by the transition from the superfluid to the nonsuperfluid and pointed out that little difference in (the density-density part of) $S(Q, \omega)$ is expected for nonsuperfluid ^{3}He and nonsuperfluid ^{4}He. Comparison of the present results for $T > T_\lambda$ and those reported previously[13] for $T = 2.3$ K with those[14] for nonsuprefluid ^{3}He supports this point of view; except at very low frequencies where spin-spin correlations are important for ^{3}He all of these distributions are similar in shape.

In summary, the description presented in this paper of the temperature dependence of $S(Q, \omega)$ for liquid helium suggests a two-component structure with the two components directly related to the macroscopic quantities ρ_s and ρ_n. At the present time there is, however, no known theoretical relationship between these macroscopic quantities and the microscopic $S(Q, \omega)$.

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Identification of the Isolated Ga Vacancy in Electron-Irradiated GaP through EPR

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An $S = \frac{1}{2}$ EPR spectrum is observed in electron-irradiated GaP:Zn with an isotropic $g = 2.0130 \pm 0.0015$ and resolved ligand hyperfine splitting from four equivalent $I = \frac{1}{2}$ neighbors. This spectrum is assigned to the isolated Ga vacancy. A molecular-orbital model for V_{Ga}^{--} is consistent with the experimental data. Analysis of the hyperfine parameters reveals some lattice relaxation although the full T_d symmetry is maintained.

Although electron paramagnetic resonance (EPR) has been successfully used to investigate vacancies in Si[1,2] and in the more ionic II-VI compounds[3-5], the current knowledge of the structure of native defects in III-V semiconductors is limited because of the lack of EPR results. The lack of EPR data is mainly due to large linewidths arising from hyperfine (hf) interactions with the group III and V nuclei, most of which have high nuclear spins. The only reported EPR identification of a native defect in a III-V semiconductor is that of P on a Ga site in GaP—an antisite defect.[6]

In this Letter, we report the observation of an

EPR spectrum in electron-irradiated GaP which, from its g value and resolved hf splitting, can be assigned to the isolated Ga vacancy (V_{Ga}). This spectrum indicates that the vacancy retains the full tetrahedral symmetry of the Ga site. A molecular-orbital model is presented which shows that the vacancy in its doubly negative charge state is consistent with the experimental observations. These results constitute the first microscopic identification of a vacancy and of a radiation-induced defect in a III-V semiconductor.

Samples of p-type (Zn-doped), undoped, and n-type (S- and Te-doped) GaP were cut into slabs $0.5\times 3\times 20$ mm^3 with the $[1\bar{1}0]$ axis along the 20-mm dimension. The room-temperature irradiations were performed with 2-MeV electrons at the Naval Research Laboratory Van de Graaff accelerator to fluences in the range $(0.2-2.0)\times 10^{17}$ e/cm^2.

No EPR is observed in the Zn-doped samples prior to irradiation. For fluences greater than 3×10^{16} e/cm^2, a weak Fe ($3d$) spectrum[7] emerges. When these samples are illuminated with near-band-gap light, a new, orientation-dependent spectrum appears (see Fig. 1). For a similar electron fluence and following optical excitation, the same spectrum is seen in an undoped GaP sample. The n-type samples exhibit a post-irradiation spectrum characteristic of an electron localized about a central phosphorus atom and interacting with three neighboring phosphorus atoms, a P-P_3 complex.[8] Following band-gap light excitation, the P-P_3 spectrum is unchanged and the spectrum of Fig. 1, if truly present, is much weaker than in the p-type and undoped samples.

The spectra of Fig. 1 exhibit moderately well-resolved hyperfine (hf) splittings and contain a center of symmetry which is independent of the direction of $\vec{H}$ to within experimental error. Thus at 77 K the center has an isotropic g factor with value $g=2.016\pm 0.002$. With $\vec{H}\parallel[001]$, the spectrum consists of five lines with intensity ratios 1:4:6:4:1, characteristic of the interaction of a spin-$\frac{1}{2}$ center with four equivalent spin-$\frac{1}{2}$ nuclei.

In order to account for the anisotropy of the splittings, we postulate the spin Hamiltonian

$$H=g\mu_B\vec{H}\cdot\vec{S}+\sum_{l=1}^{4}\vec{S}\cdot\vec{A}^l\cdot\vec{I}^l, \qquad (1)$$

with the first term describing the Zeeman interaction for the spin-$\frac{1}{2}$ electron and the second term describing the ligand hf interaction with the four

