number of free electrons is still small compared with the number of interstitial zinc atoms and the free electron contribution to the entropy is negligible in comparison with that of the interstitial zinc atoms.

In conclusion I wish to thank M. D. Earle, S. J. Angello, and members of Works Progress Administration Project 25792 for assistance in observation. I am also deeply indebted to Dr. F. Seitz for his many helpful discussions of the theoretical side of the problem in which he suggested many of the arguments presented here.

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Variation of the Magnetic Properties of Antimony with Electron Concentration

S. H. BROWNE* AND C. T. LANE
Sloane Physics Laboratory, Yale University, New Haven, Connecticut
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The principal magnetic susceptibilities of single crystals of pure Sb and solid solution alloys of Sb with Sn, Ge, Pb, and Te have been determined. It is found that as the percent of alloying metal increases the susceptibility perpendicular to the trigonal axis ($\kappa_\perp$) changes but little and remains diamagnetic. On the other hand the susceptibility parallel to this axis ($\kappa_{||}$) decreases sharply in magnitude and, in the case of Sn and Ge, changes from diagmagnetic to paramagnetic beyond 1.17 atomic percent Sn and 1.25 atomic percent Ge. This result permits us to calculate the number of electrons which overlap into the second Brillouin zone in antimony as 10^{-2} electron per atom. The bearing of these results on the current theory of metals is discussed.

IN recent years substantial advances in the theory of the solid state have been made, and at the present time we have at least a qualitative understanding of many of the properties of metals. The position on the quantitative side is less satisfactory and comparatively few experiments have been performed which can be considered to be in good agreement with theory.[1] Among the kind of experiments which could be considered suitable for a quantitative check on the theory are those dealing with magnetic susceptibility, since it is known that this quantity should depend primarily on temperature and electron concentration. This sort of experiment is particularly favorable since, in many elements, the electron concentration and temperature may be varied independently. In the present work only the effect of varying the electron concentration is studied.

A convenient method of varying this quantity in a given metal is to alloy it with known amounts of another metal whose valence is different from that of the parent substance. However, with few exceptions, the electrons in a metal cannot be considered as "free." Rather, they are coupled to the lattice ions, that is, they move in a potential field due to these ions, which varies in a periodic manner throughout the crystal. Hence in order to vary the electron concentration it is also necessary to ensure that the alloying element does not appreciably disturb the lattice structure of the pure metal to which it is added. This latter condition, of course, can never be perfectly complied with. Nevertheless, it may be closely approximated by choosing the alloying elements such that they form a simple solid solution with the parent metal. In this case the foreign atoms go into the parent lattice by simple substitution, and, provided they comprise only a few percent of the total atoms present they do not materially change either the original lattice type or its parameters.

Antimony was chosen for the present investigation, since it is possible with this element to realize all the conditions imposed above. Elements possessing one less electron per atom than

* Now with the Corning Glass Works, Corning, New York.

[1] A good modern exposition of the whole subject is to be found in F. Seitz, *Modern Theory of Solids*, (McGraw-Hill, 1940).

TABLE I. *Susceptibility data on pure antimony.*

	$\chi_\perp(10^6)$	$\chi_\parallel(10^6)$	$\chi_\parallel/\chi_\perp$
McLennan and Cohen[1]	−0.63	−1.13	1.79
deHaas and van Alphen[2]	−0.66	—	—
Shoenberg and Uddin[3]	−0.55	−1.42	2.58
Stock A	−0.51	−1.37	2.69
Stock B	−0.51	−1.41	2.77
Stock C	−0.50	−1.42	2.84

[1] J. C. McLennan and E. Cohen, Trans. Roy. Soc. Can. **23**, 159 (1929).
[2] H. deHaas and P. van Alphen, Leiden Comm. No. 255b (1933).
[3] D. Shoenberg and M. Uddin, Proc. Camb. Phil. Soc. **32**, 499 (1936).

antimony (Sn, Pb, Ge) all form solid solutions with it within a range of a few percent,[2] as does tellurium, which has one more electron per atom than antimony. In addition the theory, supported by resistivity measurements, indicates that the electric and magnetic properties of antimony are chiefly due to a few electrons which overlap into the second Brillouin zone. Hence in order to vary the pertinent electron concentration widely only small percentages of the alloying elements are likely to be necessary, and this is important, as has been stressed above.

