

## Magnetic Susceptibility of Weakly Interacting Donors in Germanium\*

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The magnetic susceptibility of *n*-type germanium with donor concentrations between  $10^{16}$   $\text{cm}^{-3}$  and  $2 \times 10^{17}$   $\text{cm}^{-3}$  has been measured by using the Faraday method in order to investigate the interactions between donors. The measurements were made between 4.2 and 1.35°K. The susceptibility of antimony-doped germanium has been contrasted to that of arsenic-doped germanium.

The results of this investigation show that the molecular theory proposed by Sonder and Schweinler predicts the observed temperature dependence of the susceptibility of the extrinsic electrons for appropriate donor concentrations. The antimony-doped samples exhibit a stronger donor interaction and a larger orbital diamagnetism than the arsenic-doped samples, consistent with the hydrogenic model.

The susceptibility for both impurity species at concentrations of about  $10^{17}$   $\text{cm}^{-3}$  is independent of temperature and the Sonder-Schweinler theory is no longer applicable. An empirical relation between the susceptibility of arsenic and antimony-doped germanium suggests that the extrinsic electrons should be regarded as localized below 4°K for donor concentrations as large as  $10^{17}$   $\text{cm}^{-3}$ .

### INTRODUCTION

IN the past few years, several studies of the magnetic susceptibility of germanium have been made. The results of these investigations have been reviewed by Bowers<sup>1</sup> and Krumhansl.<sup>2</sup> Most of these measurements have been made on samples containing impurity concentrations in excess of  $10^{17}$   $\text{cm}^{-3}$ . A few results<sup>3,4</sup> reported for the low-temperature susceptibility of germanium with donor concentrations in the neighborhood of  $5 \times 10^{16}$   $\text{cm}^{-3}$  show that the spin paramagnetism of the localized electrons does not obey the Curie law expected for un-ionized isolated donors. This paper presents an extensive study of the susceptibility of *n*-type germanium with donor concentrations between  $2 \times 10^{16}$   $\text{cm}^{-3}$  and  $2 \times 10^{17}$   $\text{cm}^{-3}$  at temperatures between 4.2 and 1.35°K. In order to study the state of the extrinsic electrons which are "frozen out" of the conduction band at these temperatures and to investigate the interactions between un-ionized donors particular emphasis has been given to the difference between the susceptibility of arsenic- and antimony-doped germanium.

The interpretation of these results is based on the model of the magnetic susceptibility of a semiconductor first proposed by Busch and Mooser<sup>5</sup> and modified by Stevens *et al.*<sup>6</sup> The susceptibility is considered to be the sum of the susceptibility of the germanium lattice  $\chi_g$  and the susceptibility of the extrinsic electrons  $\chi_e$ . It is assumed<sup>2</sup> that the addition of impurities to germanium does not affect  $\chi_g$  and that, therefore,  $\chi_g$  may be determined by measuring the susceptibility of pure germanium.

The magnetic susceptibility of localized noninter-

acting electrons occupying hydrogen atom-like states is the sum of two terms,<sup>7</sup>  $\chi_e^p$  and  $\chi_e^d$ , representing, respectively, a temperature-dependent spin paramagnetism and a temperature-independent orbital diamagnetism. Assuming that one extrinsic electron is associated with each donor, i.e., only group VA donors with negligible acceptor compensation are considered, then for  $\beta H < kT$ ,

$$\chi_e^p = g^2 \frac{\beta^2 N_D}{4\rho kT} = g^2 C_e / T, \quad (1a)$$

$$\chi_e^d = -\frac{e^2 a^{*2}}{2\rho c^2 m^*} N_D. \quad (1b)$$

$N_D$  is the donor concentration,  $g$ ,  $\beta$ ,  $m^*$ , and  $a^*$  are, respectively, the spectroscopic splitting factor, the Bohr magneton, the effective mass, and the effective Bohr radius for an electron in an impurity state. The unit of  $\chi$  is  $\text{emu g}^{-1}$ , and  $\rho$  is the density of germanium.

If the analogy to the state of atomic hydrogen were perfect, one would expect  $g=2$ . However, Feher, Wilson, and Gere<sup>8</sup> have measured the  $g$  factor of localized electrons in germanium and found its value to be considerably less than 2.

The hydrogenic model of impurity states permits the calculation of  $m^*$  and  $a^*$  in terms of the observed ionization energy of the impurity states and the dielectric constant of germanium with the result that in this model the orbital diamagnetism is inversely proportional to the third power of the ionization energy. The measured ionization energies for arsenic and antimony impurities in germanium are<sup>9</sup>, respectively,  $12.7 \times 10^{-3}$  and  $9.6 \times 10^{-3}$  eV and therefore, for donor concentrations such that interactions between the localized electrons are negligible, the orbital diamagnetism of the extrinsic electrons in an antimony-doped

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<sup>1</sup> R. Bowers, *J. Phys. Chem. Solids* **8**, 206 (1959).

<sup>2</sup> J. A. Krumhansl, *J. Appl. Phys.* **30**, 1183 (1959).

<sup>3</sup> R. Bowers, *Phys. Rev.* **108**, 683 (1957).

<sup>4</sup> F. T. Hedgcock, *J. Electronics* **2**, 513 (1957).

<sup>5</sup> G. A. Busch and E. Mooser, *Helv. Phys. Acta* **26**, 611 (1953).

<sup>6</sup> D. K. Stevens, J. W. Cleland, J. H. Crawford, Jr., and H. C. Schweinler, *Phys. Rev.* **100**, 1084 (1955).

<sup>7</sup> E. Sonder and D. K. Stevens, *Phys. Rev.* **110**, 1027 (1958).

<sup>8</sup> G. Feher, D. K. Wilson, and E. A. Gere, *Phys. Rev. Letters* **3**, 25 (1959).

<sup>9</sup> T. H. Geballe and F. S. Morin, *Phys. Rev.* **95**, 1085 (1954).

TABLE I. The donor concentrations, Hall coefficients, and resistivities at 295, 78, and 4.2°K and the susceptibilities at 295°K of the samples studied in this investigation.

