THE THERMAL CONDUCTIVITY OF ION-RADICAL SALTS OF TETRACYANQUINODIMETHANE

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Information has been gained on the details of the phonon spectrum of TCNQ salts and the participation of various groups of phonons in the transport of thermal energy from studies of the thermal conductivity.

At present great interest is being paid to studies of the ion-radical salts of tetracyanquinodimethane (TCNQ) as quasi-one-dimensional highly-conductive organic compounds (see refs. 1-3 for example). In the course of our studies of TCNQ salts [4-8] we have studied their thermal conductivities in order to gain information on the details of the phonon spectrum for these compounds and the participation of various groups of phonons in the transport of thermal energy. There is little data in the literature on the thermal conductivities of molecular crystals [9-11] and it largely refers to crystals of simple organic compounds. The salts of TCNQ are of a more complex structure and the study of their thermal conductivities will give more complete understanding of the mechanisms of energy transport in molecular crystals.

We have investigated tetracyanquinodimethane $TCNQ^0$ and its salts with alkali metals, the simple salts D^+TCNQ^- where D = Li, Na, K, and Cs and the complex salts $D_2^+(TCNQ)_3^{2-}$ where D = Rb, Cs. The investigations were carried out on polycrystalline samples made by pressing at $5 \cdot 10^3$ kg/cm^2.

The thermal conductivity $\varkappa$ was measured by an absolute stationary method between 80 and 420°K. At the same time we measured the electrical conductivity σ and the thermal e.m.f. α. To decrease the fraction of the total thermal flux transported by radiation we used planar samples with a cross section of 0.4 to 0.5 cm^2 on a side and height 0.1 to 0.15 cm. The temperature drop was measured between silver plates which were attached to the sample (Fig. 1). To create good thermal contact between the sample and the silver plates to which the thermocouples were soldered at the heater and refrigerator we used indium spacers 0.2 to 0.3 mm thick. Indium is distinguished by a high plasticity and quite high electrical and thermal conductivities. After assembling and evacuating the apparatus it was heated to 145 to 148°C which is close to the melting point of indium (156°C) which ensured good thermal contact. Control experiments with thin samples of pure silicon, whose thermal conductivity is known [12], have shown that the thermal resistance at the contacts (0.037 ± 0.010 deg·cm^2/W) is small relative to the thermal resistance of our samples. The loss of heat by radiation from the exposed surfaces of the heater and also from the current-carrying leads and the thermocouples located at the heater was determined experimentally. The correction for the heat flow along the quartz rod which fastened the heater to the sample was negligible due to the geometry of the rod and the poor thermal contact it made with the heater. The measurements made allowed us to ensure measurement of the absolute value of $\varkappa$ between 150 and 420°K with a precision no worse than ±5%. Below 150°K we sometimes observed a drop in $\varkappa$ of no more than 15%, evidently connected with the formation of small cracks in the samples at low temperatures.

The scatter of the data on the thermal conductivity and thermal e.m.f. for samples prepared under different pressing conditions (in vacuum, in air, at different temperatures) does not exceed ±10%. From this we can conclude that the intercrystalline thermal resistance has no substantial effect on the measured thermal conductivity.

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TABLE 1. Values of $\varkappa$, α, and σ for the Samples Studied

Material	Initial state	$\varkappa\cdot10^3$, W/cm deg	α, µV/deg	σ, ohm^{-1}cm^{-1}
TCNQ°	Powder	2,0	—	—
$Li^+(TCNQ)^-$	The same	2,7	−970	$3,9\cdot10^{-5}$
$Na^+(TCNQ)^-$	"	6,3	−40	$1,8\cdot10^{-5}$
$K^+(TCNQ)^-$	"	4,4	+900	$1,1\cdot10^{-6}$
$Cs^+(TCNQ)^-$	"	4,0	+570	$1\cdot10^{-4}$
$Rb_2^+(TCNQ)_3^{2-}$	"	1,5	−620	$3,3\cdot10^{-6}$
$Cs_2^+(TCNQ)_3^{2-}$	"	2,1	−580	$9,5\cdot10^{-5}$
$Cs_2^+(TCNQ)_3^{2-}$	Crystals	0,5–0,7	−615	$2\cdot10^{-5}$

