Thermoelectric power and thermal conductivity of first-stage graphite-acceptor intercalation compounds

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Measurements performed on the in-plane thermoelectric power of first-stage graphite-acceptor intercalation compounds in the temperature range $3 < T < 300$ K are reported. At high temperature, the thermoelectric power is close to that obtained for higher-stage compounds while in the lower-temperature range it drops rapidly to a negligibly small value. These low-temperature results suggest that defect scattering in first-stage compounds is qualitatively different from that of higher stages. The temperature dependence of the in-plane thermal conductivity is also reported.

Since the pioneering work of Blackman, Mathews, and Ubbelhode[1] followed by that of Ubbelohde,[2] a few reports have recently been published on the temperature dependence of the in-plane[3-12] and, to a lesser extent, c-axis[13-15] thermoelectric power of graphite intercalation compounds (GIC's). Some of them were measured with highly oriented pyrolitic graphite[1-9] (HOPG) as host material and others with graphitic fibers.[10-12] The main data pertain to acceptor compounds, though two donor compounds have also been investigated.[6,9] Oddly enough, if we except the fact that, as expected, donors have negative thermopowers and acceptors have positive ones, the temperature dependence was almost the same for all samples investigated and the magnitudes of the thermopowers were not too different for the lower-stage compounds. The in-plane thermopower was found to be a linear function of the temperature in the lowest-temperature range, then to increase monotonically with increasing temperature to reach a plateau (or a broad maximum) around 200 K. The value of the thermopower at the plateau (or broad maximum) was found to be almost stage and intercalate independent, except for dilute compounds.[7] All the published data on acceptor compounds were relative to stages higher than stage 1. It was soon pointed out that it would be hard to explain the magnitude of the high-temperature thermopower and the presence of a plateau in terms of a diffusion mechanism.[16,17] Also, the presence of more than one band for the charge carriers for stages ≥ 2 compounds complicates to a great extent the interpretation of the thermopower results, as will be shown below.

This has prompted us to investigate the thermopower of first-stage compounds, where there is a single-hole band, in parallel with their thermal conductivities. Since a simple model for the band structure of first-stage acceptor compounds is available [Blinowski-Rigaux (BR) model[18]], we have concentrated on p-type compounds. It will be shown that, contrary to higher-stage compounds, the low-temperature thermopower of first-stage compounds drops rapidly to negligibly small values. At higher tem-

peratures instead, the behavior is not qualitatively different from what is observed for higher stages.

In nonmagnetic materials, there are essentially two mechanisms for thermopower generation. The first, which is called the *diffusion thermopower* is due to the spontaneous diffusion of the charge carriers from hot to cold caused by the redistribution of the carrier energies around the Fermi energy due to the temperature gradient. Charge carriers tend to pile up at the low-temperature end of the sample giving rise to an electric field which tends to counterbalance the stream of diffusing carriers until a steady state is reached. Then the resulting current is zero all along the sample (open circuit conditions). Though the exact physics of the process is not obvious at all, since it requires a subtle knowledge of the scattering behavior of the charge carriers, the origin of the diffusion is straightforward.

The other mechanism, which gives rise to the *phonon-drag thermopower,* involves a transfer of momentum from the phonon system. Indeed, in a thermopower measurement, because of the temperature gradient, the phonon system is not in equilibrium. There are more phonons created at the hot end than at the cold one and thus phonons diffuse from hot to cold generating the lattice thermal conductivity. If there is a coupling between the charge-carrier system and the phonon system, under certain conditions the phonon system may impart some of its momentum to the charge-carrier system. This will cause, in addition to diffusion, an extra drift of the charge carriers from hot to cold, which will require an extra electromotive force to counterbalance it. The resulting voltage per unit temperature difference is the so-called phonon-drag thermopower.

The total thermopower S is given by

$$S = S_d + S_g, \qquad (1)$$

where S_d and S_g refer, respectively, to the diffusion and the phonon-drag contributions.

