Determination of the valence-electron component of the atomic scattering factor of silicon by means of a Compton effect excited by an x-ray standing wave

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A new approach for studying coherent Compton scattering has been implemented for the first time. The idea is to detect the Compton scattering under conditions corresponding to dynamic Laue diffraction of x rays. The way in which the angular dependence of the Compton scattering is shaped has been studied. The component of the atomic scattering factor of silicon, which is due to valence electrons, has been found experimentally.

Compton scattering of x rays is an effective tool for studying the electronic structure of crystals.[1] The reason is that Compton scattering is more sensitive than the intensity of diffraction reflections to the state of weakly bound valence electrons.

The possibilities of Compton scattering are substantially greater under conditions corresponding to a dynamic diffraction of x rays. In this case the coherent superposition of the incident and reflected waves in the crystal gives rise to a spatially periodic

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x-ray standing wave,[2] so the angular dependence of the intensity of the Compton scattering is determined by the distribution of the electron density with respect to the nodes and antinodes of the standing wave. The positions of these features of the wave can be controlled by rotating the crystal near the Bragg angle. The diffraction of the Compton radiation or of external radiation leads to a coherent Compton effect,[3,4] which can be utilized in particular to determine nondiagonal elements of the electron density matrix.[5]

Coherent Compton scattering has been studied previously primarily in the Bragg geometry,[4–7] which is not the optimum choice, even when the amplification of the coherent Compton scattering in the course of asymmetric diffraction is taken into account.[6,7] The reason is that there is a deep extinction dip in the angular dependence of the Compton scattering; this dip detracts from the informativeness of the method.

From this standpoint, the optimum way to carry out the experiments would be in the Laue geometry,[8] but with an energy separation between the Compton scattering and the thermal diffuse scattering. We attempted to solve this problem in the present study. In this letter we propose and report the first implementation of an experimental method based on an energy-dispersive detection of the Compton effect excited by an x-ray standing wave in the Laue geometry. The use of this method has made it possible to determine the valence-electron component of the atomic scattering factor. Since the relative contribution of the valence electrons increases with decreasing angle of the Compton scattering, the Laue geometry has the further advantage that it allows measurements to be carried out in the immediate vicinity of the passing beam.

We used a two-crystal spectrometer to measure the angular dependence of the Compton scattering. We used the (111) reflection from a silicon monochromator with an asymmetry factor of 1/18 to reduce the spectral width of Mo$K\alpha_1$ radiation. The samples were crystals of dislocation-free silicon with a (100) surface. We used a slightly asymmetric (111) Laue reflection. The Compton scattering was detected in the diffraction plane by a semiconductor detector with an energy resolution of 230 eV at an angle $\alpha = 60°$ from the exit surface of the crystal, on the side of the reflected beam. The upper energy boundary of the measurement interval, 1160 eV, was 400 eV on the low-energy side of the thermal-diffuse-scattering peak of the Mo$K\alpha$ line.

Curves of the measured Compton-scattering yield $\kappa(\Delta\theta)$, normalized to the intensity of the Compton scattering far from the diffraction region, are shown in Fig. 1 for two samples of different thicknesses l ($\mu l/\gamma_0 = 0.95$ and 4.29, where μ is the normal absorption coefficient, and γ_0 is the cosine of the angle of incidence on the crystal). The yield curve for the thin crystal (part a of Fig. 1) has a slightly asymmetric dip, which results from the contributions of the weakly and strongly absorbing fields. As the crystal thickness increases, κ acquires a clearly defined maximum at negative angles (part b of Fig. 1; see also Ref. 8). This maximum stems from the increased role of the anomalous transmission of x rays in forming the standing wave on the exit surface of the crystal. In this case the wave field is localized primarily between atomic planes, precisely where a large fraction of the valence electrons can be found.

The curve of the yield of coherent Compton scattering is described by the expression[8]

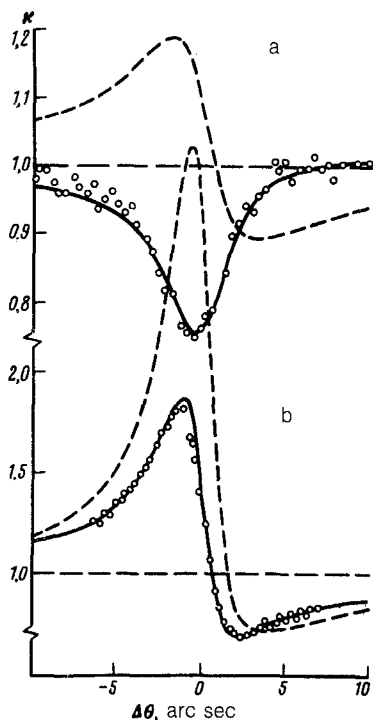

FIG. 1. Yield of coherent Compton scattering under conditions corresponding to dynamic Laue diffraction of x radiation. Points—Experimental data; solid and dashed lines—theoretical predictions for coherent and incoherent Compton scattering, respectively. a) The crystal thickness l is 0.49 mm; b) 2.2 mm.

