Semimetallic Properties of $Co_{1-x}Fe_xSi$ Solid Solutions

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The electrical resistivity, Hall coefficient, and thermoelectric power have been measured over the temperature range from 4.2 to 800°K on $Co_{1-x}Fe_xSi$ solid solutions, with x varying from 0 to 1. The specimens are n-type near $x=0$. In the purest specimen of CoSi the electron mobility reaches 800 cm²/volt-sec at 4.2°K. With increasing x, hole conduction becomes predominant. Anomalies are observed for intermediate compositions. The temperature range over which the Hall coefficient and the thermoelectric power take opposite signs is unusually wide compared with ordinary p-type semiconductors. Detailed analysis of the Hall coefficient and thermoelectric power based on a two-carrier model leads to the conclusions: (1) The upper and the lower bands overlap in energy for $Co_{1-x}Fe_xSi$ solid solutions. (2) By substitution of one iron atom for one cobalt atom in the solid solutions, approximately one hole is produced. For CoSi the best fit to the data is obtained with the overlap energy of 0.02 eV, with the electron effective mass of $2m_0$, with the hole effective mass of $4 m_0$ and with the electron-to-hole mobility ratio of 5. For the solid solutions, the observed data are qualitatively interpreted assuming that the overlap energy and the hole effective mass increase with x, but the mobility ratio and the electron effective mass remain unchanged. It is also suggested that interband scattering becomes predominant in passing from CoSi to FeSi.

INTRODUCTION

RECENTLY, some transition-metal silicides[1] acting as potential thermoelements attracted the authors' attention. Nikitin[2] observed the monotonically increasing resistivities of CoSi up to the melting point and deduced that no energy gap existed in this material. Mayer and Mlavsky[3] found that the thermoelectric power for CoSi decreased with doped FeSi, reversing the sign when doped with 7 wt. % FeSi, and suggested that there were contributions arising from sources other than the presence of carriers *per se*. All these investigations have been concerned with the resistivity, and thermoelectric power but not with the Hall coefficient, making them incomplete for a discussion of the conduction mechanism in CoSi.

Systematic investigations are now being made on some transition metal silicides on the basis of measurements of the resistivity, Hall coefficient, and thermoelectric power. It has been found that the monosilicides of Cr, Mn, and Fe show p-type conduction, while those of Co and Ni show n-type conduction. As is well known, the $3d$ electrons increase one by one in passing from Mn to Ni. This seems to be related to the conduction type. It is interesting to clarify the conduction mechanism, especially the p-n transition in $Co_{1-x}Fe_xSi$ alloys and to obtain informations about the contribution of the $3d$ electrons to conduction in transition-metal silicides.

EXPERIMENTAL

The compounds CoSi and FeSi were prepared by melting the stoichiometric amounts of their constituent materials[4] with the use of an hf generator in an argon atmosphere. This method of preparation usually gives rise to a small quantity of silicon loss, but it was found that silicon loss had less influence on the electrical properties than cobalt loss. Proper molecular proportions of the compounds once prepared were melted again to obtain $Co_{1-x}Fe_xSi$ alloys. Some of them were grown in single crystals by the Teal-Little method. X-ray powder patterns show that the alloys are single phase and that the lattice constants a vary linearly with composition x, as shown in Fig. 1. The resistivity and Hall coefficient of parallelepiped specimens cut from the ingots were measured by conventional dc-potentiometric methods. The magnetic fields used for the Hall measurements were 5000 G when $x \leq 0.1$, and 8500 G when $x > 0.1$. Measurements at low temperatures were made with soldered electrode contacts, while pressure contacts were used for high-temperature measurements. The measured resistivity ρ, Hall coefficient R, and thermoelectric power Q at 300°K are shown in Fig. 2 for the cast solid solutions. It is notable that R and Q have opposite signs over the wide composition
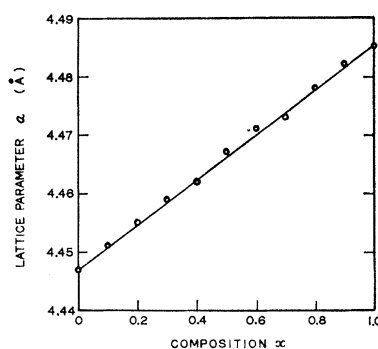
Fig. 1. Lattice parameter a versus composition x for $Co_{1-x}Fe_xSi$ crystals.