EXPERIMENTAL PROCEDURE

Three different stocks of antimony metal were used. Stocks A and B were two different lots from Eimer and Amend and listed as C.P. Stock C was from Mallinckrodt and the analysis given by them was Sb 99.96 percent. The alloying elements were all of the highest purity available, although since they were used in small amounts only, this was less important.

The specimens in every case were single crystals in the form of long rods of uniform cross section about 0.3 cm diameter and 15 cm long. The required composition of the alloy was obtained by weighing the constituents. These were melted in a quartz crucible under a hydrogen atmosphere and then cast in a graphite mold into polycrystalline rods of the required size. The casting was then placed in a second graphite mold made in two semicircular halves with a 3-mm hole down the center for the casting and converted into a single crystal by means of the horizontal traveling furnace method.[3] During this process an atmosphere of hydrogen was maintained around the crystal. By means of an etch in dilute aqua regia it could be determined whether the rod was a single crystal over its entire length. It was found that in order to obtain good single crystals of uniform composition, the speed of growing the crystals had to be increased as the amount of the alloying element was increased. This was probably due to the fact that "impurities" tend to separate out of solution during crystallization if it is carried out slowly enough.

The most desirable orientation for magnetic measurements is that in which the cleavage plane, (111), is parallel to the axis of the rod, (i.e., the principal axis perpendicular to the axis of the rod). For some crystals this condition was brought about by "seeding." Some trouble was encountered when the attempt was made to use a seed of pure antimony for alloys of 0.25 percent tin or more. A good crystal was obtained but subsequent magnetic measurements indicated that the composition of the alloy crystal varied from one end to the other; the end of the crystal nearest the seed had very little tin left in it, while at the far end the composition was essentially unchanged. It was then possible to obtain an alloy crystal of uniform composition if the seed for the new crystal was taken from the far end of the one previously grown. As long as the difference between the compositions of the seed and new crystal did not exceed about 0.25 percent, this procedure was applicable, otherwise it was necessary to repeat the process several times. Because of the labor involved, the process of seeding was discarded and in many of the subsequent crystals the orientation of the (111) plane to the axis of the rod was determined optically by cleaving the crystal at one end and

TABLE II. *Resistivity ratio versus temperature for a single crystal of Stock C antimony.*

TEMPERATURE °K	ρ_T/ρ_{297}
297	1.000
90	0.233
77.3	0.185
63	0.141
4.2	0.0092

[2] We have been unable to find in the literature a phase diagram for the system Sb-Ge. However, our results indicate very strongly that Ge must form a solid solution with Sb to at least 1.83 atomic percent Ge.

[3] M. F. Hasler, Rev. Sci. Inst. **4**, 656 (1933).

making use of optical reflections from this cleave plane in a Fuess goniometer. The error thus introduced in the magnetic measurements was not over 0.2 percent. Susceptibilities were determined by the Gouy method in which the force on a long specimen of uniform cross section is given by $F=\frac{1}{2}(\kappa-\kappa_0)A(H^2-H_0^2)$. Here κ and κ_0 are the volume susceptibilities of the specimen and surrounding medium (air), H and H_0 the field strengths at the two ends of the specimen, and A is its cross section. Since κ_0 is known and H_0^2 is negligible for long specimens, the quantities to be measured are F, H, and A.

