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[6]In Ref. 1, Keever, Jaduszliwer, and Paul reported changes in positron intensities for high-yield material like Ni in periods of a few hours after introducing the sample into the vacuum system. Similar behavior for Cu, Ni, Au was observed in our laboratory (Ref. 3) over a period of several days, perhaps because of pumping on the sample at 10^{-7} Torr. However, no significant changes in yield have been observed for any of the low-yield samples reported here over a period of one week in some cases, even though peak shifts associated with baking were very noticeable.
[7]See, for example, *Electronic Density of States*, U. S. National Bureau of Standards Special Publication No. 323, edited by L. H. Bennett (U. S. GPO, Washington, D. C., 1971), pp. 31, 54, 55, 222.

Absolute Conduction- and Valence-Band Positions for Ge from an Anisotropic Model of Photoemission*

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An anisotropic direct-transition model for single-crystal semiconductors is shown to predict the direct-transition features seen in experimental photoemission spectra for Ge(111) for $h\nu \lesssim 20$ eV. By comparing theory with experiment, all the conduction and valence bands at L and X within 1 Ry of the gap are determined. Comparison of experiment with current band models suggests that an $\sim 10\%$ self-energy correction may be needed to describe high-energy optical transitions.

Germanium is a prototype semiconductor for band-structure studies, and a variety of experimental techniques have been applied to the determination of selected aspects of its band structure. These have included optical measurements[1,2] (which determine energy-band separations), photoemission measurements interpreted using symmetry line analyses,[3,4] and photoemission valence-band overviews[5] (which give overall bandwidths).

In spite of the large amount of information represented by the above studies, many significant features of the valence and conduction bands of Ge have remained undetermined. In the present paper, we obtain from photoemission and optical data all the energy-band eigenvalues for Ge at L and at X within ~ 1 Ry of the gap using an analysis which contains two fundamental new results. There is, first, a demonstration that the anisotropy in photoexcited electron transport to and escape through a $\langle 111 \rangle$ cleaved surface is vital for obtaining calculated spectra which replicate experimental spectra for $h\nu \lesssim 15$ eV. Second, experimental band positions are determined by comparing data with features in theoretical spectra which include those which arise from transitions at *general points*[6] in the Brillouin zone (BZ).

Besides our determination of Ge band positions over a wide range of conduction- and valence-band energies, there are three other implications of this work. These are the demonstration that final-state crystal-momentum information is preserved in the transport and escape steps of the photoemission process for cleaved semiconductor surfaces; the observation that direct-transition features are seen in spectra for all $h\nu \lesssim 20$–25 eV; and the realization that a "self-energy" term, e.g., one linear in energy, appears to be needed in the Hamiltonian to produce the proper high-lying conduction-band structure.

Our anisotropic model starts with the energy bands $E_n(\vec{k})$ determined by the $l = 2$ nonlocal pseudopotential described by Phillips and Pandey.[7] This potential has been shown[7] to provide a good description of valence bandwidths and low-lying optical transitions in Ge. Photoemission spectra $P(E_i, h\nu)$ for primary (unscattered) electrons, from states of initial energy E_i, are then calculated using an anisotropic, direct-transition model[8]:

$$P(E_i, h\nu) = K \sum_{n,n'} \int d^3k \{\delta(E_n(\vec{k}) - E_i)\delta(E_{n'}(\vec{k}) - E_i - h\nu)|\vec{P}_{nn'}(\vec{k})|^2\} D_{n'}(\vec{k}) T_{n'}(\vec{k}). \quad (1)$$

Here $\vec{P}_{nn'}(\vec{k})$ is the optical matrix element between initial and final bands of band index n and n', respectively. $D_{n'}$ is an effective escape depth and $T_{n'}$ a transmission probability, both referred to a $\langle 111\rangle$ surface. The constant K is used to normalize to the quantum yield. $P(E_i, h\nu)$ represents collection of *all* emitted electrons (angle-integrated photoemission spectroscopy).

