

Incoherent and Thermal Small-Angle X-Ray Scattering in Silicon

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The intensity of small-angle x-ray scattering in single-crystal silicon has been measured with the scattering vector \mathbf{K} oriented along each of the three symmetry directions. The scattering intensity extrapolates to zero angle in reasonable agreement with the thermal scattering, calculated from the velocity of sound in each direction. The thermal scattering is calculated from known phonon dispersion relations and subtracted from the total to obtain the incoherent, or Compton, scattering. The incoherent scattering is smaller than that calculated by Freeman from Hartree-Fock wave functions for the free atom. This conclusion agrees with previous approximate measurements at small K on other crystals. Theoretical ideas about the source of the deficiency, apparently a solid-state effect, and about small-angle thermal scattering are outlined. The incoherent scattering shows little anisotropy and no sharp rise with increasing angle, which would suggest the onset of excitation of electrons across the forbidden band.

I. INTRODUCTION AND THEORY

A. Incoherent Scattering

IN a perfect, rigid crystal all the diffuse single scattering is incoherent. From the semiclassical or quantum theory, it is¹

$$I_{\text{inc}}(\mathbf{K}) = \sum_{m \neq 0} \left| \int \psi_m^* \psi_0 \sum_j^N e^{i\mathbf{K} \cdot \mathbf{r}_j} d\tau \right|^2 \quad (1)$$

$$= \int |\psi_0|^2 \sum_j^N e^{i\mathbf{K} \cdot \mathbf{r}_j} d\tau - \left| \int |\psi_0|^2 \sum_j^N e^{i\mathbf{K} \cdot \mathbf{r}_j} d\tau \right|^2 \quad (2)$$

in electron units (e.u.). $K = 4\pi \sin \frac{1}{2} \theta / \lambda$, θ is the scattering angle, λ is the x-ray wavelength, ψ_m is the wave function in state m , $m=0$ is the ground state, N is the total number of electrons, \mathbf{r}_j is the position of the j th electron, and the integrations are over all coordinates of the electrons. Then $I_{\text{inc}}(0) = 0$. The approximations that the x-ray frequency is small enough to avoid recoil and relativity corrections, but that it is much larger than the Bohr frequency ν_{0m} for any m which contributes appreciably to the sum in (1), are used. The former assumption holds in the present work. The latter assumption excludes anomalous dispersions, or Raman, terms which correspond to excited final electronic states. These terms are too small to have been observed in x-ray scattering, but are finite at $K=0$.

Thermal motion produces additional diffuse scattering I_{th} . Walker² separated I_{inc} from I_{th} in Al experimentally, by their temperature dependences. I_{th} is almost unshifted in wavelength, but I_{inc} is known, from spectral measurements at large K , to peak near a wavelength shift $\Delta\lambda = (h/m_e c)(1 - \cos \theta)$, the value for

a slow, free electron. Thus Curien and Deroche³ separated I_{inc} from I_{th} in Al with a dispersive filter. Laval⁴ measured I_{inc} in Al, diamond, and KCl by subtracting estimated I_{th} from the total diffuse scattering. Measured phonon dispersion relations were not then available. Cribier⁵ treated CaF_2 similarly. Measurements on pure, perfect crystals at small K have been difficult in the past. The weak scattering power requires an unusually strong x-ray source and low background. For convenient λ , θ is small, so that common diffraction equipment is not suitable.

If ψ_0 is a determinant of one-electron functions ψ_j , then from (2),

$$I_{\text{inc}} = N - \sum_{jj'}^N \left| \int \psi_j^*(\mathbf{r}) \psi_{j'}(\mathbf{r}) e^{i\mathbf{K} \cdot \mathbf{r}} d\tau \right|^2. \quad (3)$$

The most careful calculations have used (3) with Hartree-Fock ψ_j for free atoms or ions. A recent review⁶ lists the results. They lie above the measurements⁴ at small K , but agree otherwise.^{6,7} Coherent scattering in crystals (at large K) is also well described by free-atom orbitals.⁸ Neglect of interatomic overlap in (3), which is emphasized at small K , presumably produces much of the overestimate of I_{inc} . It may be that overlap contributions vanish when $e^{i\mathbf{K} \cdot \mathbf{r}}$ varies with large K , and that well within the atom, ψ_j is similar in free atom and crystal. Overlap effects might be estimated with simple approximate atomic orbitals. The solutions of the Hartree-Fock problem are Bloch functions, extend-

³ H. Curien and C. Deroche, *Bull. Soc. Franç. Minéral.* **79**, 102 (1956).