Sample	Doping	$N_D \times 10^{-16}$ (cm <sup>-3</sup> )	$T=295^\circ\text{K}$			$T=78^\circ\text{K}$		$T=4.2^\circ\text{K}$
			$\rho$ ( $\Omega$ cm)	$R$ (cm <sup>3</sup> C <sup>-1</sup> )	$\chi \times 10^7$ (emu g <sup>-1</sup> )	$\rho$ ( $\Omega$ cm)	$R$ (cm <sup>3</sup> C <sup>-1</sup> )	$\rho$ ( $\Omega$ cm)
<i>a</i>	As	22	0.0167	-25	1.076	0.021	-42	1.56
<i>b</i>	Sb	18	0.0186	-31	1.074	0.022	-46	0.041
<i>c</i>	As	10	0.030	-56	1.067	0.028	-99	$2.9 \times 10^4$
<i>d</i>	Sb	7.6	0.035	-74	1.066	0.027	-117	1.50
<i>e</i>	As	7.2	0.039	-78	1.065	0.031	-137	$1 \times 10^5$
<i>f</i>	Sb	5.9	0.044	-96	1.064	0.031	-148	5.2
<i>g</i>	P	5.5	0.050	-101	1.063	0.033	-161	...
<i>h</i>	As	5.4	0.050	-104	1.063	0.033	-171	$(3 \pm 1) \times 10^5$
<i>i</i>	As	4.6	0.060	-122	1.063	0.036	-191	...
<i>j</i>	Sb	3.1	0.082	-180	1.062	0.040	-251	$3.1 \times 10^3$
<i>k</i>	As	2.7	0.098	-204	1.062	0.043	-284	...
<i>l</i>	As	2.2	0.11	-251	1.061	0.044	-345	...
<i>m</i>	Sb	2.1	0.12	-262	1.061	0.047	-366	$8.7 \times 10^3$
<i>n</i>	As	1.5	0.14	-368	1.061	0.054	-427	...
<i>o</i>	...	$< 10^{-2}$	58	...	1.060	...	...	...

sample should be 2.3 times larger than the same quantity for an arsenic-doped sample with the same donor concentration.

The effective mass theory developed by Kohn and Luttinger<sup>10</sup> has shown that this description of the difference between arsenic and antimony impurities in germanium is rather naive. Kohn<sup>11</sup> has calculated the orbital diamagnetism of localized electrons using the effective-mass wave functions and its value turns out to be considerably larger than that obtained with the hydrogenic model (for example a factor of 2.5 in the case of arsenic). Kohn also suggested that the orbital diamagnetism should vary inversely with the observed ionization energy.

The determination of the orbital diamagnetism of localized electrons, especially if different impurity species are studied, would, therefore, provide valuable information about the state of the impurity electrons. Unfortunately our measurements are not sufficiently precise to allow the determination of the susceptibility of extrinsic electrons localized on noninteracting donors.

Sonder and Schweinler<sup>12</sup> have accounted for the temperature dependence of the magnetic susceptibility of electrons localized on weakly interacting donors in silicon. They take the interactions into account by treating pairs of donors as quasihydrogen molecules. The spin paramagnetism, of these electrons for specified temperatures and donor concentrations is represented in their theory by

$$\chi_c^p = g^2 C_s / T^{1-\alpha},$$

where

$$C_s = (3.7k/m^*A)(1+\alpha)^{-1}C_c, \quad (2)$$

with

$$\alpha = N_D / Bm^*.$$

$C_c$  is the Curie constant as it appears in (1),  $A$  and  $B$

are constants characterizing the energies of the singlet and triplet ground states of the hydrogen molecule scaled for the dielectric constant for silicon. Depending on the value of  $N_D$ , one finds  $0 \leq \alpha \leq 1$  and  $C_s < C_c$ . In the case of germanium  $A$  and  $B$  are found from the values for the hydrogen molecule  $A_H = 9.66$  eV and  $B_H = 7.84 \times 10^{22}$  cm<sup>-3</sup> by inserting  $K = 16$  in  $A = A_H/K^2$  and  $B = B_H/K^3$ . See, for a discussion on the choice of these values, reference 12, p. 1220.

Since the effective Bohr radius of electrons localized on antimony impurities is larger than that of electrons localized on arsenic impurities then, for equal donor concentrations, the interactions between un-ionized donors should be stronger for antimony impurities than arsenic impurities. Applied in a straightforward way the Sonder-Schweinler theory predicts a significant difference between the spin paramagnetism of electrons localized on arsenic and antimony impurities due to this difference in effective Bohr radii. Therefore, comparison of the susceptibility of arsenic- and antimony-doped germanium should prove interesting.

#### EXPERIMENTAL PROCEDURE

The magnetic susceptibility has been measured by using the Faraday method.<sup>13,14</sup> A brief description of the apparatus and a discussion of some special problems which were encountered in the low-temperature measurements will be published elsewhere.<sup>15</sup>

Single-crystal specimens of  $n$ -type germanium were prepared in this laboratory. They were first obtained in the form of bars,  $3.5 \times 3.5 \times 15$  mm. Hall coefficient and resistivity measurements were made with these bars; the results are given in Table I. Each sample used for susceptibility measurements was cut from the

<sup>13</sup> L. F. Bates, *Modern Magnetism* (Cambridge University Press, New York, 1951).

<sup>14</sup> T. R. McGuire, *Methods of Experimental Physics* (Academic Press Inc., New York, 1959), Vol. 6B.

<sup>15</sup> A. N. Gerritsen and D. H. Damon, *Rev. Sci. Instr.* (to be published).

<sup>10</sup> W. Kohn, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 257.

<sup>11</sup> W. Kohn, reference 10, p. 314.

<sup>12</sup> E. Sonder and H. C. Schweinler, *Phys. Rev.* **117**, 1216 (1960).

center of such a bar. The sample was ground with No. 600 and No. 1200 carborundum powder and etched in CP4. After this treatment the sample was approximately a cube about 3.2 mm on edge, weighing about 180 mg. Immediately before being placed in the cryostat the sample was rinsed in CP4 and distilled water. No contamination with ferromagnetic material was ever observed after this cleaning.