The effective escape depth for the final-state electron is represented by[8]

$$D_{n'}(\vec{k}) \propto \hat{S}_{111}\cdot\nabla_{\vec{k}}E_{n'}(\vec{k})\tau(E_{n'}) = \hat{S}_{111}\cdot\vec{l}(E_{n'}(\vec{k})), \quad (2)$$

where $\hat{S}_{111}$ is a unit vector normal to the $\langle 111\rangle$ surface, $\vec{l}$ is the mean-free-path vector for the final-state electron, and τ is the inelastic scattering time. To obtain the probability of transmission of the final-state Bloch wave through the $\langle 111\rangle$ surface, we sum the probability of transmission of the individual plane-wave components $|\vec{k}+\vec{G}\rangle$ of the pseudo wave function[9]:

$$T_{n'}(\vec{k}) = \sum_{\vec{G}}|C_{\vec{G},n'}(\vec{k})|^2 \times\theta(E_{n'}(\vec{k}) - \hbar^2(\vec{k}+\vec{G})_{\parallel}^2/2m - E_{\mathrm{vac}}). \quad (3)$$

The $C_{G,n'}$ are the plane-wave expansion coefficients, and θ is the usual unit step function. Also, $\vec{G}$ is a reciprocal lattice vector, and E_{vac} is the vacuum level. Equation (3) represents a low-energy electron-diffraction matching condition for a specular surface, with $\vec{k}+\vec{G}$ parallel to the surface being conserved. At a given photon energy, the primary electron spectrum calculated using Eqs. (1)–(3) was added to a secondary (inelastically scattered) electron spectrum calculated in the usual way.[10-12]

Experimental photoemission spectra for cleaved Ge(111), obtained using synchrotron radiation[5,8] for $6.5 \leq h\nu \leq 23$ eV, were compared with theoretical spectra obtained from our anisotropic model.

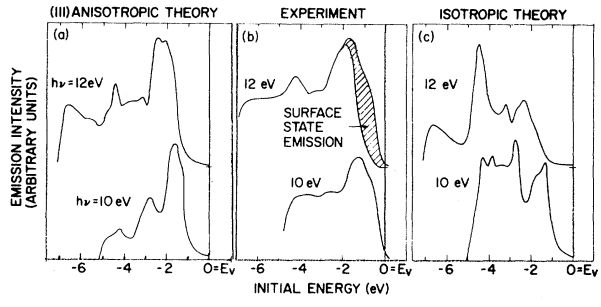

FIG. 1. Comparison of spectra at $h\nu = 10$ and 12 eV. In the 12-eV experimental spectrum, surface-state emission has been subtracted to show the shape of the bulk component alone.

For $h\nu \lesssim 15$ eV, the results for this model were in markedly better agreement with experiment than the results of the usual[10,11] isotropic "three-step model." Figure 1 compares experiment with both models at $h\nu = 10$ and 12 eV, and illustrates that the positions and intensities of peaks in the experiment and anisotropic theory agree well. In contrast, the isotropic model incorrectly produces too many peaks, which occur with rather different relative amplitudes from what are seen in the experiment.

Anisotropic-model spectra are compared with experiment in Fig. 2 for the entire 6.5–23-eV photon-energy range. Prominent peaks in both cases show the changing initial energy versus photon energy characteristic of direct-transition features. Such changing peak positions are indicated using dashed lines and demonstrate the similarity between experiment and theory.[8,13] This similarity will now be utilized to identify the BZ transitions contributing to various experimental peaks.

We start with the eigenvalue ladder at X in the BZ. The most persistent prominent peak in Fig. 2(b) is one which first appears at $E_i \approx -0.8$ eV for $h\nu = 8.5$ eV, then proceeds to lower values of E_i as $h\nu$ increases to 17 eV, and for larger $h\nu$ returns to higher-lying initial energies. At $h\nu = 17$ eV, this peak has reached its maximum ex-