The relation between the measured and principal susceptibilities (for any orientation) is

$$\kappa=\{\kappa_{\parallel}\sin^2\varphi+\kappa_{\perp}\cos^2\varphi\}\cos^2\theta+\kappa_{\perp}\sin^2\theta,$$

where φ is the azimuth of the trigonal axis with respect to the rod, and θ is the latitude with respect to the magnetic field. Since φ is known it is sufficient to determine the maximum and minimum force on the specimen in the field as it is rotated about its axis in order to find $\kappa_{\parallel}$ and $\kappa_{\perp}$.

Fields of the order of 13,000 Gauss supplied by a Weiss magnet were used and forces determined with a Sartorius microbalance. A rigid glass suspension was used to connect the crystal to the balance arm to prevent twist of the specimen in the field and this was provided with a small turn-table so that the crystal could be rotated about its axis. No dependence of susceptibility on field could be detected and hence no measurable amount of ferromagnetic impurity was present in the crystals. In all instances the crystals were measured first with one end in the strongest part of the field and subsequently with the other end so placed. If the two determinations failed to agree within the experimental error the crystal was rejected. Since, in the Gouy method, about 90 percent of the force on the crystal is due to that part of the field gradient close to the strongest part of the field, an excellent check on the uniformity of composition of the crystal could be obtained in this way. The error in the susceptibility measurements is probably less than 1 percent.

TABLE III. *Susceptibility data on alloys of single crystals of antimony.*

Atomic Percent Added Metal	$\kappa_{\parallel}(10^6)$	$\kappa_{\perp}(10^6)$	$\kappa_{\parallel}/\kappa_{\perp}$
	Sb-Sn		
0.252	−7.44	−3.31	+2.246
.489	−5.05	−3.31	+1.526
.784	−2.47	−3.10	+0.798
1.055	−0.52	−2.96	+0.176
1.543	+1.30	−2.72	−0.477
2.051	+2.46	−2.42	−1.018
3.078	+3.46	−2.05	−1.686
4.100	+3.85	−1.85	−2.080
5.321	+3.51	−1.54	−2.274
5.782	+3.16	−1.49	−2.119
7.081	+2.86	−1.41	−2.028
	Sb-Ge		
0.572	−5.29	−3.29	+1.610
1.090	−1.21	−2.87	+0.421
1.827	+3.51	−2.30	−1.530
	Sb-Pb		
0.596	−7.55	−3.36	2.249
1.484	−5.22	−3.32	1.573
2.364	−3.75	−3.16	1.188
4.207	−2.60	−3.16	0.823
	Sb-Te		
0.952	−8.97	−3.64	2.465
1.524	−8.59	−3.62	2.370
1.845	−8.56	−3.74	2.290

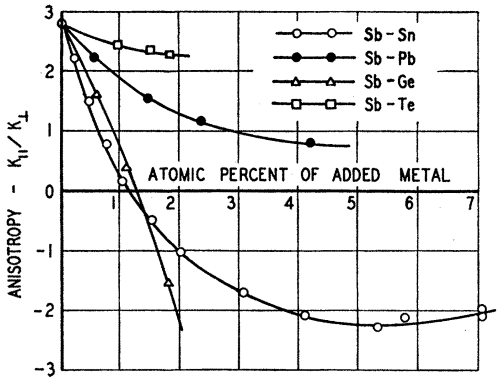

FIG. 1. Magnetic anisotropy of antimony alloys as a function of composition.

RESULTS

Table I gives the results for the Stocks A, B, and C of pure antimony, together with all other previous determinations known to us. Our results have been reduced to mass susceptibilities in this particular case for the sake of comparison. The most recent determination, apart from ours, was carried out by Shoenberg and Uddin, who used spectroscopically pure antimony. Since, as we shall show, the presence of impurities always tends to decrease the anisotropy ratio $\chi_{\parallel}/\chi_{\perp}$ we

