sistivity $\rho_0(\gg\Delta\rho_{\rm dis})$ and if this is now compared with the scattering due to dislocations in the *pure* parent metal, the results, according to the data of Table II, would differ by a factor of about 4, just because of the different anisotropies in the scattering.

CONCLUSIONS

The departures from Matthiessen's rule that we have observed in dilute alloys of Cu and Ag can all be attributed to different anisotropies of the phonon and impurity scattering. The departures found in strained specimens can likewise be accounted for. This explanation gives a qualitative account of the maximum and its concentration dependence. Some approximate quantitative estimates of the anisotropy of τ are consistent with the general theoretical picture except that they do not show any very great difference in the anisotropy due to charged and uncharged impurities.

ACKNOWLEDGMENTS

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Low-Temperature Specific Heat of Arsenic and Antimony†

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The specific heats of arsenic and antimony have been measured from 0.7 to 4.0°K and 0.5 to 4.0°K, respectively. For the electronic contributions we find 0.194 ± 0.007 mJ/mole °K^2 in arsenic, and 0.112 ± 0.005 mJ/mole °K^2 in antimony. Both values are in agreement with de Haas–van Alphen measurements on these semimetals. The lattice specific heat for arsenic is found to be $C_L=0.0880T^3+0.55\times10^{-3}T^5$ mJ/mole °K with $\Theta_D(0)=280.5\pm1.0$°K. For antimony $C_L=0.206T^3+0.0033T^5$ mJ/mole °K with $\Theta_D(0)=211.3\pm1.5$°K.

I. INTRODUCTION

THE semimetals arsenic, antimony, and bismuth make up a family of elements in which there are close resemblances. They all crystallize in rhombohedral *A*7 structures; they show metallic conduction, but much less than normal metals; they all have small Fermi surfaces made up of sets of hole and electron surfaces; and they all have at least one abundant naturally occurring isotope with a nuclear hyperfine structure due to an electric quadrupole interaction.

Phillips[1] has already measured the specific heat of bismuth below 2.0°K. He found (1) a small electronic specific heat due to the small pieces of Fermi surface, (2) a Debye temperature which is not constant at temperatures below $\Theta_D/50$ as is normally found in most metals, and (3) a nuclear specific heat due to the nuclear electric quadrupole interaction at very low temperatures.

Since arsenic and antimony have the same general electronic, lattice, and nuclear hyperfine structures, it is expected, and indeed we find, that the contributions to their specific heat at low temperatures are quite similar to those for bismuth.

The rest of this paper will deal with the expected behavior of the specific heat of arsenic and antimony in Sec. II and the measurement of the specific heat in Sec. III. The results are presented and discussed in the light of theory and other experimental results in Sec. IV.

II. COMPONENTS OF THE OBSERVED C_p

The electronic specific heat C_E obeys a linear temperature law, $C_E=\gamma T$, where

$$\gamma=(\pi^2/3)k^2N(E)\,, \tag{1}$$

and $N(E)$ is the density of electronic states at the Fermi surface. $N(E)$, and therefore γ, can be calculated from the geometry of the Fermi surface if one assumes parabolic energy bands. For an ellipsoidal Fermi surface the maximal areas can be measured by de Haas–van Alphen oscillations in a reciprocal magnetic field, which can be then converted to the effective-mass components α_{ii}. The Fermi energy is obtained from cyclotron-resonance data and the density of states can then be calculated from

$$N(E)=\left(\frac{8\pi V_m}{h^3}\right)\frac{(2E_F)^{1/2}m^{3/2}}{(\alpha_{11}\alpha_{22}\alpha_{33})^{1/2}}\,. \tag{2}$$

Here V_m is the molar volume and m is the electronic mass.

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† Based on work performed under the auspices of the U. S. Atomic Energy Commission. A preliminary report of this work was given at the Chicago meeting of the American Physical Society, October, 1965 [Bull. Am. Phys. Soc. **10**, 1104 (1965)].

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The lattice specific heat C_L for all cubic solids at sufficiently low temperatures obeys the cubic-temperature approximation from the Debye theory, $C_L = A[T/\Theta_D(0)]^3$, where $\Theta_D(0)$ is the Debye temperature at 0°K. The requirement for the approximation to hold is usually taken to be $T < \Theta_D/50$. In cases where Θ_D is not constant at such temperatures, an extra term is added so that

$$C_L = A[T/\Theta_D(0)]^3 + BT^5. \tag{3}$$

The nuclear specific heat for a nucleus of spin I, and quadrupole moment Q in an axial symmetric field gradient of q can be written[2]

$$\frac{C_N}{R} = \frac{1}{45}\left(\frac{3}{4}\frac{e^2qQ}{kT}\right)^2 \frac{(2I+3)(I+1)}{I(2I-1)}, \tag{4a}$$

or

$$C_N = D/T^2, \tag{4b}$$

where e is the electronic charge, k is Boltzmaan's constant, and R is the gas constant. Equations (4a) and (4b) hold only at temperatures well above the maximum in the nuclear specific heat.