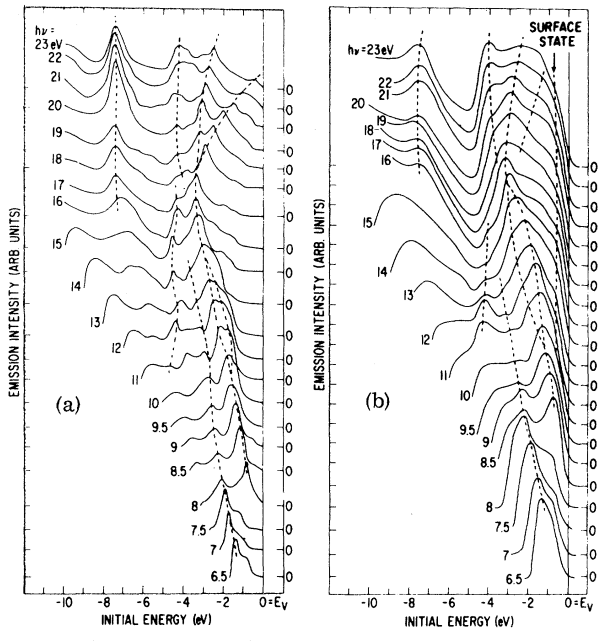

FIG. 2. Emission intensity (arbitrarily scaled) versus E_i for $6.5 \leq h\nu \leq 23$ eV, for (a) the anisotropic direct-transition model and (b) experiment.

TABLE I. Energy-band positions (in eV) for Ge, with $E_v = \Gamma_{25'} \equiv 0$. Error estimate is in parentheses.

$\Sigma_{1\,\min}$[a]	$L_{2'v}$[a]	L_{1v}[a]	$L_{3'v}$[b]	L_{1c}[c]	L_{3c}[b]	$L_{2'c}$[b]
−4.5(0.2)	−10.6(0.5)	−7.7(0.2)	−1.5(0.15)	0.84	4.25(0.2)	7.8(0.6)
L_c^{upper}	X_{4v}[b]	X_{1c}[c]	X_c^{upper}	Γ_{1v}[a]	$\Gamma_{2'c}$[d]	Γ_{15c}[d]
12.8(0.6)	−3.2(0.2)	1.3(0.2)	13.8(0.6)	−12.6(0.3)	1.00	3.25

[a]Ref. 5.
[b]Present analysis.
[c]Present analysis and optical data (Refs. 2, 7).
[d]Optical data (Refs. 2, 7).

cursion below E_v, the valence-band edge. At this point it lies at $E_i = -3.2$ eV and, as shown by our theoretical analysis, originates from transitions at X. Thus, the experimental value of -3.2 ± 0.2 eV for X_{4v} is determined, while the final-state band at X lies at $E_i + h\nu = 13.8 \pm 0.6$ eV $\equiv X_c^{\text{upper}}$, which is the center of gravity of a set of closely spaced bands (see Fig. 3). We then determine X_{1c} from X_{4v} and optical data (see Table I).

The eigenvalue ladder at L is next determined by first utilizing the values $L_{2'v} = -10.6 \pm 0.5$ eV, $L_{1v} = -7.7 \pm 0.3$ eV previously determined from photoemission spectra.[5] The peak at $E_i = -7.7$ eV corresponding to emission from states near L_{1v} is seen experimentally to increase rapidly in intensity first between $h\nu = 15$ and 16 eV, and then between 20 and 21 eV, establishing $L_{2'c} = 7.8 \pm 0.6$ eV and $L_c^{\text{upper}} = 12.8 \pm 0.6$ eV. Here L_c^{upper} is again defined as the center of the set of closely spaced bands at L shown in Fig. 3.

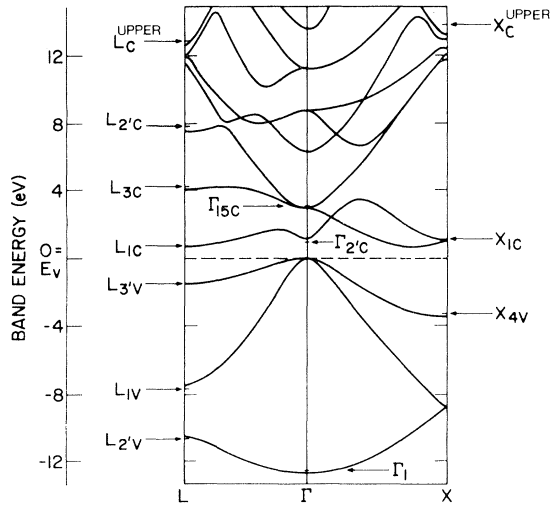

FIG. 3. Theoretical energy bands (Ref. 7 potential) for Ge along $\vec{k}$-space symmetry lines. Table I experimental band positions at X, L, and Γ are indicated by arrows.

