

state involved ($1s$, $2s$, $2p$, etc.) we have replaced the variation of ϵ_c in Eqs. (5) and (8) with the variation of the electrostatic potential at the nucleus. (This is appropriate only for deep core levels.) We have compared our results with measurements on $2s$ levels, because we feel that the atomic calculations employed in Ref. 3 are less reliable for the $1s$ levels, and p levels introduce the complication of multiplet structure. The error bars in Fig. 1 reflect only the reported uncertainty associated with the measurement of the core-level binding energy in the solid; an estimate of the additional uncertainty introduced by the use in Ref. 3 of theoretical free-atom binding energies can be obtained from the errors in these binding energies for the rare-gas atoms, for which measurements are available. For Ne and Ar, the errors are less than 1 eV; for Kr, the error is large (8 eV). The only indication we have that the errors remain small through the $3d$ transition series is the empirical one offered by the uniform level of agreement that we obtain.

¹³We use the same work functions used to define the experimental data (see Ref. 12).

¹⁴Valence electrons are affected similarly by a core hole and an extra proton. See, e.g., D. A. Shirley, *Chem. Phys. Lett.* **16**, 220 (1972). Thus, the valence charge of a screened atom containing a core hole is similar to that of the next atom in the periodic table.

¹⁵The screening electron is s -like for K, p -like for

Zn, 60% s -like and 40% d -like for Cu, and purely d -like otherwise. [In using the equivalent-core approximation to specify the screening charge (see Ref. 14), we ignore the 0.5 d electrons in Ca and the 0.1 variation in the number of non- d electrons in Ti and V.]

¹⁶R. Hoogewijs, L. Fiermans, and J. Vennik, *Chem. Phys. Lett.* **37**, 87 (1976).

¹⁷In the equivalent-core approximation (see Ref. 14), $\Delta_s = I_1(Z + 1)$. Thus, Eq. (9), together with the fact that electron affinities are smaller than ionization potentials, indicates that Δ_s should be approximately twice Δ_{relax} . (See text below.)

¹⁸L. Hedin and A. Johansson, *J. Phys. B* **2**, 1336 (1969).

¹⁹This unequal weighting of formulas (9) and (10) is slightly more accurate than the equal weighting suggested in Ref. 10.

²⁰The corresponding result for the quantity Δ_s is 6.1 eV. If, as was done in Ref. 2, Δ_s is evaluated by the Hartree-Fock method, the result is 5 eV, regardless of whether the calculations are performed on Ca, or on K with a core hole. The general tendency of the Hartree-Fock method to underestimate such total-energy differences [see J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. I, p. 392] reduces the numerical difference between Δ_s and Δ_{relax} , thereby obscuring the qualitative difference between the two quantities.

Polarization Phenomena in X-Ray Scattering

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(Received 19 January 1978)

Rotation of the plane of polarization of a linearly polarized x-ray beam by simple transmission through a (110) silicon crystal has been observed. Both the amount of rotation and the amount of absorption of x rays depend on the orientation of the crystal in the incident beam. Contemporary scattering-theory calculations are used to explain this effect, including the x-ray analog to optical birefringence, for a suitable crystal sample.

In this Letter, we report the discovery of x-ray polarization rotation for the case of simple transmission. We have used linearly polarized Cu $K\alpha$ radiation incident perpendicular to the (110) surface of Si. Avoiding Bragg or Laue conditions, we demonstrate for the first time that there is a rotation of the linearly polarized x-ray beam and an absorption in the crystal sample which depend on the orientation of the Si

crystal.

Polarization phenomena such as optical activity and birefringence are not generally expected to exist for x rays in simple transmission. For the case of x-ray diffraction, however, theoretical results of Molière¹ and Ashkin and Kuriyama² indicate that the initial and final polarization states may be different. Hōjō, Ohtsuki, and Yanagawa³ have shown, however, that as long as

atomic, hydrogenic wave functions are appropriate, this effect should not exist.

Using the theory of Ashkin and Kuriyama,² we have made numerical calculations considering only elastic scattering (with absorption) and assuming that the bonding directions are not isotropic within the (110) plane of Si. These results demonstrate that, through the choice of crystal parameters, one can derive both the "usual" case of no rotation and constant absorption, and the x-ray birefringence case of polarization rotation and crystal-orientation-dependent absorption. A particular set of physically plausible parameters can be made to reproduce the experimental results.

