OPTICAL AND MAGNETO-OPTICAL ABSORPTION EFFECTS OF GROUP III IMPURITIES IN GERMANIUM*

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(Received May 6, 1959)

The ionization and excitation spectra of Group III impurities in germanium have been measured[1] on single crystals of germanium, held at ~ 5°K, by the use of a far infrared grating spectrometer. Figure 1 shows such a spectrum for boron-doped germanium; this is typical of the Group III impurities. The absorption lines correspond to transitions of bound holes from the ground state of the impurity atom to the various excited states. The energy separations between the absorption lines give a measure of the energy spacings of the excited states. In view of the large dielectric constant of germanium and the small effective masses of its holes, the level scheme of the excited states should be relatively independent of the particular Group III impurity involved.

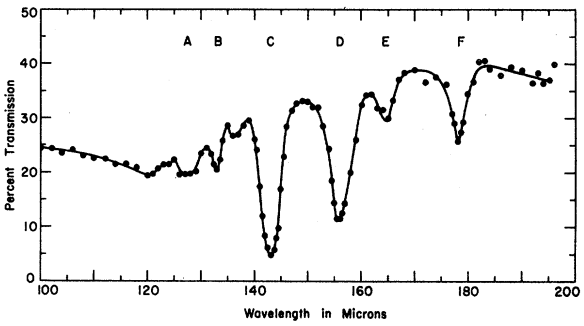

FIG. 1. Transmission spectrum of boron-doped germanium at ~ 5°K. Room temperature resistivity =14 ohm cm. Sample thickness =3.5 mm.

Table I gives the spacings between the various lines and the line D for the four impurities studied. The spacings between the excited states calculated by Schechter[2] are also listed. In comparing the theoretical and experimental values, the strong lines C and D are assigned to the $1s\rightarrow 2p^3$ and $1s\rightarrow 2p^2$ transitions, respectively. The agreement is fair, particularly when one considers the complexity of the theoretical problem. The optical ionization energies are obtained by adding the calculated binding energy of the $2p^3$ state to the energy of line C. These values are in good agreement with the thermal activation energies.

The Zeeman effect on the excitation lines of donor impurities in germanium has been reported previously[3] and satisfactorily explained. This effect has now been studied for an acceptor impurity in germanium. Figure 2 shows the Zeeman pattern of the strong C and D lines of boron impurity for $H \parallel \langle 111 \rangle$. Measurements at different

Table I. Energy level spacings and ionization energies for Group III impurities in germanium, in units of 10^{-3} ev.

Theoretical[a]			Experimental[b]			
			B	Tl	Ga	In
$2p^4-2p^2$	1.8	A-D	1.76	1.83	1.82	1.72
		B-D[c]	1.36	1.41	1.41	1.37
$2p^3-2p^2$	0.5	C-D[c]	0.71	0.73	0.72	0.73
		D-E	0.43	0.41	0.53	...
$2p^1-2p^2$	1.4	D-F	1.00	1.10	1.19	1.12
		D-G	...	1.69	1.64	1.85
Ionization energies		Optical	10.3	13.0	10.8	11.4
		Thermal	10.4[d]	14[e]	10.8[d]	11.2[d]

[a]See reference 2.
[b]Experimental error is ±0.08 unit for the spacings.
[c]Experimental error is ±0.04 unit.
[d]T. H. Geballe and F. J. Morin, Phys. Rev. 95, 1085 (1954).
[e]M. L. Schultz and G. A. Morton, Proc. Inst. Radio Engrs. 43, 1819 (1955).

