Electron Paramagnetic Resonance in Electron-Irradiated Germanium*†

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Spin-resonance studies have been made in oxygen-free p-type germanium after bombardment by 4.5-MeV electrons. Samples were bombarded and stored at 77°K, and measurements were made at liquid-helium temperatures with a superheterodyne spectrometer operating at 9500 MHz. Essentially the same resonance spectra appeared in both undoped and gallium-doped germanium samples that initially had room-temperature resistivities in excess of 40 Ω cm. No resolved hyperfine spectra were observed. The predominant set of lines represents a spin-$\frac{1}{2}$ center, designated Ge-$P1$, whose g tensor has ⟨100⟩⟨011⟩ symmetry, with $g[01\bar{1}]=2.025$, $g[011]=1.629$, and $g[100]=1.732$. The line width is 70 G. The production rate of the center is approximately 1.6 cm^{-1}. The defect exhibits some of the characteristics of a long-lived electron trap. The traps begin to empty, as evidenced by a gradual decrease in the resonance signal, when the sample is warmed above 77°K. At 135°K the traps empty in seconds. The resonance signal returns when the traps are repopulated by a short burts of ionizing irradiation at 77°K. When the sample is warmed above 220°K, the center loses its trapping property and is assumed to have disappeared or changed its form. An analysis of the g shift and the trapping behavior is not sufficient to give a definite microscopic model of the Ge-$P1$ center; however, the high degree of symmetry of the g tensor suggests that the structure of the defect is simple.

I. INTRODUCTION

ELECTRON paramagnetic resonance (EPR) is proving to be a powerful tool for the study of the detailed nature of radiation-induced defects in semiconductors. Up to now, silicon has been most extensively studied by this microscopic technique.[1,2] The first resonance results in germanium, involving impurities, were obtained rather recently and are summarized by Feher.[3] Baldwin[4] has reported results in irradiated oxygen-doped germanium.

The present paper is confined primarily to a paramagnetic center in relatively pure germanium which has been bombarded by electrons with an energy of a few MeV. The primary defects formed are presumed to be scattered vacancies and interstitials or close vacancy-interstial pairs. At the temperatures involved, these primary defects are mobile and may interact, forming a variety of different types of defects.

A limiting factor in the present system is the excessive linewidth. The observed spectra are, therefore, relatively weak, and a high electron flux is needed. This in turn puts a restriction on the initial Fermi level since germanium eventually goes p type under excessive bombardment. It is not possible to compensate without a heavy concentration of donors, which leads to impurity-band conduction. The ultimate Fermi level determines the occupation probability of the localized electronic levels associated with the defects. The charge state in turn determines the observability of a defect and in addition may influence its mobility and even its formation.[5] A large class of defects may thus be excluded from resonance measurements. It is possible to affect the charge states of the defects by properly filtered illumination; however, no such provisions were made in the present experiment.

Resolved hyperfine structure which would have greatly aided in the identification of the observed defect was not obtained. It is difficult to see such spectra in germanium because the only magnetic nucleus present in the pure material is the Ge^{73} isotope, which has an abundance of 7.8% and a spin of $\frac{9}{2}$.

The samples studied are p type, and after bombardment the equilibrium Fermi level remains near the bottom of the forbidden energy gap. The samples have an oxygen content of less than 10^{16} cm^{-3}, and the concentration of impurities other than oxygen is about 10^{14} cm^{-3}. The predominant center observed has a typical concentration of 3×10^{17} cm^{-3} and therefore does not appear to be involved with an impurity of any kind.

II. EXPERIMENTAL DETAILS

The germanium single crystals studied in this investigation were grown at Purdue by pulling in a hydrogen atmosphere. The samples, which were initially p type at 77°K and below, all came from two ingots, one gallium doped and the other undoped. The respective room-temperature resistivities before irradiation were 42 Ω cm and 50 Ω cm. The samples were cut in the shape of a thin cylinder, about 17 mm long and 2 mm in diam, and bombarded at 77°K by 4.5-MeV electrons at currents of up to 1 μA/cm². The beam

