DYNAMIC DISORDERS AND ITS RELAXATION IN ORGANIC SUPERCONDUCTOR
$k$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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In this paper, we report direct evidence of dynamic structural disorders introduced by quenching a crystal of charge transfer salt $k$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br superconductor from high temperatures to 77 K. The sample quenched from different high temperatures relaxes to an equilibrium state with a single relaxation time constant. The magnitude of the relaxation amplitude is dependent on the quenching temperature up to 140 K, above which all relaxation curves overlap with each other. The results suggest strongly that the 140 K is associated with the onset temperature of the order–disorder transition of ethylene groups and the transition is responsible for the anomalous lattice expansion observed at this temperature. © 1998 Elsevier Science Ltd. All rights reserved

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sample to a temperature $T_q$, then immersed into liquid nitrogen in about 2 s. The resistivity data was taken as a function of time immediately afterwards.

Shown in Fig. 1 is a typical time dependence of the measured resistivity for a sample quenched from 112 K. The resistivity decreases rapidly at the beginning and saturates after about 2 h. The solid line is a fit to an exponential form $\rho(t)=\rho_o \exp(-t/\tau) + \rho_{eq}$. Except for the first few points, the overall data can be fitted nicely by the exponential time dependence. For $T_q=112$ K, the fit parameters are: $\rho_o=6.9 \pm 0.2 \ \Omega \ cm$, $\tau = 500 \pm 20 \ s$, $\rho_{eq}=67 \pm 1 \ \Omega \ cm$. The inset is a plot of the resistivity as a function of temperature when the sample is slowly cooled (SC) at a rate about 1 K/min and the relaxation of resistivity at 77 K for $T_q=112$ K. Clearly, the quenched state has a higher initial resistivity than that at any temperature of the SC sample and it relaxes to the SC resistivity value. For the SC sample, it is noted that a broad peak in resistance occurs at 100 K and there is also a shoulder-like feature in resistivity near 80 K. Above 100 K, the resistivity falls gradually with increasing temperature up to above 250 K.

Shown in Fig. 2 is an overlay of relaxation data corresponding to different $T_q$s. In the temperature range between 90 K and 137 K, the initial resistivity increases with increasing $T_q$. The resistivity relaxes eventually to a common value. If we subtract the equilibrium value $\rho_{eq}$ from $\rho(t)$, i.e. $\Delta \rho=\rho(t)-\rho_{eq}$, a single exponential time dependence is observed, as shown from the semi-log plot of $\Delta \rho$ versus $t$ in the inset. The parallel curves demonstrate clearly that all the processes have a single relaxation time constant $\tau$.

For sample quenched at higher temperatures than 137 K, the relaxation data overlaps with each other. Figure 3 shows the time dependence for five different $T_q$s with $T_q=137$ K, 147 K, 157 K, 174 K, 195 K, and 225 K. The overlap shows that sample quenched from above 137 K relaxes with the same amplitude $\rho_o$ and $\tau$, independent of $T_q$.

If we plot $\rho_o$ as a function of $T_q$, a clear break in the $T_q$ dependence is observed at 137 K, as shown in Fig. 4. For $T_q$ below 137 K, $\rho_o$ is almost linear with $T_q$. Above 137 K, $\rho_o$ is nearly constant.

Two characteristics are clear from the relaxation data. First, the fact that all relaxations can be de-
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rapidly through 80 K region show that cooling has
temperature. Transport measurements on samples cooled
orders suppress the antiferromagnetic ordering tem-
amic defect,
that the relaxation is of the nature of two level process
dependence on T
ical temperature of 137 K, which separates out the
relaxations at lower temperatures
have often been observed [12,13]. Although it can not
logarithmic or stretched exponential time dependence
show that ethylene groups were ordered for both Br
V
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Structural studies by X-ray diffraction and high
resolution thermal expansion measurements show
anomalous temperature dependence of the lattice
parameters of the κ-(ET)$_2$Cu[N(CN)$_2$]Br salt. Both
experiments reported an unusual lattice expansion
of a-axis in the direction along the polymer chain in
the conducting plane. While c-axis lattice constant
decreases accordingly to keep the area of the unit cell
in the plane nearly to a constant. The a-axis expansion
occurs at around 140 K, and peaks up at near
80 K, below which a-axis lattice parameter decreases
monotonically [6,7]. The coincidence of the critical
temperature in the relaxation measurement with that
of anomalous lattice expansion suggests strongly that
they are of the same origin.

