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Thermopower of exfoliated graphites between 1.7 and 300 K

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The thermopower of three exfoliated graphites (Grafoil, Foam, and UCAR-*ZYX*) has been measured in the temperature range 1.7 – 300 K. Around 30 K a large negative anomaly similar to that of highly oriented pyrolytic graphites is observed. At higher temperatures the thermopower of all exfoliated graphites is, however, more positive. This may be a consequence of a small acceptorlike residuum remaining in the samples after the exfoliation process. Thermopower of *ZYX* graphite has been tentatively separated into its diffusion and phonon-drag components.

I. INTRODUCTION

In the past several years a variety of interesting modifications of graphite has been prepared by Union Carbide Corporation. Among these are exfoliated graphites. They offer a large ratio of area to volume and find application as substrates for monolayer adsorption of various gases[1] and for catalysis.[2] Three of the most frequently used exfoliated graphites are Grafoil, Foam, and UCAR-*ZYX*.[3]

Grafoil is made by exfoliating groundup natural crystals and rolling them into a thin sheet. The rolling process aligns the c axis so that basal planes are inclined at $\lesssim 30°$ to the sheet, but the crystallite size is only about 100 – 200 Å. Less severe rolling gives a much less dense material called graphite Foam. UCAR-*ZYX* graphite is produced by a careful exfoliation from a stress-annealed highly oriented pyrolytic graphite (HOPG) and is left unrolled. The exfoliated blocks of *ZYX* are about 0.6-mm thick. The crystallite size and orientation is estimated to be an order of magnitude better than that of Grafoil; however, the density is smaller.

It should be mentioned that exfoliation is achieved using a strong oxidizing agent (acid) followed by rinsing and rapid heat treatment. As such it is essentially an intercalation process with a subsequent expulsion of the intercalant. However, a small intercalant residue often remains trapped in the samples and this may show up as a slight excess of holes over the electrons. One of the transport effects which is sensitive to the carrier imbalance is the thermoelectric power. In this paper we present our thermopower measurements on exfoliated graphites and compare them with the data on the best pyrolytic graphites. From the data we estimate the excess carrier density of holes associated with the intercalant residue and we tentatively separate the thermopower of *ZYX* graphite into its diffusion and phonon-drag contributions.

II. EXPERIMENTAL

The thermopower was measured in the temperature range 1.7 – 300 K using a conventional cryostat. Below 4 K the temperature was stabilized by adjusting the vapor pressure above the liquid with a pressure regulator. Higher temperatures were maintained with the aid of a temperature controller.

In the case of Grafoil and Foam the thermopower was measured both along a rolling direction $S_{\parallel}$ and across the rolling plane, $S_{\perp}$. The thermopower of *ZYX* graphite was investigated only along the exfoliated leaves; the measurements across the leaves would be difficult to interpret due to frequent appearance of gaps in the stacks of graphitic layers.

The samples were cut by an air abrasive machine into parallellepipeds when measuring along the rolling direction and discs when measuring across the rolling plane. In fact, the samples are identical to those on which the thermal conductivity was recently measured.[4] For the reader's convenience, the dimensions, densities, and room-temperature resistivities are listed in Table I.

The temperature gradient was set up using a miniature resistor attached to one end of the sample and the temperature difference between two points along the sample was measured by pairs of calibrated platinum and/or carbon-glass resistance thermometers. More details concerning the ther-

TABLE I. Some parameters of exfoliated graphites. Slope of the diffusion thermopower S_d is taken as linear extention of the data to $T=0$.

Sample	Dimensions (mm)	Density ($\mathrm{g\,cm^{-3}}$)	Resistivity at 300 K (Ω cm)	Slope of S_d ($10^{-6}\,\mathrm{V\,K^{-2}}$)
Grafoil$_{\parallel}$	$2.88\times3.08\times30$	0.82	1.11×10^{-3}	
Grafoil$_{\perp}$	(dia)8.54×0.26		1.14×10^{-1}	+0.09
Foam$_{\parallel}$	$4.50\times3.75\times30$	0.172	5.87×10^{-3}	+0.08
Foam$_{\perp}$	(dia)8.30×0.98		5.48×10^{-2}	+0.04
$ZYX_{\parallel}$	$4.43\times1.9\times30$	0.5	8.16×10^{-4}	−0.25

mometers and their attachment to the samples were given previously.[4]

The thermoelectric voltage was measured using very thin, high-purity lead probes. The data were corrected for the thermopower of lead using the tables of Roberts.[5]

III. RESULTS AND DISCUSSION

The overall temperature dependence of the thermopower is shown in Fig. 1. In Fig. 2, for comparison, are presented our measurements of the in-plane S_{11} and along the c axis S_{33} components of the thermopower of high-quality (residual resistance ratio $=16.4$) highly oriented pyrolytic graphite. Two things are immediately evident: a similar behavior at low temperatures and a larger and positive thermopower of exfoliated graphites at higher temperatures.

