Thermal Conductivity of (DMe-DCNQI)$_2$Li$_{1-x}$Cu$_x$ ($x = 1$ and 0.75): Anomalous Temperature Hysteresis Depending on Cu Concentration

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We have measured the thermal conductivity of organic molecular crystals (DMe-DCNQI)$_2$Li$_{1-x}$Cu$_x$ ($x = 1$ and 0.75) over a wide temperature range between 4 and 250 K. The electronic contribution can be analyzed particularly below ~80 K. A thermal hysteresis depending on the Cu concentration $x$ has been observed between the heating and cooling processes. The system stays in a metallic state when the sample is cooled from room temperature, while a small fraction of insulating islands is created in the metallic state when heated up to room temperature. The insulating islands survive even at high temperatures. This mechanism gives rise to the hysteretic behavior. Heat conduction is sensitive to the difference in the two phases, in contrast with electrical resistivity.

KEYWORDS: (DMe-DCNQI)$_2$Cu, thermal conductivity, organic conductor, thermal hysteresis, metal–insulator transition, Wiedemann–Franz law

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1. Introduction

Organic molecular conductors have particularly attracted the interest of many researchers working on materials science because they are suitable for investigating the strongly correlated electron system that is currently the most important topic in condensed matter physics. Among them, the compound (DMe-DCNQI)$_2$Cu (copper salt with 2,5-dimethyl-dicyanomethylene-dione)$^{1,2}$ shows some unique properties. One of its exotic properties is an anomalous temperature-pressure phase diagram, which is shown in Fig. 1. In usual materials, the high pressure side should be metallic because the bond lengths between atoms are shorter under pressure, making it easier for electrons to move to neighboring atoms. However, in the (DMe-DCNQI)$_2$Cu crystal, the high temperature regime is the metallic phase, while the low temperature and high pressure region is the insulating phase.$^{3,4}$ Under ambient pressure, this material remains metallic down to low temperatures. This phase diagram has been determined initially by the helium gas pressurizing method$^5$ and then by the chemical pressure effect using the deuterium substitution technique.$^6$

The metal–insulator (M–I) transition is a first order transition, and its phase boundary is quite ambiguous. Even under ambient pressure, it is believed that a sample is locally stressed up to more than 100 bar, and thus the M–I transition occurs easily. Whether the sample is kept in the metallic phase or driven to the insulating phase when lowering the temperature depends on a slight difference in the experimental setup. A small local stress in a sample can sometimes produce an unexpected phenomenon. This situation makes any experiments on (DMe-DCNQI)$_2$Cu molecular crystals very difficult.

For this reason, no detailed study has been reported on the properties related to the M–I transition boundary. In our experiments, we aimed at examining the properties of the metallic and insulating phases. We employed the technique of thermal conductivity measurements, in which the carrier of heat is directly utilized as a probe. Thermal conductivity measurements have played an important role in the research for inorganic compounds; for instance, the magnon transport has been demonstrated in the low-dimensional quantum spin system Sr$_{14-x}$A$_x$Cu$_2$O$_{21}$ ($A =$ Ca, La)$^7$ and in the one-dimensional spin Peierls compound CuGeO$_3$.$^8$ However, the thermal transport measuring technique has little used in organic materials with some exceptions. The superconducting properties were studied in $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$,$^9$ and (TMTSF)$_2$ClO$_4$.$^{11}$ The spin–charge separation was indirectly demonstrated in quasi-one-dimensional conductors (TMTTF)$_2$X and (TMTSF)$_2$X.$^{12}$ The thermal transport of insulating (DMe-DCNQI)$_2$Li$_{1-x}$Cu$_x$ in the light doping regime ($0 \leq x \leq 0.14$) was examined over a wide range of temperatures, and the effect of the spin Peierls distortion on phonon propagation was discussed.$^{13,14}$ In this article, we report on the results of the thermal conductivity measurements of the metallic compounds (DMe-DCNQI)$_2$Li$_{1-x}$Cu$_x$ ($x = 1$ and 0.75).

Fig. 1. A schematic diagram of temperature $T$ vs pressure $P$ for (DMe-DCNQI)$_2$Cu. The solid lines indicate the M–I transition curve.$^6$ The dotted lines 1 and 2 indicate our proposed thermal cycle for hysteresis to appear; this will be discussed in §5.
2. Experiment

The typical dimension of our samples is $0.1 \times 0.1 \times 1 \text{ mm}^3$, and all the specimens used are single crystals. Measurements were made along the $c$ axis, which is the longest direction. The $c$ axis is the stacking direction of DCNQI molecules. Measurements along other directions are impossible. An experiment of the thermal transport in organic materials is, in general, very difficult since organic samples are fragile and the size of the crystals is very small.

