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Determination of the absolute structure factor for the forbidden (222) reflection in silicon using 0.12-Å γ rays

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A room-temperature determination of the absolute structure factor for the forbidden (222) reflection in silicon has been conducted at the University of Missouri Research Reactor with 103-keV gamma rays. The measured structure factor of $F(222)=1.456 \pm 0.008$ is in excellent agreement with five of the earlier intensity measurements, and is significantly different from any value determined using Pendellösung techniques. An increase in accuracy over previous intensity measurements by a factor of between 2 and 10 has been achieved and is made possible through the use of monoenergetic, short-wavelength gamma rays, which allow absolute measurements to be made in Laue geometry on relatively thick crystals (~ 1 mm) without encountering extinction problems.

I. INTRODUCTION

Ever since Bragg first measured the "forbidden" (222) reflection in diamond some 60 years ago,[1] experimentalists and theorists alike have been trying to record and model the electronic charge distribution accurately in elements with the diamond structure, such as silicon. While numerous interpretations have been used to account for the existence of the (222) reflection, the approach outlined by Roberto and Batterman[2] will be followed in large measure here. A familiar structure, the diamond lattice (Fig. 1) consists of eight atoms per unit cell arranged in the form of two interpenetrating fcc sublattices. These sublattices, denoted by A and B, are separated by one-quarter of the distance along the cube diagonal. Atoms on the A sites have their nearest neighbors on the B sites and similarly, atoms on the B sites have their nearest neighbors on the A sites. Although a center of symmetry exists in the direction of the bond between nearest neighbors, local-site symmetry is tetrahedral ($\bar{4}3m$). Assuming a spherically symmetric charge distribution at the atomic positions, the structure factor of the (222) reflection for the unit cell may be written as $F(222)=4(f_A-f_B)=0$, hence the term "forbidden" reflection. The occurrence of the (222) reflection in diamond structures results from the covalent bonding between atoms. In order for the covalent bonds to exist, a distortion of the electronic cloud must take place and conform to the site symmetry of the individual atomic positions. The corresponding charge buildup between atoms represents an antisymmetric distribution of scattering matter. This electronic redistribution from an *a priori* spherical atom is reflected in the structure factor $F(222)$ by the addition of an antisymmetric term to the atomic scattering factor.

Upon closer inspection of the diamond structure one also finds that each atom in its tetrahedral environment has, along any [111] axis, a bonded nearest neighbor in one direction and a "hole" in the opposite direction. This spatial arrangement allows the nonbonding core electrons to vibrate about a mean position slightly off the idealized diamond-lattice position and in the direction opposite that of the bonding electrons. Such anharmonic motion creates a time-averaged tetrahedral asymmetry which would be expected to increase with temperature. Combining these two effects into the structure factor for the unit cell yields

$$F(222)=8(f_{\text{asymm}}-f_{\text{anh}})=8f_{\text{bond}} \cdot$$

While the anharmonic term has not been quantitatively distinguished from the bonding term with electromagnetic radiation,[2] the anharmonic effect can be measured with neutrons. Since neutrons interact with what is basically a point nucleus, the neutron structure factor gives a measure only of the time averaged antisymmetric nuclear distribution resulting from the anharmonic thermal motion. Once determined, the anharmonic x-ray term may then be derived by noting that $F_{\text{anh x ray}}(222)=F_{\text{neutron}}(222)f_c/b$, where f_c is the x-ray scattering factor for the core electrons and b the neutron scattering length.[3] A neutron temperature-dependent study of the silicon (222) reflection has been conducted[3,4] and the results show the anharmonic contribution to be equal in magnitude to approximately 1% of $F_{\text{x ray}}(222)$ at room temperature, and confirm the choice of sign for the anharmonic term to be opposite that of the asymmetric term.

