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Thermopower measurements on arsenic from 2 to 300 K

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S_{11} and S_{33} thermopower components of arsenic have been determined in the temperature range 2–300 K. The data on trigonal (S_{33}) samples are the first reported investigations below 80 K. The measurements were made on high-quality melt-grown single crystals with resistivity ratios in excess of 3500 (S_{11}) and 5300 (S_{33}), the largest reported to date. While the thermopower S_{11} is positive above 15 K, the S_{33} component is negative throughout the investigated temperature range. Above 70 K, both S_{11} and S_{33} thermopowers are purely of diffusion origin. At lower temperatures the thermopowers show pronounced anomalies associated with phonon drag of electrons and holes. With increasing sample perfection both S_{11} and S_{33} tend to become less negative.

INTRODUCTION

Arsenic, together with its sister elements Bi and Sb, belongs to the group-V semimetals, a class of solids characterized by an overlap of the highest-lying valence band and the lowest-lying conduction band. The overlap is small but increases on going from Bi to Sb to As so that the carrier concentrations are, respectively, 3×10^{23} m^{-3} for Bi, 5.5×10^{25} m^{-3} for Sb, and 2×10^{26} m^{-3} for As. The band structure of arsenic has been established reasonably well both experimentally[1] and theoretically,[2] and it suggests that the electronic Fermi surface consists of three pockets at the L points; an equal number of holes is distributed over six pockets at H which are connected by six elongated necks to form an "arsenic crown."

What is surprising in the case of arsenic is the very limited and sketchy information regarding its transport properties, and thermal effects in particular. The primary reason for the lack of data on arsenic stems from a rather severe shortage of good quality and reasonably large single crystals, which are difficult to grow. The acuteness of the situation can best be judged from the fact that all three existing thermal-transport investigations[3–5] have been done on vapor-grown samples[6] from the same batch which were oriented so that their long dimension coincided with the binary axis. Even with such limited data, large discrepancies appear in the reports of the low-temperature thermopower. Furthermore, no information is available on the low-temperature behavior of the other thermopower tensor component S_{33}, parallel to the trigonal direction.

Recently, we have sucessfully prepared large and excellent quality melt-grown single crystals[7] with a record-high residual resistance ratio, and we have also succeeded in cutting samples with their long axis along the trigonal direction (direction of easy cleavage). Detailed thermopower investigations have been undertaken on these samples in order to (a) clarify behavior of the low-temperature thermopower S_{11}, (b) obtain information on the S_{33} thermopower component, the data not available before below 80 K, and (c) study the effect of sample quality on the phonon-drag thermopower.

EXPERIMENT

Measurements were made in a conventional liquid-helium cryostat and the thermopower data were collected on four different samples. In zero magnetic field the thermopower of the rhombohedral $A7$ structure of arsenic is fully determined by specifying two tensor components: one measured along the trigonal axis S_{33} and the other one in a plane perpendicular to the trigonal axis, such as

TABLE I. Orientation, dimensions, and residual resistance ratios of single crystals of arsenic.

Sample	Orientation	Dimensions (mm^3)	Residual resistance ratio r_R $(=R_{296\,\text{K}}/R_{4.2\,\text{K}})$
As no. 1	binary	$22.1\times3.0\times1.05$	3670
As no. 2	binary	$19.7\times2.9\times0.57$	870
As no. 3	trigonal	$11.0\times2.35\times2.37$	5310
As no. 4	trigonal	$10.5\times3.02\times4.21$	1450

e.g., along the twofold axis S_{11}. Consequently, two of the samples were cut with their long axis along the trigonal direction, the other two along the twofold axis. Dimensions and designation of the samples are given in Table I. As we have already indicated, our melt-grown arsenic crystals are of excellent quality with very high resistivity ratios. As representative specimens we have chosen one binary and one trigonal sample with residual resistivity ratios r_R of 3670 and 5310, respectively. Also, in order to facilitate a comparison with the high-temperature measurements of Jeavons and Saunders[3] and the data of Heremans *et al.*,[4] both carried out on a vapor-grown binary sample of $r_R=850$, we have also selected two less-perfect samples, a binary one with $r_R=870$ and a trigonal one with $r_R=1450$.

