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Thermal conductivity of $(\text{DMe-DCNQI})_2\text{Li}_{1-x}\text{Cu}_x$ $(0 \leqslant x \leqslant 0.14)$: Phonon propagation and the spin-Peierls lattice distortion

Kiyoshi Torizuka,[1,*] Hiroyuki Tajima,[1] and Takashi Yamamoto[2]
[1]*Institute for Solid State Physics, University of Tokyo, 5-1-5, Kashiwa-no-ha, Kashiwa, 277-8581, Japan*
[2]*Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan*

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We have measured the thermal conductivity of organic molecular crystals $(\text{DMe-DCNQI})_2\text{Li}_{1-x}\text{Cu}_x$ $(0 \leqslant x \leqslant 0.14)$ over a wide temperature range between 4 and 250 K. We observed the phonon contribution in the whole range measured. A phonon peak was observed near ~20 K. This peak denotes a crossover between the phonon mean free path that diverges as T^{-2} and the phonon specific heat that decreases as T^3. The peak height decreases with the reduction of Cu concentration x and vanishes in the $x=0$ sample. We discuss this behavior in terms of the spin-Peierls local lattice distortion.

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Organic molecular conductors have recently attracted the interest of many researchers in condensed matter physics because they are good objects to investigate the strongly correlated electron system. Among them, the $\frac{1}{4}$-filled π-electronic system $(\text{DMe-DCNQI})_2\text{Li}$ (lithium salt with 2,5-dimethyl-dicynoquinone-diimine)[1–3] is very interesting, which shows a variety of electronic states. Upon decreasing temperature, the paramagnetic dimer state is formed near room temperature due to the Peierls transition, followed by the creation of singlet tetramers through the spin Peierls transition at $T_{\text{SP}} \sim 65$ K. When decreasing the temperature through T_{SP}, the itinerant component of the magnetic susceptibility decreases drastically and finally vanishes.[4,5]

Both the Peierls and the spin Peierls states are not so simple. The Peierls state is considered to be a mixed state of the dimer and the charge disproportionation. The charge disproportionate state is the one where electrons localize on alternating sites without dimerization. Besides the on-site Coulomb repulsion, if the nearest-neighbor Coulomb interaction is strong enough, the charge disproportionate state is favored.[6] Below T_{SP}, tetramers are formed and the lattice distortion really takes place. Among these tetramers, dimer-type solitons are created, because the unsuccessful tetramerization involved with four DCNQI molecules produces isolated dimers with spins, which behave as spin solitons.[7,8]

So far considerable efforts have been devoted to a problem concerning what is microscopically happening below T_{SP}. We employed the technique of thermal conductivity measurements, in which the phonon can be used as a probe to extract informations. Thermal conductivity measurements have played an important role in condensed matter physics; for instance, the magnon transport has been demonstrated in the low-dimensional quantum spin ladder system $\text{Sr}_{14-x}A_x\text{Cu}_{24}\text{O}_{41}$ $(A=\text{Ca},\text{La})$[9] and one-dimensional spin Peierls inorganic compound CuGeO_3.[10] However, the thermal transport measuring technique has little been used in organic samples with some exceptions. The superconducting gap structure and the superconducting properties were studied in κ-$(\text{BEDT-TTF})_2\text{Cu(NCS)}_2$,[11,12] $(\text{TMTSF})_2\text{ClO}_4$,[13] and so on.[14,15] We have measured the thermal transport of $(\text{DMe-DCNQI})_2\text{Li}_{1-x}\text{Cu}_x$ $(0 \leqslant x \leqslant 0.14)$ over a wide temperature range between 4 and 250 K. In the small doping regime $(0 \leqslant x \leqslant 0.14)$, $(\text{DMe-DCNQI})_2\text{Li}_{1-x}\text{Cu}_x$ is placed into the same category as $(\text{DMe-DCNQI})_2\text{Li}$.[16] In this report, we demonstrate that for the propagation of phonons, the breakdown of the local lattice uniformity due to the spin Peierls lattice distortion may be an obstacle. Similar phenomena have been reported; in the perovskite manganite, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, the modification of the local structure due to the static distortions of the MnO_6 octahedra is responsible for the strong phonon scattering.[17]

The typical dimension of our samples is $0.1 \times 0.1 \times 1\ \text{mm}^3$, and all specimens used are single crystals. Measurements were made along the c axis, which is the longest direction. The c axis is the quasi-one-dimensional chain direction and also the stacking direction of DCNQI molecules. The measurements along other directions are impossible. The experiment of thermal transport in organic materials is, in general, very difficult, since organic samples are fragile and the size of crystals is very small. In the conventional technique, the heat conduction through the sample had been considered to be large enough compared with the heat conduction through the electrical leads for heaters and thermometers, and 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 electrical leads.