The nature of structural transition is not clear.
Possible structure disorders in the κ-(BEDT-TTF)$_2$X
system have been discussed in terms of a strain in-
dex which defines the relative changes of actual bond
length with that from van der Waals calculations [14].
The strain index can be correlated with the eclipsed or
staggered arrangement of ethylene groups. The model
has been proposed to explain the differences among
the isostructural salts κ-(BEDT-TTF)$_2$X with X being
Cl, Br and I. Room temperature X-ray diffractions
show that ethylene groups are disordered. At 127 K, it
showed that ethylene groups were ordered for both Br
and Cl samples and disordered for the I sample [15].
There were no other measurements reported for in-
termediate temperatures. Other models including a
short range modulation and a superlattice structure
have been proposed as well [16,17].

We propose that the anomalous expansion in the
a-axis is due to structural transition from the disor-
dered state with both eclipsed conformations (E) and
the staggered ones (S) to an ordered state with only the
E configuration. Above 137 K, the two configurations
are equally occupied because of large thermal energy.
Below 137 K, the E state is more energetically favored,
resulting in a gradual increase of E state or a decrease
of S state with reducing temperature. The presence
of both S and E states in the system introduces ran-
dom potential to the charge transport. In other words,
the scattering rate is proportional to the number of
S states. Since the resistivity is linearly proportional
to the scattering rate, the quasi-linear increase of $\rho_o$
with $T_q$ suggests that the number of S state is linear
in T in the temperature range investigated. The con-
tribution to the scattering rate due to the S state can
be estimated by the ratio of $\rho_o/\rho_{eq}$, which reaches a
maximum at about 15% for $T_q > 140$ K.

The relaxation time constant can be related to the
energy barrier $U$ and thermal energy $k_B T$ by $\tau = \dots$
\( \tau_o \exp (U/k_B T) \). Experimental difficulties in stabilizing the system rapidly to temperatures other than 77 K make it hard to determine the values of \( \tau_o \) and \( U \) independently. However, if we take \( \tau_o \) to be \( 2\pi \hbar /k_B T \), the activation energy \( U \) can be estimated to be around 2600 K. The large \( U \) can be interpreted in terms of collective relaxation of a cluster or a small domain of ET molecules, as in the case of many polymers [12]. If the domain has \( n \) ET molecules and each molecule has an activation energy, say about 140 K, \( n \) can be estimated to be around 18 or 9 dimers. The domain size is expected to increase with decreasing temperature. Relaxation at other temperatures should provide a test to this model.

It is worth pointing out that the transport relaxation is advantageous than many other conventional spectroscopies, such as the X-ray scattering or neutron scattering, in that it can probe the dynamic process of the transition. While a typical X-ray measurement takes hours to get an average signal and can only probe the quasi-static structure.

In summary, we have reported a novel study of transport relaxations as a function of \( T_q \). The data unambiguously shows a two-level relaxation process with a single time constant. The abrupt \( T_q \) dependence of \( \rho_o \) strongly suggests a structural transition at around 140 K, consistent with the observation of anomalous expansion of the lattice parameters. We propose that the structural transition is from the mixed E and S state to the preferred E state at temperatures below 140 K. The feasibility of probing the dynamic relaxation process sensitively by transport measurements in the ET compound makes it possible to study a large number of other molecular systems.

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