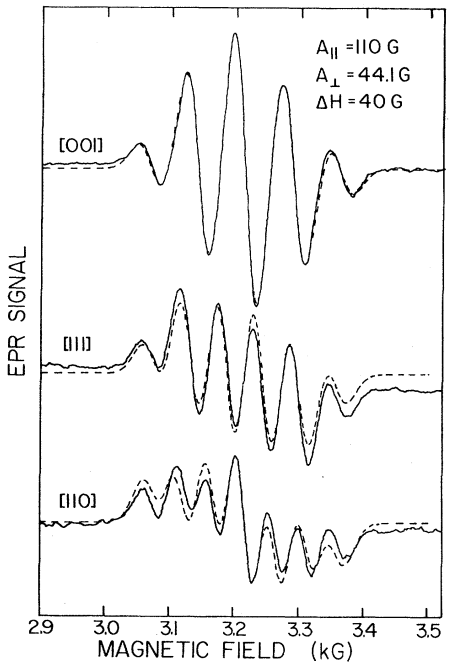

FIG. 1. EPR in electron irradiated GaP:Zn at 77 K for $\vec{H}$ parallel to the directions indicated. The solid line depicts the data. The dotted line is a simulation of the spectrum using the spin-Hamiltonian parameters shown in the upper right.

^{31}P ($I=\frac{1}{2}$) neighbors. In the strong-field case ($A_{\parallel}, A_{\perp} \ll g\mu_B H$) and with each hf interaction axially symmetric (along its [111] bond axis), transitions occur with energy given by

$$h\nu = g\mu_B H_0 + \sum_{l=1}^{4} m_l (A_{\parallel}^2\cos^2\varphi_l + A_{\perp}^2\sin^2\varphi_l)^{1/2}, \qquad (2)$$

with $m_l=\pm\frac{1}{2}$ and φ_l the angle between $\vec{H}$ and the lth bond direction. For an arbitrary value of φ_l, sixteen transitions are possible. Degeneracies occur along high-symmetry directions with additional accidental degeneracies possible depending on the values of $A_{\parallel}$ and $A_{\perp}$. The shifts from $\vec{H}=\vec{H}_0$ as a function of the angle θ between $\vec{H}$ and the [001] axis in the $(1\bar{1}0)$ plane are presented in Fig. 2. The values $A_{\parallel}=(104\pm 3)\times 10^{-4}$ cm^{-1} and $A_{\perp}=(41.5\pm 1.5)\times 10^{-4}$ cm^{-1} were used in calculating the field splittings and give, with a 40-G linewidth, the best simulation of the experimental data as shown in Fig. 1. The expected five-line spectrum occurs for $\vec{H}$ along [001] but accidental degeneracies lead to six lines instead of eight with $\vec{H}\parallel[111]$ and seven instead of nine with $\vec{H}\parallel[110]$.

The analysis and fit to the data show that the spectrum arises from a spin-$\frac{1}{2}$ center at a tetra-

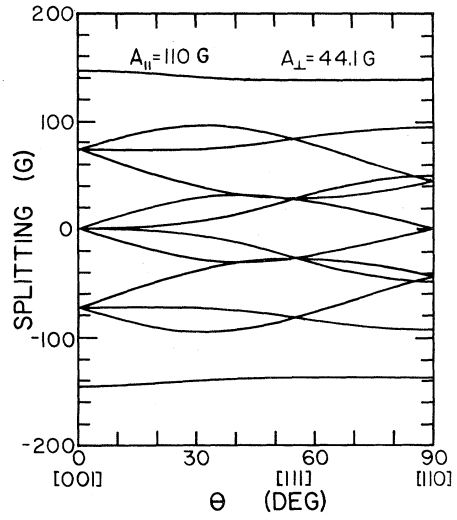

FIG. 2. EPR line positions as a function of angle in the $(1\bar{1}0)$ using the spin Hamiltonian given in the text with the hf parameters indicated.

hedral site surrounded by four ^{31}P atoms. Two such sites exist in the GaP lattice: the Ga site and an interstitial site. The hf constants can be written in terms of an isotropic contribution $a = (A_{\parallel}+2A_{\perp})/3 = 62\times10^{-4}$ cm^{-1} and a dipolar contribution $b = (A_{\parallel}-A_{\perp})/3 = 20.8\times10^{-4}$ cm^{-1}. The large dipolar component indicates substantial p-like character of the wave function of the defect, signaling broken bonds. The direction and magnitude of the shift in g from the free-electron value are also consistent with a center involving broken bonds[9] and the experimental values observed for V_{Zn}^{-} in zinc selenide[4] and for V^{+} and V^{-} in silicon.[1,10] The spectrum is therefore not what is expected for a pure (unbonded) interstitial atom. Any bonded interstitial configuration would have a symmetry lower than T_d. Thus all interstitials are ruled out and the spectrum arises from either an impurity on the Ga site or the Ga vacancy. Boron and carbon are common impurities which substitute for Ga. Both isotopes ^{10}B and ^{11}B have nuclear spins which would give rise to a central hyperfine interaction and splitting. Carbon is a shallow donor and would give rise to different EPR. From the evidence of p character in the hf constants and the g shift and from the isotropy of the g value, the spectrum is assigned to the isolated Ga vacancy.