Temperature difference was determined using a calibrated pair of carbon-glass thermometers inserted in small oxygen-free high-conductivity copper holders, soldered to the sample with Woods metal. We have also used a Au/Fe—Chromel P differential thermocouple to check the temperature difference at higher temperatures, where the sensitivity of carbon-glass sensors is reduced. Agreement between the two types of thermometers was excellent. Thermopower voltage probes were made from very thin (0.2-mm diam) high-purity Pb wires and the voltage was determined using a Keithley model 181 nanovoltmeter. The data were corrected for the thermopower of lead using the tables of Roberts.[8]

RESULTS AND DISCUSSION

The thermopower data for binary-oriented samples, S_{11} are shown in Fig. 1, while those measured on the trigonal samples, S_{33} are presented in Fig. 2. It is well known[9–11] that Bi and Sb exhibit a rather interesting temperature dependence of the thermopower with phonon drag playing an important role; the behavior of both tensor components of arsenic is even more spectacular. First, we describe the data of Fig. 1, i.e., the S_{11} tensor component.

Overall, the magnitude and the temperature dependence of the thermopower of our two binary-oriented samples is similar. At high temperatures, the data are also in good agreement with the measurements of Heremans *et al.*, indicated in Fig. 1 by a broken curve. Nevertheless, distinct differences, related to the structural perfection of the samples and also to the much higher accuracy of the present measurements, are clearly evident. In particular, the minimum at 60 K, which is of identical magnitude for both our samples, lies higher than in the measurements of Heremans *et al.* By plotting the data on a linear scale rather than as a log-linear plot (see inset in Fig. 1) it is quite clear that there is absolutely no indication of any sudden

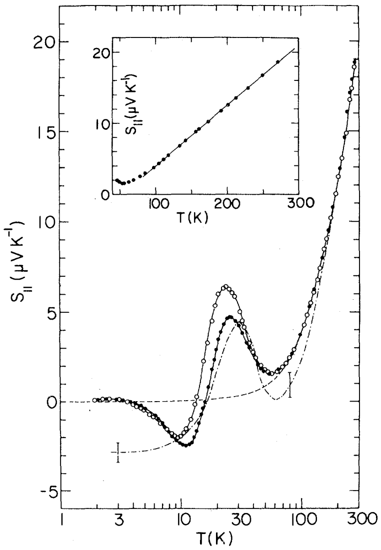

FIG. 1. Temperature dependence of the S_{11} thermopower of arsenic. Open circles correspond to a high-perfection sample As no. 1, closed circles to sample As no. 2. The data of Heremans *et al.* on a vapor-grown sample of $r_R=850$ are indicated by a chain curve; error bars show a scatter of the data points. Diffusion thermopower S_{11}^{diff} calculated from Eq. (3) is drawn by a broken curve. The inset shows the high-temperature thermopower S_{11} plotted on a linear scale.

decrease of the thermopower *below* the otherwise straight line as would have to occur had there been any "dragging" of electrons. This is in contrast to the claim of Heremans *et al.* that the thermopower minimum represents a phonon-drag contribution of electrons. We believe that this anomaly has nothing to do with dragging but arises simply as a consequence of the upturn of the curves, which culminates in a large and positive maximum in the (20—30)-K range. This dominant maximum is, indeed, of the phonon-drag origin. The evidence for this is not only a large value of the thermopower, well beyond the diffusion thermopower estimate, but also the fact that we observe a similar anomaly in the Nernst coefficient.[12] In Fig. 1 we also see an interesting trend; as the quality of crystals, judged by their r_R, improves, the height of the peak increases and is shifted to lower temperatures.