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[1] G. D. Watkins, in *Proceedings of the Seventh International Conference on Physics of Semiconductors: Radiation Damage in Semiconductors* (Dunod Cie, Paris, 1965), Vol. 3, p. 97.
[2] J. W. Corbett, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Suppl. 7.
[3] G. Feher, in *Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), Vol. II, p. 715.
[4] J. A. Baldwin, J. Appl. Phys. **36**, 793 (1965).
[5] J. W. MacKay and E. E. Klontz, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors: Radiation Damage in Semiconductors* (Dunod Cie., Paris, 1965), Vol. 3, p. 11.

passed through a 1-mil titanium window in the evacuated finger of a portable Eccofoam Dewar. Resonance measurements were made at liquid-helium temperatures in a cylindrical brass Dewar. Provisions were made to transfer and store the samples at liquid-nitrogen temperature. To obtain reasonable resonance signals, sample bombardment times ranging from 20 to 40 h were required. Electrical measurements made by MacKay and others in germanium indicate that under such bombardment the sample will tend toward or remain, p type.

A superheterodyne EPR spectrometer, using an LFE "Stalo" Model 814 as a stable X-band frequency source, was built for the present study. The operating frequency was 9500 MHz. Magnetic-field modulation and lock-in detection were employed.

A cylindrical copper sample cavity was used, operating in the TE_{011} mode, with its axis perpendicular to the dc magnetic field and the plane of rotation of the magnet. Because of space limitations, and the ultimate tuning arrangement desired, the cavity was placed on the broad face of the waveguide and was filled with ultra-pure LiF to shrink its size. This placement necessitated a diagonal slot rather than a circular hole for coupling. The sample was inserted from the top into a hole along the axis of the dielectric filler and was withdrawn for bombardment. Provisions were made to tune the frequency slightly by a plunger in the cavity and to vary the coupling by a variable short in the waveguide. Both adjustments were made remotely by a single rod leading outside the Dewar. The cavity Q with Ge sample was measured to be 3500 at 4.2°K. The sample filling factor was calculated to be 0.22, taking into account the dielectric constants of the sample and the LiF filler. The number of paramagnetic spins in a given sample was determined by comparing the resonance signal with that of a silicon calibration marker[3] obtained through the courtesy of E. A. Gere of Bell Telephone Labs.

The magnetic field was produced by a 12-in. Varian rotating electromagnet with pole caps tapered to 10 in. and making a 3-in. field gap. The magnetic was rotated through 90° about an ⟨011⟩ axis of the crystal to include the three crystallographic directions ⟨100⟩, ⟨111⟩, and ⟨011⟩. Problems of eddy current losses and mechanical vibrations were eliminated by using low field-modulation frequencies of 15 or 30 Hz. Improved resolution was obtained by employing second-derivative modulation for some of the measurements.

III. EXPERIMENTAL RESULTS

A. Characteristics of the Spectrum

The predominant center in relatively pure p-type germanium, bombarded at 77°K with high-energy electrons, has been designated Ge–$P1$, adopting Watkins' convention.[1] A pronounced anisotropy exists in the EPR spectrum associated with this defect. From an analysis of the angular variation of the spectrum, as outlined in Sec. IIIB, it is seen that the g tensor has ⟨100⟩⟨011⟩ symmetry. The spin of the center is $\frac{1}{2}$, as follows from the fact that only one set of lines is observed when the field is swept over its entire range. The irradiation was carried out in an ⟨011⟩ direction and the relative amplitudes of the lines indicate that the resulting defect has no preferred orientation in the crystal. The center was observed only at liquid-helium temperature. The linewidth, taken from peak to peak in a derivative absorption trace, is 70±5 G. The line shape is clearly Gaussian, with slight variations which may be due to unresolved hyperfine structure.

The excessive linewidth led to some degree of overlapping of adjacent lines, and in order to obtain better resolution second-harmonic detection was employed for most g-value measurements. A typical trace is reproduced in Fig. 1. The actual g values were obtained by averaging over two directions of field sweep since the sweep rates were slightly faster than that required for a completely undistorted line.

On comparing the sum intensity of all the lines with intensity of the isotropic line of the standard Gere marker, and keeping the modulation amplitude and microwave power low enough so as not to saturate the resonances, the production rate of the Ge–$P1$ center was found to be 1.6 defects/cm³ per incident electron/cm². The relative linewidths, line shapes, and filling factors were taken into account in this determination. The result is accurate to about 20% because of possible errors in the determination of filling factor and linewidth.