The expected temperature behavior of the specific heat for arsenic and antimony is then

$$C_p = \gamma T + \alpha T^3 + \beta T^5 + DT^{-2}. \tag{5}$$

III. EXPERIMENTAL

The specific heats were measured in a He^3 cryostat described previously by Lounasmaa.[3] A germanium resistance thermometer was placed in a hole in the sample with apiezon N grease for thermal contact with the sample. The leads from the thermometer were wound around the sample so that no heat was conducted directly to the thermometer. The heater was 1-mil resistance wire (both Constantan and 91% Pt–9% W alloy were used) wound on a 2-mm-diam polyethylene tube. The polyethylene tube was placed in a hole in the sample with apiezon N grease.

The mass of the addenda (grease, heater wire, etc.) was determined carefully as it was added to the sample. The heat capacity of the addenda was then calculated from the known values of the heat capacities for the materials and subtracted from the final measured heat capacity. It is estimated that the addenda can cause at most a 0.6% systematic error in the final specific heats.

The samples used were 99.9999% arsenic and antimony from Cominico Products, Inc. The only impurities detected by chemical analysis were ~5 ppm Cu in the antimony sample, and 5 ppm Pb and 10 ppm Si in the arsenic sample. The antimony sample was cut from a zone-refined ingot, and was made up of three or four large crystals. The sample was cut into a rough cylinder 2 in. long by approximately 1 in. in diameter. The arsenic sample was prepared by Cominco Products, Inc., by subliming 99.9999% arsenic into a cylindrical mold. The resulting sample was approximately the same size as the antimony sample.

The germanium resistance thermometer was calibrated against the vapor pressure of He^3 between 0.75 and 2.1°K, and against the vapor pressure of He^4 between 2.1 and 4.0°K. Below 0.75°K an uncommon method of thermometer calibration was used. The method, in brief, consists of the measurement of the amount of heat ΔQ necessary to heat a sample (platinum) from some unknown temperature T_i to a final, known temperature T_f. The heat capacity of the sample is measured in the known temperature range and fitted with an appropriate formula. The formula is extrapolated into the unknown temperature region and integrated to yield an expression for ΔQ in terms of T_f and T_i. T_i is calculated from the known values of ΔQ, T_f, and the parameters in the high-temperature heat capacity formula. The calibration obtained in this manner has been checked by measuring the specific heat of a standard calorimetric copper sample.[4] The calibration is good to within a millidegree. A more complete description of this method is to be published.

The calibration data were fitted with the formula

$$T = \sum_{n=0}^{5} \frac{1}{R^n} + (\ln R)^{-1} + (\ln R)^{-2},$$

where R is the thermometer resistance in ohms. The fit was good to better than 1.0 mdeg Kelvin.

The heat capacity was measured in the usual manner by assuming linear temperature drifts between measured heats.

IV. RESULTS AND DISCUSSION

A. Antimony

The specific-heat data for antimony are listed in Table I. The data are plotted as C/T versus T^2 in Fig. 1. Instead of fitting the data with Eq. (5), the nuclear specific heat C_N was subtracted from the data and a least-squares fit was done with the resulting data using the equation

$$C_p = \gamma T + \alpha T^3 + \beta T^5. \tag{6}$$

For the calculation of C_N we used the e^2qQ values for Sb^{121} $(I=\frac{5}{2})$ and Sb^{123} $(I=\frac{7}{2})$ from Hewitt and Williams's[5] NMR data. For the isotopic abundances we used 57.25% for Sb^{121} and 42.25% for Sb^{123}. We did

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[4] 1965 Calorimetry Conference Standard Copper Sample No. 1.4 kindly loaned to us by D. W. Osborne, H. E. Flowtow, and F. Schreiner.

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TABLE I. Specific-heat data for antimony in mJ/mole °K.

