

combination of holes and electrons can be calculated by a simple modification of the above procedure.

CONCLUSION

A method is given for the calculation of all the thermomagnetic effects based on a multiple-ellipsoidal energy surface model. It is shown that the kinetic reciprocal coefficients satisfy the generalized Onsager^{4,5}

reciprocal relations. It is thought that the formulation might be used to correlate the thermomagnetic properties of a metal with its effective masses as found from de Haas-van Alphen effects.⁶

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Electrical Properties of Germanium-Silicon Alloys*

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Resistivity measurements have been performed from 300° to 800° Kelvin on homogeneous germanium-silicon alloys. The intrinsic lines for these alloys have been established. Hall and resistivity measurements have been performed on *p*-type germanium-silicon alloys from 77° to 300°K. The variation of mobility with composition of the alloy is indicative of alloy scattering.

1. INTRODUCTION

THE preparation of homogeneous alloys of germanium and silicon was reported originally by Stohr and Klemm¹ in 1939. More recently, these alloys have been prepared by Wang and Alexander² and by Johnson and Christian.³

The availability of these alloys has stimulated considerable interest in their properties. The alloys are substitutional and the diamond crystal structure is maintained. Nevertheless, the periodicity of the lattice is disturbed by the random arrangement of the constituent atoms on the lattice sites. For this reason certain properties of germanium alone and silicon alone need to be re-examined for the alloys.

The usual energy band concept, based on a one-electron wave equation approximation, depends strongly on the assumption of a periodic potential in the crystal. In the alloys, with periodicity disturbed, one might expect that a distinct band structure would not obtain. The optical determination of forbidden band width of the alloys by Johnson and Christian³ are based on absorption curves with slopes which are similar to that for germanium alone. This seems to imply that, at least so far as the forbidden band width is concerned,

a distinct band structure does exist for each alloy. If a distinct band structure does indeed exist for the alloys, it is then possible to speculate, as Herman⁴ has, on the manner in which the band structure of germanium deforms to become the band structure of silicon as the composition of the alloy is changed from 0% silicon to 100% silicon.

On the basis of Hall mobility data which will be described in the present work, it seems likely that the aperiodicity of the lattice manifests itself on a scale which strongly affects the mobilities of carriers in the alloys. Brooks⁵ has suggested that in a random solid solution the composition will vary from region to region by virtue merely of normal statistical fluctuation. This will produce a hill and valley structure in the band edges and deformations in the energy bands which can be treated in a manner entirely analogous to the deformation potentials which arise in the theory of thermal scattering. If the mean free path for scattering by this mechanism is calculated, one loses a factor $1/T$ which appears in the calculation of the mean free path in thermal scattering. Thus the alloy scattering is treated as a "frozen-in" thermal scattering, and the anticipated temperature dependence for this scattering mechanism is $T^{-0.5}$ in contrast to the dependence $T^{-1.5}$ expected for thermal scattering. An important parameter determining the magnitude of the alloy scattering is the rate of shift of the band edge with composition of the alloy. This parameter is analogous to the parameter describing the rate of shift of the band edge with deformation in the theory of thermal scattering. Brooks

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¹ H. Stohr and W. Klemm, *Z. anorg. u. allgem. Chem.* **241**, 305 (1939).

² C. C. Wang and B. H. Alexander, American Institute of Mining and Metallurgical Engineers Symposium on Semiconductors, New York City, February 15-18, 1954 (unpublished). See also Final Technical Report, Bureau of Ships Contract No. NObsr-63180 (unpublished).

³ Everett R. Johnson and Schuyler M. Christian, *Phys. Rev.* **95**, 560 (1955).

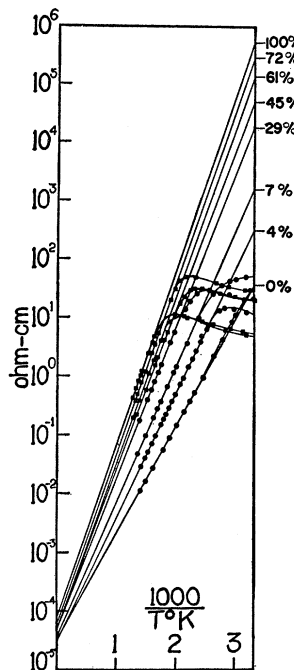
⁴ Frank Herman, *Phys. Rev.* **95**, 847 (1954).