$$\kappa(\Delta\theta) = \sum_{\nu=1}^{2} [|A_\nu|^2 + b\beta_h + 2\sqrt{b}\,\mathrm{Re}\,(A_\nu \beta_{0h})] l_\nu / 4(1+y^2) l_\infty \, , \tag{1}$$

$$l_\nu = [\exp(-\mu_\nu l) - \exp(-\mu' l/\gamma')] / (\mu'/\gamma' - \mu_\nu),$$

where $A_\nu = y \mp \sqrt{1+y^2}$; y is the normalized angular deviation; b is an asymmetry factor; l_ν are the effective scattering thicknesses; $\mu_{1,2}(y)$ are the interference absorption coefficients for the weakly and strongly absorbed fields, respectively; μ' is the absorption coefficient for the Compton radiation; $\gamma' = \sin\alpha$; and $l_\infty = l_\nu$ at $|y| \gg 1$. The parameters $\beta_h = \sigma_h/\sigma_0$ and $\beta_{0h} = \sigma_{0h}/\sigma_0$ are determined by the diagonal cross sections σ_0 and σ_h for the Compton scattering of the transmitted beam and the reflected beam, respectively, and also by the nondiagonal (interference) cross section for coherent Compton scattering, σ_{0h}. These cross sections depend on the electron density distribution and the observation direction[6]:

$$\sigma_{0,h} = Z - \sum_{ij} |f_{ij}(\mathbf{S}_{0,h})|^2, \quad \sigma_{0h} = F_h [f_h - \sum_{ij} f_{ij}(\mathbf{S}_0) f_{ij}^*(\mathbf{S}_h)] \, , \tag{2}$$

where $\mathbf{S}_0 = \mathbf{k}_0 - \mathbf{k}'$, $\mathbf{S}_h = (\mathbf{k}_0 + \mathbf{h}) - \mathbf{k}'$, $\mathbf{k}_0$ and $\mathbf{k}'$ are the wave vectors of the incident radiation and the Compton radiation, respectively; $\mathbf{h}$ is a reciprocal-lattice vector; Z is the number of atomic electrons; f_{ij} are the form factors of the electron orbitals; and f_h is the atomic scattering factor. For the (111) reflection, we would have $F_h = f_T/\sqrt{2}$, where f_T is the Debye-Waller thermal factor.

The valence-electron component of f_h is extracted from the experimental curves by the following procedure. Since the wave functions of the $2s^2 2p^6$ bound electrons are essentially the same as those for the free atoms, the cross sections for Compton scattering by these electrons were calculated with the help of the Hartree-Fock values of f_{ij} for the Si^{+4} ion core[9] (under our experimental conditions, the $1s^2$ electrons did not contribute to the detected intensity). Since the impulse approximation can be used for valence electrons,[1] we find $\sigma_0 = 10.318$ and $\sigma_h = 9.575$ for the diagonal cross sections for Compton scattering by the silicon atoms; i.e., we find $\beta_h = 0.928$. For the nondiagonal cross section for Compton scattering by the electrons of the ion core we find $\sigma_{0h}(2s^2 2p^6) = 3.752$. The yield curves described by (1) fit the experimental data best, with the value just given for β_h, at $\beta_{0h} = 0.45 \pm 0.01$. The total cross section is therefore $\sigma_{0h} = 4.64 \pm 0.1$. The contribution of the four valence electrons to σ_{0h} is therefore $\sigma_{0h}^v(3s^2 3p^2) = 0.89 \pm 0.1$. Since we can ignore the sum over i, j in $\sigma_{0h}^v(2)$, in the impulse approximation, we conclude, using $F_h = 0.699$, that the component of the atomic scattering factor due to valence electrons is $f_h^v = 1.27 \pm 0.15$. In analyzing the yield curves we allowed for the divergence and polarization of the incident beam, the detection energy interval, and the resolution of the detector. For comparison, we have shown in Fig. 1, by the dashed lines, the sharp deviation of the Compton-scattering curves from the experimental data when we ignore the angular dependence of the diagonal cross sections and—the more important point—when we ignore the coherent nature of the Compton scattering, i.e., if we assume (as in Ref. 7) $\beta_h = 1$ and $\beta_{0h} = 0$.

The value that we found for f_h^v agrees well with the result $f_h^v = 1.3$ found in Ref. 5 from measurements of the area under the nondiagonal Compton profile of valence electrons. It also agrees well with the difference between the experimental atomic scattering factor in a silicon crystal, f_h (Si) $= 10.739$ (Ref. 10), and the value calculated from the data of Ref. 9 for the ion core, $f_h(Si^{+4}) = 9.439$.

The measurement procedure which we have used allows the experimental data to be stored in the form of two-dimensional angle-energy data files (Ref. 11, for example). These files would contain, along with the curves of the integral intensity of the Compton scattering, which we have been discussing here, information on the Compton profiles. Analysis of these profiles yields further information about the nature of the electron density distribution in solids.

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