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EPR OF THE LITHIUM ION-DANGLING BOND COMPLEX IN GERMANIUM CONTAINING DISLOCATIONS

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(Received)

We have observed a new EPR spectrum in a lithium-diffused germanium crystal ($N_D - N_A \approx 10^{13} \text{ cm}^{-3}$) containing dislocations. The principal g values are 1.917 ± 0.002 , 1.896 ± 0.002 , and 0.855 ± 0.010 along the axes $\langle 1\bar{1}0 \rangle$, $\langle 11\bar{2} \rangle$, and $\langle 111 \rangle$, plus equivalent sets. As this new spectrum is seen in lieu of the dislocation dangling bond spectrum, we attribute it to a lithium ion-dislocation dangling bond complex.

The behavior of lithium in Ge is of both technological and fundamental interest and has been studied in some detail.¹⁻⁵ Lithium is a shallow donor, and as an interstitial impurity it diffuses rapidly. It can also be trapped at defects to form shallow donor complexes (for example, LiO). Reiss *et al.*¹ postulate ion pairing between lithium ions and acceptor sites in dislocations. We report here a new EPR spectrum in lithium diffused dislocated Ge, at liquid helium temperatures, which we attribute to such a complex, where the acceptor sites are the dislocation dangling bonds (DDB).

The apparatus used was a helium cooled microwave (22-26 GHz) superheterodyne spectrometer with an optical port and helium cooled shutter. Magnetic field modulation and lock-in detection were used to record the derivative of the absorption signal. Two samples, one dislocation free and one containing dislocations ($\geq 10^3 \text{ cm}^{-2}$), were cut in the shape of right circular cylinders, 12.5 mm in diameter and 8-10 mm in height (axis along $\langle 110 \rangle$). The samples were saturated with lithium by diffusion from the surface at 400°C. The lithium was then out-diffused for several days at 200°C until a net donor concentration of $\approx 10^{13} \text{ cm}^{-3}$ was achieved. After the out-diffusion virtually all the free lithium has left the crystal and one is left with lithium bound at defects. Each sample in turn was etched, mounted in the spectrometer cavity, and cooled to liquid helium temperature. At $T \approx 4\text{K}$ the Ge sample serves as its own microwave resonant cavity with a high quality factor $Q \approx 10^5$.^{5,6}

The crystals had oxygen concentrations $\approx 10^{14} \text{ cm}^{-3}$, so some of the lithium was present in the form of the LiO complex. This complex gives rise to an EPR spectrum⁵ with a g-tensor axially symmetric about the four $\langle 111 \rangle$ axes. The principal g values are $g_{\parallel} = 0.85$ and $g_{\perp} = 1.91$. This four-line spectrum is the only lithium related spectrum observed in the lithium diffused dislocation free sample.

The dislocated sample had additional lines (≈ 14 g peak-to-peak derivative width), due to lithium at dislocations, superimposed on the four LiO lines. The angular dependence of the combined spectrum, as the magnetic field is rotated in a plane close to (110) , appears in Figure 1. The figure also shows computer simulated spectra for LiO (dashed) and for Li at dislocations (solid). The simulations were done

for perfect crystal alignment and were based on the effective spin Hamiltonian

$$\mathcal{H} = \beta \vec{H} \cdot [\vec{g}_{\text{LiO}} + \vec{g}_{\text{d-Li}}] \cdot \vec{S},$$

