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Observation of a new anomaly in the low-temperature thermoelectric power of graphite: Interpretation by a phonon-drag effect acting on the H-point minority holes

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We present the results of new measurements of the basal-plane thermoelectric power S of highly oriented pyrolytic graphite between 1.3 and 300 K. In addition to the well-known large negative dip near 40 K, the curve of $S(T)$ reveals the presence of a second anomaly in the region below about 10 K. We show that this extra anomaly can be explained in terms of a phonon-drag effect acting on the H-point hole minority carriers. Such an interpretation is consistent with other experimental data.

It is well known that, in the absence of a magnetic field, the basal-plane thermoelectric power (TEP), S, of high-quality graphite exhibits a large negative minimum (or dip) as a function of temperature, of about $-20\ \mu\mathrm{V\,K}^{-1}$ near 40 K.[1-8] This negative dip in $S(T)$ is satisfactorily explained on the basis of a phonon-drag effect acting on the electron and hole majority carriers.[9-11]

Studies of the change in the TEP of graphite upon application of a magnetic field parallel to the hexagonal c axis have also been made.[12-15] The results, though essentially preliminary,[16] indicate a remarkable enhancement of the negative phonon-drag dip as well as a slight shift in its position from 40 K to near 30–35 K.

At the present time, two distinct theoretical approaches of the phonon-drag effect in graphite have been proposed to explain the dependence of the TEP at low temperatures and in the low-field limit ($H \lesssim 15$ kG) on temperature and magnetic field.[9,10,13,17,18] The theory by Sugihara and coworkers[9,13] can hardly be considered as compatible with the recent thermomagnetic transport measurements of Takezawa *et al.*,[14,15] since it was initially used to justify the very large, erroneous, dip in $S(T)$.[13,16] On the contrary, the theory first developed by Jay-Gerin and Maynard[10] and further by Jay-Gerin[17,18] on the basis of the enhanced coupling by anisotropy of the "Kohn[19] phonons" with the majority carriers has proven to give a realistic explanation of the actual thermomagnetic data.

A general survey of the thermoelectric and thermomagnetic effects in graphite can be found in the review articles by Spain[20] and by Tsuzuku and Sugihara.[21]

In addition to the large negative dip near 40 K, Sugihara *et al.*[22] have recently reported the observation of a second anomaly, in the form of a positive peak, in the curve of $S(T)$ for well-crystallized Kish graphite near 15 K.[23] These authors have also observed a rapid decrease of the size of the peak upon the application of a magnetic field $\vec{H}$ parallel to the c axis. In particular, they have found that, for $H = 6$ kG, the peak has completely disappeared.

In an attempt to explain the origin of this new phenomenon, Sugihara *et al.*[22] have carried out a calculation in which they show that the extra TEP anomaly could be attributed to a two-stage phonon-drag effect.[24] Within the framework of this interpretation, they concluded that the observation of the low-temperature peak in $S(T)$ depends critically on the quality and purity of the graphite crystals used in the experiments. In particular, according to these authors, pyrolytic graphite should not show such an extra anomaly.

The aim of the present paper is twofold. First, we present the results of new measurements of the TEP of highly oriented pyrolytic graphite in the temperature range from 1.3 to 300 K. Aside from the well-known large negative 40-K dip, these measurements reveal the existence of a second anomaly, in the form of a "plateau," below about 10 K. The observation of this extra TEP anomaly in pyrolytic graphite seems to be closely related to that reported by Sugihara *et al.*[22] in Kish graphite.[25] This suggests that the extra anomalies observed in the TEP of both pyrolytic and Kish graphite in the region near 10–15 K have the same intrinsic physical origin. Clearly, this is contrary to the prediction of Sugihara *et al.*,[22] who claimed that the extra low-temperature TEP anomaly should only be observed in well-crystallized Kish graphite.

Second, in order to explain the origin of the new S-T anomaly, we propose a mechanism which consists of a phonon-drag effect acting on the minority hole carriers near the H point on the Brillouin-zone boundary.[26] This mechanism is totally different from that previously suggested by Sugihara *et al.*[22] and relies on the Jay-Gerin–Maynard theory of the phonon-drag effect in graphite.[10,17,18] It leads to an interpretation of the extra low-temperature TEP anomaly that is consistent with the recent analysis of H-point magnetoreflection data by Toy *et al.*[26] This interpretation also agrees with the work by Sugihara *et al.*[22] regarding the disappearance of the anomaly upon the application of a magnetic field.