⁴ J. Laval, *Bull. Soc. Franç. Minéral.* **62**, 137 (1939); *Compt. Rend.* **215**, 278 (1942).

⁵ D. Cribier, *Rev. Mod. Phys.* **30**, 228 (1958); *Ann. Phys.* **4**, 333 (1959).

⁶ H. Curien, in *International Tables for X-Ray Crystallography*, edited by C. H. Macgillavry, G. D. Rieck, and K. Lonsdale (The Kynoch Press, Birmingham, England, 1962), Vol. III, p. 247.

⁷ A. J. Freeman, *Phys. Rev.* **113**, 176 (1959); *Acta Cryst.* **13**, 190 (1960).

⁸ B. W. Batterman, D. R. Chipman, and J. J. DeMarco, *Phys. Rev.* **122**, 68 (1961); M. Kuriyama and S. Hosoya, *J. Phys. Soc. Japan* **18**, 1315 (1963).

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¹ R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, Ltd., London, 1948).

² C. B. Walker, *Phys. Rev.* **103**, 558 (1956).

ing over the whole crystal, but the determinantal ψ_0 is not changed if one takes each ψ_j as a linear combination of the Bloch functions which is localized on an atom. However, for metallic or covalent bonding, these ψ_j have greater overlap than the free atom orbitals. For example, the assumption of some free electrons,² instead of isolated atoms, reduces I_{ino} at small K (except very near $K=0$). In the absence of accurate measurements on crystals at small K , no realistic calculations of I_{ino} , including interatomic effects, have been made.

To be Compton scattered in an insulator or semiconductor at absolute zero of temperature, a photon must give up at least the band-gap energy. Suppression of scattering with small $\Delta\lambda$ is reported⁹ from spectral measurements on diamond, with a 7-eV band gap. Analogous reduction of I_{ino} at angles less than a minimum, θ_c , calculated from the slow, free-electron Compton relation, has been suggested^{2,7,10} as an alternative explanation of the deficiency in I_{ino} . Si has a 1.08-eV band gap, and with $\lambda=1.542 \text{ \AA}$, as in this work, $\theta_c=7^\circ$. But the electrons in band-gap solids are not free and slow, so that large energy transfers at small θ may occur. In some cases the deficiency is by comparison with I_{ino} calculated for free closed-shell ions, which themselves have few low-lying excited levels. The idea is inapplicable, *a fortiori*, to a metal.

There is more justification for requiring conservation of quasimomentum, $\mathbf{k}'-\mathbf{k}=\mathbf{K}+\mathbf{K}_L$, from (1). \mathbf{k} , \mathbf{k}' , are the wave vectors of the excited electron in the initial and final states. \mathbf{K}_L is a vector of the reciprocal lattice. Knowledge of the band structure of Si¹¹ shows that the addition of this requirement scarcely increases the predicted θ_c , for \mathbf{K} along the [001] direction. However, this kind of description of the excited states seems inadequate.

B. Thermal Scattering

Thermal scattering involves emission or absorption of phonons, but it can be treated classically, and is well understood for harmonically vibrating crystals.^{1,12,13}

Since the two primitive sublattices in Si are identical, their amplitudes must be equal in each normal mode. Then the harmonic, one-phonon scattering is¹²

$$I_{\text{th}}(\mathbf{K}) = \frac{1}{2}m^{-1} \exp(-2M)K^2 |f|^2 \\ \times [(1 + \cos \mathbf{K}_L \cdot \boldsymbol{\rho}) \sum_{i=1}^3 E_i \omega_i^{-2} \cos(\mathbf{K}, \mathbf{e}_i) \\ + (1 - \cos \mathbf{K}_L \cdot \boldsymbol{\rho}) \sum_{i=4}^6 E_i \omega_i^{-2} \cos^2(\mathbf{K}, \mathbf{e}_i)] \quad (4)$$

⁹ K. Alexopoulos and G. Brogren, *Arkiv Fysik* **6**, 213 (1953).

¹⁰ J. Laval, *Compt. Rend.* **215**, 359 (1942).

¹¹ F. Bassani and D. Brust, *Phys. Rev.* **131**, 1524 (1963).

¹² J. Laval, *Bull. Soc. Franç. Minéral.* **64**, 1 (1941).