The apparatus consists of a polarizer, a sample chamber, and a polarization analyzer (polarimeter). The incident beam is polarized by scattering through $2\theta=90^\circ$. The polarizer (Ge powder) and the sample chamber are attached directly to the port of a Cu-target x-ray tube, and these remain stationary throughout the measurements. The polarimeter consists of a long set of Soller slits (which restrict the scattered beam to better than $90.0^\circ \pm 0.2^\circ$), a (333) Ge crystal, and a sealed Xe proportional counter. This part of the apparatus can be rotated about the azimuthal axis to measure the polarization of the x-ray beam. The intensity diffracted through 90° by the flat Ge crystal is measured at different azimuthal positions.

The system was aligned using a blank run with Ge powder, which diffracts Cu $K\alpha$ through $2\theta = 89.92^\circ$ by the (333) and (511) sets of planes. A micrometer in the polarimeter is used to orient

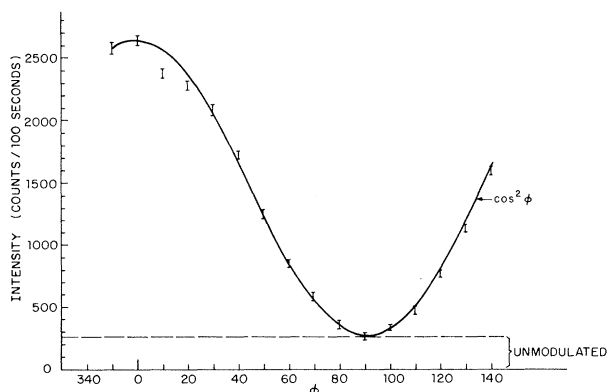


FIG. 1. Results of a blank experiment using Cu $K\alpha$ radiation on Ge powder. The error bars are 1 standard deviation, determined by the counting statistics, and the solid curve shows the $\cos^2\phi$ dependence of the modulated flux.

the (333) Ge crystal. Pulse-height analysis was used to discriminate against Ge fluorescence. The intensity versus azimuthal angle ϕ is shown in Fig. 1. The peak is located at $\phi=0^\circ$ and the modulated part of the intensity follows the $\cos^2\phi$ dependence of Malus's law.

A thin (~ 0.4 mm) Si crystal was placed in the sample chamber, with the incident beam perpendicular to the (110) face, and the polarization modulation measurements were performed. The results indicated that the modulation peak was now shifted from $\phi=0^\circ$. Measurements were made for two additional orientations of the Si crystal, derived by rotating it about the azimuthal axis (which is the $[110]$ crystal axis) by approximately 25° and 85° . The exact orientations were determined using Laue photography. Each orientation of the crystal displayed a different polarization rotation and a different absorption. Moreover, the intensity integrated over the polarization analyzer angle ϕ was different for each crystal orientation. The data points are shown in Fig. 2; we will explain below the derivation of the solid lines shown in this figure. There we define an angle θ as the angular position of the z (or unique) axis. The first modulation measurement described above corresponded to $\theta=100^\circ$.

The analysis could be made along the lines of well-established optical methods,⁴ but since we are dealing specifically with x rays we have chosen to use available x-ray theory.² We are considering only elastic scattering (with absorption) by a finite parallel-sided crystal for the case of no Bragg reflection. The scattering amplitude

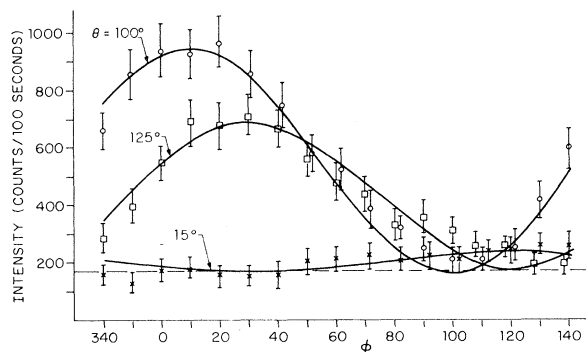


FIG. 2. Experimental results. The error bars are standard deviations about the counting statistics. The solid lines indicate a theoretical fit to the data for a single value of η and ξ . θ is the angular position of the z axis.