The sample used in the present study is a "Le Carbone-Lorraine" hot-pressed pyrolytic graphite, such as was originally made by Moore *et al.*[27] It was prepared from pyrolytic graphite deposited at 2100 °C, and hot-pressed for 10–15 min at temperatures near 3000 °C and under pressure of 20 MPa. This sample is polycrystalline, but consists of large size crystallites with their c axes aligned along the direction of compression, and mean basal-plane diameters of about 1 μm. The ratio of the 300- to 4.2-K resistivity is 4.2, and the thermal conductivity maximum near 100 K is 33 W $\text{cm}^{-1}\text{K}^{-1}$. Such values are typical of current hot-pressed pyrolytic graphites.

The dimensions of the sample were approximately $1\times5\times50$ mm^3, with the direction of the c axes perpendicular to the largest face. A steady heat-flux method was employed to measure simultaneously the thermoelectric power and the thermal conductivity along the basal graphitic planes. Gold-Iron versus Chromel thermocouples were used both for determining the temperature gradient across the sample and for measuring the thermoelectric voltage between the two Chromel wires. The absolute TEP of graphite was determined from the absolute TEP of Chromel.[28] The results of our TEP measurements as a function of temperature from 1.3 up to 300 K, are shown in Fig. 1. Details of the TEP in the region 1.3–12 K of the additional anomaly are given in the inset.

We propose to interpret the origin of the new S-T anomaly by a phonon-drag effect acting on the H-point hole minority carriers. This interpretation relies on the theory of phonon drag in graphite developed originally by Jay-Gerin and Maynard[10] to explain the large negative 40-K TEP dip, taking explicitly into account the enhanced coupling by anisotropy of the "Kohn phonons" with the majority electron and hole carriers. It is clear that this latter theory can also be applied to the case of the minority holes near the Brillouin-zone corner (the H point). In fact, the shape of the H-point minority-hole Fermi surface can be reasonably well approximated by ellipsoids elongated along the vertical edges of the Brillouin zone. The anisotropy ratio $\alpha = k_{F\parallel}/k_{F\perp}$, where $k_{F\parallel}$ and $k_{F\perp}$ are the semimajor axis wave vectors parallel and perpendicular to the c direction, respectively, is approximately 2,[29,30] and $k_{F\perp}$ is given by[20,26]

$$k_{F\perp} = \frac{2}{\sqrt{3}} \frac{[E_F(E_F-\Delta)]^{1/2}}{\gamma_0 a_0} , \tag{1}$$

which is about 0.32×10^8 m^{-1}, if we assume values

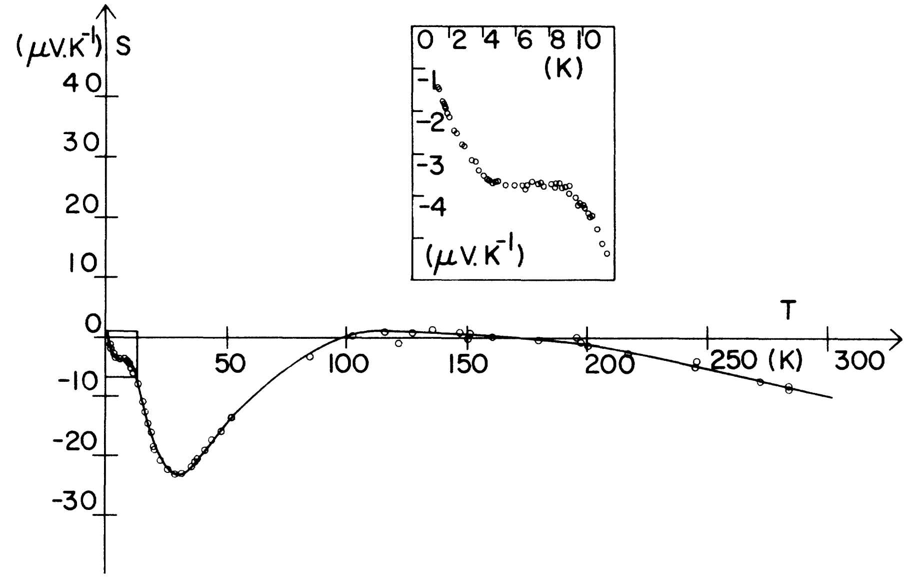

FIG. 1. TEP of graphite as a function of temperature between 1.3 and 300 K. In addition to the well-known large negative 40-K dip, the curve of S versus T reveals the presence of a second anomaly below about 10 K. The inset expands the region 1.3–12 K in order to show clearly the details of this extra TEP anomaly.