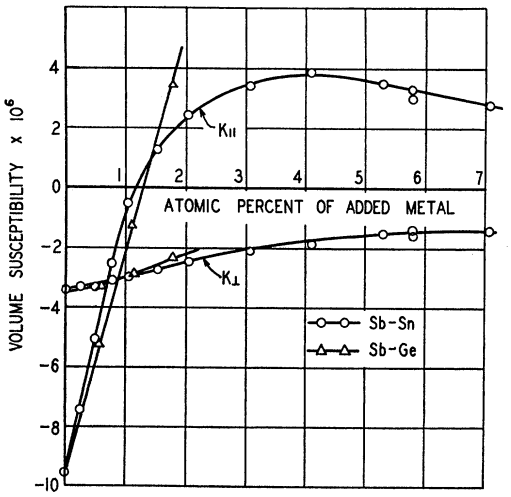

FIG. 2. Principal susceptibilities of Sb-Sn and Sb-Ge alloys.

regard Stock C as our best material and most of the alloy crystals were made from it.

As a further check on the purity of our Stock C antimony we have measured the resistivity of one of our single crystals, at various temperatures, down to the temperature of liquid helium. The result of this measurement is shown in Table II where ρ_T/ρ_{297} is the ratio of the resistivity at the given temperature to that at room temperature, 297°K in this case. The "residual resistance" of this crystal is seen to be not more than one percent of its resistance at room temperature and this low value indicates a very pure and strain-free crystal.

In Table III the composition and magnetic susceptibilities of the various alloy crystals at room temperature are given, and these results are plotted in Figs. 1, 2, and 3.

DISCUSSION

It will be noticed that, in all cases, the anisotropy ($\kappa_{\parallel}/\kappa_{\perp}$) decreases as the amount of alloying material increases and in the case of Sn and Ge eventually becomes negative. This is a rather curious result since, in the negative region, it means that the crystal is paramagnetic in one direction and diamagnetic at right angles thereto. A somewhat similar effect has been found for Bi, but only at low temperatures.[4] It will further be noted that the inversion point of the anisotropy (where the susceptibility is zero in one direction) is practically the same for both Sn and Ge alloys.[5] The Pb-Sb and Te-Sb alloys would never reach a negative anisotropy since the last points plotted in each case are very close to the limit of solubility for the required solid solution. In Figs. 2 and 3 where the separate principal susceptibilities are plotted it is seen that, for all alloys, the variation of $\kappa_{\perp}$ with composition is small. The paramagnetism mentioned previously arises solely in $\kappa_{\parallel}$.

These results can be brought into good agreement with theory if one supposes, as do Mott and Jones, that $\kappa_{\parallel}$ is due to electrons which overlap into the second Brillouin zone, while $\kappa_{\perp}$ is due mainly to positive holes in the first zone. Thus the addition of Sn or Ge, each of which possesses one electron per atom less than antimony, will result in reducing the number of overlapping electrons. Accordingly it is reasonable to suppose that, at the inversion point, the overlap has been completely removed and consequently the curves in Fig. 2 permit us to calculate the amount of this overlap. Since, however, the lattice ions also contribute a constant diamagnetism, this must be taken account of. The value of the diamagnetism of Sb^{5+} is not known experimentally with any precision; it has, however, been calculated by Van Vleck[6] as -1.32×10^{-6} per unit volume. Accordingly one must decrease the absolute magnitude of all the susceptibilities given in Figs. 2 and 3 by this amount, in other words shift the origin of coordinates downward and this will result in moving the inversion point to somewhat lower percentages of Sn and Ge, respectively. When

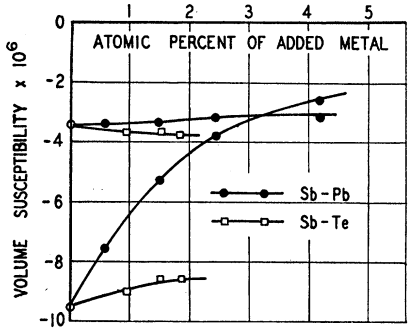

FIG. 3. Principal susceptibilities of Sb-Pb and Sb-Te alloys.

