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A NEW METHOD TO DETERMINE THE CHEMICAL COMPOSITION AND STRUCTURE OF NON-ELEMENTAL ACCEPTOR AND DONOR CENTERS IN ULTRA-PURE GERMANIUM

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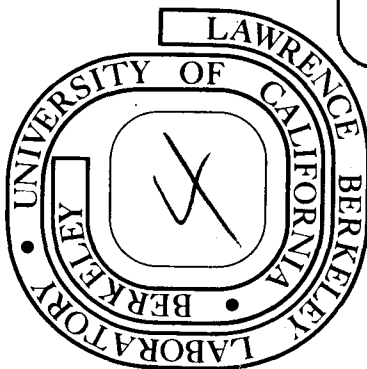
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A NEW METHOD TO DETERMINE THE CHEMICAL COMPOSITION AND STRUCTURE OF  
NON-ELEMENTAL ACCEPTOR AND DONOR CENTERS IN ULTRA-PURE GERMANIUM

E. E. Haller

October 1977

Whereas, the position of all lines due to elemental impurities coincide perfectly (B, Al, P) a large isotope shift is observed in the D-donor and the  $A_2$ -acceptor spectra. The donor D moves by  $-51 \pm 3$   $\mu\text{eV}$  closer to the conduction band edge and the acceptor  $A_2$  ground-state energy increases by  $+21 \pm 3$   $\mu\text{eV}$ . These isotope shifts are the most direct proof for the presence of hydrogen (and deuterium) in  $A_2$  and D.

It is of interest to explore the possible causes of the observed isotope shift. Deuterium has twice the mass and twice the nuclear spin of hydrogen. Using a simple hydrogen model for the description of a donor in Ge, one can estimate the effect of the mass on the ground-state binding energy  $E_{gs}$ :

$$E_{gs} = \frac{e^4 m^*}{2\epsilon^2 \hbar^2} \quad (1)$$

$e$  = charge of the electron,  $m^*$  = effective mass of the electron,  $\epsilon$  = dielectric constant of Ge ( $\epsilon = 16$ ) and  $\hbar$  = Planck's constant divided by  $2\pi$ . The effective mass of the electron,  $m^*$ , differs from the mass of a free electron due to the presence of a periodic lattice and due to the finite mass of the donor nucleus. The latter effect leads to the reduced mass  $m_r$ :

$$\frac{1}{m_r} = \frac{1}{m_e} + \frac{1}{m_N} \quad (2)$$

$m_e$  = electron mass,  $m_N$  = mass of nucleus. The influence of the reduced mass effect is largest when we assume that the  $A_2$ /D pair consists only of hydrogen or deuterium. Using equations (1) and (2) one can estimate the change in binding energy  $\Delta E_{gs}$ :

$$\frac{E_{gs}^H}{E_{gs}^D} = \frac{m_r^H}{m_r^D} \quad (3)$$

and

$$\Delta E_{gs} = E_{gs}^H - E_{gs}^D \approx E_{gs}^H \left( 1 + \frac{m_e}{m_H} \right) \left( 1 - \frac{m_e}{m_D} \right) \quad (4)$$

$$\approx E_{gs}^H \left( 1 - \frac{1}{4000} \right) \approx 3 \mu\text{eV}$$

where H and D designate hydrogen and deuterium, respectively. The estimated value is far too small to account for the observed effect.

The change in binding energy due to the interaction of the nuclear spin with the electron spin is also far too small (~50 times) to account for the observed values. A third possibility is a static or dynamic Jahn-Teller distortion. In such a model one would assume that the donor atom is not located at a highly symmetric position but is pushed to a lower symmetric site (JTD) or that it oscillates between more than one stable position (dynamic JTD). In either case more has to be known about the detailed structure of the donor before quantitative estimates about the isotope shift can be made. This leads to the second important part of the analysis of these unknown impurity centers.

## Structure of Impurity Centers

The structure of substitutional elemental acceptors and donors has tetrahedral symmetry, the same as the germanium atoms. This situation is reflected in the ground state of donors and acceptors. For reasons of simplicity, we restrict ourselves to donors in the following text.

