line broadening can be estimated to be about 0.6 gauss (*half* distance between observed absorption derivative peaks) and may be roughly compared with the square root of the second moment of the absorption calculated using the equation for dipolar broadening alone. The latter value is about 0.22 gauss for polycrystalline cadmium of natural isotopic abundance. The discrepancy of a factor 3 between the observed and calculated symmetric line broadening could be due to an exchange interaction between the nuclear spins of the two isotopes.[5]

The fact that the parallel shift is greater than the perpendicular shift indicates either that the wave function of the conduction electrons near the Fermi level has a greater density in the direction of the hexagonal axis or else that the electron spin-orbit coupling causes the g factor to be larger when the magnetic field is parallel to the hexagonal axis.

The surprising magnitude of the anisotropy is no doubt due to the extreme deviation of the c/a ratio of cadmium (1.886) from that for a close-packed hexagonal array of spheres (1.633).

Preliminary work on cadmium was done with H. E. Walchli using an enriched CdI sample provided by the Stable Isotope Research and Production Division of Oak Ridge National Laboratory.

[5] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954); N. Bloembergen and T. J. Rowland, Phys. Rev. **97**, 1679 (1955).

PHYSICAL REVIEW VOLUME 103, NUMBER 6 SEPTEMBER 15, 1956

Effect of Neutral Impurity on the Microwave Conductivity and Dielectric Constant of Germanium at Low Temperatures*

F. A. D'ALTROY† AND H. Y. FAN
Purdue University, Lafayette, Indiana
(Received June 8, 1956)

Conductivity and dielectric constant of germanium at 4.2°K were measured at a frequency of 9200 Mc/sec. The dielectric constant measured for a pure sample is 16.0±0.3. Higher dielectric constants, up to 80, were measured on n- and p-type samples doped with antimony or gallium. The conductivity and the change of dielectric constant are attributed to carriers in the impurity states. A positive contribution, ΔK_b, to the dielectric constant is given by the polarization of neutral impurity atoms and a negative contribution, ΔK_c, is associated with the conduction effect. Using ΔK_b to estimate the ionization energy of the impurity, a value of 0.0099 ev is obtained for a sample containing 1.6×10^{16} cm^{-3} antimony and 0.0084 ev is obtained for a sample containing 3.7×10^{16} cm^{-3} gallium. Samples of higher impurity concentrations showed much higher conductivity and the effect of overlapping of impurity states is shown in the variation of impurity polarizability. The relaxation time and effective mass for the conduction in impurity states are estimated from the dc conductivity and its ratio to the microwave conductivity. Large effective masses, around $1000m$, are obtained for samples of $\sim10^{17}$ cm^{-3} impurity concentration.

I. INTRODUCTION

A SEMICONDUCTOR with small impurity content and very low concentration of free carriers has a dielectric constant characteristic of the pure crystal. Free carriers give rise to conductivity as well as a change in the dielectric constant. On account of the inertia of the carriers, the current in an alternating field has a component out of phase with the field, which contributes to the electric susceptibility. From the conductivity and the change of dielectric constant, the two parameters, relaxation time and effective mass of carriers, can be determined. In order to have an appreciable out-of-phase current, it is necessary to use a sufficiently high frequency which is not too small compared to the collision frequency of the carriers. Conductivity and dielectric constant of germanium have been determined from measurements of microwave transmission through bulk samples by several groups of workers.[1–3] The measurements of Benedict and Shockley and of Goldey and Brown were made at temperatures above 160°K, while our measurements covered the range 20°K to 300°K. The results obtained on the effective masses of electrons and holes are difficult to reconcile with the cyclotron resonance data.[4] No satisfactory explanation for this has yet been found.

The present paper deals with microwave measurements of dielectric constant and conductivity near liquid helium temperature.[5] It will not be concerned with the effect of free carriers. In the samples used, most of the carriers are in the impurity states at this temperature. The samples contain Ga or Sb as im-

* Work supported by a Signal Corps Contract.
† Now at Bell Telephone Laboratories, Murray Hill, New Jersey.