[4] A. Goetz and A. Focke, Phys. Rev. **45**, 170 (1934).

[5] 1.17 atomic percent Sn and 1.25 atomic percent Ge.

[6] J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, 1932).

this is done the overlap comes out to be very close to 10^{-2} electron per atom and this is a reasonable figure. Also the fact that the corrected value of $\kappa_\perp$ is small and substantially independent of composition tends to support the correctness of the above views.

It must, however, be pointed out that the behavior of Sb-Pb and Sb-Te alloys are at variance with the theory. The $\kappa_{||}$ for Pb shows no inversion although its valence is the same as that of Sn or Ge. However the value of $\kappa_{||}$ does indeed decrease, as it should, and when it is remembered that the Pb atom (atomic weight 207) is much heavier than the Sb atom (atomic weight 121.8) it is perhaps reasonable to suppose that the structure of the antimony lattice will undergo more modification here than in the case of the lighter elements.

In the case of Sb-Te, $\kappa_{||}$ should increase since in this case we are adding to the overlap because Te possesses one more electron per atom than Sb. This is seen not to be the case, although $\kappa_{||}$ for Sb-Te does decrease much less than for any of the other alloys. Also here the atomic weights in the two cases are very similar so that the argument advanced in the case of Sb-Pb is not tenable.

Despite these imperfections, however, the results on the whole do offer a rather gratifying check on the correctness of the current theory. One of us (S.H.B.) presented part of this work to the Faculty of the Graduate School of Yale University for the degree of Doctor of Philosophy. Part of the equipment used in this work was purchased by a grant from the George Sheffield Fund.

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Temperature Variation of the Magnetic Susceptibilities of Antimony-Tin Alloys

S. H. BROWNE* AND C. T. LANE
Sloane Physics Laboratory, Yale University, New Haven, Connecticut

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The principal magnetic susceptibilities of single crystals of pure antimony and of antimony-tin alloys up to 4.1 atomic percent tin have been determined in the temperature range 77°K to room temperature. The measurements were made with a modified Sucksmith-Jackson ring balance. It is found that the diamagnetic suspectibility perpendicular to the trigonal axis ($\kappa_\perp$) is practically independent of temperature for all the alloys. The susceptibility parallel to this axis ($\kappa_{||}$) decreases in magnitude with increase in temperature, both for alloys in which $\kappa_{||}$ is diamagnetic and those in which it is paramagnetic, with one exception, the alloy of 1.06 atomic percent tin. A suitable correction for the temperature-independent diamagnetic susceptibility of the lattice ions brings this exception into agreement with the others. The experimental values of $\kappa_{||}$ are compared with Stoner's expressions for the susceptibilities of free electrons, on the assumption that $\kappa_{||}$ is due to the electrons overlapping into the second Brillouin zone. Good agreement is obtained by adjusting the parameter ζ_0, the upper limit of the Fermi distribution, and the degeneracy temperature of these electrons is found to be approximately 475°K, about 0.25 of what it would be for perfectly free electrons. This indicates that the effect of the lattice field is to suppress the value of ζ_0 by increasing the density of electronic energy levels. Values of the effective masses of the electrons, which occur as parameters in the energy equation, are computed, and the energy interval between the bottom of the second Brillouin zone and the top of the Fermi distribution is estimated as about 0.04 ev.

IT has been pointed out in a previous paper[1] that the magnetic susceptibility of a solid should depend chiefly on the concentration of the electrons in the solid and on the temperature. In that paper (referred to hereafter as I) the effect of changing the electron concentration in single crystals of antimony by alloying with small amounts of other metals was discussed. In the present discussion, the effect of temperature variation is to be considered. In particular, the principal magnetic susceptibilities of single crystals of antimony-tin alloys of from zero to approximately 4.1 atomic percent tin

* Now at the Corning Glass Works, Corning, New York.
[1] S. H. Browne and C. T. Lane, Phys. Rev. **60**, 895 (1941).