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ABSORPTION SPECTRA AND ZEEMAN EFFECT OF COPPER AND ZINC IMPURITIES IN GERMANIUM*

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The absorption spectra of group V and group III impurities in germanium have been reported previously.[1,2] For these impurities of small ionization energy, theoretical treatment based on the effective-mass formalism should be a good approximation, and the experimental results, especially in the case of donors, bear this out. Experimental investigation has been now extended to two acceptor impurities, Cu and Zn, of higher ionization energies. The ionization absorption of Cu and Zn in germanium has been seen before[3,4] but no observation of the excitation lines has been reported. Each of these impurities can bind more than one hole. Studies have been made on the neutral and the singly charged states. It may be expected that the effective-mass formalism would not apply for the ground state but may still be valid for the excited states. The absorption spectra provide the means to check this assumption and to reveal effects due to differences in the ground states.

Measurements were made at liquid helium temperature. For the observation of the Cu^- and Zn^- absorptions, samples suitably compensated by Sb impurity were used. The solid curve in Fig. 1 shows the absorption spectrum of Cu. The observed lines are labeled according to the designation used for the spectra of group III impurities.[2] As seen in Table I, the energy spacings between the *D* line and the various other lines are very close to the corresponding spacings in the group III spectra. This applies also to the spectrum observed for Zn, the data for which are included in Table I. In the case of Zn, addi-

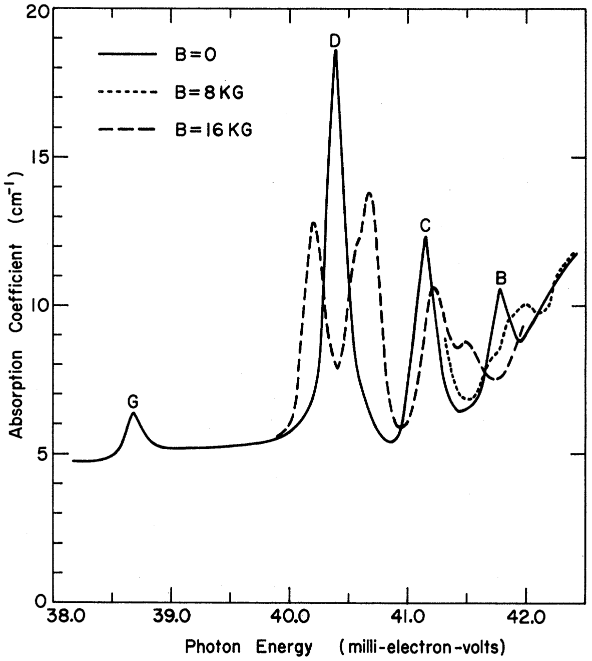

FIG. 1. Absorption spectrum and transverse Zeeman effect of Cu impurity in germanium. Copper concentration is 1.2×10^{16} cm^{-3}. Magnetic field is parallel to [111] in the (110) plane.

Table I. Ionization values and energy spacings between the excitation lines for various impurities in germanium, in units of 10^{-3} ev.

	Group III (average values)	Cu	Zn	Zn^-
B-D	1.388	1.398 ± 0.020	1.382 ± 0.051	···
C-D	0.722	0.745 ± 0.016	0.729 ± 0.033	3.33 ± 0.06
D-G	1.73	1.72 ± 0.03	1.84 ± 0.03	···
Ionization energies	Optical	42.8	32.6	85.8
	Thermal	40	30	90

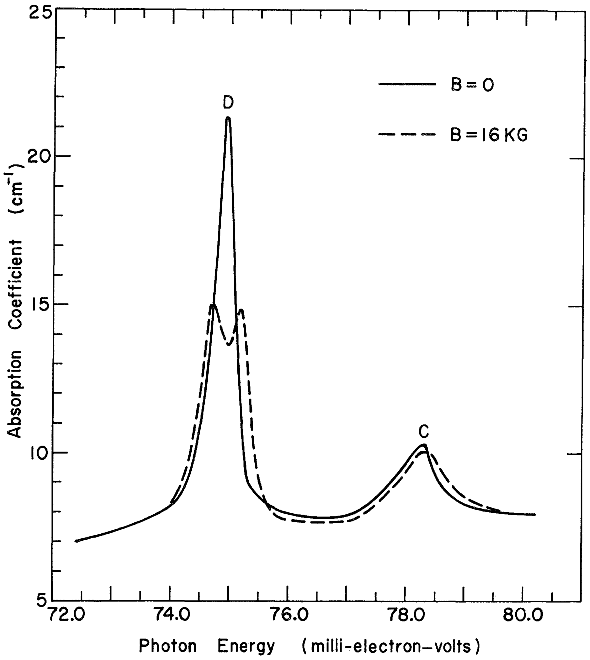

FIG. 2. Absorption spectrum and transverse Zeeman effect of Zn^- impurity in germanium. The sample is compensated with estimated 3.8×10^{15} cm^{-3} Zn and 2.2×10^{15} cm^{-3} Sb. Magnetic field is parallel to [111] in the (110) plane.

tional structure was observed on the long-wavelength side of the *G* line, the explanation for which is not yet clear. The solid curve in Fig. 2 shows the spectrum for Zn^-. Only two lines were observed which were identified with the two prominent lines *C* and *D* of the other spectra. The spacing between these two lines, as given in Table I, is about 4.6 times the corresponding spacing of the other acceptors studied. Strictly on the basis of effective-mass formalism, Zn^-, having a doubly charged center, is expected to have spacings between the excited states which are 4 times larger than those for a singly charged center. However, the excited states concerned in the cases of the *C* and *D* lines of Zn^- have binding energies already comparable to the binding energies of the ground states of group III impurities. A somewhat larger spacing between the *C* and *D* lines of Zn^- is not unexpected. In the case of Cu^-, we have not yet seen the excitation lines. However, indications of the ionization absorption have been observed.