[1] J. R. Gambino, in *Thermoelectric Materials and Devices*, edited by I. B. Cadoff and E. Miller (Reinhold Publishing Corporation, New York, 1960), p. 163.

[2] E. N. Nikitin, Fiz. Tverd. Tela 2, 633 (1960) [English transl.: Soviet Phys.—Solid State 2, 588 (1960)].

[3] S. E. Mayer and A. I. Mlavsky, in *Properties of Elemental and Compound Semiconductors*, edited by H. C. Gatos (Interscience Publishers Inc., New York, 1960), p. 261.

[4] The cobalt and iron obtained from Johnson-Matthey & Company was 99.99% pure; the silicon, n type, had a resistivity of approximately 100 ohm-cm.

range, say $0.14 \geqq x \geqq 0.05$. It is also the case for the pulled single crystals as shown in Fig. 3. In Figs. 4(a), (b), and (c), respectively, the temperature dependences of ρ, R, and Q for the cast specimens are shown. The Hall curves exhibit distinct maxima except for CoSi. As shown in Fig. 5, the electron Hall mobility, μ_H of pure CoSi reaches 800 cm^2/volt-sec at 4.2°K and is approximately proportional to $T^{-3/2}$ above 100°K. This suggests that a band model is applicable in this kind of material and that electrons are mainly scattered by acoustic phonons.

ANALYSIS

As seen in Figs. 4 (b) and 4 (c), when $0.10 \geqq x \geqq 0.06$, R and Q take opposite signs over unusually wide temperature ranges compared with ordinary p-type semiconductors. These anomalies suggest a certain high value of the electron-to-hole mobility ratio or overlapping energy bands in the solid solutions. The expression for R involves the square of the electron-to-hole mobility ratio, while that for Q involves the first power of the ratio. When the ratio is larger than unity, the effect of electrons overrides the effect of more numerous holes to a lower temperature for R than for Q. In the case of semiconductors, the temperature range over which $R<0$, $Q>0$ is wide for large values of the ratio. On the other hand, when the upper and the lower bands overlap in energy the temperature range described above is expected to be considerably
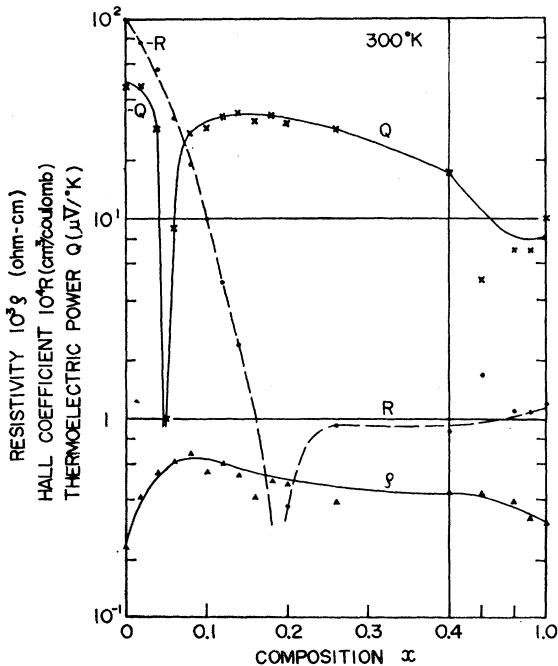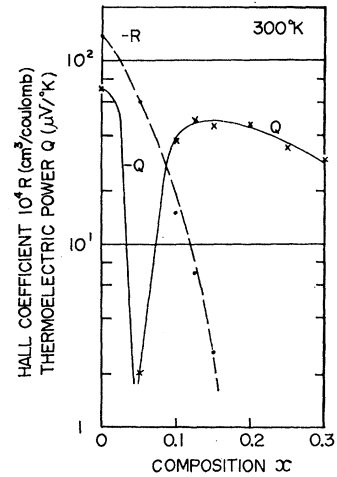
FIG. 3. Room temperature Hall coefficient R and thermoelectric power Q versus composition for pulled Co$_{1-x}$Fe$_x$Si crystals.

