Site distortion of the beryllium acceptor in germanium

W. J. Moore
Naval Research Laboratory, Washington, D.C. 20375
(Received 12 March 1984)

Beryllium in germanium is studied in high-resolution infrared transmission spectroscopy in the region of the $1s$-$2p$ transitions. The $1s$-$2p$ transitions are observed to be split in the absence of external perturbations. We interpret these data as demonstrating that the neutral substitutional beryllium impurity does not sit in the center of the germanium tetrahedron but is distorted, probably along a [111] direction.

Beryllium is a double acceptor in germanium with levels at 24.45 meV (Ref. 1) and about 64 meV (Ref. 2). It is the shallowest of the double acceptors in germanium and most nearly approximates a helium-like impurity with a small chemical shift as determined by the good agreement with the theoretical 20 meV for the ideal helium-like ground state.[3] It has recently been shown[4] that the ground to excited state ($1s$-$2p$) intrasite transitions of the shallow level are split in the absence of external perturbations similar to the splitting of the ground state of mercury.[5]

The purpose of this Rapid Communication is to demonstrate that, when studied in high resolution, the splitting of the intracenter transitions of Ge:Be is more complex than has been observed previously and is not easily explained by a simple hole-hole interaction. We are led to postulate that neutral substitutional beryllium does not sit in the center of the germanium tetrahedron but rather undergoes a Jahn-Teller-like spontaneous symmetry-reducing relaxation, probably along a [111] direction, with an associated stress sufficient to split both its ground and excited states. This is analogous to the Jahn-Teller effect observed for the nitrogen substitutional impurity in silicon[6] and to the distortion of the 0^- center in GaP.[7] This work constitutes the first observation of a distortion in an impurity site in germanium.

Samples of appropriately doped Ge:Be and Ge:Zn have been studied in infrared transmission with a low-resolution (0.5 cm^{-1}) grating instrument and a high-resolution (0.04 cm^{-1}, max) Fourier-transform interferometric spectrometer. Samples were wedged to prevent interference effects by grinding with 600-mesh SiC and were lightly cleaned in CP-4. Best results were achieved with samples doped in the 10^{14}–10^{15}-cm^{-3} range and having thicknessess of a few tenths of a millimeter. Both the sample and the detector were mounted on the cold finger of a helium cryostat with the sample serving as a cold window over the detector compartment. The cold finger was held at or below 4.2 K.

High-resolution transmission data are shown in Figs. 1(a) and 1(b) for Ge:Be and Ge:Zn, respectively. The Ge:Be D line is seen to split into at least four and perhaps as many as seven components while the Ge:Zn structure consists of the usual sequence of unsplit Lorentzian absorption lines. We see in Fig. 1(a) that the $1s$-$2p$ transitions split differently for the various excited states observed. Therefore the transitions cannot occur from a complex ground state to identical unsplit, narrow excited states but must include some excited-state splitting as well. Similar transmission spectra taken at lower resolution with samples cooled to 1.8 K show a shift in the relative amplitudes of the components of the 22.0-meV (D line) and 22.8-meV (C line) absorptions indicating that a part of the structure observed is attributable to ground-state splitting. Thus both ground-state splitting and excited-state splitting are taking place.

Since it is well known that stress can produce a splitting of both the ground and excited states of acceptors in germanium, it is necessary to investigate the possibility that the splitting observed is a result of accidental stress applied to the sample by the mounting procedure. Careful experimental investigations were undertaken in which the sample was removed, remounted, and remeasured. Only slight changes were observed when the mounting was deliberately designed to stress the sample. In all cases the mounting technique was to solder one corner of the sample to a copper foil which was then attached to the cold surface. If the indium