T(°K)	C_p	T(°K)	C_p	T(°K)	C_p
Run I		Run II		Run III	
0.7211	0.173	0.8121	0.212	0.4781	0.091
0.7514	0.183	0.8491	0.228	0.5004	0.094
0.8118	0.209	0.9039	0.258	0.5273	0.102
0.8785	0.243	0.9848	0.308	0.5740	0.114
0.9693	0.299	1.0778	0.382	0.6278	0.130
1.0768	0.380	1.1919	0.489	0.6715	0.145
1.1698	0.464	1.3136	0.627	Run IV	
1.2677	0.570	1.4162	0.762	0.4548	0.088
1.3922	0.728	1.5426	0.958	0.5294	0.103
1.4726	0.846	1.6873	1.223	0.5905	0.118
1.6323	1.118	1.8446	1.568	0.6392	0.134
1.8076	1.479	2.0184	2.025	0.6958	0.149
2.0899	2.243	2.1949	2.584	0.7906	0.200
2.2284	2.701	2.4267	3.490	0.8991	0.253
2.4040	3.391	2.6833	4.762	Run V	
2.6335	4.484	2.9154	6.156	0.6951	0.153
2.8620	5.815	3.1630	7.918	0.7501	0.173
3.0861	7.361	3.4693	10.595	0.8315	0.214
3.3242	9.312	3.7724	13.892	0.9122	0.261
3.5965	11.974	4.0072	17.207	0.9947	0.316
3.8767	15.249				

not try to include a T^{-2} term in our fitting formula since the nuclear contribution is only slightly more than 10% of the total specific heat for the lowest temperatures (~0.5°K) at which we measured the specific heat.

The best fit for Eq. (6) is shown as the solid line in Fig. 1. The coefficients for the best fit of Eq. (6) to the antimony data are $\gamma=0.112\pm0.005$, $\alpha=0.206\pm0.001$, and $\beta=0.003\pm0.0001$. The errors are 1 standard deviation.

The value for γ can be compared with that calculated from Eqs. (1) and (2) using the de Haas–van Alphen data for Sb of Windmiller and Priestley.[6] The Fermi energy was calculated using the effective masses from Windmiller's data.[7] The calculated coefficient is $\gamma=(0.115\pm0.004)$ mJ/mole °K^2 in very good agreement with the specific heat measurement. When our value for γ is compared to those from previous specific heat experiments, the agreement is poor. Ramanathan and Srinivasan[8] have reported a γ of 0.2406 mJ/mole °K^2, while Wolcott[9] has reported a γ of 0.63 mJ/mole °K^2 for antimony. The discrepancy is apparently due to the lesser purity of the samples used in these earlier experiments, although there is no information on the purity of Wolcott's sample; but his use of He^4 exchange gas puts his result in doubt. More recently, McCollum and Taylor[10] and Zebouni and Blewer[11] have measured the specific heat of antimony. They found values for γ of 0.105 ± 0.002 and 0.116 ± 0.006, respectively, in good agreement with our value.

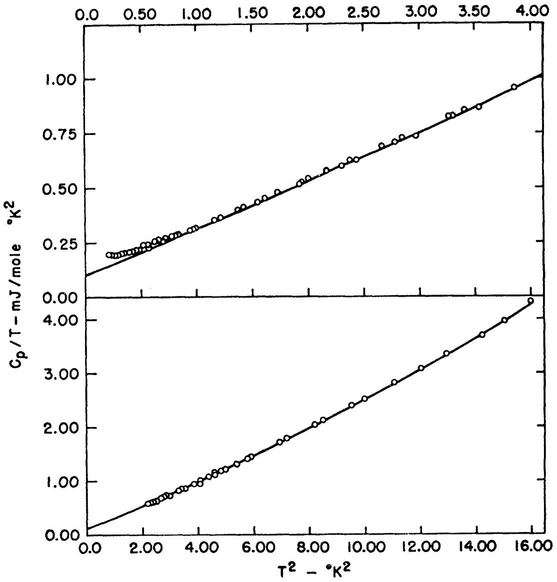

FIG. 1. Specific-heat data for antimony. The solid line is the equation $C_p=0.112T+0.2060T^3+0.0033T^5$.

TABLE II. Specific-heat data for arsenic in mJ/mole °K.

T(°K)	C_p	T(°K)	C_p	T(°K)	C_p
Run I		2.2702	1.497	Run III	
0.7013	0.180	2.5017	1.903	0.7895	0.202
0.775	0.199	2.6880	2.332	0.9062	0.243
0.8386	0.220	2.7643	2.475	1.0610	0.312
0.8900	0.234	2.9747	3.044	1.3013	0.451
0.9619	0.267	3.1710	3.667	1.4230	0.537
1.0640	0.314	Run II		1.5841	0.667
1.1482	0.359	0.8516	0.222	1.7690	0.844
1.2201	0.404	0.9307	0.252	1.9145	1.005
1.2880	0.442	1.0273	0.295	2.1049	1.254
1.3586	0.489	1.1332	0.349	2.3487	1.638
1.4340	0.544	1.2357	0.408	2.8780	2.782
1.7308	0.803	1.4350	0.545	3.2787	3.934
1.9632	1.060	1.5364	0.628	3.5707	4.977
2.2521	1.466	1.6326	0.708	3.7995	5.958
2.4141	1.748	1.7175	0.792	3.9840	6.946
		1.9065	0.996		

