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 $(1s)^4$ CONFIGURATIONS

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POSITIVELY CHARGED ACCEPTORS WITH $(1s)^3$ AND $(1s)^4$ CONFIGURATIONS

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We show that multiple acceptors in Ge can readily bind an extra hole. Experimental values for the binding energies of the extra hole for the multiple acceptors Be, Mg, Mn, Zn, Hg, and Cu in Ge are compared to model calculations. One such center (Zn^+) has been used for the first time as a long-wavelength ($\lambda < 500 \mu m$) photoconductor at $T=1.2 K$. Using the Zn^+ photoconductor in high-resolution spectroscopy, we have discovered that the linear absorption coefficients for shallow acceptor and donor transitions are substantially larger than previously reported, making possible absorption spectroscopy of lightly doped ($<10^{12} cm^{-3}$) samples.

The well-known negatively charged shallow donor D^- in semiconductors is the solid state analog of a negatively charged hydrogen ion H^- . The experimental [1-3] and theoretical [4] understanding of these "overcharged" donors is excellent. A^+ centers have also been experimentally found [1], though the data for A^+ are substantially less abundant than for D^- . From our recent studies of overcharged acceptors, it is not evident why such an imbalance in experimental data has existed. It appears that every shallow acceptor which we have studied in both germanium and silicon readily forms A^+ states [5].

Experiments with overcharged multiple acceptors have recently been reported [6,7]. Because of the fourfold degeneracy of the top of the valence bands in Ge and Si, it is possible to describe up to four holes with the same spatial wavefunction. The direct atomic analogs cannot exist because of the Pauli exclusion principle. Nevertheless we can postulate, for the purpose of binding energy calculations, pseudo atoms which can bind up to four spin 3/2 electrons in the ground state.

Evidence for the existence of positively charged zinc double acceptors in germanium is shown in Fig. 1. The same zinc doped germanium single crystal sample cooled to $T=1.2 K$ was used to record spectra A and B. A detailed description of the experimental setup has been published [6]. The rise in photoconductivity at $\sim 20 cm^{-1}$ is due to the photoionization of Zn^+ centers. Residual shallow acceptors boron and aluminum lead to continua rising sharply at $\sim 80 cm^{-1}$. The difference in amplitude of the Zn^+ response in spectra A and B is due to the difference in the free hole generation rates. In spectrum A a cold black polyethylene filter lets a small part of the 300 K blackbody radiation pass and impinge on the sample. Spectrum B was recorded using a room temperature black polyethylene filter which is a much stronger optical pumping source than the cold filter. The continuous blackbody radiation ionizes both the major dopant zinc ($E_{Zn}=E_V+32.98 meV$ [8])

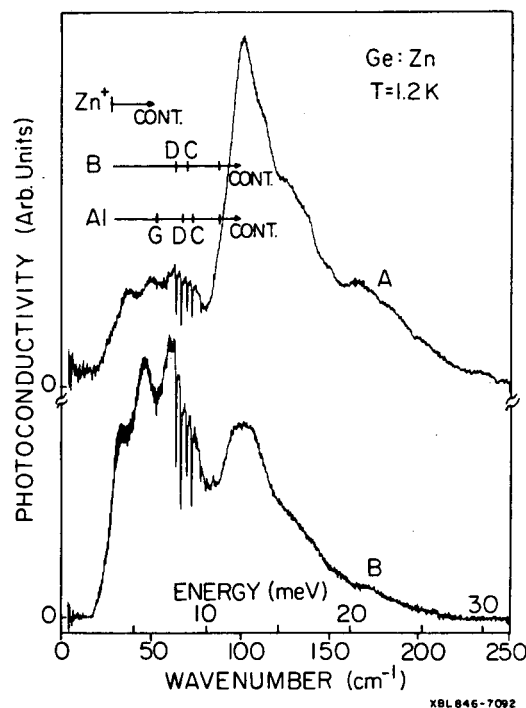


Fig. 1 - Far infrared photoconductivity spectra of a Ge:Zn crystal recorded at $T=1.2 K$. Trace A is obtained with a cold (1.2 K) and trace B with a warm (300 K) black polyethylene filter. The spectra have not been normalized with the instrument response.

and neutral residual shallow acceptors A1 and B. Variable temperature Hall effect measurements show that the total shallow acceptor concentration is larger than the residual donor concentration ($N_A > N_D$). This means that $N_A - N_D$ shallow acceptors will be neutral (i.e., bind a hole) at sufficiently low temperature and in the absence of any photon flux. A number of experiments using crystals doped with the double acceptor beryllium instead of zinc, together with various cold and warm filters, show conclusively that one can detect the A^+ continuum always and only at sufficiently low temperatures when free holes are generated from either the deep acceptors and/or from neutral shallow acceptors. Experiments using uniaxial stress further show that when the fourfold degenerate valence band top is sufficiently split, the A^+ response vanishes because the Pauli principle then permits only two holes in the (1s) state [6].