Given the small anharmonic contribution to the structure factor, an absolute measure of $F(222)$ is, essentially, a direct quantitative description of the valence-electron density. In a recent self-consistent calculation of the ground-state electronic properties of diamond within the local-density formalism, Zunger and Freeman[5] studied explicitly the role of electron exchange and correlation on the charge density. The (222) reflection turned out to be particularly sensitive to the details of the self-consistency maintained in the calculation and to the quality of the basis set. This structure factor increased by about a factor of 2 upon introducing exchange in the potential. It further increased when correlation was taken into account in the crystal potential, but only by 1.5%. For comparison, the increase in $F(111)$ due to correlation is of the order 0.25%. This calculation not only demonstrates how sensitive the forbidden (222) structure factor is to details in the charge density but it also shows how desirable it is to improve the accuracy in the experimental value from about 2% at the present time to better than 1%.

Aldred and Hart[6] performed absolute measurements of x-ray structure factors of Si up to $\sin\theta/\lambda \leq 1$ Å^{-1} by means of the Pendellösung method and the internal consistency of the results indicates that probable errors are of the order 0.1%. This is the highest accuracy in structure-factor measurements obtained until now. However, the method requires extremely perfect single crystals, especially if very weak reflections like the (222) are to be measured; that is probably the reason why Aldred and Hart did not determine the $F(222)$ experimentally. They did calculate $F(222)$ within Dawson's structure-factor formalism from their measured data[7] and compared this result with the $F(222)$ value determined experimentally by other authors. Aldred and Hart's calculated value is lower than most of the values obtained from intensity measurements but they doubt the accuracy of these experimental values. As an example they refer to the work by Roberto and Batterman,[2] who have scaled their $F(222)$ value to theoretical structure factors for the (111) and (333) reflections. Because Aldred and Hart find a different value for $F(111)$ they rescale the $F(222)$ value reported by Roberto and Batterman and find good agreement with their calculated value for the (222) reflection. This discussion shows the importance of measuring $F(222)$ on an absolute scale.

With such importance attached to a single reflection it becomes evident why many attempts have been made to determine an absolute structure factor for the (222) reflection. Experiments investigating the (222) reflection in silicon have been conducted using x-ray and neutron intensity measurements,[2–4,8–14] x-ray Pendellösung fringe spacings employing two different techniques,[14–16] and more recently an attempt has been made using gamma rays at 0.03 Å.[17] Unfortunately, reported values for $F(222)$ range from 0.88 to 1.78. Since the total scattering matter contributing to the intensity of the (222) reflection comes only from the valence electrons, the reflection is quite weak. The determination of the absolute structure factor, therefore, requires the careful consideration and

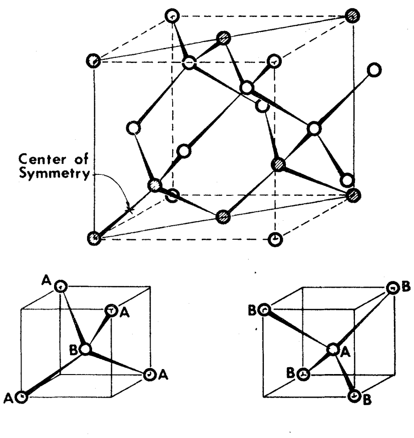

FIG. 1. Diamond lattice.

