The theorem is thus established.

For $p=1$, Eq. (3) reduces to the weak form of the Peierls variational theorem.[1]

For a boson or fermion N-particle system with two-body forces, the Hamiltonian may be written $H=H_0+H_1$, where

$$H_0=\sum_2 \epsilon_2 a_2^{+} a_2,$$

$$H_1=N^{-1}\sum_{232'3'} V_{232'3'}\delta_{2+3,2'+3'} a_2^{+} a_3^{+} a_{2'} a_{3'}.$$

Simple combinatorial considerations of the number of ways of distributing unlinked parts of a general diagram associated with $\langle H_1^m\rangle_0$ enables one to see explicitly that unlinked contributions completely cancel in each order in (3); i.e.,

$$\langle (H_1-\langle H_1\rangle_0)^m\rangle_0=\langle H_1^m\rangle_{0,\text{linked}}=O(N),$$

when diagram methods are applicable.[4]

The author is indebted to Professor B. Mühlschlegel for a lucid seminar which motivated the above work. A helpful conversation with Professor J. M. Luttinger is also gratefully acknowledged.

[1]The theorem in the original (strong) form was proved by R. Peierls, Phys. Rev. 54, 918 (1938), and with simplicity by T. Schultz, Nuovo Cimento 8, 943 (1958). The strong and weak forms of the theorem were discussed by M. Girardeau, J. Math. Phys. 3, 131 (1962), and H. Falk, Physica 29, 1114 (1963).

[2]Application to many-body systems, in general, is treated by J. Valatin and D. Butler, Nuovo Cimento 10, 37 (1958); J. Valatin, Nuovo Cimento 10, 843 (1958); V. Tolmachev, Dokl. Akad. Nauk SSSR 134, 1324 (1960) [translation: Soviet Phys. "Doklady" 5, 984 (1961)].

[3]Recent specific applications to ferromagnetism and antiferromagnetism are found in M. Bloch, Phys. Rev. Letters 9, 286 (1962); H. Falk, Phys. Rev. (to be published; based on the author's dissertation, University of Washington, 1962).

[4]For a comprehensive recent review of the application of diagram methods to the many-body problem, see C. Bloch, Diagram Expensions in Statistical Mechanics, Centre d'Etudes Nucléaires de Saclay, Gif-sur-Yvette (S&O).

POLARIZATION EVIDENCE FOR MOMENTUM CONSERVATION IN PHOTOELECTRIC EMISSION FROM GERMANIUM AND SILICON

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In this Letter we demonstrate that a sizable fraction of the electrons created by direct optical transitions can escape from germanium and silicon without loss of crystal momentum to phonons or imperfections either in the volume or at the surface. For this fraction of emitted electrons, momentum tangential to the surface is conserved while normal momentum is altered by interaction with the crystal as a whole.

The existence of a large unscattered component of photoemission was first postulated to explain linear yield vs photon-energy curves near threshold.[1,2] In view of its potential importance to the study of band structure,[3] we felt that a more stringent proof of the hypothesis of unscattered electron emission was highly desirable. We provide here such a proof by showing that the directional photoemissive yield from a (111) crystal surface is strongly sensitive to the photon polarization angle for light at normal incidence.

It is easily seen that no polarization sensitivity could be observed if the correlation between the electron's emission direction and the $\vec{k}$ state in which it was created were destroyed by scattering. In this case, every equivalent point of origin for the electron would be equally weighted and the high symmetry of a diamond-type crystal with a symmetric (111) surface would eliminate all polarization dependence. By symmetric we understand the existence of three $\{1\bar{1}0\}$ type reflection planes, a [111] threefold rotation axis, and translational periodicity. The cleaved and heated Si and Ge surfaces satisfy these requirements as is known from slow electron diffraction.[4]

The polarization dependence of the directional yield is most readily interpreted if the electrons are collimated to lie in a $(1\bar{1}0)$ plane. Such a plane will include the [111] direction perpendicular to the cleaved surface as well as the $[11\bar{2}]$ direction parallel to the surface (see Fig. 1). The symmetry of this plane enforces a strong polarization dependence on the unscattered electrons.

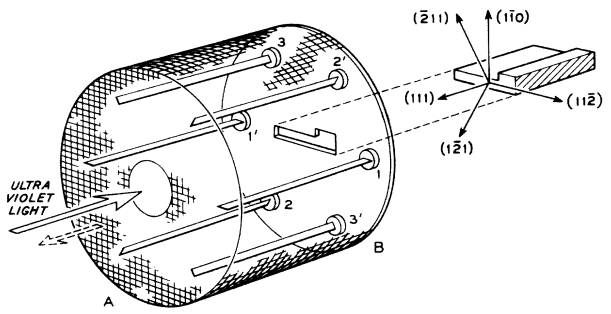

FIG. 1. Experimental arrangement for measuring the directional photoemissive yield.