The above considerations concern the thermopower of a

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given group of charge carriers that we shall thus call the partial thermopower S_i, i denoting the group of carriers considered. Thus it applies for each of the identical valleys in the case of a stage-1 compound. However, because of symmetry, the valleys will have identical contributions to the total thermopower.

Considering the different groups of carriers, the total thermopower for GIC's of a stage higher than stage 1 is given by

$$S = \left(\sum_i \sigma_i S_i \right) / \left(\sum_i \sigma_i \right) \tag{2}$$

where σ_i is the electrical conductivity of the ith charge carriers. Expression (2) shows that each group of carriers having a partial thermopower S_i contributes to the total thermopower S as is the case for emf's acting in parallel.

Now, for each type of mechanism for thermal emf generation, each group of carriers may have two contributions opposite in sign, according to whether they experience normal or umklapp collisions.[19] This shows that considering more than one group of carriers is a formidable problem to tackle, and that it is essential in order to understand, even qualitatively, the physics of thermal emf generation in GIC's, to work first on a single group of carriers, i.e., on a first-stage acceptor compound.

The general expression for the diffusion thermopower is given by the Mott formula[19,20]

$$S_d = \frac{\pi^2 k_B^2}{3e} T \left[\frac{\partial \ln\sigma}{\partial \varepsilon} \right]_{\varepsilon_F} \tag{3}$$

where ε_F is the Fermi energy, T is the absolute temperature, and σ is the electrical conductivity.

For a stage-1 acceptor compound, using the Blinowski-Rigaux model,[18] and assuming a Fermi energy of 1 eV, we find (cf. Appendix)

$$S_d = 2.45 \times 10^{-8} T (1 + p) , \tag{4}$$

where S_d is expressed in V/K, p is the scattering parameter which determines the energy dependence of the relaxation time $\tau = \tau_0 \varepsilon^p$. As a result of the linear dispersion relations for the charge carriers, it is expected that $p = 0$ for boundary scattering.

For a stage-2 acceptor compound, taking a Fermi energy $\varepsilon_F = 0.8$ eV, we obtain for each of the hole bands, 1 and 2 (cf. Appendix), a partial diffusion thermopower (in V/K)

$$S_{d1} = 2.45 \times 10^{-8} T (1.1 + 1.25 p_1) ,$$
$$S_{d2} = 2.45 \times 10^{-8} T (2.0 + 2.38 p_2) . \tag{5}$$

Since there is growing evidence that scattering in the stage ≥ 2 compounds is mainly due to large-scale defects,[21−24] one may reasonably assume that $p_1 = p_2 = 0$ in the residual resistivity range and thus $S_{d1} = 2.7 \times 10^{-8} T$ and $S_{d2} = 4.9 \times 10^8 T$. Since under such assumptions it may be easily demonstrated, using the relations expressed in Appendix, that $\sigma_1 \cong 2\sigma_2$, we finally obtain, using relation (2),

$$S_d \cong 3.5 \times 10^{-8} T . \tag{6}$$

For all samples, we have used the same type of pristine

graphite, i.e., HOPG with a mosaic spread $< 1°$, supplied by Union Carbide. The samples were parallelepipeds ($10 \times 2 \times 0.5$ mm^3) with the smallest dimension parallel to the c axis. The intercalation of the chlorides was carried out through the direct action of $CdCl_2$ (Ref. 25) or $CuCl_2$ (Ref. 26) vapor in the presence of chlorine gas (pressure $\cong 800$ mm Hg). After introduction of the graphite into the reaction tube, the chloride was purified by double distillation, the first under vacuum and the second under an atmosphere of dry chlorine. The reactor tube was then sealed under a given pressure of chlorine gas and placed in two furnaces whose temperatures determined the stage of the final compound, in our case a stage 1. The compounds were identified by (001) x-ray reflections. The principal parameters are listen in Table I.