⁵ Harvey Brooks (private communication).

performed his calculation at a time when the variation of energy gap with composition was not known. He assumed that the energy gap changes linearly with composition of the alloy, and that the change in gap is shared equally by the edges of the valence and conduction band. On this basis Brooks predicted that alloy scattering would be greater than thermal scattering at room temperature, for samples with greater than 8% of minority constituent. If we assume that the temperature dependence of the alloy scattering obtained by Brooks is correct then in the absence of scattering mechanisms other than alloy scattering and thermal scattering, the mobility will be given by

$$\frac{1}{\mu} = \frac{1}{\mu_A} + \frac{1}{\mu_T} = AT^{0.5} + BT^{1.5}. \quad (1)$$

FIG. 1. Resistivity of germanium-silicon alloys versus temperature in the intrinsic range. The extrapolation of the intrinsic resistivities to room temperature is shown.



In (1), μ_A is the mobility to be associated with alloy scattering alone and μ_T is the mobility to be associated with thermal scattering alone. For thermal scattering, the exponent 1.5, expected from acoustical mode scattering, is used for illustrative purposes. The argument which follows requires only that the exponent characterizing the thermal contribution to the reciprocal mobility be greater than the exponent characterizing the alloy contribution. With a mobility law of this form it is clear that in the absence of other scattering mechanisms the slope of the log-log plot of mobility against temperature will change from a value characteristic of thermal scattering to one characteristic of alloy scattering as the temperature is reduced. The relative magnitudes of the coefficients A and B , and the magnitude of other scattering mechanisms will determine whether or not alloy scattering is detectable.

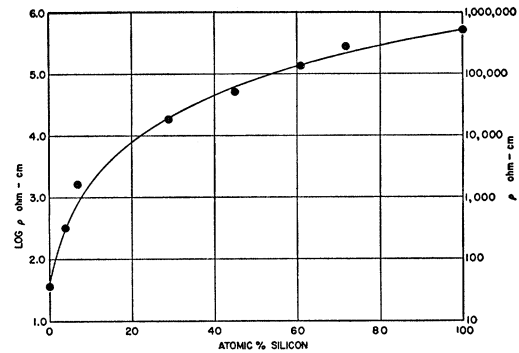


FIG. 2. Intrinsic resistivity of germanium-silicon alloys at room temperature versus composition.

The argument presented above suffers from the assumption that thermal scattering in the alloys can be represented as a simple power law in temperature. The calculation of thermal scattering requires that the lattice vibrations be described in normal coordinates. The usual transformation to normal coordinates⁶ results in a diagonalization of the configurational energy of the system provided the lattice is periodic. For the alloys, it seems clear that this problem needs to be reexamined before definite statements can be made concerning the thermal scattering.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

The alloys used in this work were prepared by C. C. Wang of this laboratory, using an isothermal solidification technique which effectively avoids the phenomenon of coring and makes it possible to produce homogeneous alloys without annealing. This technique has been previously described.² The germanium used was zone purified to room temperature resistivity better than 40 ohm-cm. The silicon was du Pont, classified as hyperpure. No chemical impurity was deliberately added to these alloys. The impurity concentrations indicated by the Hall measurements are of the

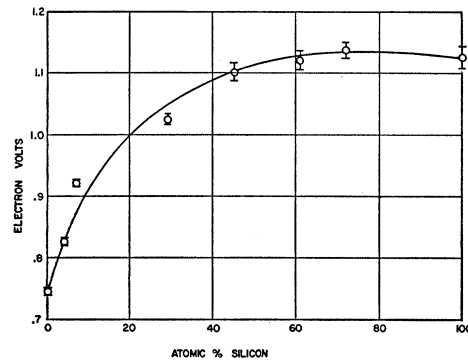


FIG. 3. The energy gap of germanium-silicon alloys versus composition.

⁶ See, for example, F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Sec. 22.

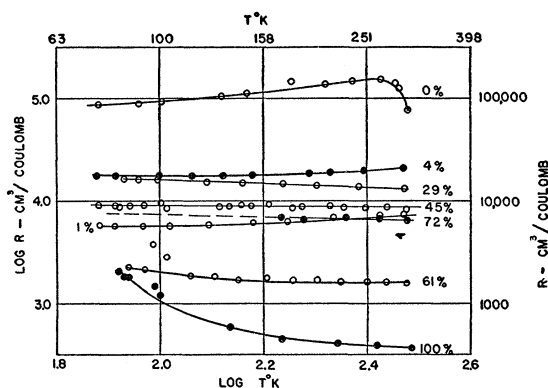


FIG. 4. Hall coefficient *versus* temperature of eight *p*-type germanium-silicon alloys.

order of 10^{14} per cc. The homogeneity of the alloys was verified by x-ray diffraction. The compositions, indicated in the figures in atomic percent silicon, were determined by chemical analysis. The alloys used in this study are mostly polycrystalline, the exceptions being the 1% and 4% samples which are single crystal.