We have developed a new technique to measure the thermal transport; two heaters and three thermometers are installed unlike the conventional technique. In our technique, we apply a heat pulse twice. By first application of the heat $\dot{Q}$, the heat flows both through the sample and through the leads, i.e.,

$$\dot{Q} = \Delta T \kappa_1 + \Delta T_0 \kappa_2, \tag{1}$$

where κ_1 and κ_2 are thermal conductivities of the sample and the leads, respectively, and ΔT and ΔT_0 are temperature differences across the sample and across the leads, respectively. Then we excite the subheater that is installed on a copper stage to which all electrical leads are thermally anchored, and thus we change the stage temperature slightly

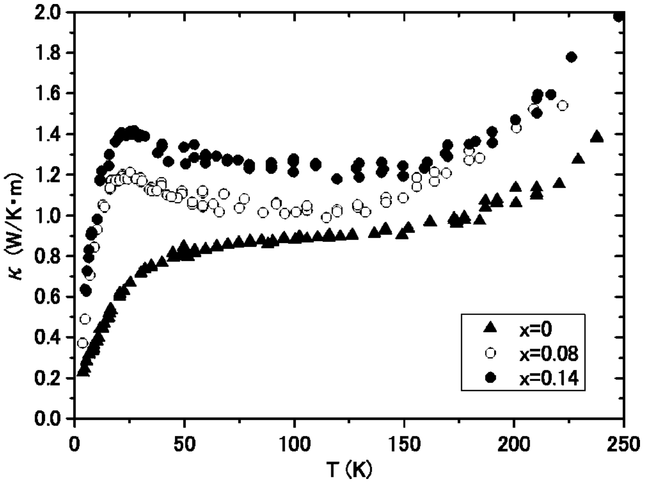

FIG. 1. The thermal conductivity vs. temperature of the $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Li}_{1-x}\mathrm{Cu}_x$ $(0 \leqslant x \leqslant 0.14)$.

$(\leqslant 0.8\ \mathrm{K})$. Under this condition, we apply second heat $\dot{Q}$, which again flows both through the sample and through the leads:

$$\dot{Q} = \Delta T' \kappa_1 + \Delta T_0' \kappa_2, \tag{2}$$

where $\Delta T'$ and $\Delta T_0'$ are temperature differences across the sample and across the leads, respectively. By solving Eqs. (1) and (2), we can obtain the thermal conductivity κ_1 of the sample. The details of our apparatus have been described elsewhere.[18]

The temperature (T) dependences of the thermal conductivity (κ) of $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Li}_{1-x}\mathrm{Cu}_x$ $(x=0,0.08,0.14)$ are depicted in Fig. 1. The absolute values of κ include the experimental error within ±10%, because the size of samples is so small that it is very difficult to estimate the effective cross section and the effective length of heat flow channel accurately. However, the shape of these three curves in Fig. 1 is not influenced seriously. The experimental data on the electrical resistivity have already been published.[16] Employing them and using the Wiedemann-Franz law, the electronic contribution to the thermal conduction is so small that what we see in Fig. 1 is the phonon contribution. A peak can be seen at ~20 K in samples $x=0.08$ and $x=0.14$. If the peak height had decreased with increasing impurity concentration, our experimental results would be trivial, because the phonon scattering with impurities naturally increases with the concentration. However, the peak height actually decreases with the reduction of x, and the peak completely vanishes in the sample $x=0$. That is why our experimental results are interesting. A small thermal hysteresis in κ between heating and cooling runs was observed around ~50 K in the sample $x=0.14$, which we do not show explicitly in the figure.