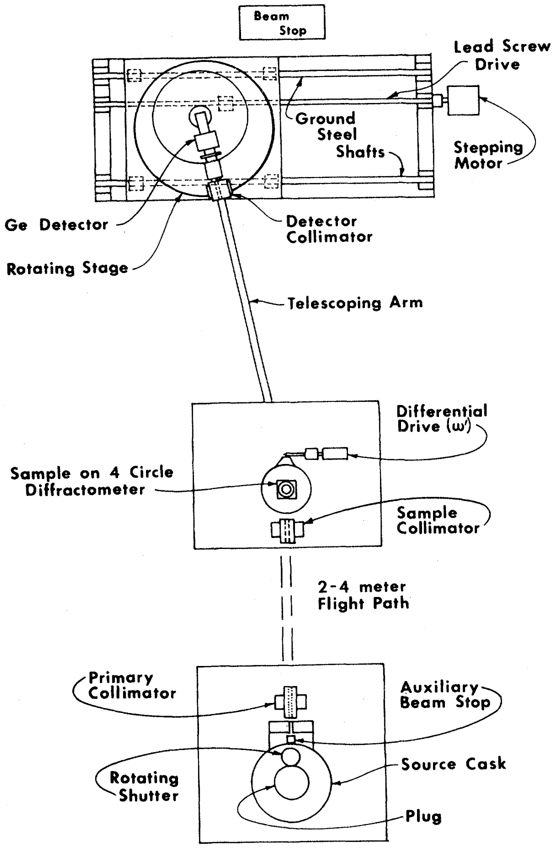

FIG. 2. Schematic of the γ-ray instrument.

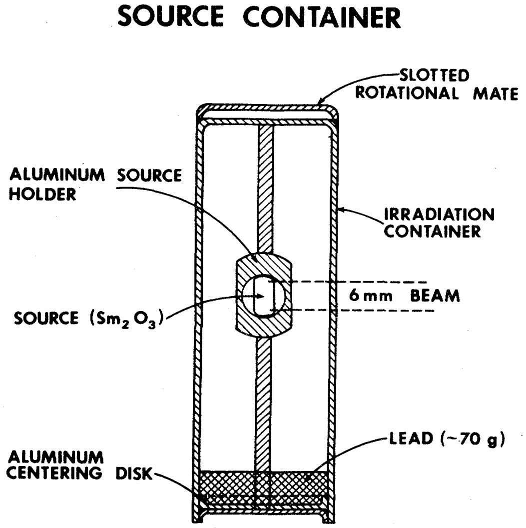

FIG. 3. $^{152}Sm_2O_3$ encapsulated into an ultrahigh-purity aluminum holder. The completed source container is designed to undergo multiple irradiations.

elimination of possible sources of error, such as multiple scattering, Compton scattering, wavelength contamination, crystal perfection (depending on the approach), and extinction.

It is the purpose of this paper to report an experimental room-temperature value for $F(222)$ determined on an absolute basis using 0.12-Å gamma rays. Potential sources of error likely to be encountered during an absolute structure-factor determination will be discussed briefly, with specific applications to the instrumentation used. It will be shown that absolute structure factors can be determined with greater than 1% accuracy while eliminating most of the problems associated with more traditional techniques.

II. EXPERIMENTAL

A detailed description of the instrument used for this study has been given elsewhere,[18] but a brief review will be presented here for clarity. The gamma-ray diffractometer consists of three principal parts: the source (inside a portable shielding cask), a full χ,ϕ circle with high-precision ω rotation, and a solid-state detector on a linear drive train (Fig. 2). A new design for the source container has been instituted (Fig. 3) which uses a 99.999% pure Al holder with a pressed fit cover to encapsulate the $^{152}Sm_2O_3$ source powder. Previously, γ rays produced from weld rod used to seal in the source material made direct beam determination difficult and contributed significantly to the overall background. In the new design, this contaminating radiation is no longer present in the beam line. Each individual source container is designed to operate through many irradiation cycles without alteration. After a one-week irradiation in a flux of 4×10^{14} neutrons/cm^2 sec at the University of Missouri Research Reactor, approximately 800–1000 Ci of ^{153}Sm are produced, with a half-life of 46.27 ± 0.07 h. Integrated intensities are collected using omega step scans. Samples with a broad mosaic structure are scanned in increments of 0.01°, while crystals with a sharp mosaic are scanned with the differential omega drive, capable of 0.225″ arc per step precision. An intrinsic germanium detector with a 13-mm thick crystal detects the 103-keV photons with $\sim$70% efficiency. Current instrument settings allow a maximum incident beam divergence of $\sim4'$ horizontal and $\sim9'$ vertical as seen by the central point of the sample. At the peak of the source activity the photon flux on the sample is 2×10^6/cm^2 sec at

103 keV and the static background is less than 0.1 Hz. Sources are exchanged every seven or eight days.