The electrical measurements performed consisted of resistivity measurements in a temperature range extending from 300°K up to 800°K and Hall and resistivity measurements in a temperature range extending from 77°K up to 300°K. The high-temperature measurements were taken on *p*-type samples with the exception of the 7% sample which was *n*-type. These measurements establish the intrinsic resistivity lines for the alloys. The low-temperature measurements were taken on *p*-type samples only. These measurements will be shown to yield evidence for the existence of alloy scattering. The magnetic field strength employed for the Hall measurements was 1300 gauss. The measuring technique consisted of the standard potential probe method. High-temperature measurements were performed in an inert atmosphere. Temperature stability for the low-temperature measurements was achieved with the use of a holder of large heat capacity, inserted in a Dewar flask. Auxiliary equipment con-

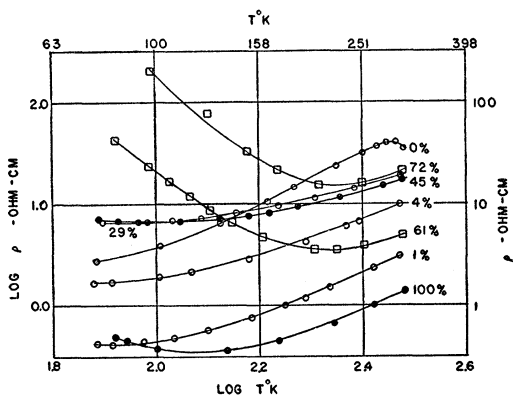


FIG. 5. Resistivity *versus* temperature of eight *p*-type germanium-silicon alloys.

sisted of appropriate switching circuits and a Leeds and Northrup type K potentiometer.

3. RESULTS AND INTERPRETATION

3.1 Intrinsic Range

The high-temperature resistivity results are shown in Fig. 1, which is a semilog plot of resistivity *versus* reciprocal temperature. The room-temperature intrinsic resistivities, shown in Fig. 2, were obtained from the results of Fig. 1 by extrapolation. It is clear that the intrinsic lines of Fig. 1 can be reconciled by a conventional law of the form:

$$\rho = A \exp(E_G/2kT). \quad (2)$$

The parameter E_G as a function of composition of the alloy is shown in Fig. 3. The parameter E_G may be considered the energy gap for the alloys, although this interpretation should be regarded with caution. If distinct band edges do not exist in the alloys, then E_G

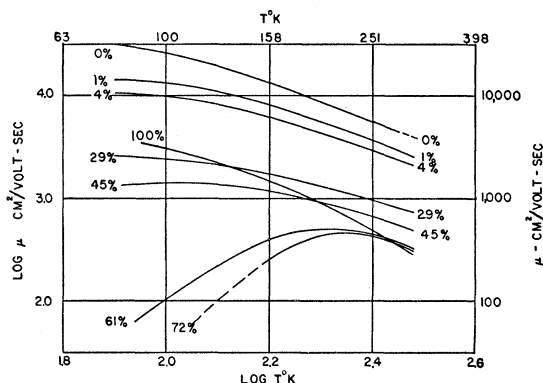


FIG. 6. Hall mobility of holes *versus* temperature in germanium-silicon alloys.

is an effective gap in the sense that it reconciles the resistivity data with the conventional law. The variation of energy gap with composition determined optically by Johnson and Christian,² exhibits the following characteristics: In the range 0 to 15% silicon, the gap increases linearly from 0.72 to 0.94 eV. A discontinuity in slope then occurs and the gap increases linearly at a lesser rate to a value of 1.20 eV for 100% silicon. Herman,⁴ explaining the optical results, has suggested that for an alloy of about 15% silicon the minimum in the conduction band shifts discontinuously in k space. If this is correct, then the resistivity data for alloys near 15% silicon would have to be interpreted in terms of a model which admitted two kinds of carriers in the conduction band and would require two parameters, E_G^1 and E_G^2 , for a complete description.

If for the moment Fig. 3 is accepted at face value, that is taken as describing the energy gap of the alloys *versus* composition, it may be noted that the slopes of this curve at the end points are consistent with recent experiments on germanium and silicon at high pressures

reported by Brooks.⁷ Brooks has reported that while the coefficient of change of the energy gap of germanium with pressure is positive, the result for silicon indicates a decreasing energy gap with applied pressure. It should be pointed out, however, that the maximum in Fig. 3 is just barely detectable within the experimental accuracy, and may be in error.