Measurements of the force on a sample at room temperature  $\Theta$  and some low temperature  $T$  yield the relative susceptibility,  $V(T) = \chi(T)/\chi(\Theta)$ . To obtain  $\chi(T)$  one must know  $\chi(\Theta)$ . Other investigators<sup>1</sup> have shown that between room temperature and 78°K the susceptibility of the extrinsic electrons in  $n$ -type germanium is that of a gas of free electrons characterized by an effective mass very nearly equal to that calculated from the results of cyclotron resonance measurements. This then permits a simple method of establishing the susceptibility at room temperature:

(1) Assume the value of  $\chi_g(\Theta)$  reported by Stevens *et al.*<sup>6</sup> as a standard;  $\chi_g(\Theta) = -1.060 \times 10^{-7}$  emu  $g^{-1}$ ;

(2.) Calculate the carrier concentration  $n$ , from the Hall coefficient;

(3.) Calculate the susceptibility of the electron gas  $\chi_e(\Theta)$  using the theoretical formula for the susceptibility of a gas of free electrons<sup>6</sup> and thus the total susceptibility  $\chi(\Theta) = \chi_g(\Theta) + \chi_e(\Theta)$ .

Ignoring compensation by acceptors<sup>12</sup> for donor concentrations greater than  $10^{16}$   $cm^{-3}$ ,  $n$  is found from

$$n = N_D = r / |R(\Theta)| e.$$

If lattice scattering predominates and the carriers obey classical statistics then<sup>16</sup>  $r = 0.92$ . For  $n \leq 2 \times 10^{17}$   $cm^{-3}$  the approximation of classical statistics is appropriate at room temperature. For  $n = 10^{17}$   $cm^{-3}$  impurity scattering is less important than lattice scattering although it is not negligible. For the samples studied in this investigation the effect of impurity scattering on the value of  $r$  should not be much larger than the experimental error in the determination of the Hall coefficient.<sup>17</sup> Therefore the value  $r = 0.9$  has been used for all the samples. Table I presents the values of  $N_D$  and  $\chi(\Theta)$  for each sample.

It is easily shown that a possible error in the determination of  $\chi_e(T)$  introduced by errors in  $\chi_g(\Theta)$  and  $\chi_e(\Theta)$  is negligible compared to the error in the measurement of the relative susceptibility with the possible exception of the two samples with donor concentrations near  $2 \times 10^{17}$   $cm^{-3}$ . The relative susceptibility has, of course, been measured at a number of different values of magnetic field strength. The value reported for any temperature is an average over these measurements. The average deviation of a measurement was found to

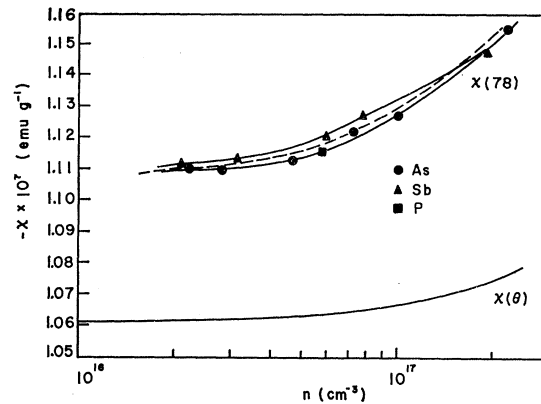


Fig. 1. The susceptibility of  $n$ -type germanium with donor concentrations between  $2 \times 10^{16}$   $cm^{-3}$  and  $2 \times 10^{17}$   $cm^{-3}$  at 78°K vs donor concentration.

lie between 0.05 and 0.2%. The precision of each average is considered to be  $\pm 0.15\%$ .

#### EXPERIMENTAL RESULTS

In order to check the procedure used to obtain the room temperature susceptibility, measurements were made at 78°K. The results are shown in Fig. 1, where the susceptibility at 78°K is plotted against the carrier concentration. There appears to be a small but consistent difference between the susceptibility of the arsenic- and antimony-doped samples below  $N = 10^{17}$   $cm^{-3}$ . The maximum difference is 0.5% of the total susceptibility which is greater than the experimental error. The dashed curve is the sum of the measured lattice susceptibility and the calculated susceptibility  $\chi_e$  of a gas of  $n$  free electrons per unit volume with an effective mass characteristic of the conduction band of germanium. (The theoretical expression for the susceptibility of an electron gas contains the factor  $1 - m^*/3m$ .<sup>6,2</sup> In the case of  $n$ -type germanium, where  $m^* \approx 0.2m$ , the electron gas is diamagnetic.) In calculating this curve, it was assumed that the electron concentration in the conduction band remained constant between room temperature and 78°K. It has further to be investigated whether the drawn curves do coincide for  $10^{17}$   $cm^{-3}$ .

In Fig. 2 the total susceptibility of some of the samples is plotted against  $1/T$  for temperatures below 4.2°K; the susceptibility of pure germanium (sample  $o$ ) is independent of temperature below 4.2°K; it will be shown in most figures as a horizontal line at  $\chi = -1.116 \times 10^{-7}$  emu  $g^{-1}$ . Throughout the range of donor concentrations studied, the low-temperature susceptibility of the antimony-doped samples is more diamagnetic than that of the arsenic-doped samples. At a donor concentration of about  $2 \times 10^{17}$   $cm^{-3}$ , the susceptibility of both arsenic- and antimony-doped germanium is, within experimental error, independent of temperature. At a donor concentration of about  $7.4 \times 10^{16}$   $cm^{-3}$  the susceptibility of the antimony-doped sample is tem-

<sup>16</sup> C. Herring, Bell System Tech. J. 34, 237 (1955).

<sup>17</sup> V. A. Johnson and K. Lark-Horovitz, Phys. Rev. 82, 977 (1951).

TABLE II. A comparison of the values of the Curie constant  $C_2$ , determined by fitting (3) to the experimental data, with the theoretical Curie constant  $g^2C_e$  as derived from the hydrogenic model.

Sample	Doping	$C_2 \times 10^9$ (emu $g^{-1}$ $^{\circ}K$ )	$g^2C_e \times 10^9$ (emu $g^{-1}$ $^{\circ}K$ )
e	As	$1.2 \pm 0.4$	5.22
n	As	$1.5 \pm 0.5$	3.92
i	As	$1.9 \pm 0.7$	3.34
j	Sb	$1.4 \pm 0.8$	3.0
k	As	$1.1 \pm 0.6$	1.96
l	As	$0.9 \pm 0.9$	1.59
m	Sb	$1.0 \pm 0.6$	2.03

perature independent whereas the susceptibility of the arsenic-doped samples has a temperature-dependent paramagnetic component.