Table 1 gives values of $\varkappa$, α, and σ for the samples studied at 300°K. It can be seen that the thermal conductivities of all of the material are extremely low. For $Cs_2^+(TCNQ)_3^{2-}$ we observed a difference in $\varkappa$ for two kinds of sample; samples pressed from fine needle-shaped crystals had a lower value of $\varkappa$ (0.5 to $0.7\cdot10^{-3}$ W/cm deg) than samples pressed from a finely-dispersed powder produced by pulverizing these crystals ($2.1\cdot10^{-3}$ W/cm deg). This difference may be related to the fact that crystals of TCNQ salts are quite anisotropic in structure and properties [1, 6]. In the preparation of the samples, the needle-shaped crystals were oriented predominantly perpendicular to the pressure and the samples also turned out to be anisotropic to some degree. Therefore we might suppose that the difference in $\varkappa$ for two kinds of sample indicates anisotropy of the thermal conductivity of the $Cs_2^+(TCNQ)_3^{2-}$ crystals in which $\varkappa_{max}$ should be observed along the needle-shaped crystals, i.e., in the direction of the $TCNQ^-$ bundles.

Figure 2 shows the temperature dependence of $\varkappa$ for the compounds of interest. Attention is called to the very weak temperature dependence of $\varkappa$ over a broad temperature range above 100 to 150°K. With T < 100 to 150°K this dependence becomes stronger and for Na^+, K^+ and Cs^+ salts of $TCNQ^-$ it approaches $\varkappa \sim T^{-1}$. An exception is Li^+TCNQ^-, whose thermal conductivity grows with temperature.

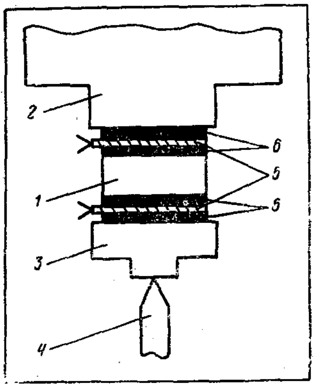

Fig. 1

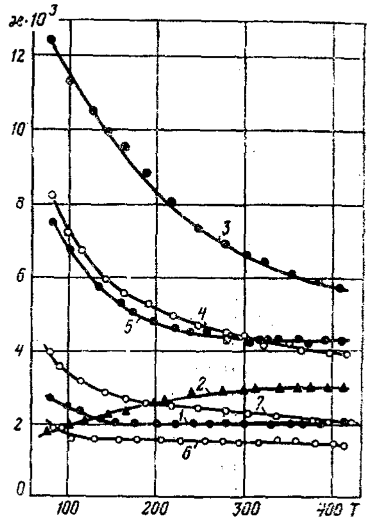

Fig. 2

Fig. 1. Operating scheme for part of the apparatus: 1) sample; 2) refrigerator; 3) planar heater; 4) quartz rod; 5) silver plate; 6) indium spacers.

Fig. 2. Temperature dependence of the thermal conductivity. 1) TCNQ°; 2) Li^+TCNQ^-; 3) Na^+TCNQ^-; 4) K^+TCNQ^-; 5) Cs^+TCNQ^-; 6) $Rb_2^+(TCNQ)_3^{2-}$; 7) $Cs_2^+(TCNQ)_3^{2-}$ $\cdot\varkappa$ is given in W/cm·deg and T is in °K.