In the conventional technique in which one heater and two thermometers are installed, the heat conduction through a sample had been considered to be large enough as compared to that through the electrical leads for the heaters and thermometers; thus, the heat leak through the electrical leads had been neglected. However, this neglect is not always allowed; in many cases, we have to take into account the heat conduction through the electrical leads, especially for the measurements over a wide temperature range. In order to carry out the measurements accurately under these conditions, we have developed a new technique where two heaters and three thermometers are installed. The sample is placed like a bridge between two resistance thermometers.

The temperature ($T$) dependences of the thermal conductivity ($\kappa$) of (DMe-DCNQI)$_2$L$_{1-x}$Cu$_x$ ($x = 1$ and 0.75) are depicted in Figs. 2(a) and 2(b). The absolute values of $\kappa$ include an experimental error within $\pm 20\%$, but the size of the samples is so small that it is very difficult to evaluate the geometry of the heat flow channel precisely. However, the shape of these curves in both the figures is not significantly influenced. Surprisingly, a large thermal hysteresis is observed above $\sim 40\text{ K}$ in both the $x = 1$ and 0.75 samples: the data taken during cooling from room temperature to $\sim 4\text{ K}$ (cooling curve) is larger than that taken during heating from $\sim 4\text{ K}$ up to room temperature (heating curve).

The features of the hysteresis are summarized as follows: (i) The temperature interval of the hysteretic region is large. It ranges between $\sim 40\text{ K}$ and room temperature. (ii) The extent of hysteresis depends on the Cu concentration $x$. The $x = 1$ sample shows a larger hysteresis. Furthermore, no hysteresis was observed in the $x = 0$ insulator sample in our previous experiments.\(^{13,14}\) (iii) The relaxation process in the hysteretic region is absent. Even if the samples are kept at a fixed temperature for hours, the measured value of $\kappa$ does not change. (iv) Each cooling curve and each heating curve are both reproducible for the two samples. We have checked for two thermal cycles between $\sim 4\text{ K}$ and room temperature.

One may claim that the Au paste that was used for pasting the specimen with thermometers may have resulted in the hysteresis, the reason for which is unknown. But this possibility is ruled out because the extent of hysteresis depends on the Cu concentration although the same pasting method was employed. One may claim that the absorbed helium gas was released when exciting the heater power during the cooling process, yielding an apparently better conductivity. But this possibility is also ruled out since the experimental chamber had been continuously pumped during the entire measurement. We are thus convinced that this anomalous hysteresis was not brought about by experimental artifacts and that the hysteretic behavior stems from some physical origin.

To our knowledge, the hysteretic behavior in the thermal conductivity measurements has been experimentally observed in high $T_c$ superconductors RBa$_2$Cu$_3$O$_x$ ($R = \text{Dy, Gd, Eu}$)\(^{16}\) and in a CDW compound Lu$_2$Rh$_2$Si$_{10,17}$.

3. Results

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4. Discussion (I)

In order to explore the origin, we have to first check whether the observed values of $\kappa$ are electronic or phononic. Let us discuss three points below. (i) Firstly, according to a literature on electrical resistivity ($\rho$) measurements on $x = 1$ and 0.75 samples,\(^{18}\) the experimental $\rho$ starts to deviate from a $T^2$ dependence at $\sim 80\text{ K}$ and shows a saturation below $\sim 40\text{ K}$ with decreasing temperature. This implies that the region below $\sim 40\text{ K}$ is impurity-dominant and the electronic mean free path $l$ should be $T$-independent. The electronic specific heat $C_e$ is expressed by $y T$ with $y = 25 \text{ mJ\text{-K}^{-2}\text{-mol}^{-1}}$ from the lowest temperature to at least $\sim 10\text{ K}$, or even higher, according to a literature on the specific heat of the $x = 1$ specimen.\(^{19}\) Since $\kappa$ is expressed by $1/2 C_{\text{eff}} v_F l$ from the kinetic theory, where $v_F$ is the Fermi velocity, we can expect that $\kappa$ is proportional to $T$. In fact, in Figs. 2(a) and 2(b), the thermal conductivity rises linearly.
with temperature from ~4 to ~20 K. We may therefore consider that this is a behavior characteristic of the electronic conduction at low temperatures. However, we know that even in insulating samples (DMe-DCNQI)$_2$Li$_{1-x}$Cu$_x$ ($0 \leq x \leq 0.14$), $\kappa$ also rises linearly with a steeper slope. We cannot rule out the possibility that this linearly rising regime does not include the phononic contribution part.

