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Abstract

A completely new phenomenon, a triply occupied double acceptor, has been observed in beryllium-doped germanium single crystals. It results in a very shallow center with a hole binding energy of ~ 5 meV. The new center, Be^+ , has been studied using photoconductive far infrared spectroscopy. The Be^+ photoconductive response can only be observed when free holes are continuously generated by ionization of either residual neutral shallow acceptors (boron or aluminum) or neutral beryllium double acceptors. The Be^+ center thermally ionizes above 4 K and it disappears at a uniaxial stress $\geq 10^9$ dyne cm^{-2} parallel to [100]. The latter observation is consistent with the lifting of the fourfold degeneracy of the top of the valence band under stress.

That single shallow donors can bind two electrons has been predicted as early as 1958¹ and has, subsequently, been established by a series of experiments²⁻⁴. These D^- centers have also been used for very far infrared photon detection⁵. Much less is known about shallow acceptors binding an extra hole. The reason for this imbalance is not readily evident. The only published experimental results deal with boron in silicon and gallium in germanium^{2,3}. Theoretical work on the behavior of D^- centers in silicon under uniaxial stress has been published recently⁶.

The model used to understand D^- and A^+ centers in semiconductors is based⁷ on the well understood, negatively charged hydrogen ion (H^-). A simple effective mass theory approach, which has been used successfully for the description of shallow levels in semiconductors⁸, yields satisfactory values for the binding energies of electrons and holes in D^- and A^+ centers respectively.

Neither theoretical nor experimental results on deep levels binding an extra electron or hole have been reported. We present in this paper the first experimental results on beryllium double acceptors in germanium binding three holes (Be^+). A simple variational calculation for the Be^+ analog, a pseudo He^- ion, clearly shows that the third hole is bound. In order to make the analogy between Be^+ and He^- useful, one has to remember that the groundstate orbital of acceptors can accommodate up to four holes because of the fourfold degeneracy at the top of the valence band. A helium atom or ion can only bind two electrons in its groundstate orbital. Resorting to electrons with a hypothetical spin 3/2, this difficulty can easily be overcome.

All of our experimental results were obtained with samples taken from large cylindrical crystals of beryllium-doped germanium. Several crystals were grown

from a melt contained in a graphite susceptor in vacuum ($\lesssim 10^{-5}$ Torr) using the Czochralski method. Doping was achieved by adding an appropriate amount of a highly doped, polycrystalline master alloy of Ge:Be to the melt. The crystal axis was in all cases parallel to the [113] orientation. The beryllium concentration N_{Be} varied between $2 \times 10^{14} \text{ cm}^{-3}$ and $2 \times 10^{15} \text{ cm}^{-3}$. Variable temperature Hall effect measurements established that the residual net shallow acceptor concentration N_A was between 10^{11} and 10^{13} cm^{-3} . The information on the shallow center concentrations is crucial for the interpretation of the infrared data in the latter part of the paper.

The samples used for low temperature, far infrared photoconductivity measurements were $7 \times 7 \times 3 \text{ mm}^3$ right-angle prisms, cut from the Ge:Be single crystals, lapped with alumina, and polish-etched in a 3:1 HNO_3 :HF mixture for two minutes. A thin layer of In-Ga eutectic rubbed onto two opposing $7 \times 3 \text{ mm}^2$ faces served as satisfactory contacts. A Far Infrared Fourier Transform Interferometer used at a resolution of 1 cm^{-1} provided IR photons in the 10 to 250 cm^{-1} range. A number of mylar beamsplitters and warm as well as cold filters were used to define and optimize the appropriate photon energy ranges.

Figure 1 shows a series of photoconductivity responses for sample temperatures between 4.2 and 1.2 K. The sharp onset of photoconductivity at $\sim 80 \text{ cm}^{-1}$ is caused by the ionization of shallow aluminum and boron acceptors. A set of cold filters blocks all the photons above 95 cm^{-1} which makes ionization of neutral beryllium double acceptors impossible. With decreasing temperature one observes a long wavelength response rising sharply at $\sim 40 \text{ cm}^{-1}$ and gaining in intensity. The presence of shallow neutral acceptors leads to clearly visible absorption lines⁹ at 66.7, 68.0, 72.8 and 74.1 cm^{-1} . There are no signs of excited state transitions close to the 40 cm^{-1} response, as are always observed for shallow acceptor or donor photoconductive responses.

We propose that the long wavelength response is due to photoionization of Be^+ centers. Supporting evidence comes from the following experimental observations: a) no Be^+ response was observed when the photon energy range was limited with a cold ($T \lesssim 4.2$ K) 50 cm^{-1} low pass filter; b) when the same filter was used at room temperature the Be^+ response reappeared. The explanation for this lies in the fact that the warm filter irradiates the Ge:Be sample with a broad band, continuous photon flux which can ionize shallow as well as deep acceptors, thereby creating free holes, some of which are captured by the abundant Be^0 centers. The cold filter on the other hand does not lead to ionization and free holes. In a further experiment a germanium sample was counterdoped with shallow lithium donors to the point where $N_A < N_D \ll N_{\text{Be}}$. This sample did not show the shallow acceptor nor the Be^+ response. Only when photons with an energy sufficient to ionize neutral Be acceptors were admitted did the Be^+ response reappear. This observation is consistent with the requirement that free holes must be present in order to create the Be^+ centers. An additional fact which supports our identification of the center as Be^+ is that it can always and only be created and observed in beryllium-doped germanium crystals.

