Isotope Shifts in the Ground State of Shallow, Hydrogenic Centers in Pure Germanium

E. E. Haller
Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

(Received 20 September 1977)

Large isotope shifts in the ground state of an acceptor A_2 ($E_{\text{val}} + 11.31$ meV) and a donor D ($E_{\text{cond}} - 12.34$ meV) have been observed for the first time with photoelectric spectroscopy in pure germanium. The shifts ($\Delta E^{A_2} = +21 \pm 3$ μeV; $\Delta E^{D} = -51 \pm 3$ μeV) occur in germanium crystals grown in deuterium instead of hydrogen. A_2 and D are observed at concentrations $< 4 \times 10^{11}$ cm^{-3}. The isotope shift is a direct proof that the centers A_2 and D contain hydrogen.

Using photoelectric spectroscopy,[1] we have investigated a previously unexplained shallow donor D and a shallow acceptor A_2 in ultrapure germanium. These shallow centers exhibit isotope shifts in their ground states when the germanium host crystal is grown in a pure deuterium atmosphere instead of the usual pure hydrogen atmosphere. This is the first time that an electronic isotope shift of shallow centers in semiconductors has been observed.

As distinct from photoconductivity measurements, the photoelectric spectroscopy[1] used for our experiments involves a two-step process, the absorption of a photon carrying an electron/hole from the ground state to a bound excited state followed by the absorption of a lattice phonon yielding a free carrier (Fig. 1). This two-step process leads to sharp lines in the conductivity spectrum below the onset of the extrinsic continuum.

Photoelectric spectroscopy has recently found application in the analysis of ultrapure semiconductors.[2,3] The sensitivity of photoelectric spectroscopy is independent of the impurity concentration over many orders of magnitude. Signal-to-noise ratios of >500 have been reported for small samples (0.5 cm^3) of ultrapure Ge containing 10^{10} acceptors.[4] For high-resolution applications, it is common to use a Fourier-transform spectrometer (interferometer) which has a high throughput and high energy resolution (typically $\Delta\nu \leq 10$ μeV). The instrument used has a resolution of 8 μeV.

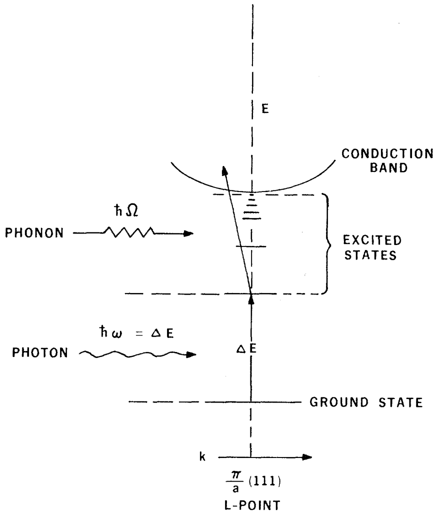

FIG. 1. Two-step process leading to photothermal ionization, the basis of photoelectric spectroscopy.

Ultrapure germanium single crystals grown in our laboratory were investigated. These crystals are extremely well characterized with respect to residual impurities and crystallography. They are grown in a palladium diffusion-purified hydrogen atmosphere (1 atm) out of a synthetic quartz crucible. The crystals typically contain between 10^9 and 10^{11} cm^{-3} boron, aluminum, and phosphorus atoms identified by photoelectric spectroscopy and Hall-effect measurements. Electrically nonactive impurities are oxygen (10^{13}–10^{14} cm^{-3}), silicon ($>10^{16}$ cm^{-3}), and hydrogen. Hydrogen is dissolved in Ge near the melting point at a concentration $\gtrsim 10^{14}$ cm^{-3} in the atomic form.[5] A large fraction of the hydrogen is trapped in crystals of several centimeters in diameter grown at rates >10 cm h^{-1}. We estimate hydrogen concentrations of 10^{13}–10^{14} cm^{-3} in the final crystal.

In addition to the known chemical residual impurities, a number of centers producing shallow energy levels have been discovered.[4] One acceptor (A_2) and one donor (D) are of special interest because we are able to link them to the presence of hydrogen in the Ge crystals. Hall[6] discovered these two centers when he rapidly quenched small Ge samples. When quenching from 400°C, the concentration of A_2 and of D is $\sim 2 \times 10^{11}$ cm^{-3} depending strongly on the cooling rate (dT/dt) and the sample's position in the original crystal.