(ii) Secondly, we notice in Figs. 2(a) and 2(b) that as far as the cooling curve is concerned, $\kappa$ of the $x = 1$ sample is larger than that of the $x = 0.75$ one in the entire temperature range. The same feature is observed in the heating curve as well. An uncertainty in the thermal conductivity is mainly caused by the uncertainty in the determination of the sample dimension. We are thus unable to claim that thermal conductivity is decisively proportional to the Cu concentration $x$ even at low temperatures. However, $\kappa$ of the $x = 1$ specimen appears to be larger because this is consistent with the experimental fact that the electrical resistivity of the $x = 1$ sample is lower than that of the $x = 0.75$ one. A metal that has better electrical conductivity also has better thermal conductivity. This observation strongly suggests that electrons significantly contribute to the thermal transport.

(iii) Thirdly, in order to check the degree of electronic contribution, we apply the Wiedemann–Franz (WF) law:

$$\kappa_e = \frac{L_0\sigma T}{\rho},$$

where $\sigma$ is the electric conductivity, and $L_0 = 2.45 \times 10^{-8}$ $\Omega$-$\text{W}$-$\text{K}^{-2}$ is the Lorenz number. Using the experimental data on $\rho$, we estimate the values of $\kappa_e$ from eq. (1). Then, we have to also take into account the phononic contribution $\kappa_{ph}$. In our previous measurements, the insulating samples (DMe-DCNQI)$_2$Li$_{1-x}$Cu$_x$ ($0 \leq x \leq 0.14$) show only a phononic contribution. The material structure of our $x = 1$ and $0.75$ samples is the same as that of insulating $0 \leq x \leq 0.14$ ones. In $x = 1$ and $0.75$ samples, neither do we consider the phononic contribution to be negligible nor do we know how significant the contribution of a phonon is. In including $\kappa_{ph}$, we employed the experimental $\kappa$ of the insulating sample $x = 0.14$; namely, we have tentatively varied the experimental $\kappa$ of the $x = 0.14$ sample from 0 to 100%, such that $\kappa_{ph} = k \times \kappa$ ($x = 0.14$) ($0 \leq k \leq 1$). Then, we add $\kappa_{ph}$ and $\kappa_{cal}$ calculated from eq. (1) as follows:

$$\kappa_{cal} = \kappa_{ph} + \kappa_{cal}.$$  

In this manner, the calculated conductivity $\kappa_{cal}$ is obtained. In Figs. 3(a) and 3(b), $\kappa_{cal}$ with $k = 50\%$ is plotted together with the experimental $\kappa$ values of the cooling curve.

We notice from Fig. 3(a) that for the $x = 1$ specimen, the shape of the calculated $\kappa_{cal}$ curve resembles that of the experimental $\kappa$ curve below ~80 K and that the absolute values of $\kappa_{cal}$ are ~2.2 times larger than the experimentally observed $\kappa$. The $\kappa$ curve reveals a peak at ~40 K, followed by a rapid decrease with decreasing temperature. This experimental feature is well reproduced in the curve of $\kappa_{cal}$. It is also clear from Fig. 3(b) that the experimental feature that the $\kappa$ values of the $x = 0.75$ sample show a broad peak at ~60 K followed by a rapid decrease with decreasing temperature is reproducible in the curve of $\kappa_{cal}$. We are thus convinced that at temperatures below ~80 K, the thermal conduction should be well described by the WF law for both the samples. In fact, we can expect that the WF law adequately holds at low temperatures below ~80 K because the experimental $\sigma$ lies in the impurity-dominant and $T$-independent region, and the experimental $\kappa$ shows a $T$-linear dependence at least up to 20 K. When further increasing $T$, however, we are out of the region where the WF law is valid because the small angle electron scattering due to phonons, which does not affect the charge current but affects the heat current, becomes dominant. Hence, $L_0$ decreases and the peak appears in the heat conduction. A disagreement in the absolute value between the experimental $\kappa$ and the WF value is not important; rather, it is very important that the experimental peak position is well explained by the WF calculation. Even if we reduce the phononic component from 100% ($k = 1$) to 0% ($k = 0$), the peak position can still be reproduced by the WF calculation. We should note here that with an increase in $x$ from $x = 0$ to $x = 1$, the phononic contribution to $\kappa$ may decrease; this is because when Li atoms are replaced by Cu ones, the difficulty in the vibration of phonons is enhanced due to an increase in the mass. From the above mentioned discussions (i)–(iii), it is evident that the thermal conduction of the $x = 1$ and 0.75 samples includes the electronic contribution to a considerable degree.