The electron which is bound to a donor can be compared to the electron of a hydrogen atom. At low temperatures, the electron occupies the lowest lying state, the ground state, in which it is most strongly bound to the positively charged nucleus. Above the ground state lies a series of bound excited states. At a certain energy above the ground state, the electron becomes unbound, i.e., it enters the continuum. The periodicity and dielectric constant  $\epsilon$  of a crystal lattice hosting a donor atom modifies the energies of the ground and the excited states.<sup>9</sup>

In pure germanium the ground state is fourfold degenerate. The continuum corresponds to the four conduction band minimas along the [111] directions. The presence of a donor "core" splits the fourfold degenerate ground state into a triplet (T) and a singlet (S) state. The energy difference is called chemical split  $4\Delta$ . However, all the bound excited states remain fourfold degenerate.

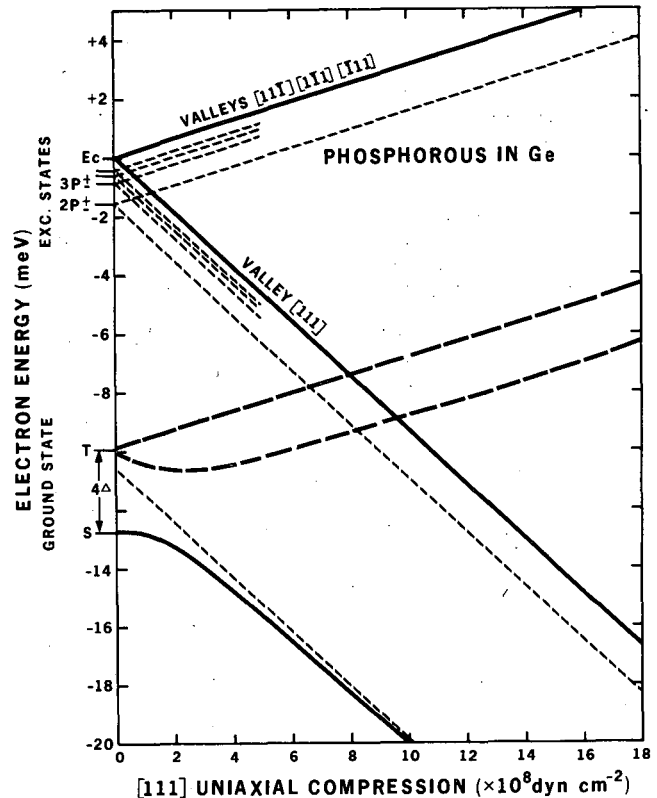


Fig. 2 Dependence of the energies of the ground- and excited-states and the conduction band minima (valleys) on uniaxial compression applied along the [111] direction. Whereas, the four valleys and the excited states show perfectly linear dependences, the ground-state components exhibits quadratic terms resulting in changes in energy differences between ground- and excited-states. These changes cause the shift of the lines in photoelectric spectra under uniaxial compression. At the temperatures used in photoelectric spectroscopy ( $\sim 7^\circ\text{K}$ ) only the lowest lying S-state is populated.

If a uniaxial stress is applied to the germanium crystal, the energies of the band edges and of the ground and excited states are changed.<sup>10</sup> The four-fold lattice symmetry is broken and this affects the degeneracy of the donor states in the way illustrated in Fig. 2. The case of compressional stress along the [111] axis is presented. The [111] valley falls proportional to the stress three times as fast as the remaining three valleys and three components of each bound excited state rise in energy. The triplet (T) component of the ground state splits into a doublet (D) and a singlet (S) both of which move parallel to the rising valleys in the high stress limit. At low stress, the lowest lying singlet (S) moves closer to its corresponding [111] valley and asymptotically reaches, in the high-stress limit, the same stress dependence. The changes in the photoelectric infrared spectrum of a substitutional donor under stress can directly be deduced from Fig. 2. At zero stress, a series of lines corresponding to the transition between the ground state and excited states is observed. The value of  $4\Delta$  is large enough ( $4\Delta(P) = 2.82$  meV) that only the singlet level of the ground state is populated at the temperatures used for photoelectric spectroscopy ( $T=8^\circ\text{K}$ ). That means that only