To analyze our data, we evaluate the phonon mean free path l based on the Debye theory. Experimental data on the specific heat C of $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Li}$ has already been published in the literature.[19] We can estimate the Debye temperature Θ_D to be ~91 K, using their low temperature $(T < 10\ \mathrm{K})$ specific heat data which show $C \propto T^3$. Furthermore, the phonon velocity v can be evaluated to be $\sim 2340\ \mathrm{m\,s^{-1}}$. Since the heat conduction is expressed by $\kappa = \frac{1}{3} C v l$ from the kinetic theory, we can obtain the temperature dependence of l, employing the published data on C and the estimated value v. In this way, the mean free paths are plotted in Figs. 2(a)–2(c). Since the experimental data on C of $x=0.08$ and $x=0.14$ samples are not available, we employed only the data on C of the $x=0$ specimen. This is justified by following two reasons. (i) The experimental specific heats of $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Li}$ $(x=0)$ and of $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Cu}$ $(x=1)$ below 35 K are available in literatures.[19,20] We notice that the specific heat of the $x=1$ sample is the same as that of $x=0$ sample, at least below 30 K. We do not think that the specific heats of the $x=0.08$ and $x=0.14$ samples are extremely different from those of the $x=0$ and $x=1$ samples. (ii) The lattice heat capacities of $(\mathrm{DI\text{-}DCNQI})_2\mathrm{Cu}$ and $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Cu}$ are $\beta = 4.12\ \mathrm{mJ\,(K^4\,mol)^{-1}}$ and $3.4\ \mathrm{mJ\,(K^4\,mol)^{-1}}$,[21,22] respectively. Both values are very close each other. In addition, the lattice heat capacities of some deuterated $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Cu}$ materials are tabulated in the literature[22] and have a similar value. Even insulating materials have almost the same β as that of undeuterated metallic $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Cu}$. These experimental facts indicate that all $(\mathrm{R_1,R_2\text{-}DCNQI})_2\mathrm{Y}$ families have the same lattice contribution.

In Figs. 2(a)–2(c), we notice that l is a smooth function of temperature even at ~20 K in all specimens. Then we have to note that in all three samples, l continues to increase with decreasing temperature. This implies that the mean free paths of samples have not reached to a limited value that is determined by impurities. If we were in the region of the impurity-determined mean free path, l should have been temperature independent. In addition, we also have to note that all samples have the same temperature dependence of the mean free path: $l \propto T^{-2}$. This fact strongly suggests that the phonon scattering mechanism is the same in all samples. The deviation from this dependence can be seen below ~10 K. But this deviation is not important in our context.

Let us first discuss the behavior of the thermal transport in high temperature regime. At temperatures $T \geqslant 150\ \mathrm{K}$, the phonon mean free paths of these three samples clearly reach to a constant ~15 Å, which is on the same order of the intermolecular separation. The experimental specific heat C increases in this temperature regime and thus κ also increases almost in proportion to T. In the intermediate region $(50\ \mathrm{K} \leqslant T \leqslant 120\ \mathrm{K})$, we can clearly see $l \propto T^{-1}$, which is typical behavior for phonons in the temperature region where the phonon-phonon interaction dominates.

Next we discuss the origin of the peak observed at ~20 K in samples of $x=0.08$ and $x=0.14$. Basically what we have to find as the origin of the peak is what increases with increasing Cu concentration. At first sight, this peak might be caused by the soliton transport, because the higher the concentration x is, the more the solitons are created. However, the possibility of the soliton transport is ruled out by following two reasons. (i) The soliton motion is diffusive with a unit hopping length $l_s \sim 4$ Å along the c axis at low temperatures. If the solitons could contribute to the thermal transport,