For experimental convenience the electrons were collimated in angle only to the extent of a 60° wedge with a $[11\bar{2}]$ direction as bisector. This will reduce the magnitude of the effect but will not eliminate it.

To obtain a quantitative expression we assume that the $\vec{k}$ vector of the electron lies in the $(1\bar{1}0)$ plane. The matrix element M for absorption is given by

$$M = (e/mc)\langle\psi_f(\vec{k})\,|\,\vec{A}\cdot\vec{p}\,|\,\psi_i(\vec{k})\rangle. \qquad (1)$$

$\vec{A}$ is the vector potential of the light (collinear with the E vector), $\psi_i(\vec{k})$ is the initial (hole) state, and $\psi_f(\vec{k})$ is the final (electron) state. Since $\vec{k}$ lies in the $(1\bar{1}0)$ plane which is a reflection plane for a perfect diamond-type crystal with a symmetric (111) surface, the wave functions must be even or odd under reflection in this plane. We define a "paritylike" quantity p, where $p = +1$ for even wave functions and $p = -1$ for odd wave functions. We also define an "optical p" given by $p_O \equiv p_i p_f$ as the product of the p's of the initial and the final state. If $\vec{A}$ is resolved into components along the $[11\bar{2}]$ and $[1\bar{1}0]$ directions, then $\vec{A}\cdot\vec{p}$ will be even under reflection in the $(1\bar{1}0)$ plane for $A_{11\bar{2}}$ and odd for $A_{1\bar{1}0}$. We designate this by $p_A = \pm 1$. Equation (1) then shows that $M = 0$ unless $p_A = p_O$ since M must be invariant under reflection. When $\vec{A}$ is in the $[11\bar{2}]$ direction, only $p_O = +1$ transitions are excited. Let N_+ be the total number of electrons escaping without scattering in this case. Similarly, let N_- be the number of escaping unscattered electrons when $\vec{A}$ is in the $[1\bar{1}0]$ direction. Let N_{scat} be the number of scattered electrons which escape. The polarization dependence of $N(\theta)$, the yield in the $(1\bar{1}0)$ plane, is given, in general, by

$$N(\theta) = N_+\cos^2\theta + N_-\sin^2\theta + N_{\text{scat}},$$

$$= (N_+ - N_-)\cos^2\theta + N_- + N_{\text{scat}}, \qquad (2)$$

where θ is the angle of the E vector measured from the $[11\bar{2}]$ direction. Transitions with $p_O = +1$ and $p_O = -1$ are expected to have thresholds at different photon energies so that N_- will go to zero before N_+, or vice versa.

Spin-orbit interaction mixes states of opposite p_O and hence will reduce the polarization sensitivity. We have not accounted for this in Eq. (2).

We have been careful to emphasize that all symmetry arguments applied to a perfect crystal with a symmetric surface. A polarization effect is therefore to be expected not only for volume states but also for surface states and for volume states strongly perturbed in the vicinity of the surface. The observed polarization effect proves only that electrons have been created and emitted without appreciable transfer of momentum to imperfections or phonons.

Turning now to the experiment, the essential task was to rotate the plane of polarization of the incident light, and to measure electrons leaving the crystal face in different directions. The apparatus is shown in Fig. 1. The directional sorting is accomplished by six symmetrically spaced collecting probes registered with the $\langle 11\bar{2}\rangle$ - type directions of the sample. The (111) sample surface, cleaved in $\sim 10^{-10}$ mm Hg by the Gobeli-Allen technique,[5] enters a closely fitting aperture at end B. The ultraviolet light enters the hole at end A, is focused to a fine image on the sample, and is reflected back through the hole. Vibrating reed electrometers measure the current to selected probes. The low kinetic energy of emitted electrons (<1 eV) makes it necessary to compensate the earth's magnetic field to maintain good spatial sorting of electrons according to emission direction.

A rotatable Glan-Thompson calcite polarizer passed light of $h\nu < 5.8$ eV from a medium pressure Hg arc. (The photothresholds of cleaved Ge and Si were ~4.8 and ~5.1 eV, respectively.) An intermediate defining slit used after the polarizer prevented "walking" of the image on the surface during rotation, but variation of intensity over the image still produced a small component with 360° period in the data. The ratios of currents to diametrically opposite probes were taken because this canceled out variations in emission current due to variation of light intensity with both time and θ.