[1] F. A. D'Altroy and H. Y. Fan, Proc. Natl. Electronics Conf. **8**, 522 (1952); Phys. Rev. **94**, 1415 and 1405 (1954); **98**, 1561 (1955).
[2] T. S. Benedict and W. Shockley, Phys. Rev. **89**, 1152 (1953); T. S. Benedict, Phys. Rev. **91**, 1565 (1953).
[3] J. M. Goldey and S. C. Brown, Phys. Rev. **98**, 1761 (1955).
[4] H. Y. Fan in *Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 1.
[5] F. A. D'Altroy and H. Y. Fan, Phys. Rev. **100**, 1260 (1955).

purities, and these have small activation energies, of the order of 0.01 ev. Carriers in the impurity states have large orbits, and appreciable polarization is obtained under applied field. The effect is to increase the dielectric constant, in contrast to the effect of free carriers which give a negative susceptibility. Furthermore, carriers in impurity states can give rise to conduction. In fact, the conductivity of the samples near 4°K is to be attributed to impurity band conduction[6] which has to be taken into account in the interpretation of the measured conductivity and dielectric constant.

II. THEORY

For sufficiently small impurity concentrations, we may consider electronic states of isolated impurity atoms. Considerable progress has been made in the study of impurities of the group III and group V elements. Ground-state wave functions as well as transition probabilities to some excited states have been calculated. However, calculations of the polarizability are not yet available. The simple hydrogenic model gives a polarizability

$$\alpha_b=\frac{9}{2}K_0a^3=\frac{9}{2}K_0\left(\frac{K_0\hbar^2}{m^*e^2}\right)^3, \tag{1}$$

where K_0 is the dielectric constant of the pure crystal and m^* is the carrier effective mass. The ionization energy being

$$E_i=h\nu_0=m^*e^4/2\hbar^2K_0^2, \tag{2}$$

we can write

$$\alpha_b=\frac{9}{8}\left(\frac{e^2}{4\pi^2m^*}\right)\left(\frac{1}{\nu_0^2}\right)=\frac{9}{8}\left(\frac{e^6}{2K_0^2}\right)E_i^{-3}$$
$$=6.56\times10^{-24}E_i^{-3}, \tag{3}$$

where the numerical factor is calculated for expressing E_i in ev. The expression is for the static polarizability. The ionization being of the order of 0.01 ev, we deal essentially with the static polarizability at microwave frequencies. Instead of the factor 9/8, more accurate model may give a different value. However, since E_i depends on the cubic root of this value, (3) may be a fair approximation for the estimation of E_i.

In the experiments, the dielectric constant is measured. Assuming isolated impurity states, we have to take into account local field correction in deducing α from the measured effect on the dielectric constant. The mutual interaction of the neutral impurities is reduced by the dielectric constant of the pure crystal,[7] giving

$$\Delta K_b=\frac{4\pi N\alpha_b}{1-4\pi N\alpha_b/3K_0}, \tag{4}$$

$$\alpha_b=\frac{\Delta K_b}{4\pi N}\left(\frac{3K_0}{3K_0+\Delta K_0}\right), \tag{5}$$

where N is the concentration of neutral impurities.

It was found that impurity concentrations over 10^{16} cm^{-3} are required for an appreciable effect to be observed. In germanium of even smaller impurity concentrations, the observed temperature dependences of resistivity and Hall coefficient indicate that the conduction at liquid helium temperatures is to be attributed to the carriers in the impurity states which may be considered as forming a band. In this picture, the polarizability discussed above is determined by the matrix elements connecting the states of the impurity band with the valence or conduction band and excitation bands of the impurity. A conduction in impurity states indicates departure from the picture of impurity states of isolated atoms. Furthermore, such conduction should give rise to an additional contribution to the susceptibility, like the effect of free carriers. In the absence of detailed knowledge about the impurity band, the effect can be estimated approximately by the Drude-Kronig theory, according to which

$$\sigma=\sigma_0/[1+(\omega\tau)^2], \tag{6}$$

$$\Delta K_c=-4\pi\sigma\tau=-\frac{4\pi\sigma}{\omega}\left(\frac{\sigma_0}{\sigma}-1\right)^{\frac{1}{2}}. \tag{7}$$

Since the microwave frequency is far below the resonance frequencies for the excitation of carriers in the impurity band to higher bands, interband transitions may be expected to give negligible contribution to the power loss and the associated conductivity. The microwave conductivity as well as dc conductivity can be attributed to conduction in the impurity band. Thus, the effect of this conduction on the dielectric constant can be estimated by using (7) and the measured dc and microwave conductivities.