The curve of energy gap *versus* composition has been previously published.⁸ It is repeated here for the reason that subsequent to the original publication the composition of the alloys were determined more precisely, and this determination required a slight revision of this curve. The energy gap determinations are based on 4 to 8 resistivity runs for each sample.

3.2 Extrinsic Range

Resistivity measurements and Hall measurements at a field strength of 1300 gauss were performed on *p*-type samples of these alloys in that portion of the extrinsic

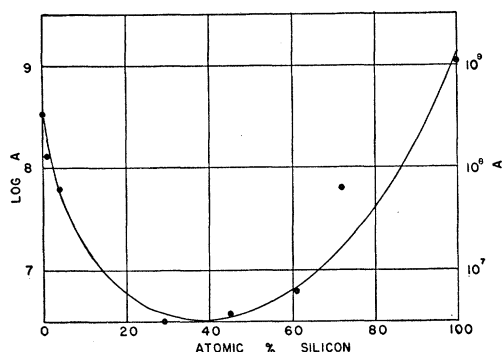


FIG. 7. The coefficient A *versus* composition of the alloy. The Hall mobility of holes in germanium-silicon alloys in the vicinity of 300°K has been reconciled to a law of the form $\mu = AT^{-x}$.

range extending from 77°K to 300°K. The Hall and resistivity data are shown in Fig. 4 and Fig. 5 respectively. These have been combined to give the Hall mobilities for holes, defined as the product of the Hall coefficient and the conductivity, shown in Fig. 6. If one examines the 1%, 4%, 29%, and 45% sample, it may be seen that the scattering mechanisms which reduce the mobilities below the values to be expected from thermal scattering are becoming successively more important and encroach more and more on the thermal scattering range. This is strongly suggestive of alloy scattering. However one would expect the effect to diminish for the 61% and 72% sample. Instead the effect becomes stronger. Moreover the reversal in slope for the 61% and 72% sample is inconsistent with the predicted temperature dependence for alloy scattering. One might attempt to explain these reversals in slope on the basis of impurity scattering. If a comparison is made with work on *p*-type single crystal silicon, for

⁷ Harvey Brooks, Phys. Rev. **98**, 244(T) (1955).

⁸ Levitas, Wang, and Alexander, Phys. Rev. **95**, 846 (1954).

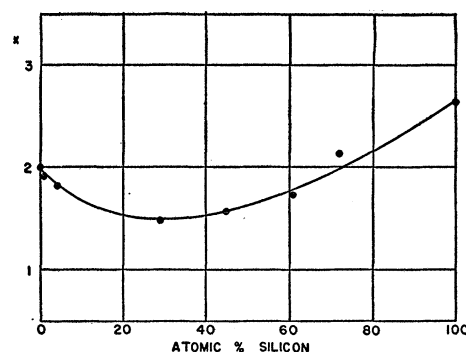


FIG. 8. The exponent x *versus* composition of the alloy. The Hall mobility of holes in germanium-silicon alloys in the vicinity of 300°K has been reconciled to a law of the form $\mu = AT^{-x}$.

instance Morin and Maita's⁹ recent work, no such reversals as found in the present work are observed in the same temperature range. If a comparison is made with earlier work on *p*-type polycrystalline silicon, for instance Pearson and Bardeen's¹⁰ 1949 work, reversals of the sort encountered in the present work are found, but for samples with impurity concentrations several orders of magnitude greater than the impurity concentrations in the samples presently under consideration. While one may ascribe some of the behavior of the 61% and 72% sample to impurity, grain boundary, and alloy scattering, the low-temperature results for these samples must be viewed as anomalous.

It seems clear that if any argument for alloy scattering is to be made for these samples, the argument will have to be based on the results in a temperature range in which impurity and grain boundary effects may be largely neglected. We therefore examine the high-temperature limit of the mobility curves of Fig. 6.

This portion of the curves may be reconciled to a law of the form AT^{-x} . In germanium and silicon it would be the lattice mobility that we would thus represent. In the alloys, if it is true that alloy scattering is important at room temperature, then the exponent x in the law AT^{-x} would be a compromise between a value typical of alloy scattering and one typical of thermal scattering. Moreover, one would expect that the coefficient A would be reduced by the operation of the new scattering mechanism. Figures 7 and 8 show plots of the coefficient A and the exponent x as functions of composition of the alloy. It is clear that these quantities are reduced in the expected manner as one moves away from the end points of these curves.