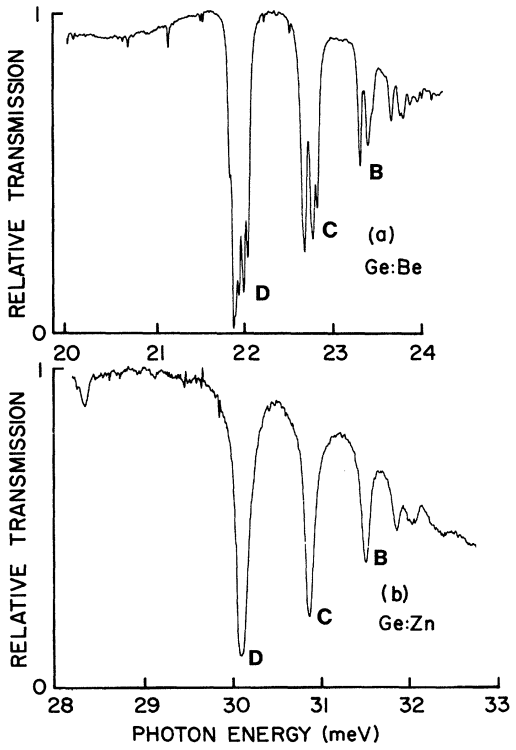

FIG. 1. High-resolution (0.1 cm^{-1}) $1s$-$2p$ spectra of (a) Ge:Be and (b) Ge:Zn. Weak residual water-vapor absorption and noise, visible in highly transmitting regions, make a negligible contribution in the highly absorbed regions.

solder was allowed to cover part of the optical path a slight modification of the spectrum was observed. When the indium was kept well away from the optical path the spectra were identical for four separate runs. In addition, we observe that the spectrum of zinc in germanium shown in Fig. 1(b) is completely free of any splitting. This sample is mounted in a manner identical to that used with the beryllium-doped sample. Therefore we can conclude that the splitting of the beryllium transitions is a property of the beryllium center itself and is independent of measurement technique.

Hole-hole interactions alone are not believed to be the dominant splitting mechanism for the following reasons: (1) It is known[5] that the hole-hole interaction at a neutral double acceptor can split the ground- to excited-state transitions if the ground-state wave functions are sufficiently compact. As the ground-state binding energy becomes smaller with diminishing chemical shift the spatial extent of the ground-state wave function becomes larger and the hole-hole interaction diminishes. Thus the hole-hole interaction was first observed for the mercury center in germanium. Mercury is the deepest double acceptor; the hole-hole splitting is maximized and the temperature dependence of the resulting structure is most easily observed. The interaction has not been observed for impurities shallower than mercury and will here be shown to be negligible for ground states as shallow as zinc. Therefore we would not expect the interaction to become larger in the case of the even shallower beryllium. (2) The temperature dependence of the amplitudes of absorption lines due to transitions from the Γ_1 and $\Gamma_3+\Gamma_5$ ground states of an interacting neutral double acceptor has been calculated using absorption coefficients determined from effective-mass wave functions, and these calculations have been found to be in good agreement with experiment.[1] These results are essentially equivalent to the result obtained by assuming the matrix elements for $1s$ to $2p$ transitions to be equal for transitions from any one of the six components of the ground state to a specific excited state and calculating the thermal population of the ground state with statistical weights equal to the ground-state degeneracies. Therefore the population of the shallower component of the ground state (Γ_1) is no more than one-fifth the population of the deeper ground state ($\Gamma_3+\Gamma_5$). The resulting absorptions reflect the population with the low-energy component of a specific line having an amplitude no greater than one-fifth that of the high-energy component. The data, however, give a different picture. If the observed structure is modeled as a hole-hole interaction plus some additional finer splitting in the excited state, then the low-energy components of given transition should have approximately one-fifth the amplitude of the higher-energy components. This is in contrast to the data which show the lower-energy components to be stronger than the higher-energy ones. Thus it is necessary to conclude that some splitting other than the hole-hole splitting is present and dominates the structure observed.