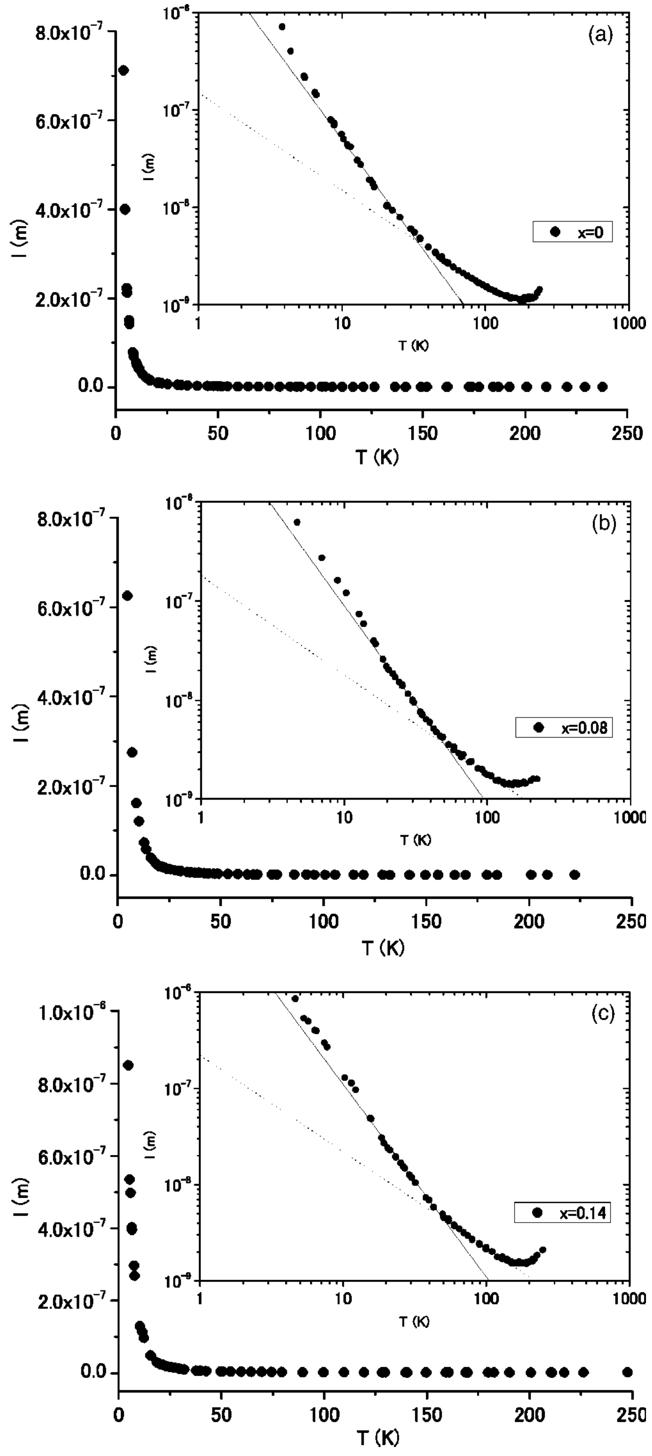

FIG. 2. The phonon mean free path vs. temperature for (a) $x=0$, (b) $x=0.08$, and (c) $x=0.14$ samples. In insets, solid and dotted lines show T^{-2} and T^{-1}, respectively.

the thermal conductivity due to solitons could be expressed by $\kappa_s = DC_s$ (D=soliton diffusion coefficient, C_s=soliton specific heat). Using the experimental data on the diffusion rate $D_\parallel$ along the c axis,[7] D is given to be $D \sim D_\parallel l_s^2 \sim 10^{10} \times (4\times 10^{-10})^2 \approx 1.6\times 10^{-9}$ m^2 s^{-1}. Furthermore, since the experimentally observed C of (DMe-DCNQI)$_2$Li shows $C \propto T^3$ at temperatures lower than $\sim$20 K, we are right in thinking that the specific heat at $\sim$20 K is due to phonons. Hence C_s might be buried in the experimental error. If the error is 5%, C_s is estimated to be 1 J (K mol)$^{-1}$=3.7×10^3 J (K m^3)$^{-1}$. Therefore we obtain $\kappa_s = (1.6\times 10^{-9}) \times (3.7\times 10^3) \approx 5\times 10^{-6}$ W (K m)$^{-1}$, which is much smaller than experimentally observed thermal conductivity near $\sim$20 K. (*ii*) If the solitons with spins were carriers of heat, they should have been influenced by the strong magnetic field. When we applied the field up to 15 T perpendicular to the c axis in the $x=0.08$ sample, no change in κ was observed.

Then the thermal channel due to the Cu^{2+} spin system might be a candidate for the extra heat conduction near $\sim$20 K. The Cu^{2+} spin system is a well-localized one, and no magnetic ordering has been detected experimentally for these specimens ($0 \leqslant x \leqslant 0.14$) at low temperatures. Above the ordering temperature, the system does not have a specific heat, because the entropy of the system is a constant $Nk_B \ln 2$ (N=number of molecules, k_B=Boltzmann constant). Therefore it is unlikely that the Cu^{2+} spin system has the contribution to the extra thermal transport.