An accurate determination of the spin-lattice relaxation time T_1 was not attempted because of the difficulty in obtaining strong signals over a wide range of microwave power. Measurements attempted under fast-passage conditions, using direct detection without

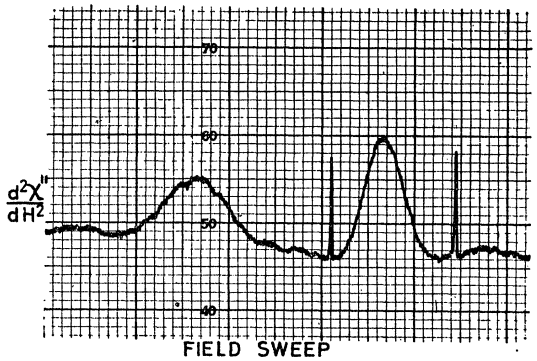

FIG. 1. ERP spectrum of Ge—$P1$ center with H along a ⟨100⟩ axis. $\Phi=2.2\times10^{17}$ electron/cm², sample annealed to 170°K. Measurement at $T=4.2$°K, $\nu=9558.4$ MHz. The weaker of the two resonance lines represents a principal g value, g[100]. The sharp lines are field markers. Ten small horizontal divisions correspond to about 116 G.

field modulation, show that T_1 is less than 0.01 sec at 4.2°K.

B. g Tensor

The spectrum can be described by the spin Hamiltonian

$$H_S=\beta\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{H}, \quad (1)$$

with $S=\frac{1}{2}$. The components of the g tensor, which determines the splitting in an external H field, are given by $g_{ij}=2.0023\delta_{ij}+\Delta g_{ij}$, where 2.0023 is the free-electron value. The shift from this value, accurate to first order in the spin-orbit interaction, is[6]

$$\Delta g_{ij}=-2\sum_n \frac{\langle 0|(\mathbf{V}_{so})_i|n\rangle\langle n|L_j|0\rangle}{E_n-E_0}, \quad (2)$$

where $\mathbf{V}_{so}=(\beta/mc)\mathbf{E}\times\mathbf{p}$ and the sum is taken over the excited states.

With a proper choice of axes, the g tensor can be represented by

$$g^2=g_1^2\cos^2\alpha+g_2^2\cos^2\beta+g_3^2\cos^2\gamma,$$

where α, β, and γ are the angles between the direction of the magnetic field and the principal axes of the tensor. When there is no preferred orientation of the defect in the crystal, one sees several g values for an arbitrary direction of the external field. The g gensor can be thought of as being viewed from several equivalent frames of reference, obtained from the point-group symmetry operations of the crystal. The germanium lattice is cubic and has the symmetry of the T_d point group. In applying these operations here, we consider the particular tensor having principal axes [100], [011], and [01$\bar{1}$], with respect to the cubic axes x, y, and z, and note the form of this tensor in the new coordinate systems obtained by the symmetry operations.[7] By constraining the field to rotate in the (011) plane of the crystal, we arrive at four equivalent but physically distinct two-dimensional matrices. The g values can then be conveniently plotted as a function of field angle in the (011) plane. The Ge–$P1$ spectrum was found to have the symmetry predicted for a g tensor with this $\langle 100\rangle\langle 011\rangle$ symmetry. The magnet was rotated about an $\langle 011\rangle$ axis and the experimental values of g^2 were plotted versus the field angle from a $\langle 100\rangle$ direction. To improve the accuracy of the plot, use was made of the consistency relations[8] which exist between the various branches of such a tensor. This was necessary because the spectrum overlapped isotropic spectra which appeared around $g=2$ and furthermore it was not easy to pinpoint the g values for the resolved lines because of their breadth. As data points, only the strongest lines were used. These occur