In the case of group III impurities, we have estimated the ionization energy by adding to the energy of the *A* line (ground state to $2p^4$ transition) the theoretically calculated binding energy of the $2p^4$ state, 0.0006 ev.[5] This procedure minimizes possible error in the theoretical estimate as the $2p^4$ state is the highest excited state calculated. The *A* line has not yet been observed for Cu and Zn. The ionization energies for these impurities may be estimated by adding to the energy of the *D* line the binding energy of the $2p^2$ state which was obtained from the spectra of the group III impurities. Since the *C*-*D* spacing is 4.6 times larger for Zn^-, we may estimate the ionization energy by adding to the *D* line a proportionately larger binding energy. The value obtained is close to the reported thermal ionization energy, but must be regarded as only an approximate estimate.

The effect of the magnetic field on the excitation lines has been investigated. The observations confirm the assignment of the lines. The dashed curves in Figs. 1 and 2 show the results obtained at a field of 16 kgauss. The *D* line splits into two components in all cases, Cu, Zn, and Zn^-. The splitting is proportional to the magnetic field and is comparable to that observed for the *D* line of boron impurity. For Cu, Zn, and B, the high-energy component appears to be broader, and there is indication that this component may further split. Studies with higher fields and polarized light are in preparation. Such measurements reported recently for aluminum in silicon[6] show rather complex Zeeman effects. The situation in silicon is complicated by the fact that the separation of the third valence band by the spin-orbit interaction is very small.

The *C* line in the Cu and Zn spectra broadens and shifts to higher energy. It resolves into two peaks at higher magnetic fields. The separation of each peak from the zero-field position of the line appears to increase quadratically with the field. The effect appears to be identical with that of the *C* line of boron. The Zeeman effect of the *C* and *D* lines reinforces the conclusion that the excited states of Cu and Zn are similar to those of the group III impurities, and indicates that the observed effect comes mainly from the excited states. In the case of Zn^-, the shift of the *C* line is much smaller as can be seen by comparing Figs. 1 and 2. This is as expected. With a doubly charged center, the dimensions of the wave functions of Zn^- should be about one-half of that for singly charged centers. The quadratic Zeeman effect being a measure of the area of the wave functions, it might be expected to be about four times smaller for Zn^-. This is consistent with the observation.

It is interesting to note that the absorption lines of impurities are very much sharper in germanium than in silicon. The full width at half absorption is about 0.19×10^{-3} ev for the observed lines of Cu and the group III impurities. The actual width is probably even smaller, since the observed width is comparable to the resolution used. This is to be compared with the width of 1×10^{-3} ev reported for boron lines in silicon.[7] The broadening of the absorption lines has been treated[7,8] theoretically on the basis of the scattering of the bound hole by the acoustical vibration of the lattice. According to these treatments which used the hydrogenic approximation for the impurity, the width is determined mainly by the broadening of the ground state, and for germanium and silicon the ratio of the widths is expected to be of the order of the reciprocal of the Bohr radius squared. On this basis, we would expect the lines of the group III impurities to be 6 to 7 times narrower in germanium than in silicon. The observation shows that the ratio of the linewidths in these two materials is at least as large as this estimate. The lines of Zn^- are considerably broader, about 0.43×10^{-3} ev in width for the *D* line. The width is considerably larger than the instrumental resolution. This result further substantiates the expectation that the broadening of the ground state increases with decreasing orbit dimension. In this connection, the failure to observe the excitation lines of Cu^- might be caused by large broadening. The orbit of the hole in the ground state may be quite small for Cu as indicated by the large ionization energy of 0.33 ev.

One additional point of interest is the difference in the relative strengths of the various lines for different impurities. This is particularly pronounced in comparing the spectrum of Zn with that of the group III impurities. The *C* line is much weaker than the *D* line in the case of Zn^-. Noticeable variations can be seen even among Cu, Zn, and the group III impurities, which should reflect mainly the difference in the ground states. Accurate data have yet to be obtained.

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HYPERFINE STRUCTURE OF THE *F* CENTER IN LiF*

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The *F* center in LiF is one of the color centers in alkali halides which has been most throughly studied experimentally by magnetic resonance[1-8] and theoretically.[9] To date there is serious disagreement between experiment and theory. Lord[2] originally reported resolved structure of the electron spin resonance, which he interpeted as arising from the hyperfine coupling of the electron to the six Li^7 atoms nearest to the vacancy. Although he failed to see all of the 19 lines predicted by this model, he later supported his contention[3] with the direct measurement of the hyperfine constants by the electron-nuclear double resonance technique (ENDOR).[10] Stimulated by this work, Gourary and Adrian[9] calculated the hyperfine coupling with the nearby nuclei. While the agreement with the nearest lithium atoms was satisfactory, the prediction for the nearest fluorine atoms was too large by a factor of 30. The picture was further complicated when Kim, Kaplan, and Bray[4] reported that they could resolve at least 10 more lines than the 19 predicted. Hyde[8]