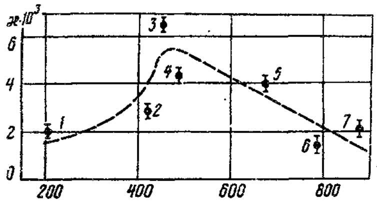

Fig. 3. Thermal conductivity as a function of the molecular weight* at 300°K; 1) $TCNQ^0$; 2) Li^+TCNQ^-; 3) Na^+TCNQ^-; 4) K^+TCNQ^-; 5) Cs^+TCNQ^-; 6) $Rb_2^+(TCNQ)_3^{2-}$; 7) $Cs_2^+(TCNQ)_3^{2-}$ $\cdot \varkappa$ W/cm·deg. The horizontal axis gives molecular weight.

Since the electrical conductivities of all the materials studied are small (see Table 1) the contribution of charge carriers to the thermal conductivity calculated from the Wiedemann–Franz ratio is small, and because of ambipolar diffusion it turns out to be insignificant. The transport of heat by phonons as shown previously [13] is also negligible. For none of the compounds, as we see from Fig. 2, can we observe the increase of $\varkappa$ with temperature above 300°K which has been discussed before [13] and which involves the transport of heat by excitons. Therefore we might suppose that the experimentally measured $\varkappa$ is the thermal conductivity $\varkappa_1$ of the crystal lattice over the whole temperature range studied.

The peculiar features of $\varkappa_1$ for $TCNQ^0$ and its salts can, in our opinion, arise from two circumstances. In the first place the unit cell of the crystal lattice contains a large number of atoms, of the order of 100 [14, 15]. The intermolecular interaction is substantially weaker. In the case of $TCNQ^0$ for example this is the Van der Waals force (with an intermolecular distance of 3.45 Å). Because of this the vibration spectrum divides into two parts.

The first, low-frequency, part of the spectrum is similar to the elastic translational vibrations in atomic crystals which propagate in the medium with the velocity of sound and have shortest wavelengths of the order of twice the lattice period. These vibrations apparently give the main contribution to the thermal conductivity for $T < 100$ to 150°K. Therefore the temperature dependence of $\varkappa_1$ for this interval in general repeats the analogous dependence for atomic crysals ($\varkappa_1 \sim T^{-1}$) with $T \geq \theta/3$ where θ is the Debye temperature. The low values of $\varkappa_1$ occur because the heat capacity due to translational vibrations amounts to only an insignificant part of the total heat capacity of the crystal, ~1/100. A similar explanation of the low value of $\varkappa_1$ was first put forth for sulfur by A. F. Ioffe [16].

The other part of the spectrum is the intramolecular vibrational and rotational motion of individual atoms and groups of atoms. The infrared spectra show [17] that in $TCNQ^0$ there are comparatively low-frequency vibrations of the group $C(CN)_2$ (100 to 400 cm^{-1}). Since these are intramolecular vibrations in the TCNQ salts they should persist with frequencies little changed. These vibrations are already excited to a significant degree at 100°K and can make an additional contribution to $\varkappa_1$ which evidently leads to the experimentally observed weak temperature dependence of $\varkappa_1$ between 100 and 150°K.

It is of interest to trace how the thermal conductivity varies in the series $TCNQ^0$, Li^+ salt, Na^+ salt, etc. up to $Cs_2^+(TCNQ)_3^{2-}$. Figure 3 shows the dependence of $\varkappa_1$ at 300°K on the molecular weight for this series of compounds. It can be seen that in going from $TCNQ^0$ to the Li^+ salt and Na^+TCNQ^-, $\varkappa_1$ increases. This increase may involve a change in the intermolecular interaction. Actually in $TCNQ^0$ the interaction forces between molecules are weaker than Van der Waals forces while in the salts they are stiffened by the Coulomb and exchange interactions. The decrease of $\varkappa_1$ in going to the following salt may be due on the one hand to an increase in the molecular weight (as is observed in atomic crystals [18]) or on the other hand to a weakening of the Coulomb interaction in complex layers.

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*In calculating the molecular weights of the simple salts we used the formula $D_2^+(TCNQ)_2^{2-}$.

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