Within experimental error, the results can be fit to an equation of the form

$$\chi = \text{const} + C_2/T. \quad (3)$$

The values of  $C_2$  so obtained for each sample have been collected in Table II together with values of  $g^2C_e$  (1a). For arsenic-doped germanium Feher *et al.*<sup>8</sup> report an isotropic value of  $g$  equal to 1.57. Comparisons of the values of  $C_2$  with  $g^2C_e$  should therefore be unambiguous. For antimony-doped germanium however, an anisotropic  $g$  factor was found. Since this anisotropy may be dependent on strains in the crystal and as we have no knowledge of the extent to which the samples used in this investigation might be strained, the comparison of the values of  $C_2$  with  $g^2C_e$  is uncertain for the antimony-doped samples. In ignorance of the true state of the samples, what might seem to be a reasonable average value of  $g^2$  has been adopted:  $g^2 = (g_{(100)}^2 + 2g_{(110)}^2)/3 \approx 3.3$  Table II shows that the values of  $C_2$  are uniformly smaller than  $g^2C_e$  for both antimony- and arsenic-doped germanium.

The difference between impurity species for practically equal concentrations is strikingly shown in the comparison of samples *f*, *g*, and *h*. Sample *g* is a phos-

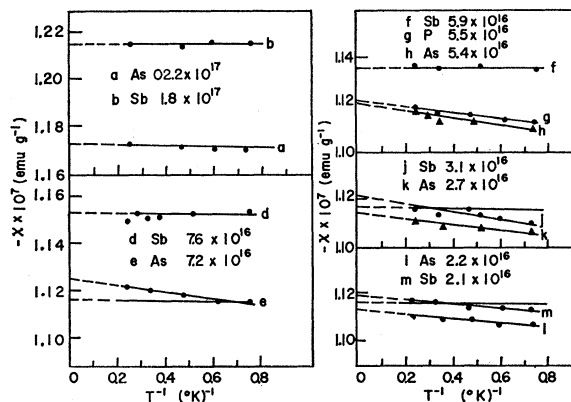


FIG. 2. The susceptibility of *n*-type germanium between 4.2 and 1.35°K vs reciprocal temperature.

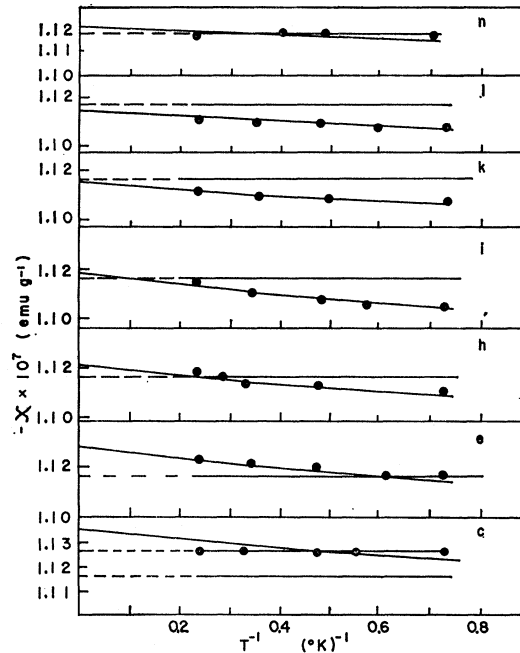


FIG. 3. The susceptibility of arsenic-doped germanium between 4.2 and 1.35°K vs reciprocal temperature. The curves are the best fit of the Sonder-Schweiner formula to the experimental points.

phorous-doped sample, the only such sample included in this investigation. With regard to both the magnitude of the susceptibility and its temperature dependence the arsenic- and phosphorous-doped samples are nearly identical and both differ markedly from the antimony-doped samples. Since the value of the impurity ionization energy for phosphorus-doped germanium ( $12 \times 10^{-3}$  eV) is much closer to that for arsenic-doped germanium ( $12.7 \times 10^{-3}$  eV) than that for antimony-doped germanium ( $9.6 \times 10^{-3}$  eV) this result may be explained, at least qualitatively, in terms of the hydrogenic model. Together with the values of  $C_2$  fit to the data, these curves indicate the existence of a molecular exchange interaction. The temperature-independent susceptibility of the antimony-doped sample *f*, suggests such a large interaction between the impurity ions that even a model of hydrogen-like molecules breaks down. The importance of this strong interaction is also demonstrated in the values of the electrical resistivity at 4.2°K for samples *f* (Sb) and *h* (As) for which the numbers 5.2  $\Omega$  cm and at least  $2 \times 10^5$   $\Omega$  cm, respectively, were found.

In Figs. 3 and 4 the experimental values of the susceptibility are compared with the Sonder-Schweiner theory. The curves represent the fit of the theory to the data plotted against  $1/T$ . This was done as follows. The Sonder-Schweiner formula (2) for the spin paramagnetism does not involve any adjustable parameters that would have to be determined by fitting the theory to the observed change of the susceptibility with

TABLE III. Values of  $\alpha$ ,  $C$ , and  $C_1$  in (4).  $\alpha$  and  $C$  have been computed using  $m^*=0.24$  and  $0.18$  for As and Sb impurities,  $K=16$ ,  $A=3.79 \times 10^{-2}$  eV, and  $B=1.91 \times 10^{19}$  cm $^{-3}$ .  $C_1$  has been chosen to fit  $[C_1 + C/T^{1-\alpha}]$  with the experimental values for  $\alpha$ .

Sample	Doping	$\alpha$	$C \times 10^9$ (emu g $^{-1}$ °K)	$-C_1 \times 10^7$ emu g $^{-1}$
<i>e</i>	As	0.27	1.7	1.128
<i>h</i>	As	0.20	1.7	1.121
<i>i</i>	As	0.17	1.6	1.117
<i>k</i>	As	0.10	1.2	1.115
<i>l</i>	As	0.08	1.1	1.114
<i>j</i>	Sb	0.27	1.0	1.120
<i>m</i>	Sb	0.19	0.95	1.120

temperature. Hence, with the values  $m_{As}^*=0.24$   $m$ ,  $m_{Sb}^*=0.18$   $m$ ,  $A=3.79 \times 10^{-2}$  eV, and  $B=1.91 \times 10^{19}$  cm $^{-3}$ , values of  $C=g^2 C_s$  and  $\alpha$  were calculated, using in (2) for each sample the donor concentration determined from the measured Hall coefficient and the  $g$  factors given above. A constant  $C_1$  was then chosen such that

$$\chi = C_1 + (C/T^{1-\alpha}), \quad (4)$$

was a best fit to the data. The values for  $C$  and  $C_1$  are given in the Table III.

