unaffected by density-of-states effects at the higher magnetic fields. A detailed analysis of these effects is complicated by energy level broadening and the fact that, for the range of absorption constants involved  $(\alpha \approx 20 \text{ cm}^{-1})$ , the absorption edge probably involves nonvertical transitions.<sup>5</sup>

The discrepancy between the experimental value for  $\gamma$  in the linear high-field region and the theoretical value for the simple model, may be due to a number of other effects: (1) Zeeman splitting of the valence band which is believed to be either p-like or d-like in character. (2) Second-order interactions between the various branches of the valence and conduction bands which may produce displacements of the top of the valence band and the bottom of the conduction band relative to one another<sup>6</sup> and which may result in a modification of the energy surfaces in the presence of a magnetic field.<sup>7</sup> (3) Spin-orbit interaction effects in the conduction band which may produce displacements in the lower magnetic levels so that they do not occur at positions predicted by the simple model.<sup>8</sup>

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## Structure Sensitivity of Cu Diffusion in Ge

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WE have observed a striking dependence of the diffusion of Cu in Ge upon the structural perfection of the Ge. Electrical-conductivity and radio-tracer (Cu<sup>64</sup>) studies have been made on Ge samples into which Cu was diffused from a  $Cu(NO_3)_2$ coated surface for 15 minutes at  $\sim$ 710°C in H<sub>2</sub>. The distance  $x_d$  from the surface at which the Cu concentration had dropped to  $C_s/2$ , where  $C_s$  is the concentration at the solubility limit for 710°C, varied from  $\sim 0.004$ 

cm in our most structurally perfect samples to >0.20cm in samples containing multitudes of small-angle grain boundaries. Samples with large numbers of dislocations  $(10^4 - 10^6/\text{cm}^2)$ , resulting from deformation at elevated temperatures, had  $x_d$ 's between these limits. We have found that a good correlation exists between the rapidity of the Cu penetration and etch pit densities as brought out with CP4 and Superoxol (1 part 49% HF: 1 part 30%  $H_2O_2$ ) on (111) planes. We have found no such correlation with very tiny etch pits brought out on (100) planes by slow etching, using a method reported by Ellis.<sup>1</sup>

If one assumes that the Cu transport obeys the usual laws of diffusion, then  $x_d \simeq (Dt)^{\frac{1}{2}}$ . For t=15 min and  $T=710^{\circ}$ C, one obtains  $D\sim 2\times 10^{-8}$  cm<sup>2</sup>/sec for the most structurally perfect specimens and  $D>4\times10^{-5}$  $cm^2/sec$  for the samples containing the small-angle boundaries. These values are to be compared with previously reported<sup>2</sup> results giving  $D \sim 4 \times 10^{-5}$  cm<sup>2</sup>/sec in this temperature range. However, we do not feel that it is possible to assign values to the diffusion coefficient on this basis. More extensive measurements have shown that there are large departures from Fick's second law in this system, and that the mass transport of Cu cannot be characterized by a single diffusion coefficient at any given temperature.

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## Effect of Melting on Positron Lifetime

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**P**OSITRONS annihilating in some liquids and solids exhibit a complex two-photon annihilation lifetime.<sup>1</sup> Experimental and theoretical evidence seems to indicate the following: (1) A certain percentage of positrons form bound states (possibly positronium) prior to annihilation. (2) The shorter lifetime,  $\tau_1$  $(2-3\times10^{-10} \text{ sec})$ , results from free and bound singlet state annihilation, while the longer,  $\tau_2(1-4\times10^{-9} \text{ sec})$ , is a reflection of either (a) conversion from bound triplet to bound singlet states and subsequent  $2\gamma$ annihilation<sup>2</sup> or (b) a pick-off process in which a positron in the triplet bound state annihilates with an overlapping antiparallel atomic electron. Because of the low cross section of the spin flipping processes, the pick-off annihilation should be predominant.