Molecular-orbital (MO) models have been used successfully to describe the simple defects in irradiated Si.[9] By analogy with the Si case, we construct a wave function from the four hybrid atomic orbitals which project into the vacancy. Overlap among the orbitals leads to removal of degeneracy and results in the formation of a triplet, t_2, and a singlet, a_1, neglecting spin. The triplet is expected to be lower in energy than the singlet to conform to the ionic limit of surrounding negative charge.[11] These states are filled with the available electrons.

In the covalent limit the gallium vacancy results from removing neutral Ga from the lattice and leaving a neutral V_{Ga}^{0} with five electrons in broken-bond states. The ionic limit would be described by removal of a Ga^{3+} ion to form V_{Ga}^{---} with eight electrons in broken-bond states. Only states of zero or small charge are expected. The most likely charge states for partially ionic GaP are therefore, V_{Ga}^{0}, V_{Ga}^{-}, and V_{Ga}^{--} with five, six, and seven electrons, respectively. The five-electron neutral state is expected to give an EPR signal. Since with five electrons the t_2 level is partially filled, this configuration is Jahn-Teller (JT) unstable and a distortion to a symmetry lower than T_d is expected. Both the V_{Ga}^{-} and the V_{Ga}^{--} states are stable with T_d symmetry since the triplet level is filled. The V_{Ga}^{-} center with six electrons would give no EPR signal, while the V_{Ga}^{--} center with one electron in the singlet a_1 state would produce an $S=\frac{1}{2}$ EPR with isotropic g value.

The doubly negative charge state is entirely consistent with the experimental EPR spectrum. However, it is also possible that the spectrum observed at 77 K is a motional average of a set of anisotropic spectra appropriate to a lower-symmetry, neutral vacancy. That is, the system may be in the dynamic Jahn-Teller limit at 77 K. Experiments at 4.2 K at 25 GHz were performed to determine whether a static distortion occurs. The isotropic vacancy spectrum was again observed with $g = 2.0130 \pm 0.0015$, identical hf parameters, and the same linewidth. This result is strong evidence for the doubly negative charge state.

Analysis of the hf interaction parameters in the MO model[9] provides a detailed description of the defect. With the wave function for the unpaired spin written as $\psi = \sum \eta_j \psi_j$ where the summation is taken over the four nearest neighbors, η_j^2 gives the fraction on each neighbor, and ψ_j is the atomic wave function $\psi_j = \alpha_j(\psi_{3s})_j + \beta_j(\psi_{3p})_j$, the isotropic (a) and dipolar (b) parts of the hf interaction can be used to evaluate η_j, α_j, and β_j. Making use of calculations of $|\psi_{3s}(0)|^2$ and $\langle r_{3p}^{-3}\rangle$ for ^{31}P by Watkins and Corbett[9] from wave functions of

Watson and Freeman,[12] we obtain the s part $\alpha_j^2 = 0.08$, the p part $\beta_j^2 = 0.92$ with 80% of the total wave function accounted for on the four nearest-neighbor P atoms. In the perfect lattice the bonding is tetrahedral sp^3, i.e., 0.25 s-like and 0.75 p-like. Thus, while the data indicate *no distortion* from T_d symmetry at the Ga site, there is evidence for *lattice relaxation* of each neighbor to more sp^2 (planar) bonding with the three remaing Ga neighbors with a predominantly p orbital left in the broken bond.

Electrical properties of radiation-induced defects in GaP have been studied by dc transport[13] and deep-level transient spectroscopy.[14] Infrared absorption[15] and luminescence[16] have also been studied. The vacancy may be a nonradiative center which degrades the performance of light-emitting diodes. Correlations between EPR and these other techniques are planned to shed light on these issues.

In conclusion, the Ga vacancy in electron-irradiated GaP has been identified through EPR. At 77 and 4.2 K, it exhibits some lattice relaxation but retains the full T_d symmetry of the lattice site. The EPR-active charge state is doubly negative.

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Acceleration of Electron-Hole Drops in Germanium by a Radiation Field: Evidence for Phonon Wind

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By heating the droplet cloud in Ge with infrared radiation, we increase the low-frequency phonon emission rate of the droplets. By measuring the resulting velocity increase, we give convincing evidence that this "phonon wind," powered by Auger decay, is the cause of droplet motion, as originally proposed by Keldysh.

The subject of the interaction of electron-hole drops (EHD) with acoustic phonons in Ge was initiated by Keldysh[1] and expanded theoretically[2-5] and experimentally[6-9] by many authors. It is now well established that this interaction with low-frequency phonons ($|q| \leq 2k_F$, where k_F is the Fermi wave vector of the liquid) is the main determinant of droplet motion. For example,