¹³ W. Cochran, *Rept. Prog. Phys.* **26**, 1 (1963); A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 3.

in e.u./atom. The two summations extend over the acoustic and optical modes, respectively. \mathbf{K} is in the zone centered on \mathbf{K}_L , $\mathbf{q}=\mathbf{K}-\mathbf{K}_L$, $\omega_i/2\pi$ is the frequency of the i th mode with propagation vector \mathbf{q} , $E_i=\frac{1}{2}\hbar\omega_i \times \coth(\hbar\omega_i/2kT)$, $2|f|^2(1+\cos \mathbf{K} \cdot \boldsymbol{\rho})$ is the usual structure factor, m is the atomic mass, and $(\mathbf{K}, \mathbf{e}_i)$ is the angle between \mathbf{K} and the polarization vector \mathbf{e}_i . The Debye-Waller factor $\exp(-2M)$ can be neglected in this work, since $2M=0.3 \sin^2\theta/\lambda^2$ in Si at 300°K. n -phonon scattering is given by the M^n term of a power series in M . Since M is so small here, multiple-phonon scattering is negligible, and it vanishes in general at $K=0$.

At $K=0$, the optical modes do not contribute, since their phase velocities $\omega_i/K \rightarrow \infty$ as $K \rightarrow 0$. Nor do purely transverse waves, for which $(\mathbf{q}, \mathbf{e}_i)=90^\circ$, contribute when \mathbf{K} is in the first zone, where $\mathbf{q}=\mathbf{K}$. Hence, in directions of such high symmetry that the modes are purely transverse or longitudinal at $\mathbf{q}=0$ ($\langle 001 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$ in cubic crystals), the harmonic thermal scattering is

$$I_{\text{th}}(0) = m^{-1} |f(0)|^2 kTV^{-2} \quad (5)$$

at $K=0$. V is the adiabatic velocity of sound in the direction of \mathbf{K} . The correction for anharmonicity is to replace V by the isothermal velocity.¹⁴ The difference is negligible in hard solids.

The calculated thermal scattering in Si is shown in Fig. 1 for \mathbf{K} along each of the three symmetry directions.

II. EXPERIMENTS AND DISCUSSION

A rotating water-cooled Cu anode was used, at 33 kV and 98 mA, with monochromatization by a Ni filter and proportional counter-pulse-height analyzer. Slits 0.6-cm high collimated and analyzed the beam. With the slit widths used for $\theta \geq 3.5^\circ$, the rms resolution was 1.0° at $\theta=3.5^\circ$, and decreased to 0.7° for $\theta \geq 10^\circ$. The resulting intense beam was needed to measure the weak scattering of Si at small K . The background was about 4 counts/min, and the smallest sample scattering at $\theta > 2^\circ$ was about 100 counts/min. Other experimental aspects have been described.¹⁵ The accuracy of the intensity standardization¹⁵ has been verified¹⁶ within a few percent.

The sample was a (110) disc of 100 Ω -cm n -type Si, made by Philco Corp. Alternate polishing and etching reduced the thickness to 0.0102 cm, uniform to 0.0005 cm over the area used, with x-ray transmission 0.237. The final treatment was an etch, to minimize the damaged surface layer. Static imperfections in this grade of Si should produce completely negligible (volume) diffuse scattering. Low dislocation density was confirmed by Laue photographs and examination of etch pits.

The orientation was accurate to 1° . Since the sample

¹⁴ S. M. Rytov, *Zh. Eksperim. i Teor. Fiz.* **33**, 166 (1957) [English transl.: *Soviet Phys.—JETP* **6**, 130 (1958)].

¹⁵ D. L. Weinberg, *Rev. Sci. Instr.* **34**, 691 (1963).

¹⁶ D. L. Weinberg, *Phys. Letters* **7**, 324 (1963).