for the various Slonczewski-Weiss-McClure band parameters of $\gamma_0 = 3.11$ eV, $\Delta = -0.0049$ eV, and the Fermi energy $E_F = -0.0235$ eV,[31] and for the in-plane lattice parameter $a_0 = 2.456$ Å. According to the Jay-Gerin–Maynard theory,[10] such an anisotropic Fermi surface should produce a predominant electron-phonon interaction at the Kohn condition. Let us thus consider that the only phonons that are effectively coupled to the H-point minority holes are the "Kohn phonons," namely, phonons with wave vector $q_\perp = 2k_{F\perp}$ (the index $\perp$ refers to the component in the plane perpendicular to the c axis). Then, those Kohn phonons should give rise to a phonon-drag effect on the H-point minority holes most effective at the temperature T_K given by

$$T_K = \hbar v_s (2k_{F\perp})/k_B \ , \tag{2}$$

where $\hbar$ is the Planck constant divided by 2π, k_B is Boltzmann's constant, and v_s is the sound velocity. Taking v_s as the longitudinal "in-plane" acoustical phonon velocity, i.e., $v_l = 2.01 \times 10^4$ m/sec, Eqs. (1) and (2) lead to a maximum phonon-drag contribution at $T_K = 9.7$ K.[32] Since S is normally positive for holes, such a contribution should be reflected in the curve of the TEP versus temperature as a positive-going anomaly near T_K. The experimental results are well consistent with such an anomaly (see Fig. 1).[25] From the results of the theory of Jay-Gerin and Maynard,[10] we can further obtain an estimate of the magnitude of this contribution. Assuming that the electron-phonon coupling constant has the same value for all types of carriers, including minority holes, and that Kohn phonons have the same bandwidth, and taking $m_\perp \approx 0.005\ \mathrm{m}_0$ (where m_0 is the free-electron mass) for the basal-plane minority-hole mass,[20,31] and $n \approx 10^{15}\ \mathrm{cm}^{-3}$ for the minority-carrier concentration,[26,33,34] yields a phonon-drag contribution due to the H-point hole minority carriers of the order of 1 $\mu\mathrm{V\,K}^{-1}$. Such an estimate should be considered as satisfactory, taking into account (i) the experimental results (see Fig. 1), (ii) the uncertainties associated with the different quantities describing the minority-hole carriers near the H point, and (iii) the fact that the purely electronic diffusion contribution to the TEP is entirely ignored.

It is worth to emphasize that, inversely, if we assume *a priori* that the extra anomaly observed in the TEP of graphite near 10 K is indeed a manifestation of a phonon-drag effect on the H-point minority holes, we can show, within the Jay-Gerin–Maynard theory,[10] that the effect corresponds to a Fermi-surface extremal cross-sectional area about the H point which agrees quite well with the recent assignment to the H-point minority-hole pocket made by Toy *et al.*[26] for the observed minority de Haas–van Alphen frequency of 3.30 kG. Such an agreement thus reinforces the interpretation of the H-point magnetoreflection data of Toy *et al.*[26] and, in turn, provides further evidence in support of a negative sign for the Slonczewski-Weiss-McClure band parameter Δ.[35]

Let us now focus our attention to the effect of a static magnetic field $\vec{\mathrm{H}}$ applied parallel to the c direction. According to the results obtained by Jay-Gerin,[18] the phonon-drag contribution to the TEP varies as a function of magnetic field essentially as the Hall coefficient, with the coefficient of proportionality depending linearly on the concentration of carriers and on the absolute value of the corresponding phonon-drag contribution in zero magnetic field. Taking account of this latter value and of the fact that n is about 10^3 smaller for the H-point minority holes than for the majority electron and hole carriers, we thus see immediately that the extra 10-K S-T anomaly should be unobservable under the presence of a magnetic field. This is consistent with the experimental results of Sugihara *et al.*,[22] who reported, in particular, that the low-temperature positive peak in $S(T)$ completely disappeared for a magnetic field strength $H = 6$ kG. A similar conclusion can be obtained regarding the Nernst-Ettingshausen coefficient,[18] which should not show such an extra anomaly at all.

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[25] The "plateau" observed near 10 K in pyrolytic graphite may be considered to originate from the combination of the large negative 40-K dip with a positively peaked anomaly such as that observed by Sugihara *et al.* (Ref. 22) in Kish graphite. However, other measurements on various samples of highly oriented pyrolytic graphite [C. Ayache, Thèse de Doctorat-ès-Sciences, Grenoble, 1978 (unpublished)], if they indeed confirm the existence of the low-temperature TEP anomaly, never show a clear-cut peak in the curve of $S(T)$.

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