4. CONCLUSIONS

The high-temperature results have established the intrinsic resistivity lines for these alloys. The slopes of the semilogarithmic plots of resistivity *versus* reciprocal temperature may be interpreted as yielding the energy

⁹ F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).

¹⁰ G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).

gap of the alloys, however, uncertainty concerning the band structure of the alloys requires that this interpretation be viewed with caution.

The low-temperature Hall and resistivity measurements are indicative of alloy scattering. If these samples were available as high-purity single crystals, a conclusive argument could certainly be made. With such samples one could apply the type of analysis which has been employed here at 300°K, to a range of temperatures. At lower temperatures one would expect that the dips in the curves of A and x versus composition would be stronger. With such samples it might be possible to establish the temperature dependence of the alloy scattering and to determine the relative magnitudes of alloy and thermal scattering. With the samples presently available, it may be possible to make meas-

urements at somewhat higher temperatures, although not entering the intrinsic range, and to observe a gradual diminution in the effects of alloy scattering. The curves of A and x would not dip as strongly.

5. ACKNOWLEDGMENTS

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Effects of Stress on Superconducting Sn, In, Tl, and Al†

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Hydrostatic pressures of 0 to 100 atmos obtained with helium gas pressure, and of 1.9×10^3 atmos obtained by an ice expansion bomb technique are used to measure the pressure displacement of critical temperature T_c . The coefficient $(\partial T_c / \partial p)$ for Sn, In, Tl, and Al is -4.7 ± 0.2 , -4.0 ± 0.2 , $+0.6 \pm 0.3$, and -2.0 ± 0.2 in units of 10^{-5} °K/atmos, respectively. The temperature dependence of $R = (\partial H_c / \partial p)_T / (\partial H_c / \partial p)_{T_c}$ above 1°K is described by $R = 0.61 + 0.029T^2$ for Sn, and $R = 0.77 + 0.020T^2$ for In. This result is discussed in connection with the similarity principle, $H_0/T_c = \text{constant}$. From an analysis combining stress and isotope effects, it is seen that T_c , or H_c , is more sensitive to volume changes, holding zero-point lattice vibration amplitude fixed, than to zero-point amplitude changes, holding V fixed: $(\partial H_c / \partial \ln V)_T^2 = 5.5 \times (\partial H_c / \partial \ln q^2)_V$ for Sn. Zero-pressure critical field data are also presented for the subject metals.

I. INTRODUCTION

THE dependence of the superconducting critical temperature T_c on mechanical stress^{1,2} has received renewed interest since the discovery of the isotope effect and the introduction of the theories by Fröhlich³ and Bardeen.⁴ The critical temperature T_c decreases under pressure for most superconductors studied so far, but increases under pressure for Tl, NiBi₃, and RhBi₄.⁵ As Marcus⁶ first noted, the stress effect is not adequately explained as the result of a change in amplitude

of the zero-point lattice vibrations. The isotope effect ($M^x T_c = \text{constant}$, where M is the isotopic mass) is usually understood as the result of a change in lattice vibration amplitude. The exponent x is approximately $\frac{1}{2}$, but varies from metal to metal; this has been explained by deLaunay⁷ from a consideration of the vibration spectrum of a real lattice. Thus understanding of the isotope effect seems as satisfactory as can be expected in the absence of a good quantum theory of superconductivity. The understanding of stress effects is less satisfactory, and there is clearly a need for more quantitative data. We have studied the displacement of T_c in Sn, In, Tl, and Al using pressures of 0 to 100 atmos obtained with helium gas pressure, and a pressure of 1.9×10^3 atmos obtained by an ice expansion bomb technique.⁸ For Sn and In, the value of $(\partial H_c / \partial p)_T$ has been measured as a function of temperature, and it is found to remain finite as T tends to 0°K. The temperature dependence of $(\partial H_c / \partial p)_T$ for tin is shown

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¹ G. J. Sizoo and H. Kamerlingh Onnes, Leiden Comm. No. 180b (1925).

² C. F. Squire, *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1955), Vol. I, p. 151.

³ H. Fröhlich, *Phys. Rev.* **79**, 845 (1950).

⁴ J. Bardeen, *Phys. Rev.* **80**, 567 (1950).

⁵ Kan, Lazarev, and Sudovstov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **18**, 825 (1948); *Doklady Akad. Nauk. S.S.S.R.* **69**, 173 (1949).

⁶ P. M. Marcus, *Phys. Rev.* **91**, 216 (1953).

⁷ J. deLaunay, *Phys. Rev.* **93**, 661 (1954).

⁸ B. G. Lazarev and L. C. Kan, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **14**, 439 (1944).