The results of a measurement on a cleaved and heated germanium surface are shown in Fig. 2, where the crystal directions relative to probes are indicated. The ratio of current to

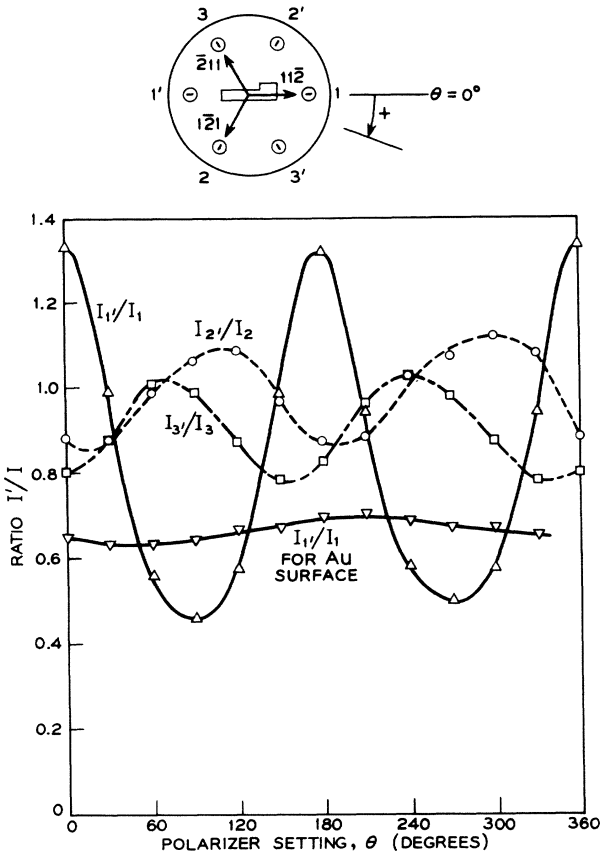

FIG. 2. Results of polarization effect measurements on a cleaved and heated germanium surface and a polycrystalline gold surface.

a given probe and its opposite, I'/I, is plotted vs polarizer angle, θ, for each of the three sets of probes. The zero of θ is chosen with the E vector along the $[11\bar{2}]$ axis. Note that each set yields a cyclic ratio having a 180° period in θ with maxima occurring when the E vector of the light lies along the appropriate $[11\bar{2}]$ direction for that set. Specifically, the ratio I_1'/I_1, or the ratio of current in the $[\bar{1}\bar{1}2]$ direction compared to the $[11\bar{2}]$ direction, is maximum when the E vector lies parallel to the $[11\bar{2}]$ direction. The same result was found for silicon. This is consistent with Eq. (2). The sign of the effect is consistent with the band structure proposed by Brust, Phillips, and Cohen[6] for Ge and Si for the transition near threshold.

The amplitude of the ratio variations as well as the mean value of the ratio depended critically upon geometrical alignment, electric fringe fields, and cancellation of the earth's magnetic field. The inequality in amplitude and mean value for the three different sets of probes shown in Fig. 2 is thus not considered significant. A lower bound on the fraction of unscattered electrons can be had directly from the amplitude of the ratio variations by Eq. (2). Since all imperfections in experimental arrangements degrade the measured amplitude by mixing electrons, the largest one observed is the most significant. Here the 1-1′ probes avoided fringe fields best because emitted electrons traveled for several mm over the perfect crystal surface before selection by the probes. The observed ratios there indicate that at least 40% of the electrons were unscattered.

That the effect was truly due to the symmetry of the crystal and not caused by some geometrical effect such as movement of the image during rotation of the polarizer is proven by the following:

The collecting geometry has 60° rotational symmetry, and therefore a simple geometrical effect would require the plots of I_1'/I_1, I_3/I_3', and I_2'/I_2 to follow each other by 60° intervals in θ. The crystal, on the other hand, has 120° rotational symmetry and would require the plots of I_1'/I_1, I_2'/I_2, and I_3'/I_3 to follow each other by 120° intervals in θ and this is what is observed experimentally.

Second, the ratio I_1'/I_1 was measured for an evaporated polycrystalline Au surface instead of a cleaved single crystal. The results shown on Fig. 2 have no component with 180° period but only the slight 360° component expected from geometrical sources.