The rate of triplet decay via  $\tau_2$  is apparently orderdisorder-dependent, as indicated by the observed difference in  $\tau_2$  between crystalline and fused quartz.<sup>1</sup> To further examine this dependence, we have measured  $\tau_2$  in the molecular crystal naphthalene, as a function of temperatures extending across the melting point of

<sup>&</sup>lt;sup>7</sup> E. N. Adams, Phys. Rev. 89, 633 (1953). <sup>8</sup> F. Herman (private communication).



FIG. 1. Representative set of delay curves at various temperatures. The 29°C curve shows the analysis of the component lifetime curves. The melting point is at 80.2 degrees.

80.2°C. No attempt has been made to form single crystals, polycrystalline naphthalene being used. The annihilation lifetimes were measured with a Bell and Graham type fast-coincidence circuit, Na<sup>22</sup> being the positron source. The percentage of positrons annihilating in the source holder was estimated to be less than 6%. This estimate was obtained by analysis of curves taken below the melting point with Na<sup>22</sup> deposited directly on naphthalene. Three different samples were run, samples II and III with improved temperature regulation (better than  $\pm 0.1^{\circ}$ C); lifetime delay curves were taken at varying temperatures. Figure 1 shows a set of four representative delay curves, the first of these (29°C) being plotted with its analysis into the two lifetime curves (obtained by the usual folding technique). Figure 2 shows the curve of  $\tau_2$  vs temperature. The points are plotted with errors computed from the least squares fitting of  $\tau_2$  for the individual runs; the larger point-to-point deviations are due to electronics and possibly differences in crystallinity of the naphthalene from sample to sample.



FIG. 2. The curve of  $\tau_2$  vs temperature. The full line is a visual fit to the experimental points. The melting point is 80.2°C.

From these curves we see that below the melting point about 9% of positrons annihilate via a  $\tau_2$  component,  $\tau_2 = 1.14 \times 10^{-9}$  sec, with  $\tau_2$  starting to rise a few degrees below melting and reaching the value of  $\tau_2 = 2.68 \times 10^{-9}$  sec at and above the melting point. The percentage of positrons annihilating with  $\tau_2$ increases sharply from 9% to 29%, the change occurring within 0.2°C of the melting point. The short lifetime,  $\tau_1$ , was of the order of  $(3-4) \times 10^{-10}$  sec for all curves analyzed.

From these measurements we draw the following conclusions:

(a) The capture cross section of positrons into bound states has a sharp increase above melting. Besides the energetics of the capture process (similar to "Ore gap"<sup>3</sup> in gases), there could exist other selection rules (conservation of momentum) that are relaxed upon destruction of long-range order during melting.

(b) Whatever the processes giving rise to triplet decay via  $\tau_2$ , the cross sections of these processes are enhanced in the ordered crystalline state. Since the change in  $\tau_2$  is less sudden than that in the percentage annihilating with  $\tau_2$ , perhaps short-range effects are here more important. The possibility of Van der Waals binding of positronium to the molecules of the crystal<sup>4</sup> could play a role.

We have also observed similar order-disorder effects in Teflon of differing crystallinities; a complete report on this work will follow shortly.

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\* Alfred P. Sloan Research Fellow, 1955–1956.
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## Ground State Energy of Two-Electron Atoms

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HE nonrelativistic energies for the ground states of ions and atoms: H<sup>-</sup>, He, Li<sup>+</sup>, · · · , have been recalculated by means of an electronic computer using 18 and finally 24 terms in the wave functions. Besides terms of the familiar type:  $e^{-s/2}$  times 1, s, u,  $s^2$ ,  $t^2$ ,  $u^2$ , su,  $\cdots$ , up to the fifth and sixth degrees, 4 additional terms:

$$P_1 = \begin{bmatrix} \frac{1}{2}(s^2 + t^2) - u^2 \end{bmatrix} \log s, \quad P_2 = \begin{bmatrix} \frac{1}{2}(s^2 + t^2) - u^2 \end{bmatrix} u/s,$$
  
st<sup>2</sup>/u, and st<sup>4</sup>/u<sup>3</sup>,