The ground-state energy of the centers A_2 and D have been determined to be $E_{\mathrm{g.s.}}{}^{A_2} = 11.31$ meV and $E_{\mathrm{g.s.}}{}^{D} \simeq 12.34$ meV.[4] By growing several crystals in a pure deuterium atmosphere (<0.03% H_2), we were able to demonstrate a large isotope shift in the ground-state binding energies of both A_2 and D. The upper spectrum in Fig. 2 was obtained with a rapidly quenched sample of the *hydrogen*-containing crystal No. 497-5.5. This sample is p type ($N_A - N_D \simeq 10^{10}$ cm^{-3}) and all the acceptor-related lines are positive while the donor lines have opposite polarity. The lower spectrum has been obtained with a *deuterium*-containing sample from crystal No. 519-4.0. The residual chemical impurities make this crystal n type ($N_D - N_A \simeq 10^{10}$ cm^{-3}) which is the reason that negative lines are produced by acceptors and positive lines by donors. The set of lines due to the donor D exhibit perfect "hydrogenic"[8] spacing and are shifted towards lower energies in the lower spectrum by $\Delta E_{\mathrm{g.s.}}{}^{D} = -51 \pm 3$ μeV. This corresponds to a shift of the ground state closer to the bottom of the conduction band. An opposite shift away from the top of the valence bands $\Delta E_{\mathrm{g.s.}}{}^{A_2} = 21 \pm 3$ μeV has been found for the acceptor A_2.

The isotope shift in the ground state of A_2 and of D is a direct proof for the presence of hydrogen in these two centers. The microscopic structures of A_2 and D are not yet known. By varying the concentrations of the residual impurities, we have established that A_2 and D are not related to chemical residual impurities B, Al, and P as had been previously assumed.[3] Experiments with crystals having strongly varying oxygen and silicon contents are in progress. Effects which could explain the observed isotope shift are the reduced mass, hyperfine interaction, and Jahn-Teller distortions. A primitive reduced-mass model yields a ground-state shift three times too small. The hyperfine constant of free hydrogen in vacuum is 507 G ($\simeq 8$ μeV). Shallow donors in germanium exhibit hyperfine constants which are typically one order of magnitude smaller than the one for free hydrogen.[9] This is about 50 times too small to account for the observed shifts.

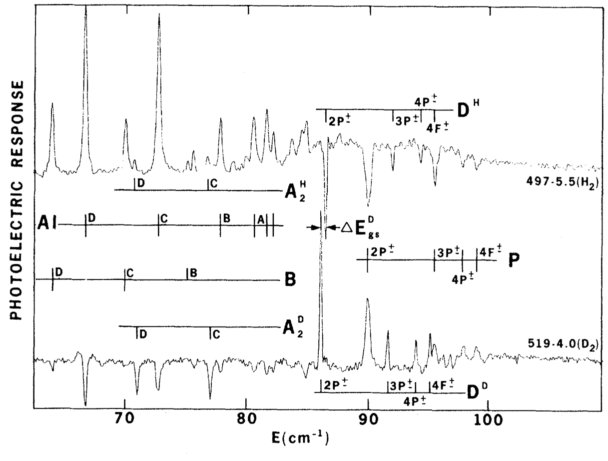

FIG. 2. Photoelectric spectra of hydrogen-grown, p-type sample 497-5.5 (H_2) and deuterium-grown, n-type sample 519-4.0 (D_2). Temperature T, 8.0°K; Al, aluminum; B, boron; P, phosphorus; $D^{\mathrm{H,D}}$, hydrogen-, deuterium-related donor; $A_2{}^{\mathrm{H,D}}$, hydrogen-, deuterium-related acceptor. The notation of Jones and Fisher (Ref. 7) was used for the acceptor lines (B, Al).

Uniaxial stress experiments[10] indicate that the donor D has lower symmetry than elemental substitutional donors.

Previously, hydrogen was thought to be a "deep" donor in analogy with muonium in germanium.[11] This would explain the fact that hydrogen is not electrically active. If hydrogen is molecular, it would not be electrically active either. Support for such an assumption comes from recent diffusion experiments[12] which show that, at temperatures below 400°C, the diffusion constant of hydrogen is more than two orders of magnitude smaller than the values extrapolated from high-temperature experiments.[6] Recent investigations show that hydrogen can form complexes with divacancies[13] and with copper.[14]

Taking into account the recent observations, we propose that the centers A_2 and D are complexes of hydrogen and other electrically nonactive impurities (the most likely candidate being oxygen). We cannot exclude the possibility that the donor D is due to atomic hydrogen, in which case the "deep" donor model would have to be revised.

We are indebted to P. L. Richards, University of California at Berkeley, for the use of the Fourier Transform Spectrometer facility. W. Frank, C. Kittel, G. Morton, and A. Seeger have contributed with many discussions. W. L. Hansen and G. S. Hubbard have assisted in the experiments. R. Markiewicz has helped in the preparation of the manuscript. We also want to thank F. S. Goulding for his continuous interest and support. This report was done with support from the U. S. Energy Research and Development Administration.

---

[1] T. M. Lifshits and F. Ya. Nad, Dokl. Akad. Nauk

162, 801 (1965) [Sov. Phys. Dokl. 10, 532 (1965)]. For a review see S. Kogan and T. M. Lifshits, Phys. Status Solidi (a) 39, 11 (1977).