The thermopower and thermal-conductivity measurements were performed using a steady-state technique in the temperature range $3 < T < 300$ K. A differential Au(0.03 at.% Fe)-Chromel-p thermocouple was used to measure the temperature gradient along the specimen. The voltage probes (Chromel-p wires) were previously calibrated below 9 K using a superconducting Nb-Ti samples as reference zero thermopower material. Similar calibration was extended at higher temperatures using a 90-K superconductor Y-Ba-Cu-O ceramic. The generated thermal emf's were measured by means of a K-140 Keithley nanovoltmeter with a sensitivity of about 5×10^{-9} V.

The temperature variation, from 3 to 300 K, of the thermopower of first stages HOPG-$CuCl_2$ and HOPG-$CdCl_2$ samples is presented in Fig. 1. For both samples, the high-temperature thermopower follows the general trend described above: the thermopower increases monotonically as the temperature increases up to about 200 K, then becomes almost temperature insensitive in the temperature range $200 < T < 300$ K. At low temperature, the thermopower drops rapidly and, below 7 K, its value does not exceed 3×10^{-8} V/K, as shown in Fig. 2. For comparison, the low-temperature thermopower of stage-2 HOPG-$SbCl_5$ (Ref. 7) and BDF-$CuCl_2$ (Ref. 12) intercalation compounds are also presented.

If we assume a Fermi energy of 1 eV for a first-stage compound, the diffusion thermopower at 7 K should take a value around 2×10^{-7} V/K in the limit of boundary scattering [relation (4) with $p = 0$] while the experimental results show that it does not exceed 3×10^{-8} V/K showing clearly that the observed diffusion thermopower is negligibly small. In order to predict an almost zero thermopower as observed experimentally, the scattering parameter p in the relation (4) should be equal to -1. Since the electrical resistivity data show clearly that we are in the residual

TABLE I. Parameters for the synthesis of the stage-1 compounds; T_r is the temperature of reaction and I_c is the c axis repeat distance.

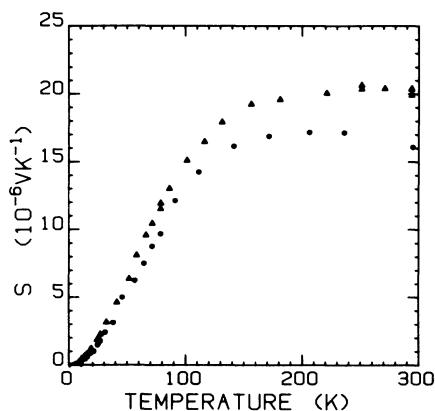| Compounds	T_r (°C)	Time (days)	I_c (Å)	Mosaic spread (deg)
HOPG-$CuCl_2$	430	30	9.39	4–5
HOPG-$CdCl_2$	510	35	9.58	4–5

FIG. 1. Temperature dependence of the in-plane thermopower of stage-1 HOPG-$CuCl_2$ (▲) and HOPG-$CdCl_2$ (●) intercalation compounds.

range at this temperature, this means that we should invoke a low-temperature defect scattering mechanism which is strengthened as the energy increases. This excludes large-scale defect scattering such as boundary scattering which is energy independent. This is also contrary to what is observed for higher stages, as shown in Fig. 2. In this case, the measured thermopower is close to that expected from relation (A5) (see Appendix) with $\varepsilon_F = 0.9$ eV and $\varepsilon_F = 0.55$ eV, respectively, for the HOPG-$SbCl_5$ and the BDF-$CuCl_2$ compounds and $p_1 = p_2 = 0$ in accordance with a boundary scattering at the limits of the Daumas-Herold domains.

So, in the light of the existing theories for the diffusion thermopower, one may conclude that the unusual negligible diffusion thermopower indicates that in the first-stage compounds the scattering of holes in the lowest-temperature range is different from that in higher stages.