5. Discussion (II)

It is highly unlikely that the M–I transition occurred in both the cooling and heating processes. The reasons are summarized as follows: (i) If the M–I transition line was
and heating curves in the $x = 0.75$ sample is smaller than that in the $x = 1$ sample is also understandable. It is known that the metallic state becomes stable with an increase in the Li substitution; hence, the excess conductivity in the cooling runs should be smaller in the $x = 0.75$ specimen. Therefore, we assert that a difference between the metallic state and the mixed state of the metallic phase and insulating islands is responsible for the temperature hysteresis.

Formerly, we have considered the metallic phase as a metallic state without insulators from the experimental results of electric conductivity, based on which the phase diagram shown in Fig. 1 was constructed. However, the hysteresis that has appeared in this study suggests that the region specified as "metallic phase" in Fig. 1 may contain insulating islands depending on the thermal history. The "metallic phase" is not as "metallic" as we have considered. If the metallic region is more than 19% in the mixed state of the metal and insulator, the percolation theory indicates that all metallic islands are connected from one end of the sample to the other. In the case that the metallic fraction is much larger, as in our case, we cannot expect to see any difference in the electrical resistivity between the metallic and the mixed states. The islands cannot be detected by the electrical conductivity. In fact, no thermal hysteresis has been reported in electrical resistivity measurements. Electrical resistivity is insensitive.

We should mention here that the temperature of $\approx 40$ K, at which the hysteretic behavior begins, corresponds to the temperature at which the M–I transition curve approaches most closely to the ordinate in Fig. 1. In the literature, the pressure needed for the M–I transition to take place at $\approx 40$ K is much less than $\approx 100$ bar; thus, the system could be transformed to the insulating phase more easily. Our scenario for hysteresis to appear is valid in this case as well. Furthermore, whether the temperature of $\approx 40$ K is passed or not seems to be important in determining which curve—cooking or heating curve—is selected. When we cooled the $x = 0.75$ sample from room temperature, after reaching $\approx 19$ K, we heated it to $\approx 70$ K and subsequently to $\approx 142$ K instead of further cooling. At both the temperatures, the $\kappa$ values were on the heating curve.

It is difficult to estimate the volume fraction of the insulating island with respect to the bulk volume because we do not know the exact respective composition of the contributions due to electrons and phonons. If the fraction of insulating islands in the metallic phase is sufficiently large, it may be possible that the hysteresis manifests in the magnetic susceptibility ($\chi$) measurement. In fact, a hysteresis in the susceptibility measurement has been reported in a literature, but the temperature region where the hysteresis appears is different from what we expect. We also measured $\chi$ of the $x = 1$ specimen in the cooling and heating runs. The specimen employed for the susceptibility measurement, which is not the same as that used for the thermal conduction experiment, has a weight of 1.786 mg. In the susceptibility measurement, about 10 needle-shaped specimens are set vertically such that an externally applied magnetic field of 1 T is parallel to the $c$ axis. They are all packed into a glass tube and are closed with glass wool caps so that all the specimens are designed to be stressed as much as possible. The experiment was performed by using an MPMS SQUID.

Table I. Symbols $\bigcirc$ and $\times$ show that the insulating islands are present and absent in the metallic phase, respectively.

<table>
<thead>
<tr>
<th>Temperature range</th>
<th>Cooling run</th>
<th>Heating run</th>
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<tr>
<td>$T \geq 40$ K</td>
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<td>$T \leq 40$ K</td>
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magnetometer supplied by Quantum Design, Inc. However, we could not observe any appreciable difference between both the curves. Assuming that the sample is sufficiently stressed in the same manner as the thermal transport experiment, this result suggests that the insulating islands in the metallic phase should be very small.

6. Conclusion

We have measured the thermal conductivity of \((\text{DMe-D}CNQI)_{2}\text{Li}_{1-x}\text{Cu}_{x}\) \((x = 1 \text{ and } 0.75)\) over a wide range of temperatures. The electron contribution is appreciable especially below \(\sim 80\) K. A hysteresis was seen above \(\sim 40\) K and is accounted for by the fact that the system remains in the metallic state when the sample is cooled to \(\sim 40\) K, while it partially contains the insulating phase when heated from the lowest temperature through \(\sim 40\) K to room temperature. This insulating region remains as islands in the metal phase even at high temperatures. The hysteresis that we have observed is not a trivial hysteresis accompanied by the first order M–I transition. The volume fraction of the insulating islands must be small such that we cannot detect it in the electric conductivity and magnetic susceptibility measurements. We have shown that heat transport is very sensitive to the difference in the two phases. Further study is in progress to detect the insulating islands by means of other measuring methods.

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