Silicon crystal slabs 20 mm × 12 mm × ($\sim$1- and $\sim$0.9-mm thickness) were used in the present experiment. The 1-mm crystal was cut with a 220-grit diamond wheel from a large single-crystal ingot. It was lightly etched in a 7:2:1 mixture of $HC_2H_3O_2$:HNO_3:HF and showed visible signs of surface damage. Four measurements were made on this crystal; these include two measurements on a single reflection (for reproducibility), one measurement on this same reflection after a 1° rotation around the scattering vector, and one measurement on a non-Friedel symmetry equivalent. Next, this same crystal was uniformly etched in a mixture of 6:3:2 HNO_3:$HC_2H_3O_2$:HF to a thickness of $\sim$0.9 mm. No signs of surface damage remained. Two non-Friedel symmetry-equivalent reflections were measured using the 0.9-mm crystal. Each of the two crystal thicknesses were measured with a micrometer gauge and average deviations in the thickness of each crystal were determined to be $\pm$0.005 mm. All six measurements were made in Laue geometry, where the crystal fully encompassed the 4-mm-diameter incident beam. An average of 4.2×10^4 counts were contained in each integrated peak after background subtraction, with a minimum of 2×10^4 counts for any single reflection. Peaks were scanned using the differential omega motion in increments of 0.005°, where each increment corresponds to 80 steps on the differential drive. Scan times for each reflection totaled approximately two days. Results are listed in Table I.

III. RESULTS AND DISCUSSION

Several sources of error have plagued traditional absolute-intensity measurements and, with the comparatively new technique of gamma-ray diffraction, it should be instructive at this time to address both the advantages and the problems unique to this diffraction method and specifically to this instrument.