As may be seen in the figures, this theory accounts very well for the observed temperature dependence of the susceptibility of most of these samples. Marked deviations from the calculated curves are found for the samples, *e*, *c*, and *n* [(7.2, 10, and  $1.5 \times 10^{16}$  cm $^{-3}$  As, respectively] and *f* ( $5.9 \times 10^{16}$  cm $^{-3}$  Sb).

From a comparison of the values for the ionization energies, the dielectric constants and the electron effective masses in *n*-type germanium and silicon, Sonder and Schweinler concluded that their theory would account for the temperature dependence of the susceptibility of *n*-type germanium for donor concentrations below  $5 \times 10^{16}$  cm $^{-3}$ . Using the same comparison but slightly different values of  $m^*$  (see Table III) we estimate that the theory should fail below 4°K for arsenic concentrations in excess of  $7 \times 10^{16}$  cm $^{-3}$  and for antimony concentrations in excess of  $3.3 \times 10^{16}$  cm $^{-3}$ . While our results are in accord with these predictions

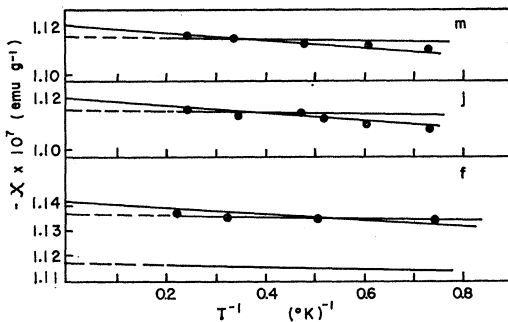


FIG. 4. The susceptibility of antimony-doped germanium between 4.2 and 1.35°K vs reciprocal temperature. The curves are the best fit of the Sonder-Schweinler formula to the experimental points.

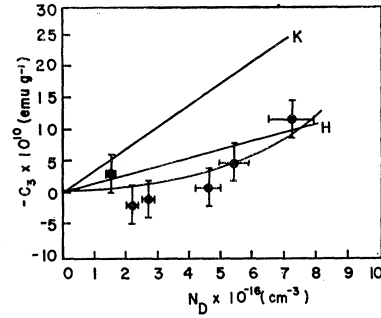


FIG. 5. The temperature-independent part of the low-temperature susceptibility of the extrinsic electrons in arsenic-doped germanium vs donor concentration for donor concentrations such that the temperature dependence of the susceptibility is described by the Sonder-Schweinler formula.

they do not show the kind of failure predicted by the theory and observed with *n*-type silicon. Sonder and Schweinler claim that their theory overestimated the effect of pairing and that at these critical donor concentrations a more strongly temperature-dependent susceptibility should be observed than predicted by the formula. It is clear that our results do not show this. For example, examine the results for samples *i*, *h*, *e*, and *c* in Fig. 3 for which the donor concentrations are, respectively, (4.6, 5.4, 7.2, and  $10 \times 10^{16}$  arsenic atoms cm $^{-3}$ ).

Inspection of the experimental data for the sample *n* shows that for this small impurity concentration the total change of the susceptibility to be expected within the temperature range considered is of the order of the experimental accuracy. We do not attach any significance to the behavior of sample *n* other than that it shows that these results cannot provide a very critical test of the Sonder-Schweinler theory.

The temperature-independent part of the susceptibility of the extrinsic electrons  $C_3$  was found by subtracting the susceptibility of the pure sample from  $C_1$ . The values of  $C_3$  found for the arsenic-doped samples are plotted against impurity concentration in Fig. 5. As may be seen from Fig. 5 the values of  $C_3$  for two samples (*k* and *l*) appear to be positive indicating a temperature-independent paramagnetic contribution to the susceptibility. However, as is indicated in Fig. 5, we do not feel that the experimental accuracy permits a definite conclusion that such a contribution exists. The line *H* represents the orbital diamagnetic susceptibility of localized electrons as calculated from the hydrogenic model and by the line *K* the same quantity is indicated but calculated from the effective mass theory.

The susceptibilities of samples *a*, *b*, *c*, *d*, and *f* are, within experimental error, independent of temperature below 4.2°K. There is no immediate way of separating the various components of the susceptibility of the extrinsic electrons. The low-temperature susceptibility of the electrons  $\chi_e$ , i.e., the difference between the

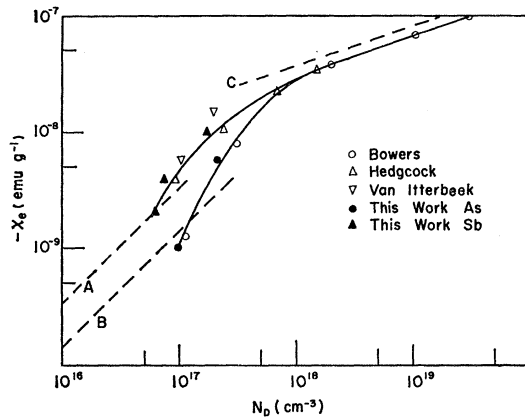


FIG. 6. The total susceptibility of the extrinsic electrons at low temperatures vs donor concentration for concentrations such that the susceptibility is independent of temperature between 4.2 and 1.35°K.

susceptibility of a doped sample and the pure sample, is plotted against donor concentration in Fig. 6, together with some previously reported results.<sup>3,4,18</sup> Taking everything into account the agreement between these various results seems reasonable. The dashed lines *A* and *B* show the orbital diamagnetism as calculated from the hydrogenic model. The dashed line *C* shows the low-temperature susceptibility of  $n=N_D$  electrons in the conduction band of germanium if the conduction band is assumed to be unaltered by the addition of impurities. It is clear that below the electron concentration range, for which Bowers found the susceptibility to vary as  $n^{\frac{1}{2}}$  the variation is much faster, even faster than the proportional variation required by the hydrogenic model. In the present investigations two different impurities have been investigated under similar circumstances. The results confirm the earlier observed but not explicitly recognized evidence that for impurity concentrations below  $5 \times 10^{17} \text{ cm}^{-3}$  the magnitude of the electronic susceptibility in germanium depends on the kind of impurity used for the doping.

