Three Holes Bound to a Double Acceptor: Be^+ in Germanium

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A double acceptor binding three holes has been observed for the first time with photoconductive far-infrared spectroscopy in beryllium-doped germanium single crystals. This new center, Be^+, has a hole binding energy of ~ 5 meV and is only present when free holes are generated by ionization of either neutral shallow acceptors or neutral Be double acceptors. The Be^+ center thermally ionizes above 4 K. It disappears at a uniaxial stress $\gtrsim 10^9$ dyn cm^{-2} parallel to [111] as a result of the lifting of the valence-band degeneracy.

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It has been predicted,[1] as early as 1958, that shallow donors can bind two electrons. The prediction was subsequently verified by a series of experiments.[2-4] These D^- centers have also been used for very-far-infrared photon detection.[5] 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 recently.[6]

The model used to understand D^- and A^+ centers in semiconductors is based[7] 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 semiconductors,[8] yields satisfactory values for the binding energies of electrons and holes in D^- and A^+ centers, respectively. The main difference between donors and acceptors is that the symmetric combination of the conduction-band minima is a twofold Γ_6 level, while the valence-band maximum, derived from p states, has fourfold Γ_8 symmetry.

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 ground-state orbital of acceptors can accomodate 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 ground-state orbital. Resorting to electrons with a hypothetical spin $\frac{3}{2}$, 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) with use of 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 2×10^{14} cm^{-3} and 2×10^{15} 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 $7\times 7\times 3$-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 2 min. A thin layer of In-Ga eutectic rubbed onto two opposing 7×3-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 beam splitters 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 ~ 80 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 tempera-

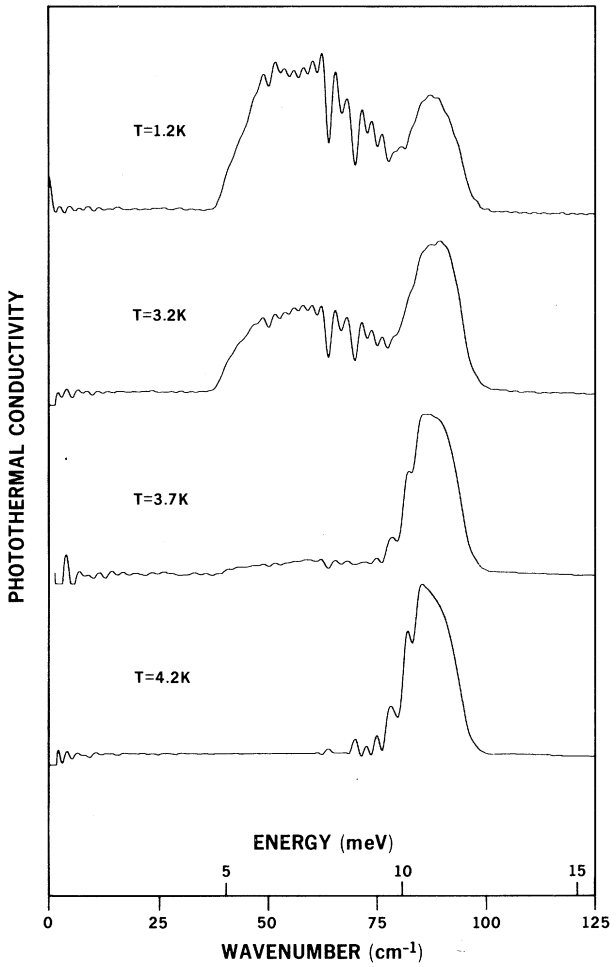

FIG. 1. Photothermal conductivity as a function of the photon energy for a Ge:Be sample at four temperatures. The cutoff at ~ 95 cm^{-1} is due to a set of room-temperature filters which irradiate the sample with blackbody radiation leading to ionization of shallow acceptors, i.e., free holes.

ture one observed a long-wavelength response rising sharply at ~ 40 cm^{-1} and gaining in intensity. The presence of shallow neutral acceptors leads to clearly visible absorption lines[9] 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. This seems to suggest that there are no optically accessible excited bound states in the system responsible for the 40-cm^{-1} structure.

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 broadband, 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 $N_A < N_D \ll N_{Be}$. 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.

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 ground-state orbitals of any acceptor can only accommodate 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.

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. The Be^+ center disappears at a uniaxial stress $\gtrsim 10^9$ dyn cm^{-2} parallel to [111] as a result of the lifting of the valence-band degeneracy.

An independent-identical-orbital variational calculation with a single, simple exponential function[10] yields (in units of $m^*e^4/\epsilon\hbar$, where m^* is the effective mass and ϵ is the dielectric constant)

$$E(H^0) = -0.500; \quad E(H^-) = -0.473;$$

$$E(He^+) = -2.000; \quad E(He^0) = -2.848;$$

$$E(He^-) = -2.836.$$

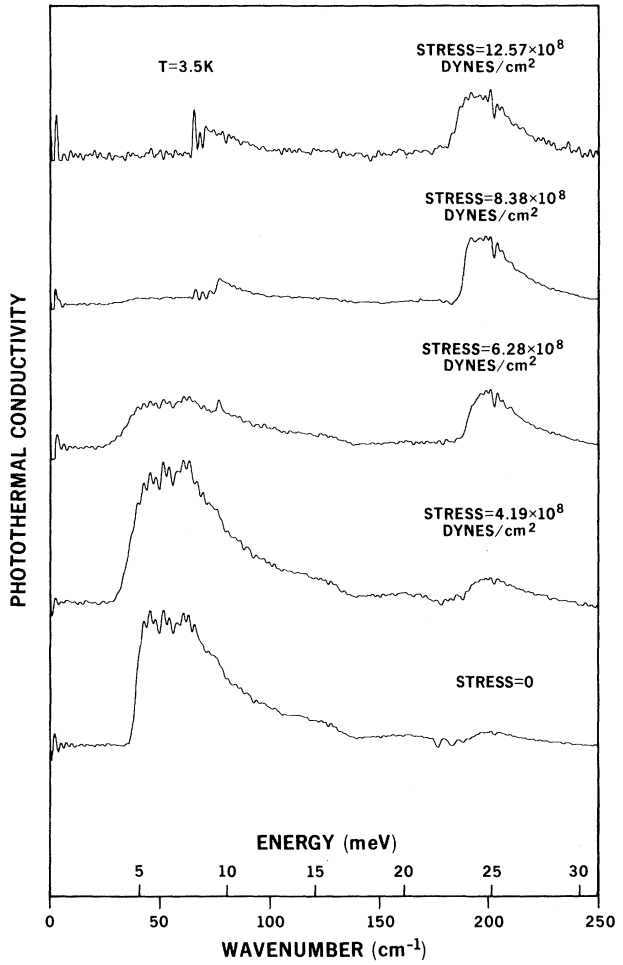

FIG. 2. Photothermal conductivity of a Ge:Be sample at $T = 3.5$ K under stress parallel to [111]. The responses at ~ 40 cm^{-1} and ~ 195 cm^{-1} are due to Be^+ and Be^0 centers. At high stress the Be^+ response vanishes and the aluminum and boron continue to become visible.

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 orbitals[11] yields

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

$$E(He^+) = -2.000; \quad E(He^0) = -2.876;$$

$$E(He^-) = -2.988.$$

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 experimentally[9] established Be^- to Be^0 transition energy of 24.5 meV ($m^*e^4/\epsilon\hbar \equiv 28.0$ 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.

It should also be remarked that, as in the case of H^-, the pseudo He^- system does not possess excited bound states,[7] in agreement with the experimental observations.

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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