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HIGH-RESOLUTION EPR AND PIEZOSPECTROSCOPY STUDIES OF THE LITHIUM-OXYGEN DONOR IN GERMANIUM

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HIGH-RESOLUTION EPR AND PIEZOSPECTROSCOPY STUDIES OF THE LITHIUM-OXYGEN DONOR IN GERMANIUM

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Lithium-oxygen donors in germanium were studied at low concentration ($<10^{14}$ cm^{-3}) by means of Electron Paramagnetic Resonance and Photoelectric Piezospectroscopy. We find unambiguously four equivalent real-space positions with <111> symmetry, which together with the four-valley conduction band lead to a 16-fold ground state. The system exhibits dynamic tunneling between the four equivalent orientations.

Lithium -- a technologically important impurity in germanium devices [1,2] -- has yielded results in IR Absorption[3] and Photoelectric Spectroscopy[4] experiments which have been controversial. The Li and Li-O donors in Si, on the other hand, [3,5] are well understood.

We have studied the Li-O-donor in Ge using improved EPR techniques and high-resolution Photoelectric Spectroscopy. The investigated Ge samples originated from ul ra-pure single crystals[6] ($|N_A - N_D| < 10^{11}$ cm^{-3}) which were doped with lithium via diffusion at temperatures between 200°C and 400°C. The crystals contain typically 10^{14} oxygen atoms/cm^3.

The EPR studies were performed with a 24 GHz heterodyne spectrometer[7] at operating temperatures ~2K. Modes with $Q > 5 \cdot 10^5$, insensitive to tuning and extremely stable were used. As few as 10^{13} Li-O-donors could be observed with signal to noise ratio of ~100.

The spectrum for magnetic fields in the $(1\bar{1}0)$ plane consists of one double and two single lines. A typical experimental curve is shown in Figure 1. The g-factors for $\vec{H}_m$ $(1\bar{1}0)$ are shown in Figure 2. A theoretical fit to the data yields donors with <111> type symmetry, and with $g_\perp = 1.9040 \pm 0.0010$.

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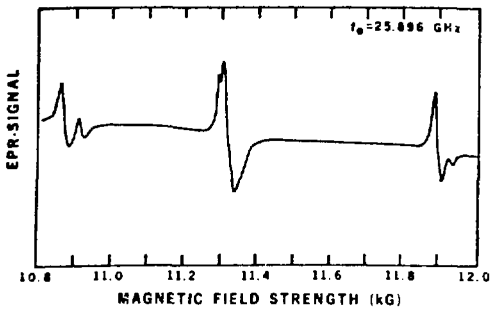

Figure 1. Typical EPR spectrum of the Li-O donor in Ge.

and $g_{\parallel}$ = 0.8585 ± 0.0010.

Attempts to saturate the Li-O EPR lines failed due to ionization of the donors; this is seen by a rapid increase in the free-electron cyclotron line intensities. Under these circumstances ENDOR experiments are impossible.

Photoelectric piezospectroscopy was performed using a Fourier transform IR-spectrometer. High resolution was achieved by keeping the Li concentration below 10^{13} cm^{-3}. Figure 3 shows two spectra at T = 6.5K with and without stress. Both spectra show "hydrogenic" character[8]. A series of spectra at intermediate stress shows that the broad features at ~62 and 67 cm^{-1} in the zero stress spectrum develop continuously into the two sharp lines at