wide so long as the ratio is larger than unity, because the electron concentration is not so rapidly increased with temperature as it is for semiconductors. In either case, in order to expect occurrence of the anomalies associated with the Hall maxima, it should be concluded that both electrons and holes are present, giving rise to mixed conduction. Furthermore, it is required for holes to have higher concentration and lower mobility than electrons. These concepts also seem to be consistent with the observed Hall maxima for $x=0.02$ and 0.04 in which the anomalies are not seen in the temperature range investigated.

Detailed analysis based on the two-carrier model are carried out on the following assumptions:

(i) The difference p_0 between the concentration of holes p and that of electrons n depends on x and not on temperature:

$$p_0 = p - n. \tag{1}$$

(ii) The mean free path of carriers is independent of their energies.

(iii) Both the upper and the lower bands are spherically symmetric. The effective mass of electrons m_n is independent of x, but that of holes m_p depends on x. This implies that the characteristics of a transition element, if any remain, may be involved in the heavier band.

(iv) The ratio, $b(>1)$ of the electron mobility μ_n to the hole mobility μ_p is independent of temperature and can be expressed as

$$b = (m_p/m_n)^\alpha, \tag{2}$$

where α is equal to either $\frac{5}{2}$ or 1. The former is expected in the case of intraband scattering associated with acoustic phonons and the latter in the case where the relaxation time of electrons is equal to that of holes due to predominating interband scattering.