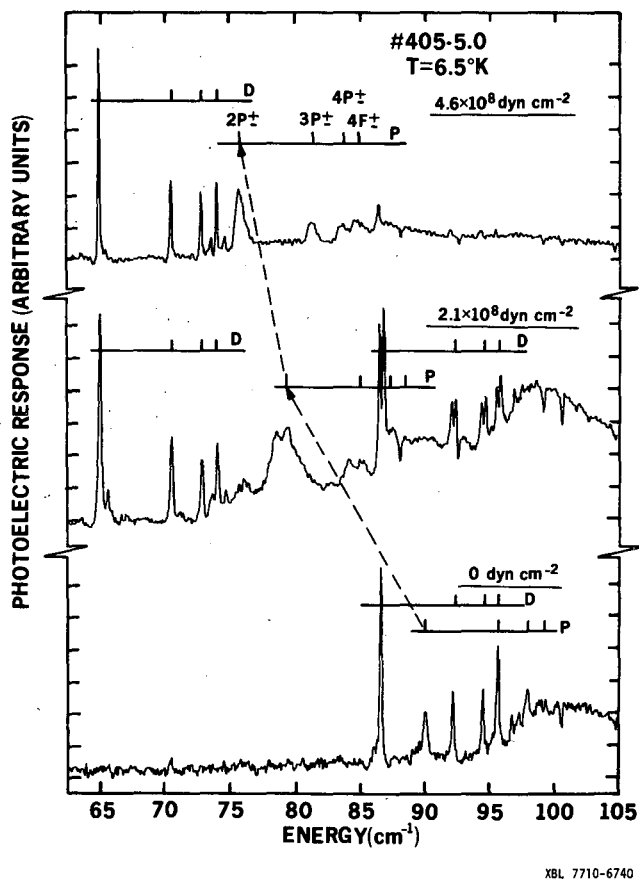
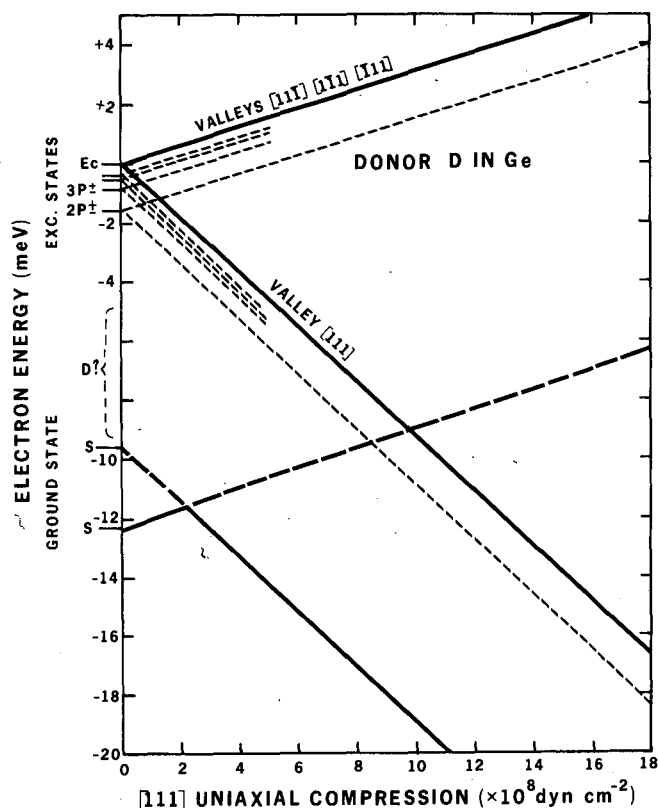


Fig. 3 Spectra of Ge-samples 405-5.0 recorded for three uniaxial stress values. The phosphorous spectra move to lower energies as illustrated in Fig. 2. The hydrogen-related donor D spectra exhibit two sets of exceptionally sharp lines which do not move but which change their intensities. Around  $2.1 \times 10^8$  dyn  $\text{cm}^{-2}$  the ground state components cross and produce some interferences which result in a line splitting.