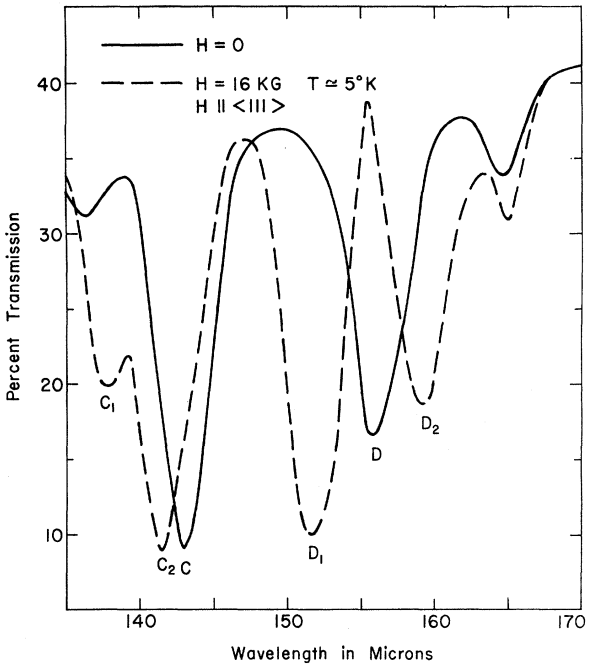

FIG. 2. Effect of a magnetic field on the two strong excitation lines of boron in germanium.

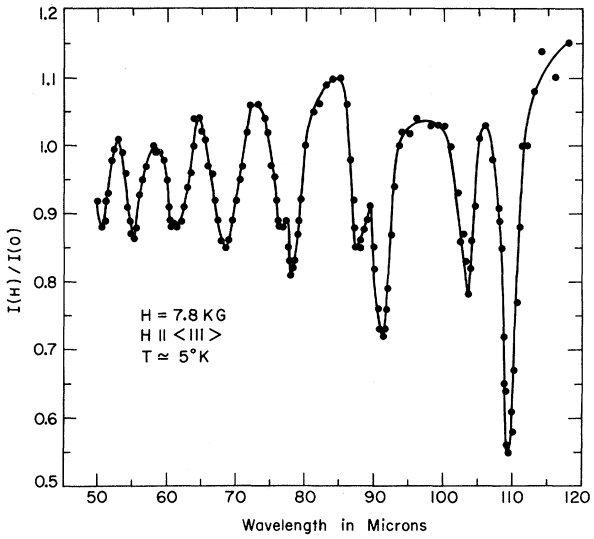

FIG. 3. Effect of a magnetic field on the ionization absorption of boron in germanium. The ordinate is the ratio of transmitted intensity through the sample with and without field.

field strengths show that the splitting of the D line is linear with field (2.5×10^{-8} ev/oersted) with no observable shift in its mean position. The C line appears to be split into two lines, the splitting, however, being only about half that seen for the D line. The C line exhibits a shift of its mean position to higher energies; this shift appears to be a quadratic function of field.

Schechter's analysis shows that the $2p^2$ and $2p^3$ states are fourfold and twofold degenerate, respectively. Thus we may expect a difference between the Zeeman patterns of the C and D lines. According to Wallis and Bowlden,[4] Kohn has shown that the degeneracy of the ground state is lifted in the presence of a magnetic field. However, for the fields used here the expected splitting would be unresolvably small. Even so, it is difficult to understand why the pattern of the D line does not show more multiplicity. A measurement made with $H \parallel \langle 100\rangle$ gave substantially the same result.

Luttinger's[5] theory for the effect of a magnetic field on the degenerate valence band of germanium predicts two pairs of ladders of energy levels. Roughly, each pair is associated with one of the degenerate bands. Thus the ionization absorption spectrum of a Group III impurity in germanium should show structure under an external magnetic field. Figure 3 shows this effect for boron-doped germanium. The pattern appears to consist of two series of peaks, one series being weaker than the other. Only three of the weak peaks are resolved. Better resolution has been obtained at higher fields. The absorption peaks may be identified with transitions from the impurity ground state to the two light-hole ladders.

The difference between the energy of the first peak in each series and the ionization energy for $H=0$ (see Table I) is 11.0 and 18.3, in units of $(e\hbar/mc)H$. Comparing these values with the theoretically estimated levels[6] in the two light-hole ladders, one can identify the first peak in each series with the level for which $n=1$, where n is the quantum number defining the levels in a ladder and takes the values 0, 1, 2, 3, ... etc. The observed energy spacings between the successive peaks is approximately uniform, 24.8 units in the first series and 23.4 units in the second series. The theoretically estimated spacing is ~23 units for both ladders, provided $n>2$, which is in fairly good agreement with either of the two experimental values. However, within the ladder which has been associated with the first series of peaks the estimated spacing between the levels for $n=1$ and $n=2$ is ~19 units. This value is appreciably smaller than the spacing between the first two peaks in the first series.