The following table summarizes all of our experimental data on positively charged double acceptors and the triple acceptor copper in germanium. The experimental results are compared with calculations [9] using pseudo He or Li atoms with all of the electrons in the (1s) state. An effective Rydberg (Ry^*) is obtained by using the experimentally determined energy for the transition from the neutral to the singly ionized state ($A^0 \rightarrow A^-$) and setting it equal to the calculated value of 1.77 Ry for the double acceptor and 2.72 Ry for copper. These variational calculations give only upper bounds for the ground state energies in each configuration. The general agreement is surprisingly good. It is expected that more accurate results can be obtained with Monte Carlo methods [10]. However, one has to keep in mind that the pseudo atom model cannot account for chemical effects without modification of the potential. The acceptors Be, Mg, Mn, Zn, Hg and Cu have deep level character and exhibit a wide range of binding energies reflecting rather strong chemical shifts.

Table (all energies are in meV)

| Acceptor | $E(A^+ \rightarrow A^0)$ | | $E(A^0 \rightarrow A^-)$ Experiment [8] | $E(A^- \rightarrow A^{--})$ | |
|----------|--------------------------|--------|--|-----------------------------|--------|
| | Experiment | Theory | | Experiment | Theory |
| Be | 5.1 | 3.1 | 24.81 | 58.02 | 56.07 |
| Zn | 4.1 | 4.1 | 32.98 | 86.51 | 74.53 |
| Mg | 2.9 | 4.5 | 35.85 | — | 81.02 |
| Mn | 3.2 | 6.9 | 55 | ~100 | 124.3 |
| Hg | 12.2 | 10.2 | 91.88 | ~230 | 183.8 |
| Cu | 2.0 | 10.4 | 43.21 | 330 | 87.6 |

Let us now focus our attention on the sharp negative-going peaks in the Zn^+ continuum in Fig. 1. The energies at which these peaks occur correspond accurately to transitions of the holes from the ground state to bound excited state of A1 and B acceptors (transitions D and C [11]). The concentration of B and A1 residual acceptors in these samples has been accurately determined by variable temperature Hall effect, and is of the order of a few 10^{12} cm^{-3} . The strength of the negative-going lines was found to vary with the concentration of B and A1 in the sample, indicating that they are indeed internal absorption peaks. An unexpected feature of these internal absorption lines is their great strength. The observed lines exhibit values of α larger than 1 cm^{-1} when fully resolved at an instrumental resolution of 0.5 cm^{-1} . In order to determine if the internal absorption is enhanced by configuration interaction [12] or by some other unknown effect we performed a number of absorption experiments using pure crystals acting as absorbers in front of the Ge:Zn crystal which was used to record Fig. 1. The result of such an experiment is shown in Fig. 2. A 0.4 cm thick slice of a germanium crystal doped with antimony and arsenic ($[Sb]=1.6 \times 10^{12} \text{ cm}^{-3}$, $[As]=0.4 \times 10^{12} \text{ cm}^{-3}$) was inserted directly in front of the Ge:Zn crystal. The absorption lines of Sb and of As in the Zn^+ , B and A1 continua are clearly visible. The strength of the Sb and As lines approximately doubles when the thickness of the absorbing specimen is doubled.

This is expected for small values of αx , if a simple absorption law is obeyed:

$$I = I_0 \exp(-\alpha x)$$

For shallow acceptor concentrations of the order of 10^{11} to 10^{12} cm^{-3} linear absorption coefficients of the D and C lines of the order of ~ 0.01 to 0.1 cm^{-1} are extrapolated from published data [13]. In making this estimate we have taken the line width differences into account by linearly scaling α for a constant line area. It has been experimentally established that this is an appropriate procedure [14] for fully resolved lines. In order to clarify the large discrepancy between the old data and our present experiments we repeated our absorption experiment but with a more highly doped 1.2 mm thick n-type Ge crystal ($[\text{Sb}] = 3 \times 10^{14}$ cm^{-3}). This doping range is representative of the earlier experiments. Fig. 3 shows that the $2p_{\pm}$ line absorbs more than 99% of the light at 69 cm^{-1} , making an accurate determination of α very difficult. Several of the other lines show absorption in excess of 90%, confirming very large values of α . Computing the logarithm of the ratio between the spectrum shown in Fig. 3 and a spectrum obtained with an ultra-pure Ge slice of similar thickness leads to a plot of α as a function of the wave number (Fig. 4). Lines belonging to the p_0 and the p_{\pm} series originating from both groundstate components (A_1, T_2) are clearly visible. From our experimental results we must conclude that the previously reported values for α must, in general, have been substantially too small. A likely reason is insufficient instrumental resolution. It can be easily shown that lines which are not resolved have peak linear absorption