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Fig. 4 Dependence of the energies of the ground-state components of the hydrogen related donor D on uniaxial compression along the [111] direction. The excited states and the [111] valleys are the same as in Fig. 2. Contrary to elemental substitutional donors the lines of the D-spectrum do not move under uniaxial compression but, their intensity drops rapidly around  $2.1 \times 10^8$  dyn  $\text{cm}^{-2}$ . A new set of lines appears at 2.7 meV lower energies. This behavior is explained by a crossing of two singlet states (S). A doublet (D) or two more singlet (S) components of the ground state must exist close to the conduction band minima but, they cannot be populated and are therefore not observed at the temperatures used.

one set of infrared lines appear in the spectrum. When stress is applied this set of lines will move to lower energies because the ground-state singlet moves closer to the conduction band valley minimum. All elemental donors follow exactly the described pattern which proves that they are substitutional.

The spectrum of the hydrogen related donor D does not follow the pattern described above. From spectra recorded at various values of stress (Fig. 3), we obtained the situation displayed in Fig. 4. The position of the lines does not change at all under stress. At a stress of  $2.1 \times 10^8$  dyn  $\text{cm}^{-2}$  ( $0.981 \times 10^6$  dyn = 1 kg force) the intensity of the lines reduces rapidly and new set of lines appear at 2.7 meV lower energy. No further changes occur up to very large stresses.

Preliminary group theoretical considerations lead to the conclusion that the donor has a symmetry axis along a [111] direction and does not occupy a substitutional site. It follows that D is interstitial, located at a low symmetry site. This is the case of a static Jahn-Teller distortion. A more detailed

analysis is necessary to obtain the exact location of D in the lattice.

### Discussion and Conclusion

The isotope shift and the uniaxial stress experiments do not yield a complete picture of the acceptor/donor pair  $A_2/D$ . The choice of impurities other than hydrogen involved in the formation of  $A_2$  and D is however very limited. Only oxygen and silicon are present at sufficiently high concentrations to be possible candidates. Experiments with lightly doped crystals have shown that  $A_2$  and D are not affected by the presence of B, Al, or P. Silicon takes a substitutional position when introduced into the germanium lattice. Its valence is equal to the valence of germanium. Itself, it produces no electronic states in the forbidden gap of germanium. We assume that silicon is most probably not a candidate for the  $A_2/D$  pair. Oxygen is the only remaining choice as an impurity component of  $A_2$  and D. With only one possible choice left, we can try to make models for the precise nature of  $A_2$  and D. Considerable help in this task comes from the detailed observations on the annealing properties of  $A_2$  and D. Hall<sup>5</sup> observed that while  $A_2$  anneals rapidly away at room temperature, the concentration of D increased. The maximum values of the concentrations of D and  $A_2$  are nearly equal. Hall's model which implies that  $A_2$  combines with an unknown impurity to form D, fits quantitatively the experimental data. We put forward two new models.

1) Our first model requires only the impurity hydrogen. We assume that at 400°C, the temperature from which the Ge-samples are quenched, a fraction of the hydrogen is dissociated into atomic hydrogen. The acceptor  $A_2$  is postulated to be a hydrogen atom near a vacancy or divacancy. The donor is created when the vacancy or divacancy is released and the hydrogen becomes interstitial. In analogy to lithium, we assume that D is a shallow donor formed by interstitial hydrogen. At temperatures around 160°C, the donor D anneals through the formation of molecular hydrogen. This reaction would be of second order exactly as observed by Hall.

2) In a second model, we identify  $A_2$  with an oxygen-hydrogen molecule. The molecule captures a hydrogen molecule forming  $OH_3$ , the donor D. At 160°C this configuration becomes unstable and one hydrogen atom is split off producing a neutral water molecule and an electrically inactive hydrogen atom. The latter reaction of the second model is of first order and does not agree with the experimental observations. Experiments with Ge crystals containing strongly varying amounts of oxygen are in progress, and they should show if oxygen is involved in the formation of  $A_2$  and D.

At this time, we feel that since Model 1 fits experimental observation better than Model 2 (or any previous model), we have discovered an atomic interstitial hydrogen donor.

Using the  $A_2/D$  pair as an example, we have demonstrated that isotope effects and uniaxial stress can be successfully used to determine composition and structure of unknown acceptor and donor centers in germanium. The same technique will be applied to other unknown centers and also to the case of lithium which has not been solved satisfactorily up to the present time.<sup>11</sup>

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