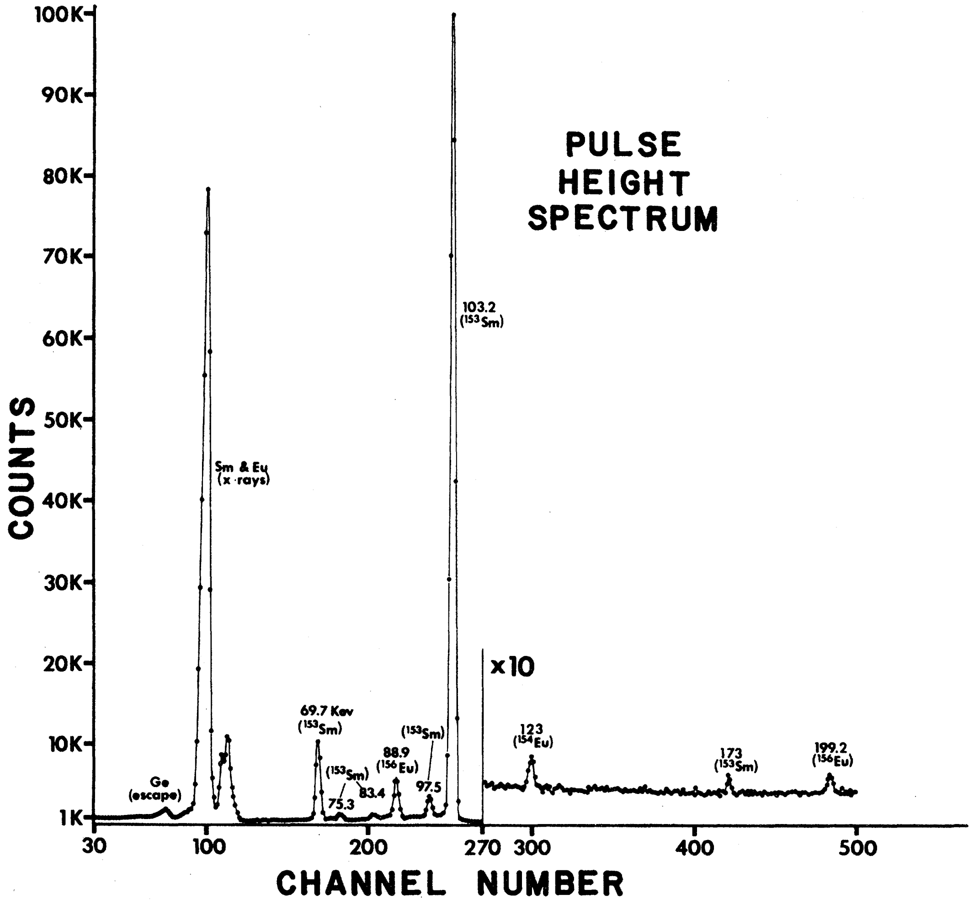

FIG. 4. Multichannel analysis of the ^{153}Sm spectrum after multiple irradiations.

Unique to radioactive sources is the inherent monochromatic beam. Figure 4 illustrates the energy spectrum obtained from the ^{153}Sm source using a multichannel analyzer. For the intense 103-keV gamma ray, $\Delta\lambda/\lambda$ is of order 10^{-6}. Although a 97-keV gamma ray from the source does exist, the excellent energy resolution of the intrinsic germanium detector can easily separate it from the main energy of interest. The dead time (τ) of the counting chain was determined to be 6.0 μsec using a Bragg diffracted beam. A few ^{153}Sm gamma lines do exist which are higher in energy than the principal 103-keV gamma line, and the Compton scattering from them into the electronic window is 0.6% of the photopeak intensity of the main gamma line. Source stability is based strictly on the exponential decay making intensity corrections possible over 3 or 4 half-lives with less than 0.2% uncertainty.

While "umweganregung" and "aufhellung" conditions[19] are readily calculated, it has been pointed out[20] that the conditions for multiple Bragg scattering are, basically, always satisfied using short-wavelength gamma radiation. However, given the narrow linewidth of the 0.12-Å radiation, the Ewald sphere is quite thin. With the incident-beam divergence controlled to avoid excitation of intense, low-order Bragg spots on the sphere of reflection, the remaining reflections which are simultaneously on the Ewald sphere with the desired (222) peak have such high $\sin\theta/\lambda$ values that their participation in the diffraction process can be considered negligible. It has been demonstrated with 0.12-Å radiation,[18] however, that specific conditions can arise which allow multiple Bragg events to influence the outcome of a measurement. In the present work, no measurement taken on either crystal showed signs of multiple scattering.