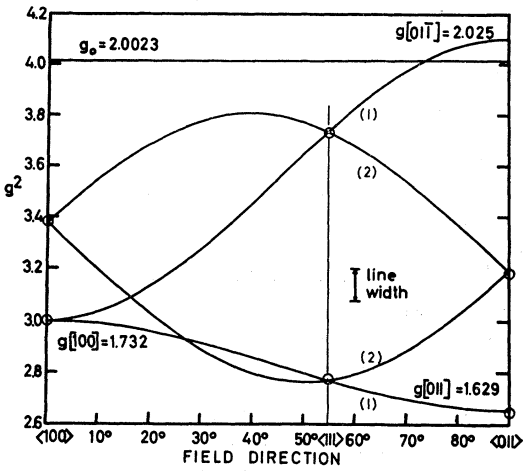

FIG. 2. Angular variation of Ge–$P1$ center with H in a {011} plane. Curves are calculated from the six data points by a least-squares method.

at angles where the branches intersect and do not overlap other spectra. The branches intersect at seven points in the three crystalographic directions $\langle 100\langle$, $\langle 111\rangle$, and $\langle 011\rangle$. Only six of the points were observable, and expressions were obtained for these experimental points in terms of the three principal g values. The best possible values for the principal g values, consistent with the six equations, were found by a least-squares fit. An improved angular variation plot, computer calculated, is shown in Fig. 2. Data taken at 7.5° field intervals fitted this plot to within about 5 G at every point where the signal was observable. The principal g values may be obtained directly from the plot. The numbers in parentheses indicate the relative branch intensities expected when the center has no preferred orientation. The usefulness of such an internal-consistency method can be seen by the fact that one of the principal g values, near $g=2$, is not directly observable. The principal g values for the Ge–$P1$ center are

$$g_1\equiv g[01\bar{1}]=2.025\pm0.001,$$
$$g_2\equiv g[011]=1.629\pm0.001,$$
$$g_3\equiv g[100]=1.732\pm0.001.$$

C. Annealing

Temperature studies were made by allowing the brass Dewar system to warm up of its own accord after each run. In the range 80 to 250°K the rate of sample warming, monitored by a copper-constantan thermocouple, was very nearly constant at 8°/h. The gallium-doped sample was isochronally annealed at this rate in steps of between 5° and 20°. After each annealing stage, the sample was cooled to 4.2°K and resonance measurements were made. The behavior of the Ge–$P1$ resonance is compatible with that of a metastable

[6] G. D. Watkins and J. W. Corbett, Phys. Rev. 134, A1359 (1964).
[7] M. Nisenoff and H. Y. Fan, Phys. Rev. 128, 1605 (1962).
[8] W. Jung, Ph.D. thesis, Purdue University, 1963 (unpublished).

electron trap. At temperatures above 77°K the resonance signal gradually decreases with time. During the annealing run the emptying of the traps was accelerated, and at 135°K the traps emptied in seconds. The traps were refilled and the resonance signal was brought back to full strength by an ionizing irradiation at 77°K, of a few minutes duration, which was too short to introduce much damage. At the higher stages of annealing, the traps emptied immediately and the resonance was observed only after an ionizing irradiation, carried out every few stages of anneal. Measurements were made within 3 h after every such irradiation. Above 220°K, the defects were assumed to have disappeared or changed their form since they could no longer be populated. A plot of the annealing behavior is given in Fig. 3. The solid line is a chronological plot of the relative strengths of the resonance signals. The dashed line indicates the fraction of defects remaining.

Assuming first-order kinetics and isothermal annealing, the activation energy ϵ for emptying of the traps or annealing of the defect can be estimated from the relation

$$\ln(1/f)=t\nu e^{-\epsilon/kT},$$

where f is the fraction of the signal remaining at a temperature T, k is Boltzmann's constant, and ν is a constant with the dimensions of frequency. The time t can not be specified exactly here because the anneal is not strictly isothermal. It is therefore not possible to determine the jump frequency ν to any degree of precision. Assuming the same time interval t for each annealing point, the activation energy for emptying of the traps is found to be approximately 0.10 eV. The activation energy for the 220°K anneal with traps empty is found to be 0.12 eV. The assumption of isothermal annealing and the errors in the resonance measurements at low amplitudes limit the accuracy of these results to about a factor of 2.