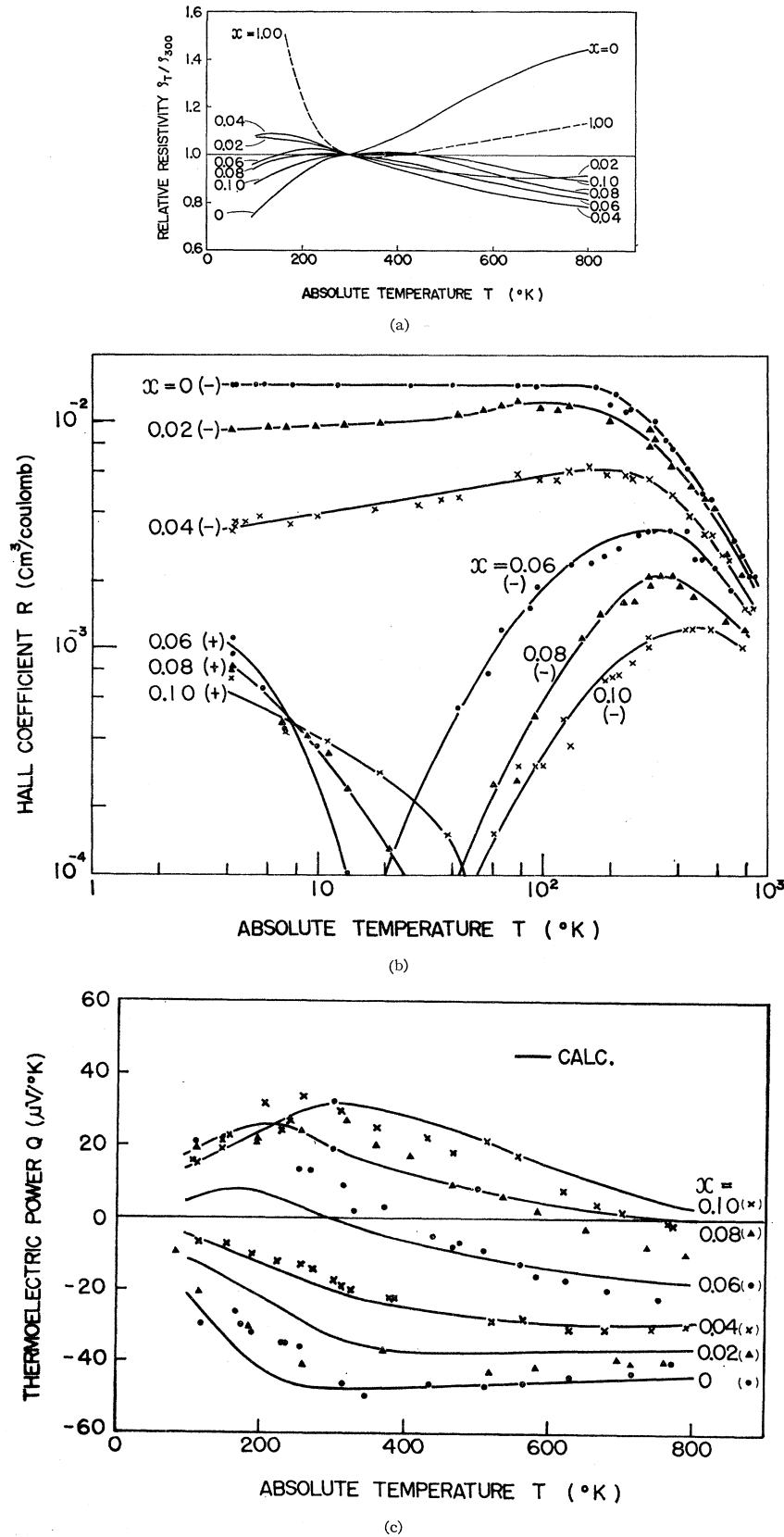On the four assumptions described above, R, n, p,

FIG. 2. Room temperature resistivity ρ, Hall coefficient R, and thermoelectric power Q versus composition for cast Co$_{1-x}$Fe$_x$Si crystals.

(a)

(b)

FIG. 4. (a) Relative resistivity ρ_T/ρ_{300}, (b) Hall coefficient R, and (c) thermoelectric power Q versus absolute temperature for cast $Co_{1-x}Fe_xSi$ crystals. Solid curves in (c) are calculated with use of parameters shown in Table I.

(c)

and Q can be written as follows[5]:

$$R = (p - nb^2)/e(p + nb)^2,$$ (3)

$$n = 4\pi h^{-3}(2m_n kT)^{3/2} F_{1/2}(\zeta^*),$$ (4)

$$p = 4\pi h^{-3}(2m_p kT)^{3/2} F_{1/2}(\eta^*),$$ (5)

$$Q = \frac{k}{e(nb+p)}\left[p\left\{ 2\frac{F_1(\eta^*)}{F_0(\eta^*)} - \eta^* \right\} \right.$$

$$\left. - nb\left\{ 2\frac{F_1(\zeta^*)}{F_0(\zeta^*)} - \zeta^* \right\} \right],$$ (6)

where ζ^* and η^* are the reduced Fermi energies relative to the bottom of the upper band and to the top of the lower band, respectively. The energy difference ΔE is then given by

$$\Delta E = -(\zeta^* + \eta^*)kT.$$ (7)

A positive value of ΔE indicates energy separation and a negative value energy overlap. The scattering constant in the Hall expression is choosen to be unity in Eq. (3). In Eqs. (4), (5), and (6), F_r is a Fermi-Dirac integral.