The Debye temperature for antimony calculated from the coefficient of the T^3 term in Eq. (6) is $\Theta_D(0)=(211.3\pm1.5)$°K. In spite of this fairly high value for $\Theta_D(0)$, it was necessary to use a T^5 term in the fitting equation. A similar effect was found by Phillips in his specific heat measurements on bismuth (Θ_D not constant below 2°K). The absence of low-temperature measurements of the elastic constants of antimony make it impossible to check this behavior for the lattice specific heat. Previous specific-heat measurements on antimony give values for $\Theta_D(0)$ in rough agreement with

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ours: Ramanathan and Srinivasan[8] reported $\Theta_D(0) = 206.8°\mathrm{K}$, Wolcott[9] reported $\Theta_D(0) = 204°\mathrm{K}$, McCollum and Taylor[10] reported $\Theta_D(0) = (210\pm0.7)°\mathrm{K}$ and Zebouni and Blewer[11] reported $\Theta_D(0) = 209.6°\mathrm{K}$.

B. Arsenic

The arsenic specific-heat data are listed in Table II and plotted as C_p/T versus T^2 in Fig. 2. The data were fitted with Eq. (5). There are no NMR data available for arsenic and thus no correction was made for the nuclear specific heat before fitting. The specific heat was measured only down to 0.7°K on arsenic and so there is a great deal of uncertainty in the T^{-2} coefficient. We venture only to say that the nuclear term for arsenic appears to be smaller than the nuclear term for antimony, and we report no definite value.

The γ value for arsenic from Eq. (6) is (0.194 ± 0.007) mJ/mole °K^2. Priestley *et al.*[12] have determined the shape of the Fermi surface of arsenic. Although the hole surface is a multiply connected set of six distorted ellipsoids, Priestley *et al.* have calculated γ assuming parabolic bands, ellipsoidal pockets, and cylindrical connecting necks. They calculate $\gamma = 0.192$ mJ/mole °K^2, which agrees with the specific-heat measurement much better than expected.

The lattice specific heat for arsenic was found to be

$$C_L = 0.0881T^3 + 0.55\times10^{-3}T^5 \text{ mJ/mole °K}. \qquad (7)$$

The Debye temperature calculated from the T^3 coefficient is $(280.5\pm1.0)°\mathrm{K}$. It is interesting that with such a large Debye temperature, the lattice specific heat is not a simple cubic function of T below 4°K. The noncubic behavior of the specific heats of arsenic and antimony below 4.0°K may be due to the presence of so-called "soft" modes in the vibrational spectrum. Desorbo[13] and Kothari and Tewary[14] have discussed these modes in terms of atomic displacements perpendicular to the "puckered" layers in the $A7$ crystal structure. Desorbo suggests that 11.1% of the total modes of vibration in the antimony crystal are "soft" and have a characteristic temperature (Desorbo's Θ_2) of 70°K. With such a large fraction of the modes still able to be excited at low temperatures, one might well expect to find more than a cubic temperature term in C_L at low temperatures.

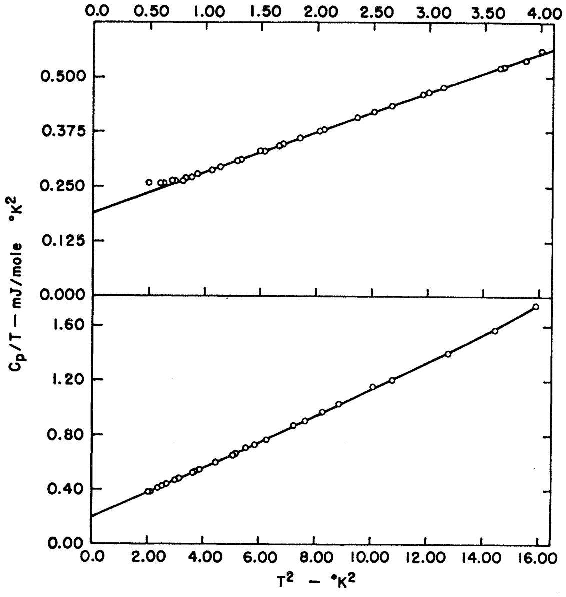

FIG. 2. Specific-heat data for arsenic. The solid line is the equation $C_p = 0.194T + 0.08801T^3 + 0.00055T^5$.

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