Interactions between a hole in a ground state and one in an excited state are possible but should be even weaker than those between ground states. Interactions between holes in the ground state and holes in excited states may, however, be present and may couple the perturbation which splits the ground state to the excited states. Such a mechanism could explain some of the fine structure but, again, is not the dominant mechanism.

Therefore we conclude that hole-hole splittings are not the dominant splittings in the observed spectra and that some additional source of splitting must be found to explain the data.

Having concluded that neither accidental stress nor hole-hole interactions are the principal cause of the observed splitting we consider the possibility that a Jahn-Teller-like distortion of the beryllium substitutional site is occurring. Analogous examples from the literature are nitrogen donors in silicon for which a Jahn-Teller distortion has been observed by EPR studies,[6] aluminum acceptors in silicon for which a trigonal site distortion was proposed to explain uniaxial stress splitting of $1s$-$2p$ transitions,[8] and the oxygen center in gallium phosphide for which a local distortion is proposed to explain optically detected magnetic resonance (ODMR) spectra and an anomalously large binding energy for the 0^- state.[7] In the latter case no observable distortion occurs if the oxygen is neutral. This interesting behavior can be given as an example of the general principle that splitting of ground states becomes more favorable energetically as the occupation of the low-lying components of the ground state is increased.

A distortion of the impurity center would produce a reduction in symmetry analogous to that produced by uniaxial stress and should produce $1s$-$2p$ transitions which are similar to those observed with uniaxial stress. Fortunately, the effect of uniaxial stress on a group-II double acceptor in germanium has been measured with a resolution of approximately 0.5 cm^{-1} for stress along [111] and [100] directions in Ge:Zn.[9] If the E parallel to stress and E perpendicular to stress results for [111] stress are averaged, shifted to the applicable spectral region and compared with the data of Fig. 1(a), smoothed to 0.5-cm^{-1} resolution, one gets excellent agreement. Comparison with [100] stress yields poor agreement. Data for [110] stress are not available.

The agreement with the uniaxial stress spectrum suggests that a symmetry-reducing distortion of the beryllium center is responsible for the observed splitting and that this distortion may occur along a [111] direction.

Recent results[4] also indicate that the singly compensated beryllium acceptor does not show such a splitting. This is consistent with the expected behavior in that it is more favorable energetically for the netural center to split since two holes reside in the ground state which becomes deeper. It should be noted that the ground state of both double-hole and single-hole acceptors in germanium can have Jahn-Teller-like distortions if it is sufficiently favorable energetically. The ground state of even the single acceptor has more than the Kramers degeneracy due to crystal-field effects. This is in contrast to systems which have a simple hydrogen-like ground state.

The author acknowledges helpful conversations with T. A. Kennedy and N. D. Wilsey.

[1]W. J. Moore, J. Phys. Chem. Solids 32, 93 (1971).
[2]N. D. Tyapkina, M. M. Krivopolenova, and V. S. Vavilov, Fiz. Tverd. Tela (Leningrad) 6, 2192 (1964) [Sov. Phys. Solid State 6, 1732 (1965)].
[3]W. C. Dunlap, Jr., Phys. 96, 40 (1954).
[4]J. W. Cross, L. T. Ho, A. K. Ramdas, R. Sauer, and E. E. Haller, Phys. Rev. B 28, 6953 (1983).
[5]R. A. Chapman, W. G. Hutchinson, and T. L. Estle, Phys. Rev. Lett. 17, 132 (1966).
[6]K. L. Brower, Phys. Rev. Lett. 44, 1627 (1980).
[7]See, e.g., B. C. Cavenett, in *Defects and Radiation Effects in Semiconductors–1980,* edited by R. R. Hasiguti, IOP Conf. Proc. No. 59 (IOP, Bristol and London, 1981), p. 69.
[8]H. R. Chandrasekhar, A. K. Ramdas, and S. Rodriguez, Phys. Rev. B 12, 5780 (1975).
[9]R. L. Jones, Ph.D. thesis, Purdue University, 1968 (unpublished).