An interesting relation between the susceptibilities of these arsenic- and antimony-doped samples is shown in Fig. 7 where  $\chi_e$  is plotted against  $a^{*3}N_D$ ;  $a^*$  is the effective Bohr radius of electrons localized on isolated impurities as calculated from the hydrogenic model. It is clear that a single curve represents the susceptibility of the impurity electrons considered as a function of  $a^{*3}N_D$  for both impurity species. For  $5 \times 10^{-3} \leq a^{*3}N_D \leq 10^{-2}$  the susceptibility is given by  $\chi_e = -5.5 \times 10^{-5} \times (a^{*3}N_D)^2$  (emu g<sup>-1</sup>), with  $a^* = 47$  and  $36 \text{ \AA}$ , respectively, for antimony and arsenic impurities.

#### DISCUSSION AND CONCLUSION

The results obtained for 78°K (Fig. 1) not only indicate that there is a diamagnetic contribution by the electrons in the conduction band but they seem to

suggest that this contribution depends on the impurity species. It is somewhat larger for antimony and smaller for arsenic than follows from a straight-forward calculation of the susceptibility of the electrons in the conduction band. However, the magnitude of the Hall coefficient is for each sample considerably larger at 78° than at 300°K (Table I). While part of this change in the Hall coefficient almost certainly will be due<sup>17</sup> to an increase in the value of  $r$ , part also should be due to a decrease in the number of carriers in the conduction band as the temperature is lowered from 300 to 78°K.

It will be shown that the difference between the susceptibilities of arsenic- and antimony-doped germanium for concentrations below  $10^{17} \text{ cm}^{-3}$  and at 78°K can be attributed to the difference between the susceptibility of electrons localized at these impurities without supposing any effect of the impurities on the conduction band.

Assume that at 300°K there are  $n=N_D$  extrinsic electrons in the conduction band, but that at 78°K only a fraction  $f$  of these electrons are in the conduction band, the remaining fraction  $1-f$  occupying localized states of the impurities. The susceptibility of a sample at 78°K may therefore be represented by

$$\chi = \chi_c + f\chi_e^{\text{C.B.}} + (1-f)\chi_e^{\text{p}} + (1-f)\chi_e^{\text{d}},$$

where  $\chi_e^{\text{C.B.}}$  represents the susceptibility of free electrons in the conduction band and the other quantities have been previously introduced. If for equal donor concentrations the value of  $f$  is assumed to be the same for arsenic- and antimony-doped germanium, then the difference between the susceptibility of an arsenic-doped sample and an antimony-doped sample is, for the most part, to be found only in the last term (the first two terms cancel and the third is small at 78°K). Using Eq. (1b), the effective Bohr radii calculated from the hydrogenic model, and the data shown in Fig. 1, values of  $f$  (within about 50%) may be calculated. For  $N_D = 6 \times 10^{16} \text{ cm}^{-3}$ ,  $f$  turns out to be 0.6. This value is not inconsistent with the measured Hall coefficients. One might question the assumption that  $f$  is the same for both impurity species particularly if the

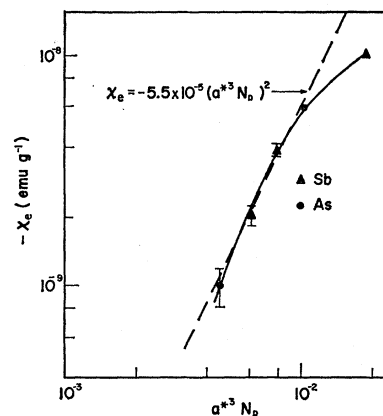


FIG. 7. The total susceptibility of the extrinsic electrons at low temperature vs  $a^{*3}N_D$ .

<sup>18</sup> A. Van Itterbeek and W. Duchateau, *Physica* 22, 649 (1956).

dissociation equation, containing an exponential factor with the donor ionization energy, is used to calculate  $f$ . However, if both the Hall mobility and the ratio of the Hall coefficient at 78°K to the same quantity at 300°K are plotted against donor concentration, no significant difference between the antimony- and arsenic-doped samples is observed. While this does not prove the assumption about  $f$ , it does indicate that it is perhaps not unreasonable. In view of the poor accuracy in the values of the susceptibility differences and in absence of precise information about the value of  $r$  further speculation seems unwarranted.

These uncertainties do not affect the conclusion that the results at 78°K are in good agreement with previously published studies.<sup>6</sup> It seems therefore justified to conclude that the described method for the determination of the susceptibility of the samples at room temperature is to be considered reliable.

The Sonder-Schweiner theory was shown to give a good account of the observed values of the susceptibility for appropriate donor concentrations in the range 1.3 to 4.2°K. The present results are not sufficiently precise to claim that they provide a critical test of the theory. This theory introduces a twofold modification of the Curie law; both the temperature dependence of the spin paramagnetism and the Curie constant are altered. However, it was shown that the temperature dependence of the susceptibility could be accounted for within experimental error by a paramagnetic contribution varying as  $1/T$ . The results, therefore, are not sensitive to the difference between  $1/T$  and  $1/T^{1-\alpha}$  even though  $\alpha$  is as large as 0.27 for the concentrations considered. The significant feature of the theory in accounting for these results is the modification of the Curie constant.

Differences between impurity species are accounted for in (2) by the values of  $m^*$  and  $g$ . Though the susceptibility values for the antimony-doped samples  $j$  and  $m$  seem to satisfy (4) when the appropriate values of  $m^*$  and  $g$  are used, the uncertainty in the value of  $g$  for antimony and the accuracy of the experimental results do not allow any conclusion to be drawn regarding the extent to which the Sonder-Schweiner formula accounts for differences in donor characteristics.