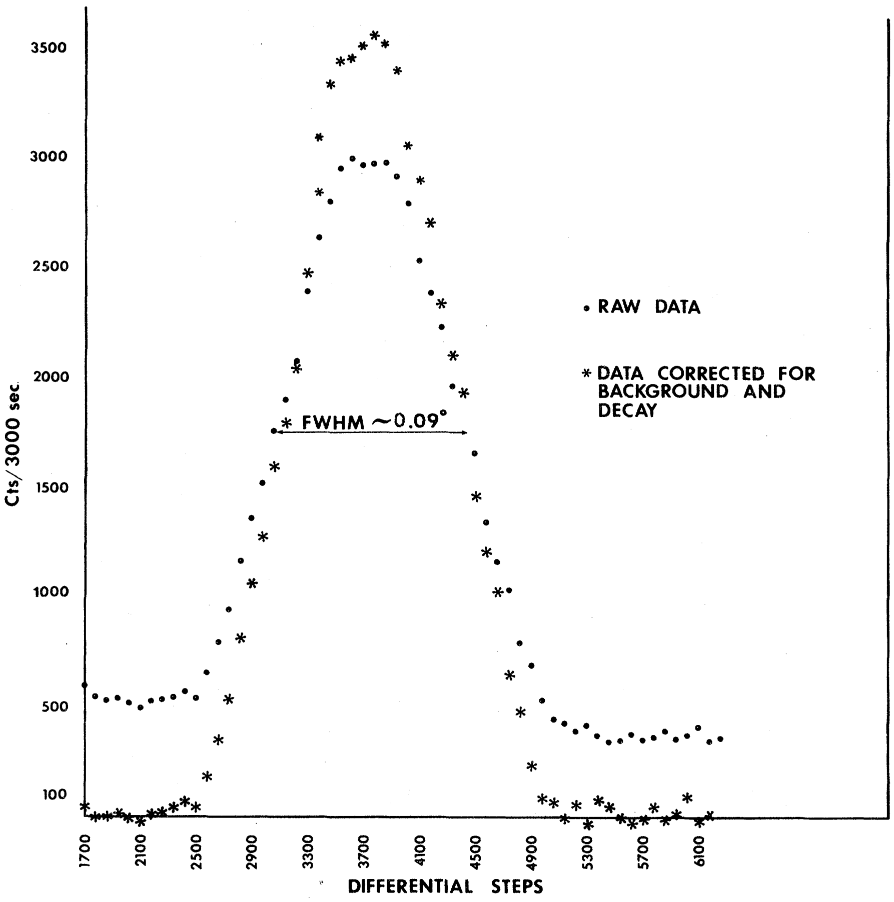

FIG. 5. Rocking curve of the (222) reflection in silicon, before and after corrections for background and decay.

Owing to the complexity of the source container, Bragg peak measurements have underlying background levels which decay at a rate different from that associated with the ^{153}Sm source alone. Figure 5 illustrates raw data taken during the beginning of a measuring period and the same data corrected for background and decay. Contributions to the background come from ^{24}Na produced by the aluminum construction materials and from the ^{153}Sm source. In addition, trace amounts of alloying metals present in the irradiation container eventually become activated. These isotopes are generally long-lived compared to ^{153}Sm and thus require lengthy irradiation times before they influence the background or, more importantly, the spectral properties of the incident beam. Cumulative background levels measured during peak ^{24}Na activity were, in the worst case, 0.2 Hz. Background corrections were made by subtracting the static source-independent contribution first, then fitting the residuals to an exponential function. A linear least-squares fitting procedure was used on the exponential function to compute a smooth curve which represented the overall background. Values from this curve were chosen to represent the background beneath the main peak.

Quantifying the power of the incident beam is simplified with a radioactive source of short half-life yet, at the same time, can be potentially the largest source of error. During the active data collection period a ^{153}Sm source will decay through 3 or 4 half-lives, making the incident flux at least an order of magnitude less than its original value. Two or three aluminum blocks (approximately 2.5-cm thick each) are used at this point to lower the count rate to about 1000 Hz for the incident-beam measurement. When measuring the incident beam the full complement of gamma rays from the source container impinge upon the detector crystal. Although counting rates monitored after passing through the single channel analyzer (i.e., from the 103-keV gamma ray only) may be relatively low, detector dead time is dependent on the overall count rate per unit area of the detector crystal. "Extra" counts on the crystal are the result of short- and long-lived isotopes produced from materials present in the aluminum source container as well as photons from Bremsstrahlung radiation and gamma rays present in the ^{153}Sm source other than the principal one used. In order to minimize change in incident beam characteristics which could affect dead time corrections, present measurements have been made using sources irradiated not more than two times. In the future, Al as container material will be replaced by graphite.

TABLE I. Silicon $F(222)$ by γ-ray diffractometry ($\lambda = 0.12$ Å).