As seen in Fig. 4(b), the values of R for $x=0$, namely for CoSi, are invariant with temperature below 100°K and down to 4.2°K, showing no signs of exhibiting a

TABLE I. Description of various parameters giving the best fits to the experimental data.

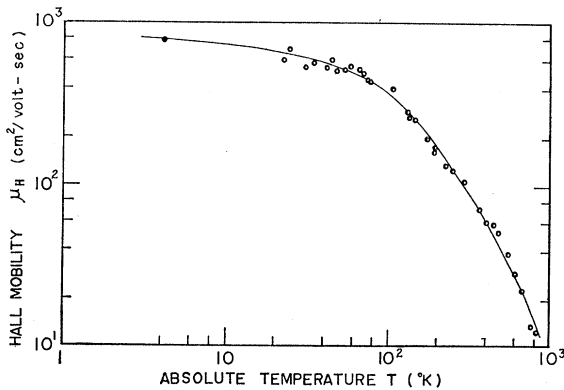| x	p_0 (cm^{-3})	m_n	m_p	α	b
0	-4.5×10^{20}	$2\,m_0$	$4\,m_0$	$\frac{5}{2}$	5
0.02	4.1×10^{20}	$2\,m_0$	$4\,m_0$	$\frac{5}{2}$	5
0.04	8.0×10^{20}	$2\,m_0$	$4\,m_0$	$\frac{5}{2}$	5
0.06	1.5×10^{21}	$2\,m_0$	$6\,m_0$	$\frac{3}{2}$	5
0.08	2.3×10^{21}	$2\,m_0$	$10\,m_0$	1	5
0.10	3.3×10^{21}	$2\,m_0$	$10\,m_0$	1	5
0.10~1.00	extrapolated	$2\,m_0$	$10\,m_0$	1	5

FIG. 5. Electron Hall mobility μ_H ($= |R|/\rho$) versus absolute temperature for a pure CoSi crystal.

[5] V. A. Johnson, in *Progress in Semiconductors*, edited by A. F. Gibson (Heywood & Company, Ltd., London, 1956), Vol. 1, p. 65.
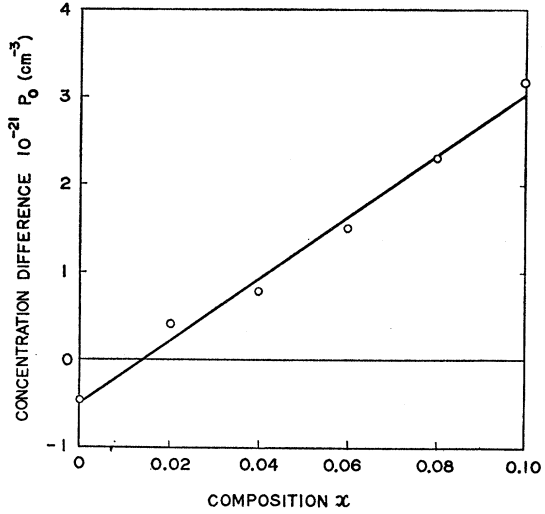

FIG. 6. Concentration difference p_0 between holes and electrons versus composition for cast Co$_{1-x}$Fe$_x$Si crystals.

maximum. This gives evidence that in CoSi only electron conduction takes place, or $n \gg p$ at low temperatures. In such a case, the value of m_n is evaluated from the low-temperature values of R and Q according to the usual expression: $n = 1/e|R|$. The estimated value of m_n is $2m_0$. For Co$_{1-x}$Fe$_x$Si, where $x \leq 0.1$, the values of p_0 are determined by

$$p_0 = \frac{1}{e|R_{\max}|} \frac{(b-1)^2}{4b}.$$ (8)