Both Grafoil$_{\parallel}$ and ZYX show a substantial negative anomaly around 30 K, i.e., at the same temperature where S_{11} of HOPG is dominated by a large negative contribution which is believed to arise from the phonon drag.[6–8] The negative dip ($25-30\ \mu\mathrm{V\,K^{-1}}$) is a result of partial compensation between the phonon-drag contributions of electrons and holes, individual drag terms are estimated to be an order of magnitude larger.[8] From a close similarity of anomalies we can assume that, despite an imperfect crystallographic structure of Grafoil$_{\parallel}$, and ZYX graphite, especially in the stacking direction, the phonon drag still represents a large contribution to the thermopower of exfoli-

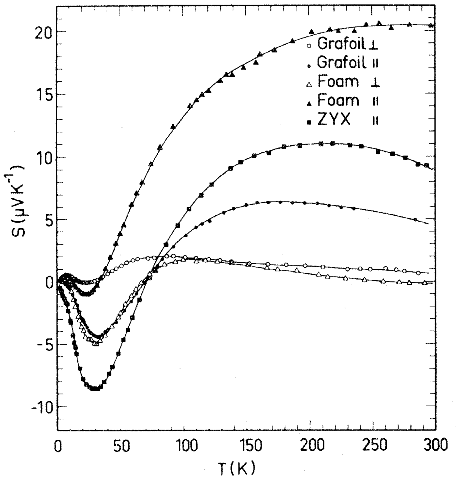

FIG. 1. Overall temperature dependence of the thermoelectric power of exfoliated graphites.

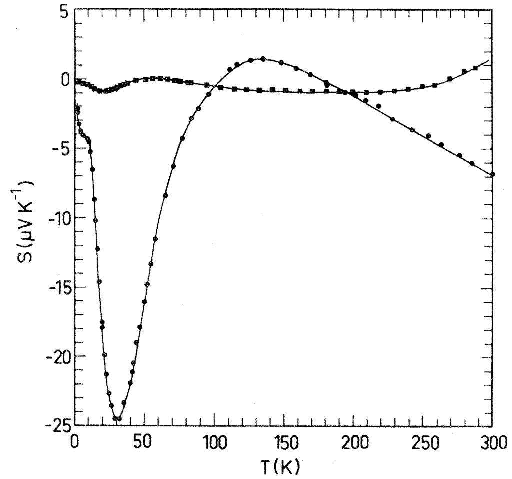

FIG. 2. Temperature dependence of the thermoelectric power of stress-annealed pyrolytic graphite (HOPG). ● thermopower measured along the planes (S_{11}), ■ thermopower measured across the planes (S_{33}).

ated graphites at low temperatures. This is reasonable since the in-plane carbon bonding is unlikely to be disturbed by the exfoliation process. Furthermore, since the minima for Grafoil$_{||}$, *ZYX*, and HOPG are observed at the same temperature, and the in-plane sound velocities are unlikely to be much different for the reason given above, the Sondheimer's condition[9] for the effective interaction of the in-plane long-wavelength phonons with the carriers located in small Fermi pockets

$$1.6k_B\Theta_D^* = 2k_{F_\perp}\hbar s \qquad (1)$$

suggests that the diameter of the Fermi surface $2k_{F_\perp}$ ($k_{F_\perp}$ being a semimajor axis wave vector perpendicular to the c axis) of both Grafoil and *ZYX* is very similar to that of pyrolytic graphite. Here s is the in-plane sound velocity, Θ_D^* is the effective Debye temperature, the coefficient 1.6 comes from the dominant phonon mode at the phonon cutoff,[10] and $\hbar$ and k_B are the Planck and Boltzmann constants, respectively. The out-of-plane acoustic vibrations, while absolutely vital for the heat transport of graphite in both principal crystallographic directions below 100 K,[11] do not couple strongly to charge carriers[12] and, therefore, can be neglected.