III. EXPERIMENTAL METHOD

The experiment consists of measuring the attenuation and phase shift in the transmission of microwaves through germanium specimens.[1] Microwaves of 9200 Mc/sec was supplied by a klystron modulated at 1000 cycles/sec. Samples of suitable thicknesses, a few mm, were prepared to fit closely the cross section of the rectangular wave guide. The phase shift was measured by using a bridge circuit, one arm of which contains the sample and the other a calibrated phase shifter. A section of the wave guide containing the sample was immersed in liquid helium and was filled with helium gas at a slightly lower than atmospheric pressure to prevent condensation of helium in the guide. The sample dimensions were made slightly smaller than the

[6] C. S. Hung, Phys. Rev. **79**, 351, 727 (1950).
[7] G. W. Castellan and F. Seitz in *Semiconducting Materials* (Butterworths Publications, London, 1951).

TABLE I. Results of dc and microwave measurements at 4.2°K.

Sample	*n* type *S2H*	Sb14*b*	Sb11*A*	*PN4I*	*p* type Ga10*C1*	Ga10*C4*	Ga10*C2*	*PN3E*
n_{ex} (10^{16} cm^{-3})	6×10^{-3}	1.2	6.3	12	2.9	5.1	6.3	2.8
N_{maj} (10^{16} cm^{-3})			8.9	90	3.7	6.3	9.9	22.2
σ_0 (ohm cm)$^{-1}$	$<10^{-6}$	1.58×10^{-5}	0.69	0.435	5.25×10^{-4}	0.46	0.81	0.095
σ (ohm cm)$^{-1}$			0.095	0.61		0.102	0.11	0.132
K	16.0	17.1	27.2	79.5	20.4	27.8	15.1	32.3
ΔK_b		1.1	35.0	<107	4.4	30.9	26.9	<25.8
α_b (10^{-17} cm^3)		0.680	2.58	<2.29	1.10	2.95	2.17	<4.86
		(0.695)	(4.45)	(<7.40)	(1.20)	(4.85)	(3.40)	(<7.50)
E_i (10^{-2} ev)		0.99	0.64	>0.66	0.84	0.61	0.68	>0.52
		(0.99)	(0.53)	(>0.45)	(0.82)	(0.52)	(0.58)	(>0.45)
τ (10^{-11} sec)			4.33	<1.8		3.24	4.3	<1.8
m_i/m			1100	<1300		1020	975	<1430

inner cross-sectional dimensions of the guide, and the sample is pressed into the wave guide with a foil of indium in between, in order to insure an intimate contact and to prevent at the same time excessive pressure on the sample when the guide was cooled. The peripheral surface of the sample was prepared in such a way as to minimize the contact resistance between the sample and the indium: rhodium plating was made on *p*-type samples and a thin layer of solder was applied to *n*-type samples. The contact resistance was less than 1 ohm.

The dielectric constant and conductivity were deduced from the observed attenuation and phase shift. Assuming that there is no contact resistance between the sample and the wave guide, the wave in the sample and the transmitted wave are of the same mode as the incident wave. The calculation is then straightforward. Under the assumption, there is no tangential component of electric field at the contact surface. In the presence of a contact resistance, the electric field may have a tangential component at the sample surface, even though there is no field in the wall of the wave guide. The values deduced for the conductivity and dielectric constant will be then in error. We shall estimate an upper limit for the effect by assuming a thin insulating layer at the contact.

Let t be the thickness of the layer and let the x axis be along the length of the guide. We have at the sample surface

$$\mathcal{E}_x+t(\partial\mathcal{E}_{yt}/\partial x)=(i\omega/c)H_{zt}t, \tag{8}$$

$$\mathcal{E}_{yt}=\mathcal{E}_y+4\pi q, \tag{9}$$

where $\mathcal{E}_{yt}$ and H_{zt} are the fields in the insulating layer. The surface charge density, q, on the sample is related to the current density, $\mathbf{j}$, by

$$-\partial q/\partial t=\mathrm{div}\mathbf{j}, \tag{10}$$

or

$$-i\omega q=-(\sigma+i\omega\alpha)\mathcal{E}_y+i\omega\alpha_t\mathcal{E}_{yt}.$$

