K by $^1\text{H-NMR}$ measurement⁹ for the Cl salt. The glass transition temperatures of the Br and the Cl salts at which the τ is equal to a daily time scale ($\approx 10^3$ s) are determined as 77 K and 75 K, respectively, from the extrapolation of the Arrhenius plot shown in Fig. 8. It is emphasized that the estimated glass transition temperature

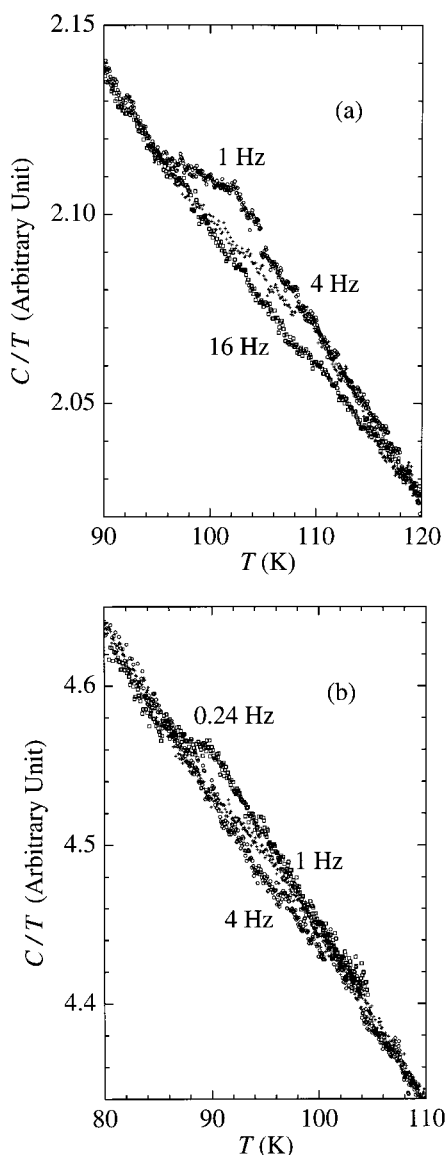


FIG. 7. Frequency dependent C/T plotted against T of (a) κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br (1, 4, and 16 Hz) and (b) κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Cl (0.24, 1, and 4 Hz) around 100 K.

just corresponds to the temperature where the anomaly has been reported in the resistivity¹³ and the thermal expansivity for the Br salt.²⁰

One may claim that the glass transition has another origin other than the conformational freezing of the ethylene group on the basis of the fact that no apparent disorder was detected at 127 K by crystal structure analyses for both salts.¹² The sensitivity of calorimetry is, in fact, much higher than the diffractometry concerning the disorder. For example, the population of the wrong conformation is about 5% at the temperature where heat capacity shows a maximum in the simple two-level Schottky case.

Now, the consistency between the glass transition and the other results concerned with the ethylene motion of the Br salt is considered. The keyword is time scale. Tanatar *et al.*¹⁶ reported that the anomaly was observed at 60 K in the resistivity if the sample was annealed at 66 K about 10 h (4×10^4 s). The annealing time may be regarded as an effective

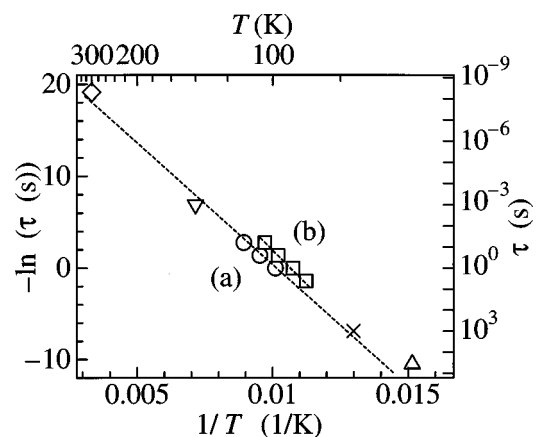


FIG. 8. Arrhenius plots of the anomalies of (a) κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br in the present ac calorimetry (circle), the resistivity after annealing 10 h at 64 K (triangle) (Ref. 16), the resistivity of the rapidly cooled sample (inverted triangle) (Ref. 15), and the conformational correlation time at 300 K by NMR (diamond) (Ref. 21), and (b) κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Cl in the present ac calorimetry (square).