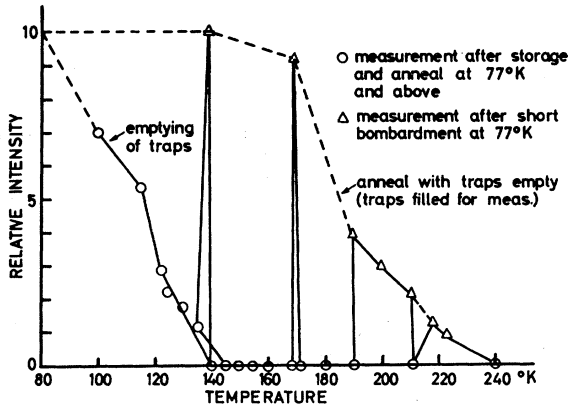

FIG. 3. Isochronal anneal of the Ge—$P1$ center. The annealing rate was 8°/h and at each point the sample was cooled to 4.2°K for resonance measurements.

D. Summary of Related Work

Electrical measurements made at Purdue[9] and elsewhere[10] in p-type germanium, bombarded by electrons at 77°K, have shown the existence of a defect with trapping and annealing properties that identify it as the Ge–$P1$ center. Measurements[11] on the introduction rate of these metastable energy levels, for 4.5-MeV electrons incident upon degenerate p-type germanium, indicate a value of 1.45 states/cm^3 per electron/cm^2, in reasonable agreement with the value of 1.6 obtained from resonance measurements in the nondegenerate material. The defect is not immediately observable when the bombardment is carried out at 4.2°K, even upon subsequent warming to 77°K, although there is evidence of its appearance at a very low ultimate production rate upon warming to 120°K.[12] The defect behaves somewhat like a long-lived minority carrier trap, which can communicate with the valence band only by means of the conduction band. The level can be filled with electrons by means of white light or a short burst of electron irradiation and can be emptied by light filtered through germanium or by warming the sample to about 135°K for a few minutes.

Callcott and McKay[13] have determined that the defect gives up its electron with an activation energy of 0.22 eV, and from the behavior of mobility change it was concluded that the trap-filled state is neutral and the trap-empty state is positively charged. It is unlikely that the defect is actually a simple electron trap because of its very low capture cross section for holes.[10] Flanigan and Klontz[14] have made measurements on the annealing of the defect which are in fair agreement with the resonance results. North and Buschert[15] have measured the dependence of sample length on the electron population of the level. Microscopic models that have been proposed from electrical measurements are summarized by Hasiguti and Ishino.[16]

E. Additional Resonance Spectra

Isotropic spectra which were observed around $g=2$ in the electron-bombarded germanium have shed little light on the nature of the defects giving rise to these spectra. However, since the line strengths indicate a relatively large concentration of defects, they are cataloged here for reference (Table I). All of the adjacent lines overlapped to a degree, and as a conse-

[9] J. W. MacKay and E. E. Klontz, J. Appl. Phys. **30**, 1269 (1959).
[10] W. L. Brown, W. M. Augustyniak, and T. R. Waite, J. Appl. Phys. **30**, 1258 (1959).
[11] J. E. Whitehouse (private communication).
[12] J. E. Whitehouse, Phys. Rev. **143**, 520 (1966).
[13] T. A. Callcott and J. W. MacKay (to be published).
[14] T. M. Flanagan and E. E. Klontz (to be published).
[15] J. C. North and R. C. Buschert, Phys. Rev. **143**, 609 (1966).
[16] R. R. Hasiguti and S. Ishino, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors: Radiation Damage in Semiconductors* (Dunod Cie., Paris, 1965), Vol. 3, p. 260.

TABLE I. Isotropic resonance lines observed at 4.2°K in the electron-irradiated germanium.

Line designation	Effective g value (± 0.001)	Production rate (defects/cm³ per electron/cm²)	Microwave power saturation (mW)	Annealing temp. (°K)
X_1	2.058	~0.1	1 - 10	170–200
X_2	2.038	~0.2	0.1 - 1	200–230
X_3	2.027	<0.1	1 - 10	170–200
X_4	2.014	<0.1	10 -100	140–170
X_5	1.996	~0.7	0.001- 0.01	210
X_6	1.973	<0.1	1 - 10	?
X_7	1.965	~0.2	0.1 - 1	200–230

quence it was difficult to accurately measure the liue-widths, which are of the order of 15 G. Two of the lines, X_1 and X_3, exhibited an anisotropic broadening, presumably arising from a distribution of g values due to local strain.[17] The minimum width was in the [100] direction. There was no observable shift in g values in any of the lines as the external magnetic field was rotated. The centers are thought to be spin $\frac{1}{2}$ since variations in amplitude and linewidth, and behavior under saturation and annealing, seem to exclude the possibility of any pair of lines forming a spin-1 center. However, because of the weakness and overlap of some of the lines, definite conclusions can not be made until measurements are performed at different microwave frequencies.