Summarizing the experimental results, we have observed the long wavelength photoconductive response starting at 40 cm^{-1} in all beryllium-doped germanium samples at temperatures below $T = 4.2$ K when free holes were present. It is not important whether the free holes are created by ionization from shallow residual acceptors or from the deep beryllium centers. A pseudo He^- ion is the analog of the Be^+ center when hypothetical $3/2$ spin electrons are assumed.

An independent-identical-orbital variational calculation with a single, simple exponential function¹⁰ yields [in units of $(m^* e^4 / \epsilon \hbar)$, m^* = effective mass, ϵ = dielectric constant]:

$$E(\text{H}^0) = -0.500; E(\text{H}^-) = -0.473;$$

$$E(\text{He}^+) = -2.000; E(\text{He}^0) = -2.848; E(\text{He}^-) = -2.836.$$

It corresponds to both unbound H^- (which is well known to bind) and slightly unbound pseudo He^- .

A better calculation involving symmetrized products of two or three single exponential orbitals¹¹ yields:

$$E(H^0) = -0.500; E(H^-) = -0.514;$$

$$E(He^+) = -2.000; E(He^0) = -2.876; E(He^-) = -2.988.$$

It gives bound states for both H^- (binding energy 0.014; experimental value 0.028) and pseudo He^- (binding energy 0.112).

The experimental observables are the energy differences between subsequent ionization stages. If the He^+ to He^0 transition is equated with the experimentally⁹ established Be^- to Be^0 transition energy of 24.5 meV ($m^*e^4/\epsilon\hbar^2 = 28.0$ meV), we get estimates for both the Be^{--} to Be^- (variational calculation: 56.0 meV, experimental value: 58.02 meV) and the Be^0 to Be^+ (variational calculation: 3.3 meV, experimental value: 5.0 meV) transitions. Given the extreme simplicity of the variational calculation, we are satisfied with the agreement between theory and experiment.

An excellent test for the validity of our Be^+ (or He^-) model can be obtained with a uniaxial stress experiment. Stress in the [111] direction pushes the light hole band through the heavy hole band. The fourfold degeneracy at the top of the valence band is lifted and the groundstate orbitals of any acceptor can only accomodate two holes. The Be^+ response, therefore, must vanish under sufficiently high uniaxial stress. Figure 2 shows precisely this behavior in a sequence of spectra taken at increasing stress.

As a final remark we want to point out that preliminary results with copper-doped germanium show that Cu^+ centers (four holes bound to a triple acceptor) do exist. Furthermore, we are in the process of evaluating whether the Be^+ centers can be utilized as very long wavelength infrared detectors.

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References

- ¹M. A. Lampert, Phys. Rev. Lett. 1, 450 (1958).
- ²E. I. Gershenzon, G. N. Gol'tsman, and A. P. Mel'nikov, JETP Lett. 14, 185 (1971).
- ³M. Taniguchi, M. Hirano, and S. Narita, Phys. Rev. Lett. 35, 1095 (1975).
- ⁴E. A. Schiff, Phil. Mag. B 45, 69 (1982).
- ⁵P. Norton, J. Appl. Phys. 47, 308 (1976).
- ⁶D. M. Larsen, Phys. Rev. B 23, 5521 (1981).
- ⁷H. A. Bethe and E. E. Salpeter in Quantum Mechanics of One- and Two-Electron Atoms, (Springer, Berlin, 1957) pp. 154-7.
- ⁸A. Natori and H. Kamimura, J. Phys. Soc. Japan 43, 1274 (1977).
- ⁹See for example: A. K. Ramdas and S. Rodriguez, Rept. Progress in Phys. 44, 1297 (1981) or E. E. Haller, W. L. Hansen, and F. S. Goulding, Adv. Phys. 30, 93 (1981).
- ¹⁰L. I. Schiff, in Quantum Mechanics, second ed. (McGraw Hill, New York, 1955) pp. 174-6.
- ¹¹S. Chandrasekhar, Astrophys. J. 100, 176 (1944).

Figure Captions

Fig. 1. Photothermal conductivity as a function of the photon energy for a Ge:Be sample at four temperatures. The cutoff at $\sim 95 \text{ cm}^{-1}$ is due to a set of room temperature filters which irradiate the sample with black body radiation leading to ionization of shallow acceptors, i.e. free holes.

Fig. 2. Photothermal conductivity of a Ge:Be sample at $T = 3.5 \text{ K}$ under stress $||[111]$. The responses at $\sim 40 \text{ cm}^{-1}$ and $\sim 195 \text{ cm}^{-1}$ are due to Be^+ and Be^0 centers. At high stress the Be^+ response vanishes and the aluminum and boron continue to become visible.

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Fig. 1

Fig. 2

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