Finally, $L_{3'v}$ and L_{3c} are determined by comparing our calculation with optical data, photoemission conduction-band state-density overviews,[14] and cesiated-Ge photoemission data[15] near $h\nu = 5.8$ eV. We arrive at[15] $L_{3'v} = -1.5 \pm 0.15$ eV, $L_{3c} = 4.25 \pm 0.2$ eV. We then obtain $L_{1c} = 0.8$ eV from our value for $L_{3'v}$ in conjunction with optical data (see Table I).

The energy-band positions at L and X are listed in Table I and shown in Fig. 3. ($\Sigma_{1\,\min}$ and also eigenvalues at Γ have been determined previously from photoemission[5] and optical data.[2,7]) Figure 3 presents a graphic demonstration of our overall determination of the total band structure for Ge. This figure shows that the theoretical bands near L_c^{upper} and X_c^{upper} lie ~10% too low. This disagreement cannot be corrected by adjusting the pseudopotential, but only by adding a term linear in energy to the Hamiltonian, such as that due to self-energy effects.[16] Finally, we note that the $l = 2$ nonlocal term in the pseudopotential was required to give the proper high-lying conduction-band topology, for it is this term that brings $L_{2'c}$ close to the experimental position.[8]

We are grateful to John Freeouf and M. Erbudak who assisted in obtaining the data, and to J. Shaw for programming assistance.

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[9]We need not sum amplitudes since individual beams (of finite coherence width) do not overlap at the detector.

[10]J. F. Janak *et al.*, in *Electronic Density of States*, edited by L. H. Bennett, U. S. National Bureau of Standards Special Publication No. 323 (U. S. GPO, Washington, D. C., 1971).

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[12]The $\vec{k}$-space integration employed the algorithm described in Ref. 5, and eigenvalues, pseudo wave functions, and their momentum matrix elements calculated at ~1600 points in the reduced BZ.

[13]Note that direct-transition features are still seen weakly even at large $h\nu$ and short escape depths (see Ref. 8).

[14]D. E. Eastman and J. L. Freeouf, in Proceedings of the International Topical Conference on Tetrahedrally Bonded Amorphous Semiconductors, Yorktown Heights, N. Y., 20–22 March 1974 (to be published).

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Theory of ac Conductivity Based on Random Walks

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It is shown that a simple random-walk formalism is not sufficient to derive ac conductivities when the influence of the first–waiting-time distribution is considered.

The continuous-time random walk of Montroll and Weiss[1] has been employed by Sher and Lax[2] and subsequently by Moore[3] to derive ac conductivity in situations where the conduction is primarily by hopping. The treatment ostensibly has applications to amorphous materials where at moderate frequencies the conductivity is frequently proportional to ω^{ν}, where ω is the angular frequency and ν is a constant of the order of unity. Sher and Lax are able to fit theoretical curves to experimental data quite successfully through a frequency-dependent term of the form

$$i\omega\psi(\omega)[1-\psi(\omega)]^{-1}, \qquad (1)$$

where $\psi(\omega)$ is the Fourier transform of the probability density of the waiting time between hops in a random walk.

Firstly I shall derive a formula for the ac conductivity in a much simpler fashion than Sher and Lax and secondly show that expression (1) is incorrect.

Suppose a potential gradient is suddenly applied to a material in which the carriers perform a Montroll-Weiss type of random walk. In this walk, independent electrons (say) are trapped at sites which may be distributed at random. Hopping takes place between sites; the transitions themselves are virtually instantaneous with a waiting time between hops with probability density $f(t)$. The potential gradient naturally causes the probability of a hop in the forward direction to be greater than that in the reverse direction so that a steady component of current is produced.

With the use of a type of argument employed by Feller,[4] the probability that a transition takes place in interval dt at time t after application of