The thermopower of Grafoil measured across the planes, Grafoil$_\perp$, is much smaller than the in-plane component and resembles very closely the c-axis thermopower of HOPG.

Thus, judging from the position, temperature dependence, and the depth of the thermopower anomaly there appears to be no shrinking of the electron Fermi surface as one would expect had Grafoil or *ZYX* possessed a large excess density of holes originating from the exfoliation process. However, the shift of the thermopower curves upwards to less negative values in comparison to HOPG suggests a small residue of holes.

The thermopower of Foam is a less clearcut case. A minimum in the thermopower of Foam$_{||}$ appears at around 23 K while the thermopower measured across the rolling direction Foam$_\perp$ is surprisingly more negative and virtually identical to that of Grafoil$_{||}$ below 80 K. It is difficult to draw any conclusion from this behavior since the c axes of the microcrystallites of Foam are highly misaligned due to only very weak rolling process applied in its preparation.

More details concerning the low-temperature thermopower of the exfoliated graphites are given in Fig. 3. At temperatures below the negative phonon-drag anomaly the absolute value of the thermopower decreases and, with the exception of *ZYX* graphite, changes sign and approaches the thermodynamically required $\lim_{T\to 0} S = 0$ with positive values. Slopes of the linear extrapolations of the thermopowers to $T = 0$ are given in Table I. The behavior we observe in exfoliated graphites is in contrast to that shown by high-quality pyrolytic graphites where the low-temperature thermopower never attains positive values down to 1.2 K, the lowest temperature investigated so far. *ZYX*, while approaching zero with negative values has, nevertheless, much smaller slope than HOPG.

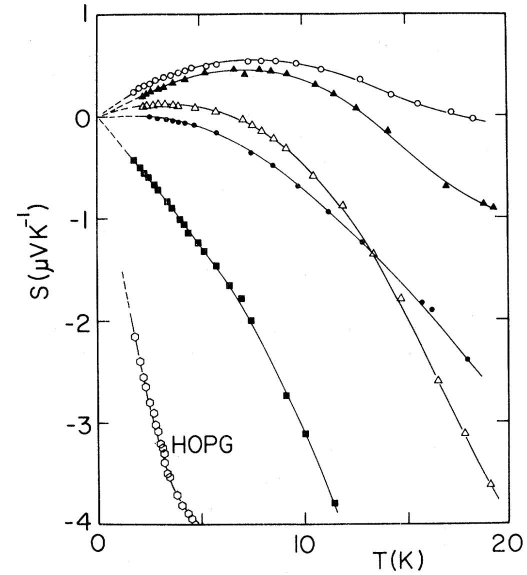

FIG. 3. Low-temperature details of the thermoelectric power of the samples in Fig. 1. O indicates the thermopower of HOPG measured along the planes (S_{11}).

Persistence of a large phonon-drag anomaly in exfoliated graphites is, in view of the measurements[13] of Tsuzuka *et al.* of the effect of structural imperfections on the thermopower, rather surprising. It is well known, see e.g., Moore,[14] that the best graphitic structure is achieved by annealing at around 3600 °C under a uniaxial pressure applied in the c-axis direction. With lowering the temperature of the heat treatment, the structural perfection deteriorates in the sense that the misorientation of crystallites around the common c axis increases and the size of the crystallites decreases. Initially, on going from 3600 to 3200 °C, Tsuzuku *et al.* find a more negative dip, $-39\ \mu\text{V K}^{-1}$ instead of $-29\ \mu\text{V K}^{-1}$, which they explain in terms of imperfections affecting the hole contribution more than the electronic one. However, on further lowering of the annealing temperature down to 2800 °C the phonon drag is strongly attenuated and only a shallow, $-8.5\ \mu\text{V K}^{-1}$, dip is observed.

The authors argue that a strong scattering of phonons on the defects (they mention an appearance of small regions of turbostratic graphite) is now very effective. Thus, structural perfection has a rather profound effect on the phonon-drag thermopower. Yet, one should remember that all three HOPG graphites of Tsuzuku *et al.* are still rather good, solid samples with the density close to 2.266 $\mathrm{g\,cm^{-3}}$; certainly far from exfoliated samples with densities well below 1 $\mathrm{g\,cm^{-3}}$. One would therefore expect that the scattering of phonons on imperfect structure of exfoliated graphites would be so strong as to prevent any sizable momentum transfer into the charge carrier system and, hence, phonon drag should vanish. Since the effect of exfoliation is primarily to expand the lattice along the c axis with only a relatively small effect on the in-plane structure, the presence of the phonon drag would suggest that the in-plane long-wavelength phonons are rather insensitive to interlayer coupling.