It was not possible to carry out accurate saturation measurements over a wide range of microwave power. Measurements attempted under fast-passage conditions indicate that T_1 is under 0.01 sec at 4.2°K for lines X_1 and X_2, the only lines observed under these conditions. A relative indication of where the lines begin to saturate is given in Table I. It is seen that T_1 is shorter than 0.01 sec for all lines, with the probable exception of X_5.

Lines X_3, X_4, and X_6 were not observed in the undoped sample. These lines were relatively weak and may have been present but masked by noise. Lines X_2, X_5, and X_7 were observed in resonance measurements made at 77°K as well as at 4.2°K.

IV. DISCUSSION

An analysis of the g shift and the trapping behavior is not sufficient to give a definite microscopic model of the Ge–$P1$ center. However, the results are suggestive. Probably the simplest paramagnetic configuration, consistent with the symmetry of the g tensor, is that of an electron in an antibonding orbital formed between two broken-bond orbitals oriented toward the center of a tetrahedron from its corners. Two simple defects which fit this condition are the isolated vacancy in a negative charge state and the oxygen-vacancy complex.[1] The latter possibility is ruled out by the purity of the crystal. The vacancy leaves four broken bonds pointing in ⟨111⟩ directions (toward the center of the tetrahedron). As shown in Fig. 4(a), they pair off in bonding orbitals between the remaining Ge atoms. The system becomes paramagnetic when an electron is added or removed. The vacancy in a positively charged state is ruled out here because it should result in a g tensor axially symmetric along a ⟨100⟩ direction.[18] The negatively charged vacancy has the desired symmetry, but with such a model it is difficult to explain the small hole capture cross section which results in the long lifetime of the trap-filled state of the defect. This model is examined more closely in the Appendix.

It seems unlikely that the Ge–$P1$ spectra can arise from an isolated interstitial because such a model does not appear to account for the symmetry of the g tensor. One model, which might have the trapping features observed, as well as the required symmetry, is that of a vacancy and interstitial separated by a few lattice spaces. (A close pair would probably recombine at the temperatures involved.) Such a defect, taken as a whole, might be positively charged in its paramagnetic state, thus providing a small-hole capture cross section. Its wave function would presumably be spread over many lattice sites. Further speculation must await more detailed experimental findings.

The Ge–$P1$ resonance line is inhomogeneously broadened,[19] as seen by the observed Gaussian shape of the line. The linewidth is isotropic, which suggests there is little contribution from local strains. Presumably the linewidth arises from unresolved hyperfine interactions of the defect electron with the Ge^{73} isotope,[17] which has spin $\frac{9}{2}$ and is 7.8% abundant. An average electron will interact with many such randomly located nuclei, each having 10 possible spin orientations. The excessive linewidth and the Gaussian shape indicate that the defect electron interacts quite strongly with magnetic nuclei at many sites. It is possible that

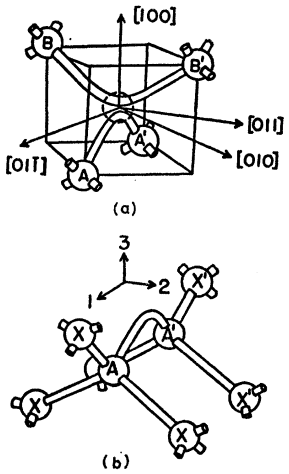

FIG. 4. Germanium lattice. (a) Primative cell showing tetrahedral bond arrangement, with vacancy at center; (b) localized molecule considered in g-shift calculation.

[17] D. K. Wilson, Phys. Rev. 134, A256 (1964).

[18] G. D. Watkins, J. Phys. Soc. Japan 18 II, 22 (1963).