Below 10 K, our measurements and those of Heremans *et al.* are in qualitative disagreement. In the latter case the thermopower is shown as negative ($-2.5\ \mu V K^{-1}$) and temperature independent with widely scattered data points. We have already pointed out from our high-precision [superconducting quantum interference device (SQUID) detector] ultralow-temperature measurements,[5] which are made on the same vapor-grown sample as the one used by Heremans *et al.*, that the component S_{11} cannot continue to stay negative as $T \rightarrow 0$, but rather it must approach $T=0$ with positive values. We have predicted, as a consequence of the temperature dependence, that in the liquid-helium range one should observe a negative minimum of S_{11}. In Fig. 1 such a minimum is, indeed, clearly seen on our two samples designated as As no. 1 and as As no. 2 at 9.5 K and 11 K, respectively. We point out that the negative sign and the large magnitude of thermopower observed on a strongly degenerate system, such as arsenic at these temperatures, is not compatible with the small and positive values expected for diffusion thermopower. Hence, we believe this minimum is associated with a phonon-drag contribution of electrons. Below 4 K the phonon-drag contribution gradually diminishes; the thermopower S_{11} changes sign back to positive, reaches a small maximum near 2.5 K, and approaches zero T with positive values as expected for a purely diffusion transport. This behavior is thus entirely consistent with our previous ultralow-temperature measurements.

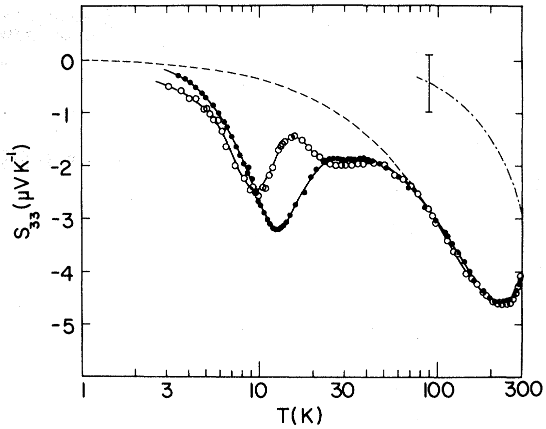

FIG. 2. Temperature dependence of the S_{33} thermopower of arsenic. Open circles designate the data of a high-perfection sample As no. 3, closed circles correspond to sample As no. 4. The data of Jeavons and Saunders obtained on a vapor-grown sample are indicated, with appropriate error bars, by a chain curve. The diffusion thermopower S_{33}^{diff} calculated from Eq. (4) is shown by a broken curve.

We now turn our attention to the S_{33} tensor component of the thermopower which is shown in Fig. 2. With the exception of the measurements made in a limited temperature range 80—300 K by Jeavons and Saunders (broken line in Fig. 2), our data represents the only investigation of the S_{33} thermopower of arsenic. Unlike the S_{11} component which was large and predominantly positive, the S_{33} thermopower is rather small and negative throughout the temperature range. Nevertheless, its temperature dependence is, again, rather dramatic. Despite the fact that the r_R's are considerably different, both our trigonal samples show an identical behavior above liquid-nitrogen temperature. A characteristic feature here is the occurrence of a minimum near 230 K. In comparison, the data of Jeavons and Saunders show only about half as large a magnitude of the thermopower and no indication of a minimum. In that study there is a large scatter and only a few data points, and it is conceivable that the minimum could not be resolved. Below 50 K pronounced anomalies are observed. First, at around 30 K the thermopower shows a shallow minimum which is well resolved on the high-quality As no. 3 but it is more difficult to resolve on the less perfect As no. 4 sample. At still lower temperatures, the thermopower becomes strongly dependent on the degree of sample perfection. Thus, the thermopower of As no. 3 reaches a peak near 16 K, followed by a minimum at 10 K and, finally, the magnitude of thermopower decreases towards zero as $T \rightarrow 0$. On the other hand, As no. 4 does not exhibit any clear maximum (if there is one it most probably occurs at 25 K, 10 K higher than for As no. 3), and its minimum is deeper and shifted up relative to a minimum on As no. 3 by about 3 K. Regarding this minimum, both S_{11} and S_{33} components show the same trend; with increasing sample perfection the thermopowers become less negative, and the minima shift to lower temperatures. Below 10 K the thermopowers of As no. 3 and As no. 4 become again comparable in their magnitudes as well as temperature dependences.