The evaluation of b and α is accomplished by substituting trial values of these parameters into the aforementioned equations, calculating Q as a function of temperature, and selecting those values which give the best fits to the experimental data. The values of b and α thus selected, along with p_0, m_n, and m_p, are shown in Table I. Figure 4 (c) also includes curves of Q calculated using the values of the parameters shown in Table I. It is seen that better agreement is obtained with $\alpha = \frac{5}{2}$ when $x \leq 0.04$ and with $\alpha = 1$ when $x > 0.06$.[6] For $x = 0.06$, neither $\alpha = \frac{5}{2}$ nor $\alpha = 1$ gives qualitative agreement but $\alpha = \frac{3}{2}$ does. This value may be physically meaningless but is taken for the purpose of convenience. In Fig. 6 it is shown that the values of p_0 thus determined increase linearly with increasing x. For $x > 0.1$, the values of R are too small to be measured at various temperatures. The analysis is made only at 300°K. Comparison between the observed and the calculated

[6] This is easily demonstrated by simple consideration on the experimental results as follows: $nb = p$ for $R = R_{\max}$. From Eqs. (2), (4), and (5), one obtains $F_{1/2}(\eta^*)/F_{1/2}(\zeta^*) = (m_p/m_n)^{\alpha-3/2}$. For $\alpha \geq 3/2$, one gets $\eta^* \geq \zeta^*$; accordingly $Q \leq 0$. The experimental results show that at the temperatures at which $R = R_{\max}$, $Q < 0$ when $x = 0.04$, and $Q > 0$ when $x \geq 0.06$. This indicates that α should be larger and smaller than 3/2 when $x = 0.04$ and when $x \geq 0.06$, respectively.
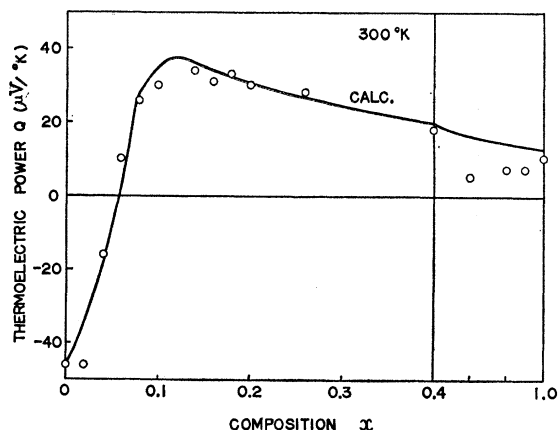
FIG. 7. Comparison between calculated and observed values with respect to room-temperature thermoelectric power versus composition for cast $Co_{1-x}Fe_xSi$ crystals.

values of Q at 300°K for $x=0\sim1$ are illustrated in Fig. 7. The parameters used for the calculation for $x>0.1$ are also included in Table I.

Determination of the parameters giving the best fits to the experimental data allows us to evaluate n and p at $100\sim800°K$ when $x\leqq0.1$ and at 300°K when $x>0.1$. The calculated values of $\mu_p(\mu_n)$ are fairly large at low temperatures and vary approximately as $T^{-3/2}$ above 200°K when $x\leqq0.1$. These results support the theory that the band model may be applicable and that the assumption (ii) may be valid in the present analysis. The calculated values of ΔE for $x\leqq0.1$ can approximately be expressed by $\Delta E=-(\Delta E_0+\beta T)$ over the temperature range investigated. The estimated value of ΔE_0 is 0.02 eV when $x=0$ and it seems to increase with x. The values of β are in the range $3\sim6\times10^{-4}$ eV/deg, which seem reasonable compared with those in well-known semiconductors. In Fig. 8 are shown the calculated values of n, p, and ΔE for $x=0\sim1$ at 300°K.

DISCUSSION

It should be noted in Fig. 8 that the signs of ΔE are negative over the entire compositions. That is, $Co_{1-x}Fe_xSi$ solid solutions are semimetals rather than semiconductors. The values of $|\Delta E|$ increase almost linearly with increasing x. Assuming that the coefficient of thermal expansion in the solid solutions is of the order of 10^{-5}/deg, a value comparable to those of other hard, brittle, and refractory materials, and taking into account that the lattice constants of $Co_{1-x}Fe_xSi$ increase linearly with x, the increase in $|\Delta E|$ with x seems to be of a reasonable order of magnitude.