for a system including a crystal, an incident beam, and a scattered beam may be given by

$$\langle \vec{k}', \nu'; \text{out} | \vec{k}, \nu; \text{in} \rangle \propto \delta(\vec{k} - \vec{k}') \{ \vec{\epsilon}(\nu') \}_{\vec{i}} \{ D \}_{\vec{i}\vec{j}}^{(\sigma)} \{ \vec{\epsilon}(\nu) \}_{\vec{j}} \exp(i\lambda_{\sigma} L), \quad (1)$$

where \vec{k} and \vec{k}' are the momenta of the incident and scattered beams, $\{ \vec{\epsilon}(\nu) \}_{\vec{i}}$ is the i th component vector labeled by a polarization index ν , and \vec{i} and \vec{j} imply sums over "out" and "in" polarization states, respectively. L is the crystal thickness. σ indicates that a sum is taken over the two beams (or modes) $\sigma=1$ and 2. The derivation of the matrix $\{ D \}_{ij}^{(\sigma)}$ and the quantity λ_{σ} is explained in the following.

The experimental situation consists of a linearly polarized x-ray beam incident on a crystal. The crystal is assumed to have at least one unique axis in the plane orthogonal to the beam. A unique axis may be thought to arise due to anisotropy of bonding electron densities. We assume that the beam emerges from the exit surface of the crystal with an arbitrary polarization distribution, which is to be measured by the analyzer system. If we assume biaxial rather than uniaxial sym-

metry for the crystal, then the symmetry of the results about the angular position $\theta=0^{\circ}$ change, but the basic properties of the solutions are the same. Thus, for simplicity, we will allow the crystal to deviate from isotropy by having one unique axis. The generalized polarizability can be given in the crystal-coordinate representation by a matrix $\{ \Gamma \}$, whose diagonal elements $\{ \Gamma \}_{xx} = \{ \Gamma \}_{yy}$ and $\{ \Gamma \}_{zz}$ are nonvanishing. The crystal axes are labeled x, y, z and the x-ray-optical axes (i and j) are 1, 0, 2, with the y and 0 axes coinciding with the beam propagation direction. The crystal axes undergo a transformation to determine the polarizability in terms of the experimental x-ray-optical system, where the angle θ is defined as the angular distance between the vertical (i axis) and the z axis. Then the crystal polarizability in the optical system representation is written as

$$\{ \Gamma \}_{ij} = \begin{pmatrix} \Gamma_{xx} \cos^2 \theta + \Gamma_{zz} \sin^2 \theta & 0 & (\Gamma_{xx} - \Gamma_{zz}) \sin \theta \cos \theta \\ 0 & \Gamma_{xx} & 0 \\ (\Gamma_{xx} - \Gamma_{zz}) \sin \theta \cos \theta & 0 & \Gamma_{zz} \cos^2 \theta + \Gamma_{xx} \sin^2 \theta \end{pmatrix}.$$

Now we obtain the matrix $\{ D \}^{(\sigma)}$ for the σ mode (or wave)

$$\{ D \}_{ij}^{(\sigma)} = \frac{1}{2} \begin{pmatrix} 1 - (-1)^{\sigma} \frac{\Delta}{R} & (-1)^{\sigma} \frac{\Gamma_{12}}{R} \\ (-1)^{\sigma} \frac{\Gamma_{21}}{R} & 1 + (-1)^{\sigma} \frac{\Delta}{R} \end{pmatrix},$$

and

$$\lambda_{\sigma} = (\frac{1}{2}k) [\Delta + \Gamma_{22} - (-1)^{\sigma} R],$$

with $\Delta = \frac{1}{2}(\Gamma_{11} - \Gamma_{22})$ and $R = (\Delta^2 + \Gamma_{12}\Gamma_{21})^{1/2}$.

The intensity is given by the modulus square of Eq. (1). We have calculated this intensity for various physically plausible cases. We write, for the optical system

$$\Gamma_{ij} = v(0) \delta_{ij} + \kappa_{ij},$$

where $v(0)$ is the ordinary complex refractive index. In the crystal representation, we set

$$\kappa_{xx} = \text{Re}(\kappa_{xx})(1 + i\eta),$$

and

$$\kappa_{zz} = \text{Re}(\kappa_{xx})(1 + i\eta)\xi,$$

where we vary the parameters η and ξ . As a first approximation we have used the tabulated linear absorption (μ) to set

$$\text{Im}[v(0)]/k \simeq \mu/2$$

and

$$\text{Re}[v(0)]/k^2 = -10^{-6}$$

from the refractive index. Finally, we assume that the $\text{Re}(\kappa_{xx})$ is of the same order of magnitude as $\text{Im}[v(0)]$ because both arise from the photoelectric effect ($\vec{p} \cdot \vec{A}$ term). The calculated intensities for two interesting cases are shown in Fig. 3. Figure 3(a) shows the standard x-ray scattering case where a linearly polarized beam enters a sample and an unrotated linearly polarized beam leaves the sample. The absorption in the sample is independent of the orientation (angle θ) of the crystal. Here, the real parts of κ_{xx} and κ_{zz} are much greater than their imaginary parts. As the real and imaginary parts of the $\{ \kappa \}_{ij}$ approach equal magnitude, one sees an orientation-dependent absorption, but, at first,