$F(222)=8fe^{-M}$	
1.041-mm crystal	0.932-mm crystal
1.459 ± 0.007	1.462 ± 0.007
1.457 ± 0.009	1.455 ± 0.008
1.459 ± 0.007	
1.441 ± 0.009	mean = 1.456 ± 0.008

Following Zachariasen[21] the integrated reflecting power of a perfect single crystal as measured in an omega scan in symmetrical Laue geometry is equal to

$$R_H^{\theta} = \frac{r_e \lambda^2 F_H R_H^{y}}{\pi \sin(2\theta_B) V} ,$$

where r_e is the classical electron radius, λ the wavelength, θ_B the Bragg angle, and V the volume of the unit cell. F_H represents the structure factor for the unit cell which, in this case, can also be written as $F_H = 8fe^{-M}$ where f is the atomic scattering factor and e^{-M} the Debye-Waller factor. R_H^{y} is given as a function of a parameter $A = t_0/t_{\text{ext}}$, which is the ratio of the crystal thickness t_0 and the extinction length

$$t_{\text{ext}} = \frac{V \cos\theta_B}{r_e \lambda F_H C} ,$$

where C is the polarization constant. In the case of negligible absorption one finds

$$R_H^{y} = \frac{\pi}{2} \int_0^{2A} J_0(x) dx .$$

For $t_0 \gg t_{\text{ext}}$, that is $A \gg 1$, the integrated intensity becomes $R_H^{y} = \pi/2$. In the case of a very thin crystal with $t_0 \ll t_{\text{ext}}$, that is $A \ll 1$, one reaches the kinematical limit and the integrated reflecting power is equal to $R_H^{y} = \pi A$ or

$$R_H^{\theta} = \frac{r_e^2 F_H^2 \lambda^3 [1 + \cos^2(2\theta_B)] t_0}{2V^2 \sin(2\theta_B) \cos\theta_B} .$$

We have performed absolute measurements of the (111) structure factor on the sample used for the measurement of $F(222)$ by reducing the intensity of the incident beam to about 3000 Hz using attenuators. The integrated Bragg-diffracted intensity R_m was then normalized by the intensity of the transmitted beam measured on both sides of the Bragg peak, which means R_m can be compared with theoretical values calculated for zero absorption. The parameter A for the (111) reflection calculated for $t_0=0.932$ mm is equal to $A=11.82 \gg 1$. Therefore, it is reasonable to compare the measured value of the integrated reflecting power with the theoretical one calculated for a "thick" perfect crystal. Within the experimental uncertainty, we find agreement between the experimental and the average theoretical value. We conclude then that the crystal on which the $F(222)$ was measured is very close to being perfect.

In the first step $F(222)$ was calculated from the integrated reflectivity measured at the (222) reflection within the kinematical limit. We found a value of $F(222) \sim 1.432$, which was then used to calculate the parameter $A(222)$ for the two thicknesses, or 0.29 and 0.32, respectively. Apparently the limit $A \ll 1$ is not reached and therefore the exact formula for R_H^y has to be used. The R_H^y values calculated this way are 2.8% or 3.5% smaller than the value for the kinematical limit for the respective sample thickness, which increases the value of the (222) structure factor by 1.4% or 1.8%, respectively. In other words, imperfections in the sample which could influence the diffraction process and which we excluded because of the good agreement between measured and calculated integrated reflecting power obtained for the (111) reflection would reduce the reported $F(222)$ value by at most $\sim 1.5\%$.

Since orientation of the single-crystal ingot was known before cutting, it is assumed that the diffraction planes are perpendicular to the face of the crystal. In this case, θ represents the Bragg angle in all parts of the reflectivity equation, which is computed with $a_0=5.431$ Å. Any error introduced by this assumption should be quite small, since the diffraction angle for the (222) reflection is only 2.2° with 0.12-Å radiation. Each variable involved in the calculation of $F(222)$, such as wavelength, thickness, half-life and the attenuator transmission coefficient, contributes to the error in the final value. However, in all cases, the major source of error was due to counting statistics, background, and direct beam measurements. In diffraction experiments with 0.12-Å gamma rays, multiple scattering is always present from reflections at large $\sin\theta/\lambda$. However, the effects attributed to these reflections are extremely small and can be considered a constant, both on the peak and in the background. Therefore, these effects are considered negligible. When multiple scattering from low-order peaks occurs it is obvious, and in the present case was not observed.