The experimental results are qualitatively interpreted under the assumptions that $\alpha=\frac{5}{2}$ when $x\leqq0.04$ and that $\alpha=1$ when $x\geqq0.08$. The relation $\alpha=\frac{5}{2}$ may be expected for nonpolar semiconductors[7] and $\alpha=1$

[7] G. L. Pearson and J. Bardeen, Phys. Rev. 75, 865 (1949).

for transition metals.[8] The latter is generally interpreted in terms of the s-d scattering because of the large effective mass of the d band. Although the scattering mechanism in $Co_{1-x}Fe_xSi$ cannot be elucidated by the present analysis, the transition of α from $\frac{5}{2}$ to 1 seems to be ascribed to predominating interband scattering, because both m_p and η increase with x.

An interesting feature is that the values of p_0 increase linearly with x. If the $3d$ electrons partly contribute to conduction, the values of p_0 are expected to be proportional to x. They increase by 3.5×10^{20} cm^{-3} for every substitution of 1% Fe atoms. Since CoSi includes four Co atoms in its unit cell, every substitution of 1% Fe atoms for Co atoms produces 4.5×10^{20} cm^{-3} Fe atoms. Good agreement between these two values indicates that one Fe atom substituting for one Co atom produces approximately one hole when $x\leqq0.1$. Furthermore, this idea is extended to the case that $x>0.1$ to interpret successfully the observed values of Q. From this it may be concluded that by substitution of one Fe atom for one Co atom in $Co_{1-x}Fe_xSi$ solid solutions, approximately one hole is produced over the entire composition.

As seen in Fig. 8, the values of p increase with x, while those of n remain almost unchanged. This may be qualitatively interpreted as follows: With increasing x, both electrons and holes increase due to increasing $|\Delta E|$. In addition, holes are produced by substituting Fe atoms for Co atoms. Cancellation may take place to some extent between increased electrons and holes, resulting in nearly constant values of n over the entire composition. Even in such a case, the increase in p_0 with x is equal to that in holes produced by substitu-
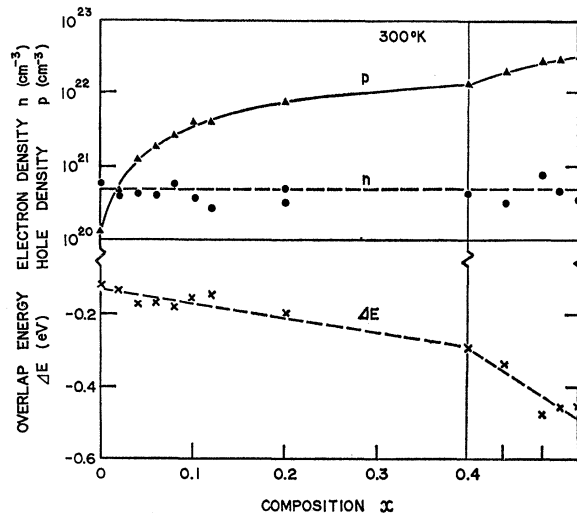

FIG. 8. Electron density n, hole density p, and overlap energyΔE at 300°K versus composition for cast $Co_{1-x}Fe_xSi$ crystals.

[8] H. Jones, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XIX, p. 265.

tion, since the increase in $|\Delta E|$ gives rise to the increase in electrons and that in holes by equal numbers.