In general, all details of the molecular model remain obscured by the rather low experimental precision. It should be remarked that silicon is a much more favorable material to investigate than germanium. For example, between 20 and 3.5°K a change of  $26 \times 10^{-9}$  emu  $g^{-1}$  is found<sup>7</sup> in the susceptibility of a silicon sample containing  $6 \times 10^{17}$  cm<sup>-3</sup> arsenic atoms, compared to the largest change  $1.1 \times 10^{-9}$  emu  $g^{-1}$  observed for sample  $i$  in this investigation between 4.2 and 1.3°K.

The present results strongly suggest that for certain concentrations to consider the impurity atoms in germanium as forming hydrogen molecule-like pairs is a fair approach to reality.

The error in the determination of the temperature-independent contribution  $C_3$  is, without doubt, rather large. Still it is difficult to avoid concluding that the orbital diamagnetism calculated from the effective mass theory is too large, the observed values of the orbital diamagnetism are much closer to those suggested by the simple hydrogenic model. The success of the Sonder-Schweiner theory in accounting for the spin paramagnetism suggests that a calculation of the orbital diamagnetism on the basis of the hydrogen molecule might be more rewarding. An exact calculation might turn out to be rather difficult; the state of an isolated impurity atom is not perfectly represented by a hydrogen-like  $^2S$  state nor the states of a pair by  $\Sigma$  states. Two problems that should be considered in such a calculation may be pointed out. First, if the orbital diamagnetism of an electron pair in a  $^1\Sigma$  state should differ significantly from that in a  $^3\Sigma$  state then the orbital diamagnetism of the extrinsic electrons would no longer be independent of temperature. A simple Heitler-London calculation using  $^2S$  hydrogen wave functions scaled for impurity atoms in germanium shows<sup>19</sup> that this difference is small and probably would not cause the orbital diamagnetism to become significantly temperature dependent. Second, in adopting a molecular model the possibility of a significant Van Vleck paramagnetic contribution must be considered. In this regard it is interesting to note the tendency of the values of  $C_3$  to become positive for arsenic concentrations of the order of  $2 \times 10^{16}$  cm<sup>-3</sup> although considering the accuracy in the values of  $C_3$  it is hardly justified to attribute much significance to this tendency. Van Vleck and Frank<sup>19</sup> estimated an upper limit to this paramagnetic contribution attributed to the non-vanishing mean square of the electronic angular momentum in the  $^1\Sigma$  state for the normal hydrogen molecule. A similar estimate<sup>20</sup> of the upper limit to this term for an impurity pair in germanium with a donor concentration of the order of  $10^{16}$  cm<sup>-3</sup> gave a value of the same order of magnitude as the orbital diamagnetism. While the estimate is questionable, it does suggest that further investigation of this contribution might be warranted.

We find it extremely difficult to give a quantitative account of the results shown in Fig. 7. As previously mentioned there does not appear to be any way of straightforwardly separating the spin paramagnetism and the orbital diamagnetism of the extrinsic electrons in these samples whose susceptibility is independent of temperature. Furthermore, it is not clear<sup>21</sup> that the sum of a spin paramagnetic contribution and a diamag-

<sup>19</sup> H. Van Vleck and A. Frank, Proc. Natl. Acad. Sci. U. S. **15**, 539 (1929).

<sup>20</sup> D. H. Damon, Ph.D. thesis, Purdue University, 1961 (unpublished).

<sup>21</sup> In recent years there have been many attempts to derive a more general theory of the magnetic susceptibility of an electron gas; see, for example, J. E. Heblorn and E. H. Sondheimer, J. Phys. Chem. Solids **13**, 105 (1960).

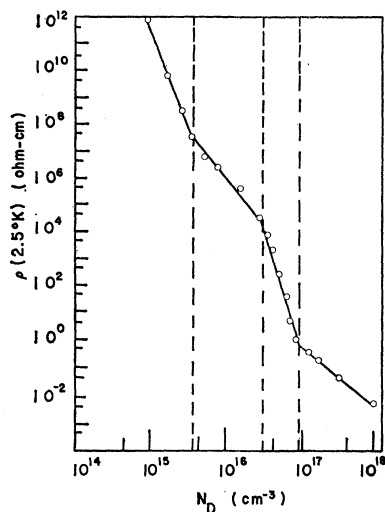


FIG. 8. The electrical resistivity of antimony-doped germanium at 2.5°K vs donor concentrations (Fritzsche, reference 22). The line segments through the experimental points and the division of the concentration range are proposed by the present authors.

netic contribution proportional to  $\langle r^2 \rangle$  provides an adequate description of the susceptibility of the extrinsic electrons. The fact that the effective Bohr radii characteristic of localized electrons can be used to "normalize" the susceptibility strongly suggests that the electrons should be regarded to a considerable extent as localized at helium temperatures for arsenic concentrations as large as  $2 \times 10^{17} \text{ cm}^{-3}$  and for antimony concentrations as large as  $1 \times 10^{17} \text{ cm}^{-3}$ . Since the dependence of the electron susceptibility on the square of  $a^{*3}N_D$  extends over only a very limited range of values of this parameter, it is not clear whether this has any fundamental significance or is only fortuitous. Outside the range  $5 \times 10^{-3} < a^{*3}N_D < 10^{-2}$ , the state of the extrinsic electrons in germanium at helium temperatures seems to be rather well understood. For  $a^{*3}N_D > 10^{-2}$ , electrons presumably occupy band-like states. At and below  $a^{*3}N_D = 5 \times 10^{-3}$  the electrons are most certainly localized on impurity atoms grouped in hydrogen molecule-like pairs and at still lower concentrations the localization is at the single impurity atoms.

In Fig. 8 we reproduce some results published by Fritzsche.<sup>22</sup> The electrical resistivity of antimony-doped germanium at 2.5°K is plotted against antimony concentration. We have added the line segments through the experimental points and the fourfold division of the concentration range. The division at  $N_D = 3.5 \times 10^{16} \text{ cm}^{-3}$  corresponds very well with the upper limit of antimony concentration for which the Sonder-Schweiner theory should be applicable. It is somewhat smaller than the concentration given by  $a^{*3}N_D = 5 \times 10^{-3}$  which is  $N_D = 5 \times 10^{16} \text{ cm}^{-3}$ . The division at  $N_D = 9 \times 10^{16} \text{ cm}^{-3}$  corresponds very closely to the concentration given by  $a^{*3}N_D = 10^{-2}$ . The division at  $N_D = 4 \times 10^{15} \text{ cm}^{-3}$  is, arbitrarily, at the donor concentration for which  $C$  in the Sonder-

Schweiner formula equals 90% of  $g^2 C_e$ . The very close correspondence between the sharp drop in the electrical resistivity at 2.5°K between antimony concentrations of  $3.5$  and  $9 \times 10^{16} \text{ cm}^{-3}$  and the abrupt rise in the diamagnetic susceptibility of the extrinsic electrons in that concentration region is remarkable indeed. It is clear from the values of the electrical resistivity at 4.2°K of the arsenic-doped samples used in this investigation (Table I) that a similar correspondence can be expected to exist for arsenic-doped germanium.