One other point is worth mentioning. The second, minority hole-type, phonon-drag anomaly reported recently[15] at around 10 K on HOPG and evident also on our sample in Fig. 2 is not resolved in the case of the exfoliated graphites. The strength of this small anomaly is estimated to be only about $\frac{1}{20}-\frac{1}{30}$ of the 30-K anomaly and this is probably too small to survive the "wash out" due to imperfections. The 10-K anomaly is observed only on the best pristine graphites.

At higher temperatures the thermopower of $\mathrm{Grafoil}_{\perp}$ and $\mathrm{Foam}_{\perp}$ is small and is similar to the thermopower of pure pyrolytic graphite measured along the c axis, S_{33}. One does not expect a large thermopower for any c-axis oriented graphite due to very small mobilities along this direction.

On the other hand, the in-plane thermopowers of exfoliated graphites are larger and more positive compared to the S_{11} component of HOPG. At low temperatures, where the phonon-drag contribution extends down to the liquid-helium range, an attempt to separate the diffusion and phonon-drag terms would be unreliable since phonon drag varies as the lattice specific heat, and in graphite at low temperatures this obeys a T^2 rather than T^3 power law.[16] However, at high temperatures, above about 150 K, the phonon-phonon collisions dominate and the thermopower is essentially of diffusion origin. Within the framework of a simple two-band model of Klein[17] which treats graphite as a two-dimensional solid, the diffusion thermopower of graphite is given as

$$S_d=\frac{k_B}{e}\frac{a-b}{a+b}\left[\frac{2F_1(E_0/2k_BT)}{F_0(E_0/2k_BT)}-\frac{E_0}{2k_BT}\right], \tag{2}$$

where $a=p/n$ is the ratio of holes to electrons, $b=\mu_e/\mu_h$ is the mobility ratio, F_n are the Fermi integrals, and E_0 is the band overlap.

Equation (2) has been frequently used[17–19] to fit the high-temperature thermopower behavior of HOPG under the assumption of perfect carrier compensation, i.e., $a=1$. The ratio of the carrier mobilities b can be obtained from the fit or, alternatively, it can be determined independently from galvanomagnetic data,[20] if such exist. A rather good agreement between the two methods has been demonstrated.[19] However, it should be noted that in all cases[17–19] the fit had been done with an unrealistically low value of the band overlap, 0.010–0.016 eV. For a two-band model the band overlap is given as $2\,|\gamma_2|$ where γ_2 is the next-nearest-layer interaction parameter of the Slonczewski-Weiss-McClure model[21,22] responsible for the semimetallic character of graphite. The absolute value of γ_2 determined from the galvanomagnetic[23] and magnetoreflection[24] data lie in the range 0.018–0.019 eV, hence, E_0 used in previous works should have been two to three times larger. The value of the band overlap adopted by us is $E_0=0.036$ eV.

Since Eq. (2) is based on the cylindrical model, i.e., it neglects the interlayer interaction, it should apply equally well to exfoliated graphites which show much enhanced c axis spacing but only a relatively small distortion of the in-plane carbon bonds. As our low- as well as high-temperature thermopower data suggest *a small* excess of holes over electrons, we will drop the assumption of carrier equality and instead, attempt to estimate this carrier imbalance. We shall concentrate here mainly on *ZYX* graphite and Grafoil, the Foam being so highly misaligned that the analysis would probably be meaningless.