where β is the Bohr magneton, \vec{H} the magnetic field, and \vec{S} the spin (the same effective spin, $S=1/2$, was used for both centers). \vec{g}_{LiO} is the spectroscopic splitting tensor for the LiO complex and has the principal g values quoted above. $\vec{g}_{\text{d-Li}}$ is the spectroscopic splitting tensor for the Li-dislocation complex and was selected in such a way as to best reproduce the data. $\vec{g}_{\text{d-Li}}$ has principal g values $g_1 = 1.917$, $g_2 = 1.896$, and $g_3 = 0.855$, and principal axes $\vec{g}_1 = \langle 1\bar{1}0 \rangle$, $\vec{g}_2 = \langle 11\bar{2} \rangle$, and $\vec{g}_3 = \langle 111 \rangle$ (plus equivalent sets). Note that $\vec{g}_{\text{d-Li}}$ deviates by only $\sim 1\%$ from being axially symmetric about the $\langle 111 \rangle$ axes. For each of the four $\langle 111 \rangle$ axes (i.e. \vec{g}_3) there are three $\langle 110 \rangle$ directions lying in the corresponding $\langle 111 \rangle$ plane, and \vec{g}_1 can be along any of these three $\langle 110 \rangle$ directions. \vec{g}_2 also lies in the plane and is perpendicular to \vec{g}_1 . Consequently, the spectrum resulting from $\vec{g}_{\text{d-Li}}$ consists of four branches of three lines each, or 12 lines. For \vec{H} restricted to the $\langle 110 \rangle$ plane, degeneracies reduce this number to seven lines. In practice, a slight misorientation of the sample can break some of the degeneracies and result in more than seven lines. These are, of course, in addition to the four LiO lines.

Recalling that dislocation lines in the tetrahedral structure are oriented along $\langle 110 \rangle$ directions,⁷ we see that the departure of the $\vec{g}_{\text{d-Li}}$ tensor from axial symmetry is correlated to the directions of dislocation lines. If we consider in particular the 60° dislocation of the shuffle set, Figure 2, then \vec{g}_1 is parallel to the dislocation line, \vec{g}_3 is parallel to the DDB's, and \vec{g}_2 is perpendicular to \vec{g}_1 and \vec{g}_3 .

A previous paper⁶ reported the observation of the spin resonance of the Ge DDB electrons. The DDB g -tensor is axially symmetric about the $\langle 111 \rangle$ axes tilted by 1.2° along the $\langle 110 \rangle$ directions and has principal g values $g_{\parallel} = 0.73$ and $g_{\perp} = 1.89$. We did not observe the DDB spectrum in the lithium diffused Ge sample containing dislocations. In order to explain the absence of the DDB spectrum and the appearance of the d-Li spectrum, we propose a model in which lithium ions form a complex with the DDB's. The complexing of the Li to the DDB could also account for the suppression of the 1.2° tilt of the DDB, resulting instead in the 1% nonaxiality of the

g-tensor. One might have expected an atomic Li-DDB complex in which the Li saturates the dangling bond. In such a case, however, one would have an $S = 0$ configuration and no EPR signal.

An interesting feature arises when one considers the neutral configuration of the Li ion-DDB complex, in which an electron is shallowly bound in some roughly hydrogenic orbit. Rather than being distributed throughout the bulk of the crystal, these donors are lined up along the dislocations, where even at concentrations below 10^{12} cm^{-3} considerable overlap of the donor electron wave functions occurs, resulting in a conducting path along the dislocations. (As in the case of dislocated Si, where the microwave conductivity was found to be seven orders of magnitude larger than the D.C. conductivity,⁹ we expect this conductivity to be most pronounced at high frequencies, due to kinks and/or other breaks in the translational symmetry along the dislocations.) Supporting this model is our observation of an electron cyclotron resonance signal for the optically shielded dislocated sample comparable to that for the optically pumped dislocation-free sample. The shallow donor electrons are evidently being accelerated along dislocations by the microwave electric field until ionization into the conduction band takes place.

The presence of mobile electrons at the dislocations would open up the possibility for spin dependent scattering of those electrons by the Li ion-DDB complex, similar to the previously reported⁶ spin dependent scattering of photo-excited electrons by dangling bonds in dislocated Ge. In the latter case, the spin resonance of the DDB electrons was electrically detected, i.e., the magnetic dipole transition triggered a change in conductivity which resulted in an observable change (both increases and decreases were seen, depending on the sample) in absorption of energy from the microwave electric field. We cannot rule out the possibility that the d-Li spectrum has also been electrically detected (although only increases in absorption were observed), particularly in view of the small number of spins involved which, considering the number of lines and their width, would be difficult to detect using conventional EPR magnetic dipole transitions.

In summary, we have found that when lithium is diffused into a Ge crystal containing

dislocations, a new EPR spectrum emerges. This new spectrum is not observed in a lithium-diffused, dislocation-free crystal. The principal axes of the g-tensor correspond to the orientation of dislocation lines and their dangling bonds. The DDB EPR spectrum seen in ultrapure dislocated Ge is not observed in the lithium-diffused sample. The simple model of a lithium ion-DDB complex is consistent with all of our observations. Electrons are apparently so shallowly bound to these ions that they are easily promoted by the microwaves into the conduction band, resulting in a strong electron cyclotron resonance signal in the absence of optical excitation.