[2]E. E. Haller and W. L. Hansen, Solid State Commun. 15, 687 (1974).

[3]M. S. Skolnik, L. Eaves, R. A. Stradling, T. C. Portal, and S. Askenazy, Solid State Commun. 15, 1403 (1974).

[4]E. E. Haller, in Proceedings of the First Seminar on Photoelectric Spectroscopy of Semiconductors, Moscow, May 1977 (to be published).

[5]R. C. Frank and T. C. Thomas, J. Phys. Chem. Solids 16, 144 (1960).

[6]R. N. Hall, in *Lattice Defects in Semiconductors 1974,* Institute of Physics Conference Series No. 23, edited by F. A. Huntley (Institute of Physics, London, 1975), p. 190.

[7]R. L. Jones and P. Fisher, J. Phys. Chem. Solids 26, 1125 (1965).

[8]R. A. Faulkner, Phys. Rev. 184, 713 (1968).

[9]D. K. Wilson, Phys. Rev. 134, A265 (1964).

[10]E. E. Haller, to be published.

[11]S. T. Wang and C. Kittel, Phys. Rev. B 7, 713 (1973).

[12]R. N. Hall and T. J. Soltys, to be published.

[13]E. E. Haller, G. S. Hubbard, W. L. Hansen, and A. Seeger, in *Mechanical Properties at High Rates of Strain,* Institute of Physics Conference Series No. 21, edited by J. Harding (Institute of Physics, London, 1974), p. 309.

[14]E. E. Haller and G. S. Hubbard, in Proceedings of the First Seminar on Photoelectric Spectroscopy of Semiconductors, Moscow, May 1977 (to be published).

Evidence for a Ferromagnet-Spin-Glass Transition in *Pd*FeMn

B. H. Verbeek, G. J. Nieuwenhuys, H. Stocker, and J. A. Mydosh
Kamerlingh Onnes Laboratorium der Rijka-Universiteit, Leiden, The Netherlands

(Received 9 January 1978)

Measurements of the low-field ac susceptibility on ternary alloys of Pd+0.35 at.% Fe and a Mn concentration of 0 to 8 at.% reveal, for three distinct regimes of Mn concentration, (a) a giant-moment ferromagnetism, (b) a high-temperature ferromagnetic phase followed by a lower-temperature spin-glass transition, and (c) a spin-glass phase. Our results for the susceptibility and the T-c phase diagram are satisfactorily explained by the spin-glass theory of Sherrington and Kirkpatrick.

Competing interactions in magnetic systems lead to a diversity of magnetic structures and critical phenomena. Particularly in insulating compounds, variations of the space and the spin dimensionalities provide important criteria for the theory of phase transitions. In metallic systems, and especially dilute alloys, the situation is more complex because of the long-range nature of the magnetic interactions mediated by the conduction electrons. If we focus upon dilute magnetic alloys and neglect the Kondo effect which produces a weakened magnetic moment, there exist two distinct types of ordering for randomly distributed magnetic impurities. The first is the so-called "giant-moment" ferromagnetism[1] which occurs in a few systems with a large exchange-enhanced host susceptibility. Secondly, there is the more common spin-glass type[2] of random freezing of the moments without long-range order in the usual sense.

An interesting combination of these two types of ordering is found at different concentrations of the *Pd*Mn system. For $c \leq 3$ at.% Mn, giant-moment ($\mu_{\text{eff}} \simeq 7.5\mu_B$) ferromagnetism prevails.[3] However, upon further increasing the Mn concentration ($c \geq 4$ at.%), the probability of having two Mn atoms at first, second, and third nearest neighbor increases. This then supplies the essential element of "conflict" or "frustration" for the appearance of the spin-glass phase. Mn nearest neighbors couple antiparallel and thereby produce Mn-Mn antiferromagnetic exchange competing with the longer-ranged ferromagnetic interaction.[4] An anomalous mixed phase with peculiar magnetization and remanence behavior occurs between 3 and 4 at.% Mn.[5]

In order to better control and understand the competition between these two exchange mechanisms, we have studied the ternary alloy *Pd* + 0.35 at.% Fe and a Mn concentration of $0 \leq c \leq 8$ at.%. *Pd*Fe is a strong giant-moment ferromagnet with $\mu_{\text{eff}} \simeq 10\mu_B$ and $T_c = 8.7$ K for 0.35 at.% Fe. Only at very low concentrations ($\simeq 0.015$ at.% Fe) and temperatures ($\simeq 0.1$ K) is there some experimental evidence for the onset of a spin-glass ordering.[6] By adding Mn to this *Pd*Fe alloy we now have a wide Mn concentration range at favorable temperatures (1 – 20 K) with which to investigate the resulting magnetic ordering. Low-field susceptibility measurements offer a convenient and sensitive method to determine the type of magnetism present, and an external