Thus

$$\mathcal{E}_{yt}(1+4\pi\alpha_t)=\mathcal{E}_y(1+4\pi\alpha+4\pi\sigma/i\omega). \tag{11}$$

Substituting (11) into (8), we get

$$\mathcal{E}_x+t[(K+4\pi\sigma/i\omega)/K_t](\partial\mathcal{E}_y/\partial x)=t(i\omega/c)H_{zt}. \tag{12}$$

The samples used in the experiments had sufficient thicknesses to give a large attenuation and we may assume for the present purpose that we have a traveling wave in the sample, giving

$$\partial\mathcal{E}_y/\partial x=\gamma\mathcal{E}_y=(i\omega/c)H_z, \tag{13}$$

where γ is the wave propagation constant of the sample. With $H_{zt}\sim H_z$, we get

$$\mathcal{E}_x=\mathcal{E}_y t\gamma[(K_t-K)-4\pi\sigma/i\omega]/K_t. \tag{14}$$

Thus, the tangential field, $\mathcal{E}_x$, is small compared to the normal field, $\mathcal{E}_y$, so long as

$$t\ll|\gamma[(K_t-K)-4\pi\sigma/i\omega]/K_t|^{-1}. \tag{15}$$

Assuming that the contact resistance originates in a surface potential barrier in the sample, the thickness, t, can be estimated and is of the order of 10^{-4} cm for the samples used. The right-hand side of (15) is more than an order of magnitude larger in all cases, so that the error due to the contact resistance should be small.

IV. RESULTS AND DISCUSSION

The results of the experiments are summarized in Table I. All samples used were single crystals. The *p*-type samples were doped with Ga and the *n*-type samples were doped with Sb. The carrier concentrations, n_{ex}, in the exhaustion range were determined from Hall coefficients measured in the temperature range 77°K to 300°K. The concentration, N_{maj}, of majority impurity were determined from n_{ex} and the total concentration of donors and acceptors, the latter being estimated from the Hall mobility at 77°K. The accuracy of the N_{maj} values is probably no better than 20%. Samples *PN3E* and *PN4I* were from ingots doped with both Ga and Sb. Both showed a large difference between n_{ex} and N_{maj}, indicating a high degree of compensation between the donor and the acceptor impurities. With double doping, it is possible to obtain samples having high concentrations of majority impurity and few free carriers at low temperatures.

For all the samples, the conductivity at 4.2°K was at least 40 times smaller than that at room temperature. The Hall coefficient, on the other hand, had comparable values at the two temperatures. The behavior is in line

with the observations of Hung and Gliessman[8] and Fritzsche and Lark-Horovitz,[9] the low-temperature conductivity being determined by carriers in the impurity states. Sample *S2H* was from an undoped ingot having a room temperature resistivity of 31 ohm cm. The conductivity at 4.2°K was less than 10^{-6} (ohm cm)$^{-1}$. The dielectric constant measured for this sample can be taken as that of the pure crystal, giving

$$K_0=16.0\pm0.3.$$

At room temperature, measurements made on pure samples gave a dielectric constant of 16.2 ± 0.3; Benedict and Shockley[2] obtained a value of 16.0 ± 0.5, while Goldey and Brown[3] deduced a value of 16.4 ± 0.2 from measurements on n-type samples and a value of 16.6 ± 0.3 from p-type samples. Thus, the dielectric constant of pure germanium may be somewhat lower at 4.2°K than at room temperature but the difference is uncertain in view of the experimental error. All other samples, excluding Ga10*C*2, showed higher dielectric constant than the pure sample, clearly indicating the effect of ΔK_b due to the polarization of neutral impurity atoms. In the case of sample Ga10*C*2, the negative contribution, ΔK_c, associated with the conduction in impurity states, apparently more than compensated for ΔK_b.

Samples Sb14*b* and Ga10*C*1 had very low dc conductivities and it was not possible to determine the microwave conductivity reliably. According to (7), ΔK_c should be negligible and the difference between K_0 and the measured K gives ΔK_b. The values of α_b and E_i were calculated by using (5) and (3). The value of E_i for the n-type sample is in good agreement with the known ionization energy, 0.0094 ev, of Sb in germanium. The value obtained for the p-type sample is somewhat lower than the accepted value of ionization energy, 0.0108 ev, for Ga.