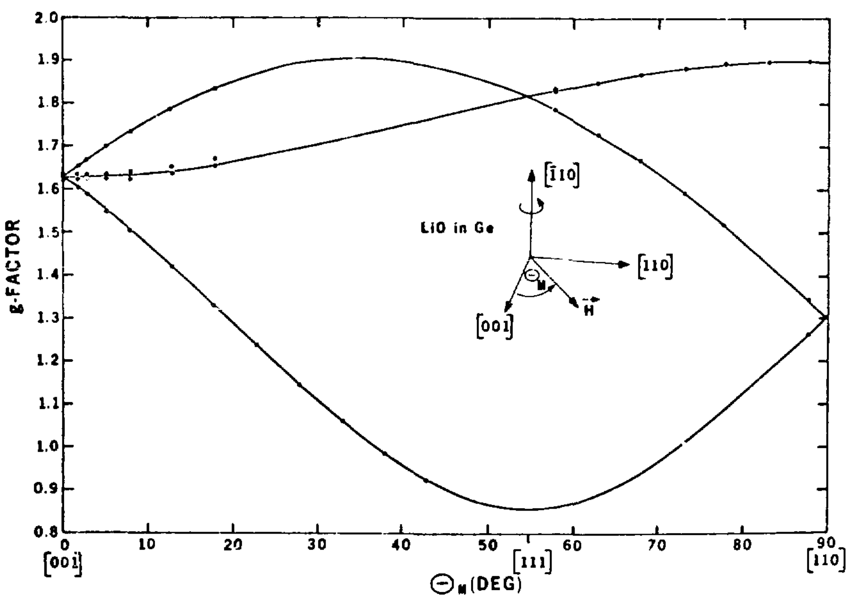

Figure 2. The g-factors of the Li-O donor in Ge.

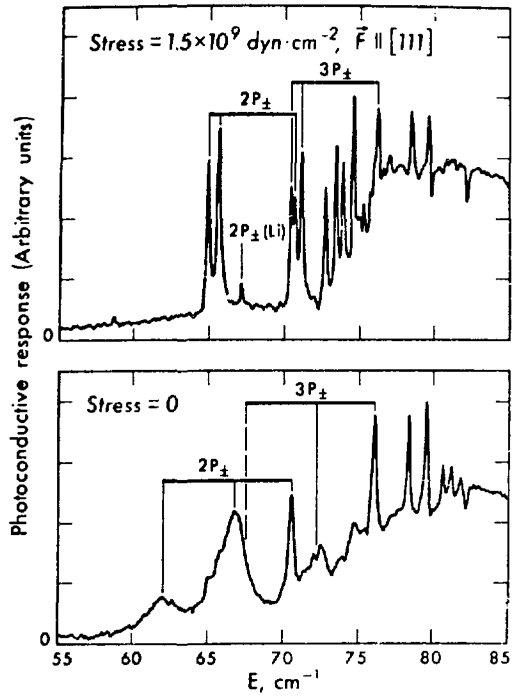

Figure 3 (above, left). Photoelectric spectrum of the Li-O-donor in Ge at T = 6.5K.

~65 and 66 cm^{-1} in the high stress limit. The sharp line at ~70.5 cm^{-1} does not change its position under stress.

The weak line at ~67 cm^{-1} at high stresses and its hydrogenic partners are the only ones due to free Li donors: they are very sensitive to total Li and O concentrations and they increase rapidly when $N_{Li} > N_O$. At low stresses the 67 cm^{-1} line blends into Li-O broad lines.

The EPR and IR spectra of Li-O can be interpreted unambiguously in terms of donors with axial symmetry along <111> -- e.g. a diatomic complex oriented along <111> axes -- which tunnels between all four possible real space orientations.

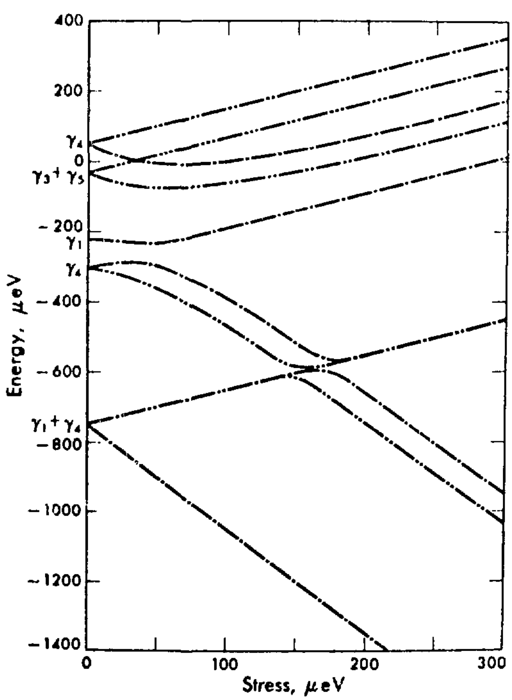

Figure 4 (below, left). The energy levels of the Li-O-donor ground manifold as a function of stress. Degeneracy is shown by the number of dots.

Figure 4 shows the eigenvalues of the 16-fold ground-state multiplet as a function of stress[9]. This degeneracy arises from the 4 real-space orientations and the 4-valley degeneracy of the Ge conduction band.

In summary we have observed an electronic effect caused by a dynamic tunneling of the nuclei of the Li-O complex. This model, including the high multiplicity and the tunneling, explains the puzzling features of previous work [3,4] and eliminates the discrepancies found in the interpretation of the data.

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