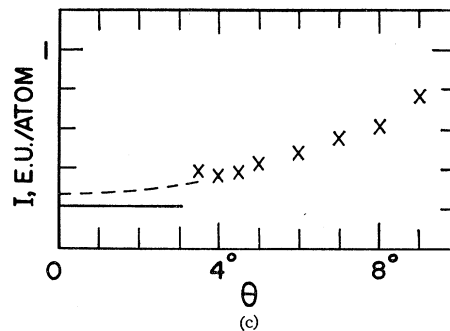
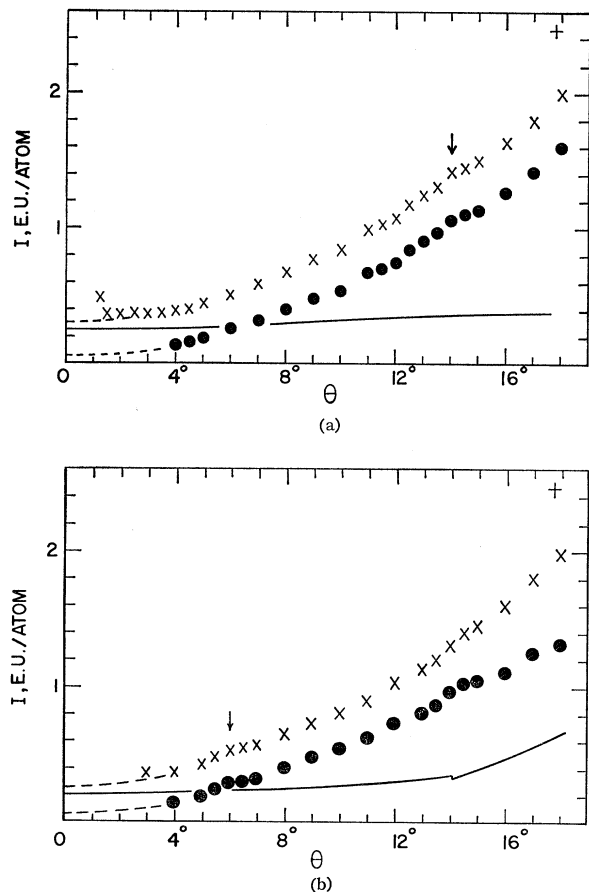


FIG. 1. Scattering of 1.542 Å x-rays in Si, measured by transmission through a thin plate of (110) orientation, held perpendicular to the incident beam. At $\theta=0$ the scattering vector \mathbf{K} is along the (a) [001], (b) [111], (c) [110] direction. For scattering at angle θ , \mathbf{K} deviates by $\frac{1}{2}\theta$ from the symmetry direction. + Incoherent scattering at $\theta=17.7^\circ$, theoretical. [A. J. Freeman, *Acta Cryst.* **12**, 929 (1959).] × Total scattering, experimental. — Thermal scattering, theoretical. • Incoherent scattering, obtained by subtracting the thermal scattering from the total scattering. — — Extrapolation of the experimental curves to $\theta=0$ as $a+b\theta^2$. The two vertical arrows indicate verified, but unexplained irregularities. The thermal scattering was calculated according to (4) with measured dispersion relations {G. Dolling, in *Inelastic Scattering of Neutrons in Solids and Liquids*, (International Atomic Energy Agency, Vienna, 1963), Vol. 2, p. 37. These measurements of the dispersion relations in Si agree approximately with x-ray scattering measurements by J. Corbeau, *Compt. Rend.* **256**, 1275, 4641 (1963), and with calculations by T. I. Kucher, *Fiz. Tverd. Tela*, **4**, 992 (1962) [English transl.: *Soviet Phys.—Solid State* **4**, 729 (1962)].} except near $\theta=0$, where (5) was used. The polarization of modes with \mathbf{K} along the [110] direction is not known, except at one point of high symmetry in each zone of (periodically extended) reciprocal space, where the vibrations are purely longitudinal or transverse. Therefore, the measurement and calculations for the [110] direction are confined to angles near $\theta=0$.

was normal to the incident beam, \mathbf{K} varied in direction at half the rate at which θ changed, when the analyzing slits were rotated. Figure 1 shows the measurements, corrected for background (angularly dependent), absorption, polarization, and slit-height smearing. The correction¹⁵ for this last effect is a factor $[1+(b/a)\times(\theta^2-4.76)]/[1+(b/a)\theta^2]$, b/a in deg^{-2} , where the expression $a+b\theta^2$ is fitted to the experimental total-scattering curve at θ . The factor is 0.90 to 0.91 at $\theta=0$.

The experimental values for $I(0)$ are from 16 to 30% too large in the three directions. Only measurements made during the first month after the final etch are reported because the scattering is found to increase with time, most conspicuously at the smallest θ . The increase must represent deterioration, either surface corrosion or possibly x-ray damage. Scattering from surface roughness is known¹⁷ to be prominent at small θ , especially in otherwise perfect crystals, where the

¹⁷ D. L. Weinberg, *J. Appl. Phys.* **33**, 1012 (1962).

volume scattering is small. Comparison of surface conditions shows that it accounts at least primarily for the deviation, at $\theta<4^\circ$, of the experimental curves in Fig. 1 above the expected $a+b\theta^2$ variation. The observed excess in $I(0)$ is attributed to this cause. The time variation in $I(\theta)$ is approximately independent of θ , so that it is believed the final curve should be lowered uniformly by about 0.05 e.u./atom.

Similar experiments on quartz, in two directions, also show surface scattering, similar agreement with (5) (piezoelectric effects are negligible), and I_{inc} less than theory.⁶ However, the phonon dispersion relations are not known.

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