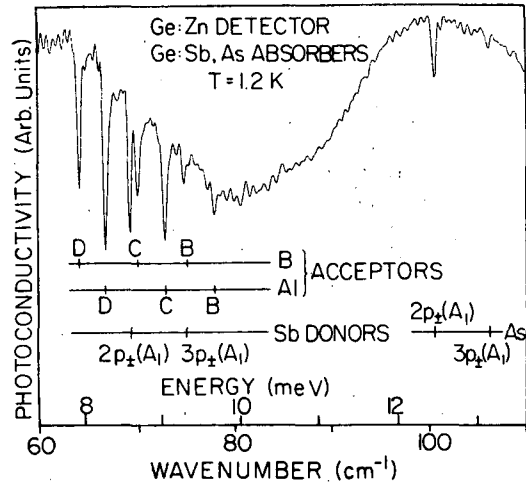


Fig. 2 - Part of a photoconductivity spectrum recorded as in Fig. 1B but with a 4 mm thick slice of Ge:Sb,As at $T=1.2$ K. The net donor concentration $= 2 \times 10^{12}$ cm^{-3} .

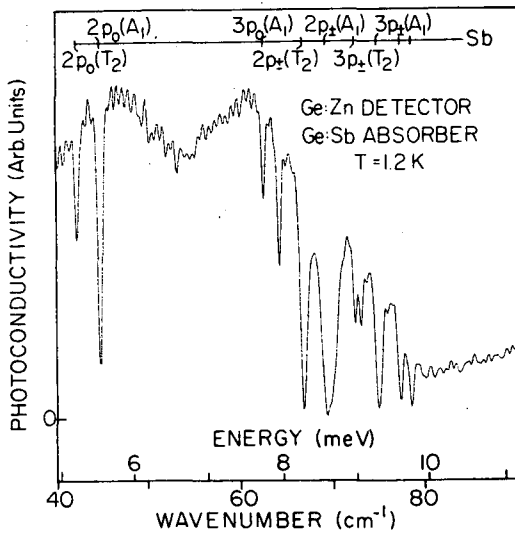


Fig. 3 - Part of a photoconductivity spectrum recorded as in Fig. 1B but with a 1.2 mm thick Ge:Sb slice acting as absorber at $T=1.2$ K. $[\text{Sb}] = 3 \times 10^{14}$ cm^{-3}

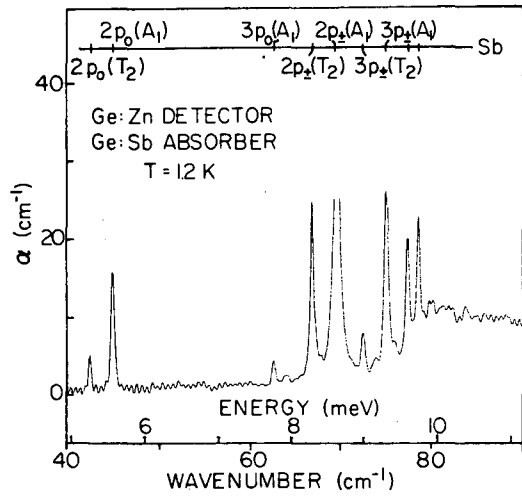


Fig. 4 - Linear absorption coefficient as a function of photon energy computed from the spectrum shown in Fig. 3 and a normalization spectrum obtained with an ultra-pure Ge absorber.

coefficients and areas which are both too small because α is the logarithm of a transmittance ratio. Line-broadening caused by physical phenomena within the absorber on the other hand does not appreciably change the line areas when the lines are fully resolved.

In summary, we have shown that double and triple acceptors readily form A^+ states. A theoretical model using pseudo atoms with $3/2$ spin electrons gives satisfactory values for the binding energy of the extra hole. We further show for the first time that these A^+ centers are good photoconductors up to wavelengths of $500 \mu\text{m}$, though an evaluation of responsivity and noise equivalent power is needed for quantitative specifications. The discovery that the absorption coefficients of lines of the hydrogenic spectrum of shallow acceptors and donors are approximately an order of magnitude larger than previously reported may be important for certain experiments. It shows that absorption spectroscopy with very pure crystals with negligible orbital overlap between the shallow centers is possible. This will permit the study of special centers which are only present at low concentrations without having to resort to photo-thermal ionization spectroscopy [11]. It will also allow absolute oscillator strength measurements of electric dipole transitions in the absence of impurity-impurity interactions.

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