It seems interesting to compare the present results on $Co_{1-x}Fe_xSi$ with our recent work on $Co_{1-x}Ni_xSi$ ($0.14 \geqq x \geqq 0$) solid solutions. In the latter case, the experimental data are qualitatively interpreted on the assumptions that (1) the solid solutions are semi-metallic, (2) m_p, η, and $\alpha(=\frac{5}{2})$ remain unchanged with x, and (3) one Ni atom substituting for one Co atom produces approximately one electron. Since Ni has one more $3d$ electron while Fe has one less $3d$ electron in

comparison with Co, the results on these two solid solutions seem to be quite reasonable. Details of the work on $Co_{1-x}Ni_xSi$ will be published elsewhere in the near future.

ACKNOWLEDGMENTS

Galvanomagnetic Effects in n-Type Germanium

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The galvanomagnetic coefficients of n-type Ge have been calculated theoretically and compared with previously published experimental data. Calculations have been made for material containing from 10^{11} to 10^{18} impurity centers per cm³, and comparisons were made with samples having free-carrier concentrations from 5×10^{13} to 2×10^{17} per cm³. The calculations were made primarily at 77 and 300°K, but also as functions of temperature. A solution of the Boltzmann transport equation with a collision time which was anisotropic, energy-dependent, and which depended on the impurity content was used. In the expressions Herring and Vogt's equations were used for the acoustic lattice scattering, the Brooks-Herring equation modified by Ham's calculation of the anisotropy was used for the ionized impurity scattering, and the Erginsoy formula for neutral impurity scattering was used to account for the energy-independent scattering. It is shown that even though a constant mean collision time can be used to qualitatively predict the dependence of the coefficients on the magnetic field, the quantitative agreement with experiment is considerably improved when a more realistic form of the collision time is used for the calculations. Scattering functions which take the temperature dependence of the scattering and the presence of ionized impurities into account enable quantitative predictions of the behavior of the galvanomagnetic coefficients to be made quite successfully.

INTRODUCTION

A LARGE amount of accurate experimental data has been published on the galvanomagnetic effects, the Hall effect and the magnetoresistance, for the elemental semiconductors germanium and silicon. Qualitatively, the theoretical calculations are in good agreement with the experimental data as functions of the orientation and field dependence of the effects. However, quantitatively the dependence on temperature and impurity content of the semiconductor is not in as good agreement as might be hoped for.[1-9] Primarily, this is due to the difficulty of calculating the conductivity tensor when the relaxation time equations

are complicated because of the presence of more than one effective scattering mechanism. With the present relatively easy access to large computers, this calculation problem is greatly eased. Such a calculation has been made for the case of n-type silicon by one of the authors[3] with fairly good agreement between experiment and theory. Therefore, it seems appropriate to perform these calculations for n-type germanium and to compare the results with the extensive previously published experimental data.

THEORY

The formal theory of conductivity was used in the usual manner to evaluate the conductivity for a single ellipsoidal energy surface with an anisotropic energy-dependent relaxation time.[1-3,10] For this development

[1] W. M. Bullis and W. E. Krag, Phys. Rev. 101, 580 (1956).
[2] W. M. Bullis, Phys. Rev. 109, 292 (1958).
[3] W. E. Krag, Phys. Rev. 118, 435 (1960).
[4] C. Goldberg, Phys. Rev. 109, 331 (1958).
[5] C. Goldberg and W. E. Howard, Phys. Rev. 110, 1035 (1958).
[6] R. A. Laff and H. Y. Fan, Phys. Rev. 112, 317 (1958).
[7] D. Long and J. Myers, Phys. Rev. 115, 1107 (1959).
[8] D. Long and J. Myers, Phys. Rev. 120, 39 (1960).
[9] H. Miyazawa and H. Maeda, J. Phys. Soc. Japan 15, 1924 (1960).

[10] The development for a single-energy minimum is exactly the same as that followed in Ref. 3. It is done in considerable detail in W. E. Krag, PhD. thesis, Massachusetts Institute of Technology, June 1959 (unpublished). The procedure for combining the conductivities of the several [111] oriented ellipses is also the same as in the above references, modified of course by the different orientations of the ellipsoidal energy surfaces.