The size of the anomalies observed on the S_{33} thermopower and their dependence on the quality of samples suggests that they have an origin in phonon drag, a situation similar to that of S_{11} thermopower. To substantiate this point further, we shall make an estimate of the diffusion thermopower for both S_{11} and S_{33} tensor components. The difference between the experimental and the diffusion thermopowers will then be identified, from Eq. (1), as the phonon-drag contribution,

$$S_{\text{expt}} = S_{\text{diff}} + S_{\text{drag}} \ . \tag{1}$$

In general, the thermopower of a multicarrier system, such as arsenic, is a weighted difference between the contributions of positive and negative carriers,

$$S = \sum_i \alpha_i \sigma_i \Big/ \sum_i \sigma_i \ , \tag{2}$$

where σ_i represents conductivity associated with ith carrier pocket and α_i is its partial thermopower. We shall assume that arsenic is exactly compensated, and we also neglect the contribution of a small number of γ holes residing in narrow connecting necks.[13] The Fermi energies of electrons and holes, as determined from de Haas–van Alphen measurements,[1] are large ($\epsilon_F^- = 0.190$ eV; $\epsilon_F^+ = 0.177$ eV), and the carrier spectrum may be considered to be strongly degenerate even at room temperature. The diffusion thermopowers for the two directions are obtained from Eq. (2) by taking the partial thermopowers α^- and α^+ as isotropic quantities,

$$S_{11}^{\text{diff}} = \frac{(\pi^2 k_B^2/3|e|)(1/\epsilon_F^+ - A_x/\epsilon_F^-)T}{1+A_x} \ , \tag{3}$$

$$S_{33}^{\text{diff}} = \frac{(\pi^2 k_B^2/3|e|)(1/\epsilon_F^+ - A_z/\epsilon_F^-)T}{1+A_z} \ . \tag{4}$$

Here $A_x = \mu_{11}^- / \mu_{11}^+$ and $A_z = \mu_{33}^- / \mu_{33}^+$ are the mobility ratios for the two crystallographic directions of interest. Assuming that the experimental thermopower above about 80 K is purely of diffusion origin, the ratios A_x and A_z can be calculated from Eqs. (3) and (4) and the results are shown in Fig. 3. Extrapolating the ratios A_x and A_z to lower temperatures and relying on the fact that the diffusion thermopower must smoothly approach zero as $T \rightarrow 0$, estimates of S_{11}^{diff} and S_{33}^{diff} are shown in Figs. 1 and 2 by dashed curves. The anomalies are clearly seen against this background, and one must invoke phonon drag in order to explain their origin. In this sense, the thermopowers of all three group-V semimetals (Bi, Sb, and As) are similar; their low-temperature behavior is dominated by phonon drag.

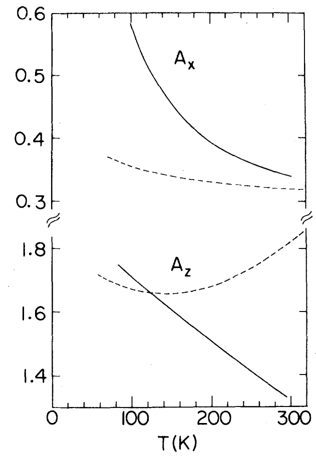

FIG. 3. Temperature dependence of the mobility ratios $A_x = \mu_{11}^- / \mu_{11}^+$ and $A_z = \mu_{33}^- / \mu_{33}^+$ calculated from Eqs. (3) and (4) assuming the Fermi energies of electrons and holes as given by Priestly *et al.* The broken curves represent A_x and A_z of Jeavons and Saunders obtained from their galvanomagnetic measurements (Ref. 18).