A summary of the accumulated works to date involving the absolute determination of $F(222)$ are presented in Table II. At the outset, the measurements made by Hewat *et al.*[13] and Cramb[15] reportedly suffered from problems due to intensity scaling and crystal defects, respectively.[16] In comparison to previous intensity measurements (as opposed to Pendellösung fringe measurements) our value of 1.456 is in excellent agreement with five of the earlier measurements. The measurements by Schneider *et al.*[17] were also performed using gamma-ray diffraction ($\lambda=0.03$ Å) but they suffer from very poor statistics. Additionally, an extrapolation to the limit of zero extinction had to be applied which has to be considered as a major source of error. For those experiments where the reported value is outside the quoted error bars from the present results, the difference may be explained as due to scaling problems or to multiple Bragg scattering. The Pendellösung fringe measurements of Fujimoto[14] and of Fehlman and Fujimoto,[16] for which excellent precision is claimed, do not agree either with our results or between themselves. Our value of 1.456 ± 0.008 clearly disagrees with the $F(222)$ of 1.35 ± 0.04 calculated by Aldred and Hart[7] from the structure factors measured of the "allowed" reflections.

TABLE II. Values of the structure factor $F(222)$ for silicon at room temperature.

Authors	$F(222)=8fe^{-M}$
Hewat, Prager, Stephenson, and Wagenfeld (1969)	0.88
[a]Aldred and Hart (1973)	1.35 ±0.04
DeMarco and Weiss (1965)	1.44 ±0.08
Present	1.456±0.008
Roberto and Batterman (1970)	1.46 ±0.04
Jennings (1969)	1.48 ±0.03
Fujimoto (1974) Cu$K\alpha_1$	1.48 ±0.02
[b]Schneider, Hansen, and Pattison (1980)	1.50 ±0.05
[c]Fujimoto (1974)	1.50 ±0.015
Fujimoto (1974) Ag$K\alpha_1$	1.51 ±0.02
Colella and Merlini (1966)	1.54
Renninger (1960)	1.55
[c]Fehlman and Fujimoto (1975)	1.65 ±0.03
Cramb (1970)	1.76 ±0.03
Göttlicher and Wölfel (1959)	1.78

[a] Model value.
[b] Extrapolated value ($\lambda=0.03$ Å).
[c] Pendellösung value.

IV. CONCLUSIONS

Many attempts have been made to determine the absolute structure factor of the silicon (222) reflection because it is extremely sensitive to details in the electronic charge density and this is regarded as a stringent test on the various concepts used to describe the chemical bonding in this system. The present measurement was performed on an absolute scale and yielded a value of $F(222)=1.456\pm 0.008$. This value is of significantly higher accuracy than those reported earlier and therefore it is considered to open a new perspective for a comparison between experimental and theoretical data in terms of the physical concepts on which the various theoretical approaches are based. The present result is in excellent agreement with five of the previous intensity measurements, and certainly disagrees with the results obtained by means of Pendellösung fringe measurements. This discrepancy, however, can hardly raise doubts concerning the validity of the present measurement because there were two independent measurements performed by means of the Pendellösung method in the same laboratory which do not agree and the authors do not explain the reason for this discrepancy. It is interesting to note that our value for the (222) structure factor in silicon is also in clear disagreement with the value calculated by Aldred and Hart using Dawson's structure-factor formalism and their structure factors measured of the "allowed" reflections by means of the Pendellösung method.

The reasons for the improvement in accuracy of the silicon $F(222)$ measured with gamma rays compared to previous x-ray intensity measurements are essentially the following: The incident beam intensity could be measured with high accuracy so that the measurements are on an absolute scale; we could work with relatively thick crystal plates (~ 1 mm) so the sample thicknesses could be measured accurately, and yet the difference between the kinematical and dynamical limit for the integrated reflecting power of the very weak (222) reflection is only of order 3%.

ACKNOWLEDGMENT

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