If we now compare at higher temperatures the predicted diffusion thermopower with that observed experimentally (Fig. 1), we may see that the situation is reversed
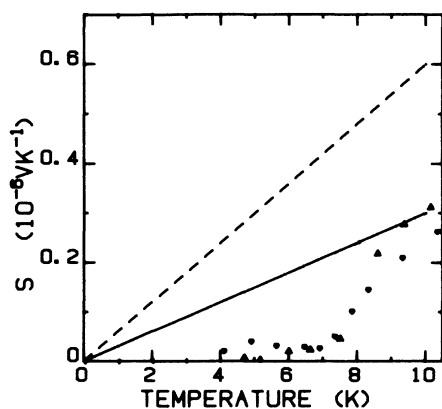
and that the observed values are higher than the predicted ones. At 100 K, for example, the computed thermopower is 2.45×10^{-6} V/K, while the experimental value is more than six times higher. This suggests that there is an additional mechanism for thermal emf generation, which could probably be attributed to phonon drag. In that context, it is interesting to note that a phonon-drag mechanism has been invoked to interpret the high-temperature thermopower of stage-2 acceptor compounds.[27] However, we believe it is rather premature to explain our results on this basis since there is no evidence that the underlying physical mechanism (Rayleigh scattering) invoked to explain the plateau is operative.

Figure 3 shows the temperature variation of the thermal conductivities of the two first-stage HOPG-$CuCl_2$ and HOPG-$CdCl_2$ samples whose thermopower are presented in Figs. 1 and 2. At high temperatures, the thermal conductivities of both samples are substantially smaller than that of the stage ≥ 2 HOPG-$FeCl_3$ and HOPG-$CoCl_2$ compounds[5,8] but are close to that of stage ≥ 2 HOPG-$SbCl_5$ compounds.[7] At liquid-helium temperature, the thermal conductivity of the $CdCl_2$ compound is about two times higher than that of the $CuCl_2$ compound. Recent studies on intercalated graphite fibers[11,12,28] have established that the heat transport at low-temperatures in acceptor GIC's is governed by the quasi-two-dimensional hole gas and by an extra phonon contribution resulting from intercalation. However, for HOPG-based compounds, electrical and thermal measurements cannot be performed simultaneously on the same sample so that an accurate separation into the lattice and the electronic thermal conductivities is not possible to realize in low-stage compounds even with high magnetic fields.[7]

We have reported the results of measurements of the in-plane thermopower and thermal conductivity of first-stage HOPG-$CuCl_2$ and HOPG-$CdCl_2$ compounds from room temperature down to 3 K. In the higher-temperature range, the thermopower results are similar to those previously obtained for higher-stage compounds. Thus it may be concluded that at high temperature, the thermopower follows the same general trend whatever the stage and the intercalate considered.
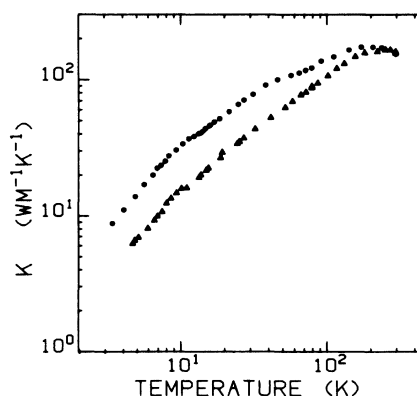
FIG. 2. Low-temperature behavior of the thermopower. Symbols represent the thermopower of stage-1 HOPG-$CuCl_2$ (▲) and HOPG-$CdCl_2$ (●) intercalation compounds. Solid line and dashed line designate, respectively, the temperature variation of the thermopower of stage-2 HOPG-$SbCl_5$ (Ref. 7) and BDF-$CuCl_2$ (Ref. 12) intercalation compounds.

FIG. 3. Temperature dependence of the in-plane thermal conductivity of first-stage HOPG-$CuCl_2$ (▲) and HOPG-$CdCl_2$ (●) intercalation compounds.