*Work supported by the Office of Naval Research.

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Ser. II, 4, 145 (1959).

[2]Reported by W. Kohn, in Solid-State Physics, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1957), Vol. 5. p. 257.

[3]H. Y. Fan and P. Fisher, J. Phys. Chem. Solids 8, 270 (1959); W. S. Boyle, J. Phys. Chem. Solids 8, 321 (1959).

[4]R. F. Wallis and H. J. Bowlden, J. Phys. Chem. Solids 8, 318 (1959).

[5]J. M. Luttinger, Phys. Rev. 102, 1030 (1956).

[6]Values of the constants used for this calculation are $\gamma_1 = 13.2$, $\gamma_2 = 4.4$, $\gamma_3 = 5.4$, and $\kappa = 4.0$; this last value is estimated from Kohn's value for K (see reference 5). The calculation is made for $H \parallel \langle 111 \rangle$.

RANGE OF ORDER OF SUPERCONDUCTING ELECTRONS*

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(Received April 30, 1959)

In the following it is proved that just as superconducting electrons can drift into an adjoining normal conducting layer and make it superconducting, normal electrons can drift into an adjoining superconducting layer and prevent superconductivity.

It has been found earlier that an interposed normal conducting barrier does not necessarily prevent the superconductivity of a contact between two superconducting wires.[1] This has been explained by the assumption that the density of the superconducting electrons in the normal conducting barrier decreases relatively slowly with distance from the superconductor. Observations of the barrier thickness at which superconductivity disappears therefore provide an estimate of the "range of order" of the superconducting electrons. The following thicknesses in 10^{-6} cm have been observed for the metals listed:

Group	I*B*	VI*A*	VIII		
Metal	Cu: 30	Cr: 4	Fe: 0.7	Co: 2	Ni: 1.0
	Ag: 40	...	...	...	...
	Au: 35	...	...	...	Pt: 7.5.

The lower values of the thicknesses observed for the ferromagnetic barriers may be caused by quenching of superconductivity in the neighborhood of the contact due to the high magnetic fields emerging from the barrier layers.

The experiments have been extended to measurements of the contact resistance (transverse resistance) and the resistance along the wire (longitudinal resistance) of normal conducting wires plated with tin. While it is known[2] that films of tin evaporated onto glass are superconducting at thicknesses as low as 1.6×10^{-6} cm, it has been observed that films of tin electroplated onto gold wire do not become superconducting if their thickness is less than 60×10^{-6} cm. Similar measurements of tin plated onto copper wire showed that these do not become superconducting below 20 $\times 10^{-6}$ cm.

These observations confirm early measurements by Burton, Wilhelm, and Misener[3] on tin, and by Misener and Wilhelm[4] on lead. These and subsequent measurements by Misener[5] were usually believed to be unreliable (see the remark by Feigin and Shal'nikov[6] and by Shoenberg[7]), because they disagreed with the measurements of superconducting films evaporated onto glass or quartz surfaces. Since in the present experiments the time between plating and measurement in liquid helium was less than 2 hours, it is unlikely that the results are falsified by alloying or diffusion. It is much more likely that just as the superconducting electrons "spill over" into the normal conducting barriers, also the normal conducting electrons of the base metal can prevent superconductivity of the film. This effect is to be expected in view of the recent treatment of "dirty" superconductors by Anderson.[8]

The measurements of the contact resistance represent in a way the "transverse" resistance of the film. Their results are very similar to those observed on contacts between normal-conducting and superconducting wires.[9] At lower temperatures the resistance disappears partially, but is, at least for the thinner films, still measurable even at 5 μa and 1.48°K. A decrease in transverse resistance is observed already for films thin enough that the longitudinal resistance is almost independent of current and temperature.

It is planned to repeat the experiments by simultaneous evaporation of tin onto glass and metal