time scale. Su *et al.*¹⁵ reported that the anomaly was observed at 140 K in the resistivity if the sample was suddenly immersed into liquid nitrogen. It is difficult to estimate the effective time scale but will be very short, perhaps may be in order of 10^{-3} s. Much faster motion is directly probed by the relaxation measurement of $^1\text{H-NMR}$. The conformational correlation time τ was reported as 4.8×10^{-9} s at 300 K.²¹ Finally, most usual measurements of physical properties are done in a time scale of 10^3 s. These results are included in the Arrhenius plot in Fig. 8. As clearly seen from the figure, all points show a reasonable linearity within tolerable scatter. This clearly indicates that the assignment of the glass transition to the conformational freezing of the ethylene motion is fully consistent with all the existing results. Besides, the important point is that one needs not assume the presence of phase transition at 77 K as an origin of the anomalies in resistivity and thermal expansivity. Of course, however, the discussion given here cannot rule out a possibility of some phase transition.

The possibility of the existence of an unobservable phase transition can be discussed on the basis of the shape of the steplike thermal anomaly. The magnitude of the step is almost constant against the measurement frequency, and consequently temperature, in cases of (DMET) $_2$ BF $_4$ and (DMET) $_2$ ClO $_4$.²³ These results were interpreted as the anomaly locates around a broad top of a two-level Schottky heat capacity. Namely, the interaction between adjacent ethylene moieties was unnecessary for the interpretation of the thermal anomaly of (DMET) $_2$ BF $_4$ and (DMET) $_2$ ClO $_4$. On the other hand, the magnitude of the steplike anomaly in the Br and Cl salts depends strongly on the frequency. The magnitude is decreasing with increasing frequency. This strong temperature dependence cannot be reproduced while assuming a simple two-level system. This implies some cooperativity between adjacent ethylene moieties.²⁴

The conformation of the ethylene moiety only indirectly influences the electronic structure. The most probable indirect mechanism is the change in volume, or more precisely

the average transfer integrals between BEDT-TTF molecules.²⁴ Since these systems are very sensitive to pressure, the volume will be one of the most important parameters to control the physical properties. Besides the change in volume, spatial disorder would make some effects. It is therefore very difficult to predict what change in the properties results from the glass transition. Posselt *et al.*²⁹ speculated that the conformational disorder thermally activated was related to the rather high electrical resistivity and the observed maximum in resistivity. The experimental results shown in this paper clearly demonstrate that the conformational change is really active around the resistivity maximum. The microscopic study is therefore in order on the relation among the resistivity maximum, averaged system volume and frozen-in disorder in the κ -type salts. Such a study will also contribute to understanding of the spin-density-wave transition in quenched (TMTSF)₂ClO₄ (Q -state), which is believed to arise from the nesting of quasi-one-dimensional Fermi surfaces blurred by the frozen-in orientational disorder of ClO₄.³⁰

IV. CONCLUSION

Heat capacities of κ -(BEDT-TTF)₂Cu[N(CN)₂]X (X = Br and Cl) were measured by chopped-light ac calorim-

etry. A small anomaly involved in the superconducting transition was clearly observed for the Br salt. While no anomaly was observed at a magnetic transition into a weak ferromagnetism at 22 K, a small anomaly was observed at 45 K for the Cl salt. For the Cl salt, a thermal anomaly probably due to a similar structural phase transition to that of the Br salt was detected at 233 K. In both salts, the steplike anomalies were detected around 100 K, the location of which was dependent on the frequency. The anomalies are attributed to the conformational freezing of the terminal ethylene moiety in BEDT-TTF molecules. The normal glass transition temperature (corresponding to the time scale of 10³ s) coincided well to the temperature of anomalies in resistivity and thermal expansivity. The motion plays no significant role in the electric properties of the Cl salt, but plays a crucial role in the electronic properties including superconducting properties of the Br salt.

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