## SUMMARY AND CONCLUSIONS

The following conclusions about the susceptibility of  $n$ -type germanium with moderate donor concentrations may be drawn.

(1) For impurity concentrations below about  $5 \times 10^{17} \text{ cm}^{-3}$  there is a marked and consistent difference between the electronic susceptibility for samples doped with different impurities.

(2) At high temperatures (around 80°K) the difference in susceptibility for arsenic- and antimony-doped germanium can be explained quantitatively by a decrease in the electron concentration in the conduction band relative to the concentration at room temperature and the difference between the effective Bohr radii of the electrons localized on arsenic and antimony impurities.

(3) There exists for each of the impurities, arsenic and antimony, a range of concentration within which the susceptibility of the extrinsic electrons at helium temperatures can be qualitatively described by a hydrogen molecule-like pairing of the impurities.

(4) Straightforward application of such a model as suggested by Sonder and Schweiner accounts for the magnitude of the electronic susceptibility below 4°K but the results do not permit a determination of the exact functional form of the temperature dependence of the susceptibility.

(5) Qualitatively the hydrogen-molecule model accounts for the observed differences between the susceptibilities of arsenic- and antimony-doped germanium at these concentrations but the results are not sufficiently precise to permit a quantitative check of the theory on this point.

(6) The diamagnetic contribution of extrinsic electrons below 4°K is quantitatively best in agreement with the hydrogenic model for those concentrations for which the Sonder-Schweiner theory is applicable.

(7) At concentrations slightly greater than those for which the Sonder and Schweiner theory is applicable, the susceptibility of the extrinsic electrons varies rapidly with donor concentrations. This variation, observed over a relatively small range of concentrations, is distinctly different from the variation observed both at higher and lower concentrations.

<sup>22</sup> H. Fritzsche, J. Phys. Chem. Solids **6**, 69 (1958).



(8) On the basis of the susceptibility measurements, the range of impurity concentrations in germanium may be divided into at least three parts. A close correspondence between the dependence of the low-temperature electrical resistance and the magnetic susceptibility on donor concentrations was observed. This division may be associated, at least qualitatively, with the strength of the donor interactions.

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## Uniformly Moving Dislocations of Arbitrary Orientation in Anisotropic Media\*

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The dynamical behavior of uniformly moving dislocations in anisotropic media is considered for the general case in which the dislocation involves three components of displacement. It is found that both edge and screw dislocations can display an anomalous behavior. It appears that, in general, the force of interaction between two parallel dislocations on the same slip plane changes sign with increasing dislocation velocity; this result obtains whether the dislocations involved be two edges, two screws, or an edge and a screw. The threshold velocity at which the force of interaction changes sign is a function of the orientation and type of dislocation. However, the limiting velocity, at which the energy of the dislocation becomes infinite, is a function only of the orientation of the dislocation and is the same whether the dislocation be pure edge, pure screw, or mixed in character. Numerical results are presented for  $(\bar{1}10)$   $[11\bar{1}]$  dislocation motion in lithium.

### I. INTRODUCTION

THERE has been a renewal of interest in the dynamical properties of dislocations since Weertman<sup>1</sup> pointed out that in isotropic materials high-speed dislocations of like sign attract rather than repel one another. The velocity range for this anomalous behavior extends from the Rayleigh wave velocity to the shear wave velocity; the latter is the limiting velocity of the edge dislocation since its energy becomes infinite at that velocity. Screw dislocations, however, behave "normally" at all velocities up to their limiting velocity, which also is the velocity of shear sound.

The dynamical behavior of dislocations in anisotropic media was considered previously by this author<sup>2,3</sup> for those orientations of the dislocation for which the problem could be treated as one of plane strain, i.e., for those orientations for which a pure edge dislocation requires only two components of elastic displacement, a pure screw dislocation only one. Again it was found that the force field of an edge dislocation changes sign at

some velocity below its limiting velocity, whereas a screw dislocation is well-behaved at all possible velocities. However, in the anisotropic case the threshold velocity for the anomalous behavior of edge dislocations (the generalized Rayleigh wave velocity) can be any velocity from zero to the limiting velocity, depending on the elastic constants of the material and the orientation considered. The limiting velocity of a screw dislocation is different from that of an edge for these orientations, and it is possible for the limiting velocity of an edge dislocation to be less than the corresponding shear sound velocity.

Specific orientations of moving edge dislocations in cubic materials for which the plane strain analysis is not applicable have been treated by Weertman and co-workers.<sup>4,5,6,7</sup> This paper presents an analysis of the dynamical behavior of a uniformly moving dislocation of arbitrary orientation in any anisotropic elastic medium.

### II. UNIFORMLY MOVING DISLOCATIONS

The equations of equilibrium for an anisotropic elastic medium are

$$F_{ijk}u_{k,jl} = \rho\ddot{u}_i, \quad (1)$$

<sup>1</sup> J. Weertman, *Phil. Mag.* **7**, 617 (1962).

<sup>2</sup> J. Cotner and J. Weertman, *Acta Met.* **10**, 515 (1962).

<sup>3</sup> J. Weertman, *J. Appl. Phys.* **33**, 1631 (1962).

<sup>4</sup> A. Van Hull and J. Weertman, *J. Appl. Phys.* **33**, 1636 (1962).

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<sup>1</sup> J. Weertman, *Response of Metals to High-Velocity Deformation*, edited by P. G. Shewmon and V. F. Zackay (Interscience Publishers, Inc., New York, 1961).

<sup>2</sup> L. J. Teutonico, *Phys. Rev.* **124**, 1039 (1961).

<sup>3</sup> L. J. Teutonico, *Phys. Rev.* **125**, 1530 (1962).