Finally, the polarization effect was compared for two silicon crystals, identical except that one was cut with the $[11\bar{2}]$ axis pointing to the left, and other with the $[11\bar{2}]$ axis to the right as shown in Fig. 2. The resulting ratio plots were just inverted for the two crystals so that I_1'/I_1 for one was the same as I_1/I_1' for the other, as expected for the true effect.

Strong evidence that the polarization effect is a highly sensitive test for surface perfection was obtained by depositing Cs^+ ions on the Ge surface in controlled doses. It is known from slow electron diffraction work[7] that Cs does not form an ordered phase on Si at room temperature, and the same presumably holds true for Ge. It was observed that the amplitude of the polarization effect decreased as Cs was added and that it had disappeared from experimental view at a coverage of ~0.3 monolayer. We attribute this disappearance to the increased

scattering of the emitted electrons by the random array of Cs ions on the surface.

The polarization effect from a cleaved Ge surface was observed both before and after annealing. The effect increased in amplitude upon annealing but did not change in phase. We emphasize this point because a polarization effect not requiring momentum conservation could be generated by a surface having domains of low symmetry such as the ladderlike structure given by cleavage.[4] The presence of the enhanced effect, after annealing has produced a surface of threefold rotational symmetry, proves that such a surface domain structure is not the cause of the present effect.

In conclusion, it is believed that the polarization effect hss proven the existence of unscattered electrons in photoelectric emission, and has itself provided a highly sensitive new technique to study the perfection of a surface.

[1]G. W. Gobeli and F. G. Allen, Phys. Rev. 127, 141 (1962).
[2]E. O. Kane, Phys. Rev. 127, 131 (1962).
[3]E. O. Kane, following Letter [Phys. Rev. Letters 12, (1964)].
[4]J. J. Lander, G. W. Gobeli, and J. Morrison, J. Appl. Phys. 34, 2298 (1963).
[5]G. W. Gobeli and F. G. Allen, J. Phys. Chem. Solids 14, 23 (1960).
[6]D. Brust and J. C. Phillips, Phys. Rev. Letters 9, 94 (1962); D. Brust, M. L. Cohen, and J. C. Phillips, Phys. Rev. Letters 9, 389 (1962).
[7]G. W. Gobeli and J. J. Lander (unpublished).

IMPLICATIONS OF CRYSTAL MOMENTUM CONSERVATION IN PHOTOELECTRIC EMISSION FOR BAND-STRUCTURE MEASUREMENTS

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Compelling evidence[1] has been obtained that a sizable component of the photoelectric yield from silicon and germanium consists of electrons produced optically which have undergone no scattering events in escaping from the solid. In this case momentum tangential to the surface is conserved while normal momentum is altered by interaction with the crystal as a whole. Good evidence exists[2] that this is also true in GaAs and it may be quite generally true whenever clean, cleaved surfaces of high perfection can be produced.

Subject to several important limitations, the existence of crystal-momentum conservation implies that energy vs $\vec{k}$ for the solid may be inferred directly from measurements of the energy and momentum of the emitted electrons. The first and most obvious limitation is that the lifetime of the electron in the solid be sufficiently long. Energy vs $\vec{k}$ is, of course, always limited as a physical concept by the lifetime broadening uncertainty. The second important limitation is that the optical absorption must be assumed to occur sufficiently deep within the volume that no significant exchange of momentum normal to the surface takes place during the act of absorption. In this case we may write

$$h\nu = E_c(\vec{k}) - E_v(\vec{k}), \tag{1}$$

assuming direct transitions and ignoring the k vector of the light. The photon energy is $h\nu$, E_c and E_v are conduction and valence-band energies, respectively. Equation (1) defines an optical energy surface in k space. If normal momentum is not conserved during excitation, transitions occur over a volume in k space rather than a surface. Evidence supporting normal momentum conservation is found in the work of Gobeli and Allen,[3] and Kane,[3] since the explanation of the linear yield vs $h\nu$ characteristics observed in silicon are based on this assumption. In what follows we assume the validity of Eq. (1).

Let k_1, k_2 be the components of momentum tangential to the surface. Since k_1, k_2 are conserved during emission they can be measured directly. For a given value of k_1, k_2 a set of two or more discrete values of the energy $E_c(k_1, k_2, k_3')$ is determined by the intersection of the line $k_1 = \text{const}$, $k_2 = \text{const}$ with the optical energy surface of Eq. (1). Although there are generally at least two points of intersection, half of the intersections will correspond to group velocities directed into the crystal for which escape without scattering is imposible. k_3' is the momentum normal