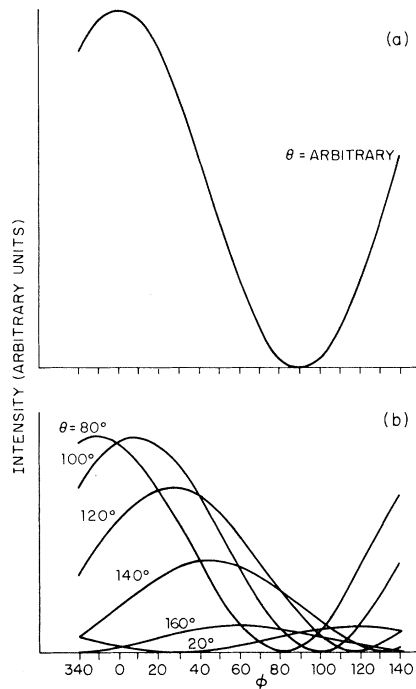


FIG. 3. (a) "Usual" x-ray case. (b) X-ray birefringence case.

no polarization rotation. If the imaginary parts of the $\{\kappa\}_{ij}$ exceed their real parts, there is rotation of the angle of polarization and a strongly crystal-orientation-dependent absorption. The situation approaches the x-ray analog to optical birefringence shown in Fig. 3(b). It is interesting to note that there exists a crystal position for which the linearly polarized beam is almost entirely attenuated.

Using these techniques of varying η and ξ we are able to fit the basic features of the experimental results. The fit for $\eta=2$ and $\xi=2$ is shown as the solid lines in Fig. 2. We have identified $\theta = 15^\circ$ as being 15° from the $[111]$ axis.

The intensities integrated over the polarization analyzer angle ϕ varied as the crystal orientation was changed. Since the beam path is the $[110]$ axis, these intensities would have been identical for each crystal orientation if the effect (as shown in Fig. 2) has been caused by Bragg diffraction

alone. In fact, Laue pictures were taken for both transmission and back reflection to enable us to verify that no accidental simultaneous diffraction took place. Attempts to change the polarization modulation curves were made. These included tilting the crystal (about 1°) in the sample chamber, and reversing the direction of the crystal in the beam. Both experiments showed no change in the basic features of the modulation curve. This may be taken as additional evidence that the Si crystal was not diffracting.

Measurements were made with the same system for three orientations of a thin (111) Si crystal. No rotation of the plane of polarization or crystal-orientation-dependent absorption was seen. We also performed measurements on a thin, commercially supplied, (110) Si crystal. The perfection of this crystal (as determined by x-ray topography⁵) was very poor. It appeared also to be heavily strained. This was in contrast to the excellent quality of the (110) crystal used for the measurements reported in Fig. 2. The three modulation curves taken from this low-perfection crystal were all identical, and no polarization rotation or change in absorption was observed. It appears that the strain field in this crystal was more significant than any deviation from isotropic bonding symmetry.

The reason that orientation-dependent absorption has not been reported earlier can be related to the choice of crystal orientation, the question of crystal perfection, and the fact that linear absorption is generally not measured on a crystal in simple transmission using a polarized x-ray beam.

¹G. Molière, *Ann. Phys. (Paris)* **35**, 272 (1939).

²M. Ashkin and M. Kuriyama, *J. Phys. Soc. Jpn.* **21**, 1549 (1966).

³A. Hōjō, Y. H. Ohtsuki, and S. Yanagawa, *J. Phys. Soc. Jpn.* **21**, 2082 (1966).

⁴For example V. M. Agranovich and V. L. Ginsburg, *Monograph and Text in Physics and Astronomy* (Wm. Clowes and Sons, Ltd., London, 1966), Vol. 18.

⁵W. J. Boettinger, H. E. Burdette, M. Kuriyama, and R. E. Green, *Rev. Sci. Instrum.* **47**, 906 (1976).