As the most possible origin for the peak near $\sim$20 K, we will point out a crossover effect. First, at the high temperature side of the peak just above $\sim$20 K, we have obtained the relation $l \propto T^{-2}$ by the calculation that employed both the experimental values of κ in the temperature range just above $\sim$20 K and the experimental values of C in the temperature range just above $\sim$20 K. [See Figs. 2(a)–2(c).] We emphasize here that in this temperature range ($T \geqslant 20$ K), we cannot see relations of $\kappa \propto T$ nor of $C \propto T^3$, but nevertheless we have obtained $l \propto T^{-2}$ for all three samples. If both relations of $\kappa \propto T$ and of $C \propto T^3$ were seen experimentally, the relation $l \propto T^{-2}$ would be apparent and trivial. Next at the low temperature side of the peak below $\sim$20 K, we are allowed to expect that the relation $l \propto T^{-2}$ continues even to low temperatures below $\sim$20 K. In fact this is true, because as revealed in Figs. 2(a)–2(c), we can see the relation $l \propto T^{-2}$ at temperatures down to $\sim$10 K. Since the experimental low temperature specific heat of (DMe-DCNQI)$_2$Li is now $C \propto T^3$ at temperatures below $\sim$20 K, the thermal conductivity should be $\kappa \propto T$. Actually the relation $\kappa \propto T$ is appreciable at approximately $\sim$10 K for all samples shown in Fig. 1. Accordingly, the relation $\kappa \propto T$ observed experimentally at the low temperature side of the peak is consistent with the relation $l \propto T^{-2}$ evaluated at the high temperature side of the peak. This fact strongly suggests that the peak is created by the crossover between the mean free path that diverges as T^{-2} as decreasing temperature and the specific heat that vanishes as T^3 as lowering temperature.

According to the theory on the phonon scattering,[23] the relation $l \propto T^{-2}$ is equivalent to the fact that the scattering probability of phonons is proportional to ω^2: $1/\tau \propto \omega^2$, where ω and τ are the frequency and the lifetime of phonons, respectively. In addition, it is believed that this relation occurs when the scatterers are sheetlike faults in a crystal. Then the problem we have to address is what is the phonon scattering mechanism that brings to $1/\tau \propto \omega^2$.

To solve the problem mentioned above, we propose the following scenario. Among these three samples, the lattice distortion due to the spin Peierls state may be the largest in the $x=0$ sample. We guess that with increasing Cu concentration x, the spin Peierls lattice distortion may decrease and, rather, the charge disproportionate state may increase. The phonon wavelength at ∼20 K is estimated to be ∼15 Å, as long as we employ the dominant phonon approximation in which the dominant phonons are those that are most dominant in the phonon specific heat. For the propagation of phonons with this wavelength, the local breakdown of the lattice uniformity due to the spin Peierls lattice distortion may be a serious obstacle. Therefore the phonon propagation may be significantly affected in the $x=0$ sample. It may be possible that the nonuniformity of the lattice is considered to be the sheetlike fault.

One of authors (T.Y.)[24] measured the infrared reflectance spectra of these materials. In the spectra he observed the e-mv mode, which indicates the existence of the lattice distortion in the sample. The intensity of the e-mv mode decreased with increasing x. These observations suggest the spin Peierls lattice distortion decreases with increasing x. Our proposal is consistent with his observations.

In summary, we have measured the thermal conductivity of $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Li}_{1-x}\mathrm{Cu}_x$ ($x=0$, 0.08, and 0.14) over a wide temperature range. We have found a phonon peak near ∼20 K. The peak height decreases with decreasing Cu concentration x and vanishes in the $x=0$ sample. This peak indicates the crossover between the phonon mean free path that diverges as T^{-2} and the phonon specific heat that decreases as T^3 when $T \to 0$. We have proposed the phonon scattering mechanism that the spin Peierls lattice distortion may seriously suppress the phonon propagation. The effect of the spin Peierls lattice distortion on the phonon propagation has been discussed for the first time.

We have measured the thermal conductivity of $x=1$ and $x=0.75$ samples as well, which are metals and are classified into a different class from samples of $0 \leqslant x \leqslant 0.14$. Experimental results will be published later.

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*Part-time Lecturer of Kanagawa Institute of Technology, Shonan Institute of Technology, and Hosei University.

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