At low temperature, however, a surprising behavior is observed since the thermopower exhibits negligibly small values below $T \approx 7$ K. Using the two-dimensional (2D) BR band model and assuming that a diffusion mechanism is dominant in the liquid-helium-temperature range, this result implies that the scattering via the static defects is different in first-stage compounds from that in higher stages, where the Daumas-Hérold domain boundaries are probably the main scattering source.

APPENDIX

The diffusion thermopower may be calculated using the general Mott formula given by Eq. (3). In the frame of the BR model,[18] the carrier dispersion relations for a stage-1 acceptor GIC is given by

$$-\varepsilon_v(k) = \varepsilon_c(k) = \tfrac{1}{2}\gamma_0 b k , \tag{A1}$$

where b and γ_0 are the in-plane nearest-neighbor distance and overlap energy, respectively, and the indices c and v correspond to the conduction and valence bands, respectively.

For a stage-2 acceptor GIC, taking into account the nearest neighbor out of plane energy γ_1 (≈ 0.38 eV), the dispersion relations for bands 1 and 2 are given by

$$-\varepsilon_{v1}(k) = \varepsilon_{c1}(k) = \tfrac{1}{2}[(\gamma_1^2+9\gamma_0^2 b^2 k^2)^{1/2} - \gamma_1] ,$$
$$-\varepsilon_{v2}(k) = \varepsilon_{c2}(k) = \tfrac{1}{2}[(\gamma_1^2+9\gamma_0^2 b^2 k^2)^{1/2} + \gamma_1] . \tag{A2}$$

The electrical conductivity σ for a stage-1 compound may be expressed as $\sigma \approx Ne^2\tau v_F/I_c \hbar k_F$, where N is the 2D hole density, v_F is the Fermi velocity, k_F is the Fermi wave vector, τ is the relaxation time, and I_c is the c-axis repeat distance. Since $N \approx k_F^2/\pi$, $v_F \approx \hbar^{-1}d\varepsilon/dk$ is energy independent and, using $\tau \approx \tau_0\epsilon^p$, we obtain, from Eq. (3),

$$S_d \approx 2.45\times10^{-8}\, T\frac{1+p}{\varepsilon_F} . \tag{A3}$$

For a stage-2 compound, the diffusion thermopower is computed by taking into account the partial electrical conductivities σ_j and the partial diffusion thermopowers S_{dj} from the two-hole bands ($j = 1,2$),

$$S_d \approx \frac{\sigma_1 S_{d_1}+\sigma_2 S_{d_2}}{\sigma_1+\sigma_2} . \tag{A4}$$

In this expression $S_{dj} \approx 2.45\times10^{-8}T\, (\partial\ln\sigma_j/\partial\varepsilon)_{\varepsilon_F}$ and $\sigma_j \approx N_j e^2\tau_j v_{Fj}/I_c hk_{Fj}$. Since $N_j \approx k_{Fj}^2/\pi$, $v_{Fj} \approx \hbar^{-1}d\varepsilon_j/dk$ and using $\tau_1 \approx \tau_{01}\varepsilon^{p_1}$ and $\tau_2 \approx \tau_{02}(\varepsilon-\gamma_1)^{p_2}$ we obtain

$$S_{d_1} \approx 2.45\times10^{-8}\, T\left[\frac{2\varepsilon_F+\gamma_1}{\varepsilon_F^2+\varepsilon_F\gamma_1} + \frac{p_1}{\varepsilon_F} - \frac{2}{2\varepsilon_F+\gamma_1}\right] ,$$
$$\tag{A5}$$
$$S_{d_2} \approx 2.45\times10^{-8}\, T\left[\frac{2\varepsilon_F-\gamma_1}{\varepsilon_F^2-\varepsilon_F\gamma_1} + \frac{p_2}{\varepsilon_F-\gamma_1} - \frac{2}{2\varepsilon_F-\gamma_1}\right] .$$

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