From Eq. (2) one thing is immediately obvious: In order to fit a positive high-temperature thermopower of exfoliated graphites the coefficient a must necessarily be larger than b. In the absence of direct information on the mobility ratio b we shall rely on the values in the literature.[19,20,25,26] Over a wide range of structural perfection the value of b at 300 K lies invariably between 1.025 and 1.1, HOPG samples are close to the upper limit. We shall therefore adopt a room-temperature value of $b=1.1$. Substituting for b in Eq. (2) and assuming that at 300 K the experimental thermopower is purely of diffusion origin, the carrier imbalance as expressed through coefficient a is 1.23 for *ZYX* and 1.15 for Grafoil. Since graphites are semimetals, once the carrier density ratio is known it will change very little with temperature and we can assume it constant. Substituting the values of coefficient a thus obtained back into Eq. (2) and equating the experimental thermopower above 200 K with the diffusion thermopower, the temperature dependence of the mobility ratio b can be extracted and is shown for *ZYX* in the inset of Fig. 4. A similar curve results for mobility ratio of Grafoil. A linear term of the coefficient b of both *ZYX* and Grafoil is comparable to that of single-crystal graphite ($\sim 5\times 10^{-4}$ K^{-1}) as determined by Takezawa *et al.*[19] As already indicated, the workers used an unreasonably low value for E_0 and the agreement is probably fortuitous. If we linearly extrapolate b to low temperatures (this may not be fully justified for imperfect graphitic structures as the data of Ayache and Spain[21] seem to indicate; it could lead to overestimating of the low-temperature diffusion thermopower and hence more negative phonon drag), the diffusion thermopower can be computed. Subtracting this from the experimental thermopower gives the phonon-drag contribution. Such a separation for *ZYX* graphite is shown in Fig. 4 and a similar one can be achieved for Grafoil.

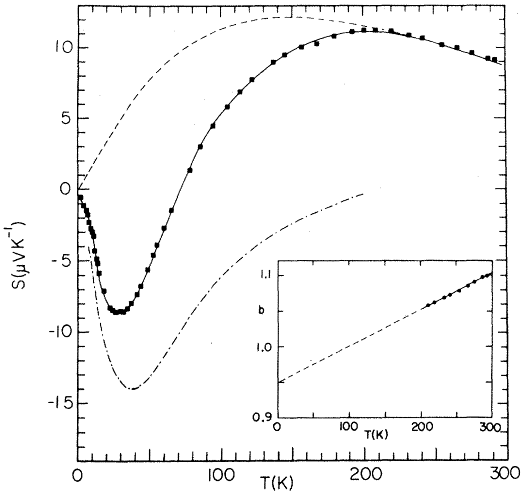

FIG. 4. Separation of the thermopower of *ZYX* graphite. Dashed curve indicates the diffusion thermopower S_d calculated from Eq. (2). Dash-dot curve is the phonon-drag thermopower obtained as a difference between the experimental data and S_d. In the inset is given the mobility ratio b calculated from Eq. (2) above 200 K under the assumption of $a=1.23$. The straight-line extension can be described by an equation $b=5.13\times 10^{-4}T+0.95$. The band overlap is assumed to be equal to 0.036 eV.

From Fig. 4 we observe that the phonon drag indeed represents a surprisingly large contribution to the thermopower of exfoliated graphites at low temperatures: Around 30 K the magnitude of the drag term is about twice as large as that of the diffusion term. We should, however, keep in mind that the accuracy of the separation given in Fig. 4 is subject to an uncertainty in the mobility ratio b at low temperatures. In particular, the depth of the minimum on the phonon-drag curve would be affected had the mobility ratio differed drastically from an assumed linear dependence on temperature. However, even if the mobility ratio did deviate from the linear extrapolation and reached near 30-K values as large[25] as $b=1.09$ it would merely make the phonon-drag term smaller (-11 $\mu V\,K^{-1}$ as against -13.6 $\mu V\,K^{-1}$) but, qualitatively, the argument would stand. Furthermore, the position of the minimum on the phonon-drag curve (~ 37 K) and the shape of the curve itself is in good agreement with the theory of Jay-Gerin and Maynard[8] and it thus adds confidence to the separation procedure used here.

IV. CONCLUSION

Measurements of the thermopower of exfoliated graphites indicate the presence of a strong phonon-drag contribution near 30 K, behavior similar to that observed in highly oriented pyrolytic graphites. Persistance of phonon drag in exfoliated graphites is, we believe, associated with the in-plane acoustic phonons insensitivity to the stacking disorder. All investigated samples show a small hole residue which has its origin in the exfoliation process. From the thermopower data of *ZYX* and Grafoil we estimate about 20% excess of holes over the electrons. We have separated the thermopower of *ZYX* graphite into its diffusion and phonon-drag components. However, in view of uncertainties in the behavior of the mobility ratio at low temperatures, this separation should be treated as tentative only. Extension of the thermopower measurements to temperatures well below 1 K should allow a more precise determination of the diffusion thermopower contribution and, hence, also of the phonon drag-term.

The first thermal transport measurements on intercalated graphites have only recently been carried out.[27] It is hoped that our data on exfoliated graphites will be useful in the interpretation of these results. In particular this applies to *ZYX* material which is based on HOPG graphite, also the preferred starting material for the highest quality samples of intercalation compounds.

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