We should like to stress that the ratios A_x and A_z as well as the theoretical diffusion thermopowers should be taken as a guide only. They are sensitive, particularly the magnitudes of A_x and A_z, to values of the Fermi energy, which may not be known very accurately even if obtained from the de Haas–van Alphen measurements, normally one of the most precise probes of the Fermi surface. The reason for this is as follows: An estimate of the Fermi energies from the effective masses, which are in turn obtained from the temperature dependence of the oscillations, is virtually always made under the assumption of a parabolic ellipsoidal model. For a highly nonellipsoidal Fermi surface, such as is known to represent holes in arsenic, this may easily lead to a large error in their Fermi energy. Since electronic surfaces resemble ellipsoids more closely, the Fermi energy of electrons could conceivably be more reliable.

The mechanism of phonon drag in semimetals is subject to one important qualification: Owing to the small size of the Fermi surface, the intravalley scattering of charge carriers can occur only with phonons whose momenta satisfy the condition

$$q \lesssim 2k_F \ , \tag{5}$$

where $2k_F$ is the maximum dimension of the Fermi surface. Thus, as noted first by Sondheimer,[14] the effective phonon cutoff is not determined by the true Debye temperature ($\Theta_D = 282$ K), but by an effective Debye temperature

$$\Theta_D^* = 2k_F \hbar s / 1.6 k_B \ . \tag{6}$$

Here $\hbar$ and k_B are the Planck and Boltzmann constants, respectively, and s is the speed of sound. The factor 1.6 comes from the dominant phonon mode at the cutoff.[15] Whenever the phonons acquire sufficient momentum to scatter the carriers across the entire Fermi surface, i.e., when their temperature is Θ_D^*, one expects a large phonon-drag contribution. In fact, in the case of bismuth[10] and its alloys,[16] excellent agreement has been obtained between the temperatures of the thermopower extrema and the effective Debye temperatures calculated from Eq. (6). This applies to both the electron and hole Fermi surfaces and also includes their anisotropy.

Unfortunately, in the case of arsenic, such an interpretation is not very successful. For instance, using a parabolic ellipsoidal approximation and appropriate sound velocities,[17] the effective Debye temperatures of electrons along the binary and trigonal axes are, from Eq. (6), 38 K and 24 K, respectively. Experimentally, large minima are observed for both axes near 10 K. The reason for such a large discrepancy is seen in the fact that the Fermi surfaces of arsenic are strongly nonelliposidal and, in the case of holes, they even lack a center of symmetry. Consequently, it is difficult to estimate the exact values of the Fermi wave vectors along various crystallographic directions.

CONCLUSION

Thermopowers S_{11} and S_{33} have been measured on high-quality single crystals of arsenic in the range 2–300 K. At high temperatures, above 70 K, the S_{11} thermopower is in a good agreement with the measurements of Heremans *et al.* and Jeavons and Saunders, and the thermopower is here entirely due to charge carrier diffusion. We confirm, in agreement with Jeavons and Saunders, that the S_{33} thermopower is negative. The magnitude of the S_{33} is, however, about twice as large and, furthermore, a distinct minimum is observed near 230 K. At lower temperatures, both tensor components show large anomalies which are of phonon-drag origin. Contrary to measurements of Heremans *et al.*, which indicate saturation of the S_{11} thermopower ($-2.5\ \mu\mathrm{V\,K^{-1}}$) below 10 K, our data show clearly that S_{11} reaches a pronounced minimum followed by a change of sign, and the thermopower then approaches absolute zero with positive values. This behavior is thus in excellent agreement with our previous ultralow-temperature measurements.

The low-temperature behavior of S_{33}, reported here for the first time, is typified, for samples of high perfection, by two negative minima. The first, a shallow one, is near 30 K and a much stronger second one is near 10 K. The exact position as well as the depth of the minima depends rather strongly on the perfection of the samples.

At low temperatures, the thermopowers of all three group-V semimetals, Bi, Sb, and As, are dominated by phonon-drag effects. Unfortunately, due to large uncertainties in the magnitudes of the Fermi wave vectors arising from highly nonellipsoidal nature of the Fermi surface of arsenic, we are, in this case, unable to make a direct comparison between the temperatures of the extrema and the calipers of the Fermi surface for any given crystallographic direction.

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