[19] A. M. Portis, Phys. Rev. 91, 1071 (1953).

interactions with nearest neighbors are resolvable with EPR, but lost in noise. The observed linewidths in germanium are about one order of magnitude larger than in silicon.

Further experiments in germanium are needed for a complete interpretation of the structure of the Ge–$P1$ center. Electron irradiation at liquid-helium temperature may give rise to new EPR spectra, and may shed some light on the primary damage processes related to the Ge–$P1$ center. Because of its high degree of symmetry, and its prominence in both electrical and EPR studies in germanium, the Ge–$P1$ center should provide a fruitful topic for research directed toward a more basic understanding of radiation-damage processes in germanium.

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APPENDIX

The model of a negatively-charged vacancy is examined by means of a simplified molecular-orbital treatment,[20] making use of Eq. (2). Referring to Fig. 4(b), we assume that the ground-state wave function of the unpaired electron is completely localized on the $A-A'$ sites, and we consider only the nearest excited states, which are the bonding and antibonding orbitals AX and $A'X'$. We assume that the dangling bonds from the A and X atoms are p in character, and we write the AA' and AX molecular orbitals as linear combinations of these atomic orbitals. All AX bonds are assumed to have equal strength and the AA' bond is assumed weak enough so as to neglect the AA' overlap. Following the procedure of Watkins and Corbett,[8] we arrive at

$$\Delta g_1=\tfrac{1}{3}\lambda(1/E_b-1/E_a),$$
$$\Delta g_2=\lambda(1/E_b-1/E_a),$$
$$\Delta g_3=\tfrac{2}{3}\lambda(1/E_b-1/E_a),$$

where E_b and E_a are the energies to the bonding and antibonding orbitals which lie below and above the level of the unpaired electron, and λ is the spin-orbit interaction constant. In this result the ratios of the g shifts, $\Delta g_1:\Delta g_2:\Delta g_3=1:3:2$, depend only on the angles between principal axes and the direction of the broken-bond A orbital.

The model, as it stands, does not account for the signs and ratios of the g shifts for the Ge–$P1$ center, which are $\Delta g_1\approx+0.023$, $\Delta g_2\approx-0.373$, $\Delta g_3\approx-0.270$. An identical treatment of the localized molecule BB' in Fig. 4(b) gives ratios $\Delta g_1:\Delta g_2:\Delta g_3=3:1:2$, which are in poorer agreement. If the A and A' atoms were assumed to pull together into the vacancy to any extent, the broken-bond A orbital would tend to point toward A', and the present treatment of the AA' molecule would predict a smaller g shift along the 1 axis together with larger shifts, of nearly equal magnitude, along the 2 and 3 axes. This improvement is in the right direction, since the ratios approach $\Delta g_1:\Delta g_2:\Delta g_3=0:1:1$, but there is no positive evidence that the contribution will be large. Within the framework of the present treatment, the assumption of different relative bonding energies for the AX orbitals will affect only the magnitude, and not the ratios, of the g shifts. Similarly, had we assumed a partial s character of the atomic orbitals, only the magnitude and not the ratios would be changed.

The magnitude of the g shift can be accounted for in a reasonably satisfactory way by the present simplified treatment. The predominantly negative g shift expresses the fact that the unpaired electron interacts more strongly with the antibonding AX orbitals than with the bonding ones. This is reasonable because the energy level of the Ge–$P1$ center is thought to lie near the conduction band. If we assume $E_a\ll E_b$, then the maximum g shift will be given by $g\approx-\lambda/E_a$. The spin-orbit coupling constant for germanium is $\lambda\approx0.12$ eV,[21] and the largest observed g shift is $g_2\approx-0.373$. This is consistent with an energy $E_a\approx0.3$ eV, which may correspond to the conduction-band edge or to a suitable average over the available states in the conduction band.

The magnitudes and signs of the Δg_i could be altered significantly by a more detailed treatment, which took into account the spread of the wave function over nearby sites. Unfortunately, little can be said about the spread of the wave function without resolved hyperfine data. If only a small fraction of the wave function were found to be localized, the above simplified treatment of the negatively charged vacancy would break down.

[20] G. D. Watkins and J. W. Corbett, Phys. Rev. 121, 1001 (1961).

[21] *Atomic Energy Levels*, edited by C. E. Moore, Natl. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).