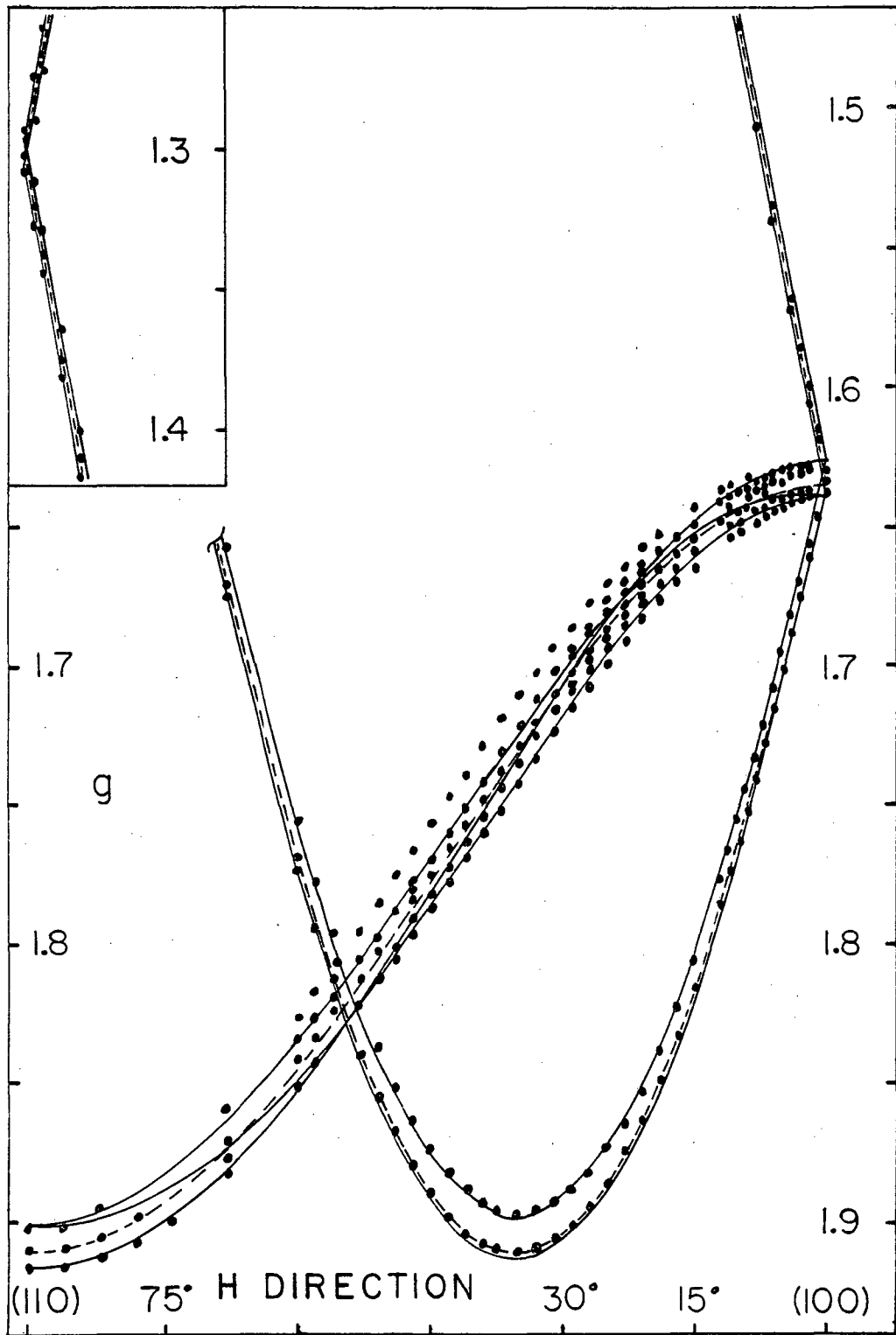
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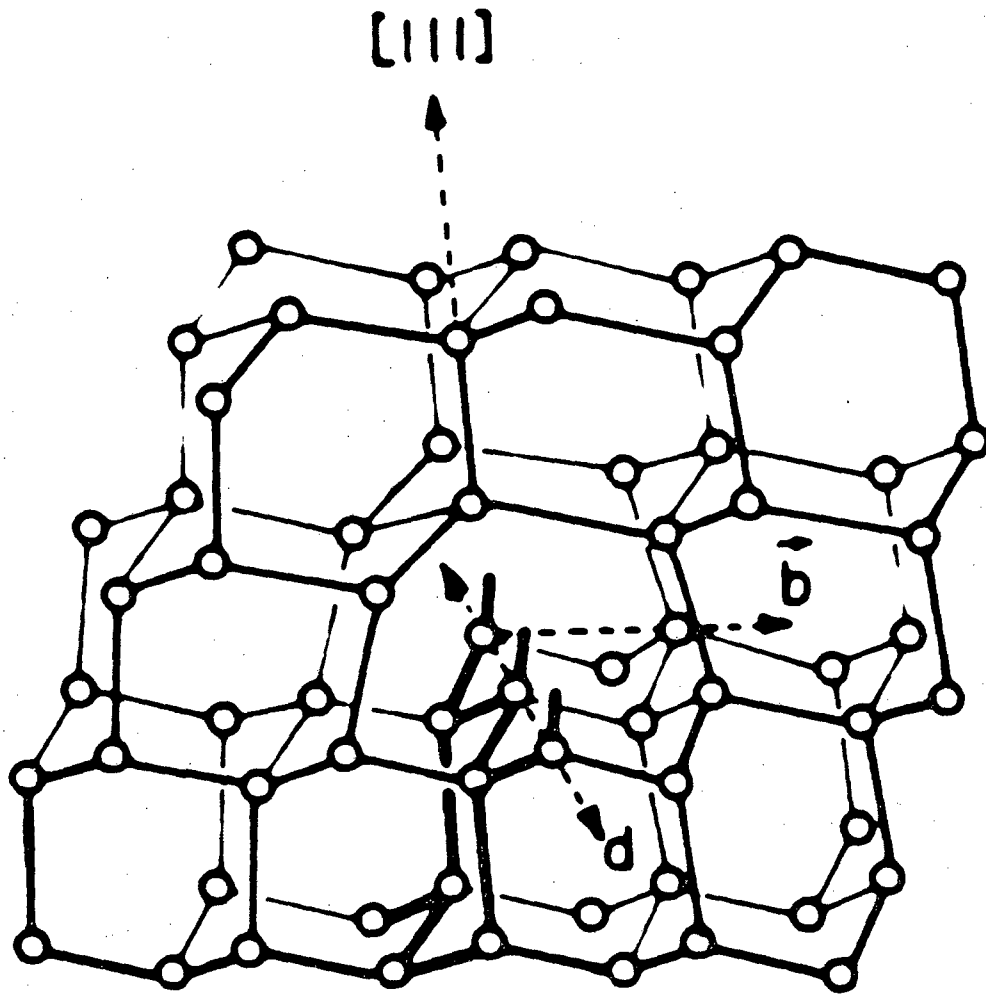
Figure 1 - Angular dependence of the EPR lines observed for the lithium-diffused Ge sample containing dislocations as the magnetic field is rotated in the approximate (110) plane. Insert shows the continuation of the lines for low values of g near $\langle 110 \rangle$. $N_D - N_A \approx 10^{13} \text{ cm}^{-3}$. Dislocation density $\approx 10^3 \text{ cm}^{-2}$. $T = 2\text{K}$. $f = 23.49 \text{ GHz}$. Points are measured values. Lines are computer simulations based on perfect crystal alignment and g values quoted in the text. Solid lines: lithium at dislocations. Dashed lines: LiO complex. The size of the deviation from calculations is consistent with a misorientation $\approx 1^\circ$. Note that lines degenerate for perfect alignment can become resolved for other orientations.

Figure 2 - Germanium crystal structure including one 60° -dislocation line, d , with its row of dislocation dangling bonds, and Burgers vector, \vec{b} . See Reference 8.



XBL 826-10393

Fig. 1



XL 819-6501

Fig. 2

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