Theory indicates that the wave function of donor states is pancake-like because of the large anisotropy of the effective mass in the conduction band. In the plane of large extension, the ground-state wave function varies as $\exp(r/r_D)$, where $r_D\sim60$ A according to Kittel and Mitchell[10] and $r_D\sim(4/3\pi)(K_0\hbar^2/m_te^2)=44$ A according to Kohn and Luttinger.[11] Thus considerable overlapping of states of neighboring atoms may be expected for impurity concentrations of the order of 10^{17} to 10^{18} cm^{-3}. For acceptor states, Kohn and Schechter[12] showed that the ground-state wave function has terms decaying as $\exp(r/43.3\times10^{-8})$ and $\exp(r/33.8\times10^{-8})$. Thus, overlapping may be expected at similar impurity concentrations as in the case of donors. Overlapping of excited states, which also affects the polarizability, should take place at much smaller concentrations. The low value of E_i given by sample Ga10*C*1 may be, therefore, the consequence of too high a concentration of impurities. In fact, the conductivity of this sample was much higher than that of sample Sb14*b*, which indicates more overlapping of the impurity states. On the other hand, part of the discrepancy may be the error involved in using Eq. (3) based on the simple hydrogenic model.

The remaining samples showed fairly high conductivity. It is necessary to take into account the quantity ΔK_c associated with the conduction. For samples Sb11*A*, Ga10*C*4, and Ga10*C*2, the conductivity at the microwave frequency is many times smaller than the dc conductivity. Using the conductivity ratio σ_0/σ, the values of ΔK_c were calculated according to (7) and the values of ΔK_b were then obtained:

$$\Delta K_b=K-K_0+|\Delta K_c|.$$

Equation (5), which can be used for calculating α_b, contains the local-field correction. However, it is only certain that the correction should be applied in the case of electrons tightly bound to atoms and is not needed for perfectly free electrons. With conductivities as high as in these samples, it is questionable that the correction should be applied. Values calculated both with and without the correction are given in the table; the values without the correction are given in brackets. In samples *PN*3*E* and *PN*41, the microwave and dc conductivities were about the same; in fact the high frequency value is somewhat higher, due probably to experimental inaccuracy or some inhomogeneity of the samples. Equation (7) cannot be used to determine ΔK_c; however, it gives $4\pi\sigma/\omega$ as an upper limit for $|\Delta K_c|$, since $\sigma\sim\sigma_0$ indicates that $\omega\tau\ll1$. The increase of α_b, as compared to that of the purer samples Sb14*b* and Ga10*C*1, shows the effect of the overlapping of impurity states. The values of E_i, calculated by using (3), can only be regarded as a crude measure for the ionization energy of the impurity band.

The values of relaxation time τ for the samples Sb11*A*, Ga10*C*4, and Ga10*C*2 were estimated by using (6). The values are seen to be of the same order of magnitude as that observed for free carriers in cyclotron resonance experiments. An effective mass can be obtained from τ and the dc conductivity:

$$m_i=n_{ex}e^2\tau/\sigma_0,$$

which characterizes the conduction in the impurity band. The carrier concentration is taken to be equal to the concentration of free carriers in the exhaustion range. For these samples with about 10^{17} majority impurity atoms per cm^3, m_i turned out to be around $1000m$. The large effective mass is responsible for the small mobility as indicated by the product of Hall coefficient and conductivity. It is to be expected that m_i should decrease with increasing impurity concentration. Samples *PN*4*I* and *PN*3*E* had much higher impurity concentrations. However, for these samples, we can infer only that $\tau<1/\omega$; hence only an upper limit can be obtained for m_i.

[8] C. S. Hung and G. R. Gliessman, Phys. Rev. **96**, 1226 (1954).
[9] H. Fritzsche and K. Lark-Horovitz, Physica **20**, 834 (1954).
[10] C. Kittel and A. H. Mitchell, Phys. Rev. **96**, 1488 (1954).
[11] W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955).
[12] W. Kohn and D. Schechter, Phys. Rev. **99**, 1903 (1955).