$$H_{n+1}(x)=xH_n(x)-nH_{n-1}(x) \quad (n\geq 1) \qquad (A5)$$

$$H_0(x)=1 \quad \text{and} \quad H_1(x)=x \qquad (A6)$$

$$\begin{aligned} D^kJ_0(x)=2^{-k}\bigg[&J_{-k}(x)-\binom{k}{1}J_{-k+2}(x)\\ &+\binom{k}{2}J_{-k+4}(x)+\ldots+(-1)^kJ_k(x)\bigg]. \qquad (A7)\end{aligned}$$

Calculation of $D^8[\log J_0(x)]$

Substituting $\alpha_n(x)=J_n(x)/J_0(x)$ for $|x|\leq 2$ one obtains

$$\begin{aligned} D^8[\log J_0(x)]=&-5040[\alpha_1(x)]^8-5040[\alpha_1(x)]^6\\ &\times\{2[1-\alpha_2(x)]-[1-\tfrac{1}{3}\alpha_3(x)/\alpha_1(x)]\}\\ &-[\alpha_1(x)]^4\{6300[1-\alpha_2(x)]^2\\ &-5040[1-\alpha_2(x)]\\ &\times[1-\tfrac{1}{3}\alpha_3(x)/\alpha_1(x)]\\ &-630[1-\tfrac{4}{3}\alpha_2(x)+\tfrac{1}{3}\alpha_4(x)]\\ &+945[1-\tfrac{1}{3}\alpha_3(x)/\alpha_1(x)]^2\\ &+210[1-\tfrac{1}{2}\alpha_3(x)/\alpha_1(x)\\ &+\tfrac{1}{10}\alpha_5(x)/\alpha_1(x)]\}\\ &-[\alpha_1(x)]^2\{1260[1-\alpha_2(x)]^3\\ &-945[1-\alpha_2(x)]^2\\ &\times[1-\tfrac{1}{3}\alpha_3(x)/\alpha_1(x)]\\ &-472{\cdot}5[1-\alpha_2(x)]\\ &\times[1-\tfrac{4}{3}\alpha_2(x)+\tfrac{1}{3}\alpha_4(x)]\\ &+157{\cdot}5[1-\alpha_2(x)]\\ &\times[1-\tfrac{1}{3}\alpha_3(x)/\alpha_1(x)]^2\\ &+105[1-\alpha_2(x)]\\ &\times[1-\tfrac{1}{2}\alpha_3(x)/\alpha_1(x)\\ &+\tfrac{1}{10}\alpha_5(x)/\alpha_1(x)]\\ &+157{\cdot}5[1-\tfrac{1}{3}\alpha_3(x)/\alpha_1(x)]\\ &\times[1-\tfrac{4}{3}\alpha_2(x)+\tfrac{1}{3}\alpha_4(x)]\\ &+17{\cdot}5[1-\tfrac{3}{2}\alpha_2(x)+\tfrac{3}{5}\alpha_4(x)\\ &-\tfrac{1}{10}\alpha_6(x)]\\ &-26{\cdot}25[1-\tfrac{1}{3}\alpha_3(x)/\alpha_1(x)]\\ &\times[1-\tfrac{1}{2}\alpha_3(x)/\alpha_1(x)\\ &+\tfrac{1}{10}\alpha_5(x)/\alpha_1(x)]\\ &-4{\cdot}375[1-\tfrac{3}{5}\alpha_3(x)/\alpha_1(x)\\ &+\tfrac{1}{5}\alpha_5(x)/\alpha_1(x)-\tfrac{1}{35}\alpha_7(x)/\alpha_1(x)]\}\\ &-\{39{\cdot}375[1-\alpha_2(x)]^4\\ &-39{\cdot}375[1-\alpha_2(x)]^2[1-\tfrac{4}{3}\alpha_2(x)\\ &+\tfrac{1}{3}\alpha_4(x)]\\ &+4{\cdot}921\,875[1-\tfrac{4}{3}\alpha_2(x)+\tfrac{1}{3}\alpha_4(x)]^2\\ &+4{\cdot}375[1-\alpha_2(x)]\\ &\times[1-\tfrac{3}{2}\alpha_2(x)+\tfrac{3}{5}\alpha_4(x)-\tfrac{1}{10}\alpha_6(x)]\\ &-0{\cdot}273\,437\,5[1-\tfrac{8}{5}\alpha_2(x)+\tfrac{4}{5}\alpha_4(x)\\ &-\tfrac{8}{35}\alpha_6(x)+\tfrac{1}{35}\alpha_8(x)]\}. \end{aligned}$$

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Phase Observation in an Organic Crystal (Benzil: $C_{14}H_{10}O_2$) Using Long-Wavelength X-rays

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Abstract

The phase-related asymmetry effect near a multi-beam excitation point has been observed for a noncentrosymmetric organic crystal, benzil ($C_{14}H_{10}O_2$), by using 3·5 keV X-ray synchrotron radiation. A multi-beam theoretical calculation shows good agreement with the experimental data when mosaic spread of the crystal is taken into account. A practical method to extract the cosine of the phase triplet for noncentrosymmetric crystals is also discussed.

Introduction

It has been recognized that multi-beam X-ray diffraction, especially the concept of virtual Bragg scattering

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(Chapman, Yoder & Colella, 1981), can be used in a diffraction experiment to obtain phase information on the structure factors of a crystal (Shen & Colella, 1986). The idea is to measure the intensity of a weak reflection (main reflection) in the neighborhood of a strong multiple reflection, by rotating the crystal around the scattering vector. The intensity on the wings of the multiple-reflection peak usually shows an asymmetric pattern, higher than the value of the main reflection on one side and lower on the other side, over an angular interval of a few degrees. This asymmetric pattern is related to the phases of the structure factors involved. Successful phase determinations have been obtained for some forbidden reflections of silicon (Tischler, Shen & Colella, 1985) and V_3Si (Schmidt & Colella, 1985).

Problems have been found, however, when organic crystals are considered, because of their relatively large unit cells that cause densely populated multiple reflections. As an example, benzil ($C_{14}H_{10}O_2$) is an organic crystal isomorphous with quartz (space group $P3_121$ or $P3_221$). Its Bravais lattice is simple hexagonal with $a = 8{\cdot}376$ and $c = 13{\cdot}700$ Å (Brown & Sadanaga, 1965, hereafter BS). For its 606 reflection with Cu $K\alpha$ radiation, there are more than 5000 multiple reflections in a 360° azimuthal rotation acccording to calculation, which means that, on the average, one Renninger peak is calculated for every 4′ arc. Since a typical mosaic spread is ~2-3′ arc, it is almost impossible to see the asymmetry effect in an experiment, even with a highly collimated beam like that obtainable from a synchrotron.

One way to attack this problem is to make use of soft X-rays which give rise to a smaller sphere of reflection. This smaller Ewald sphere will obviously intersect a smaller number of reciprocal-lattice nodes during its rotation.

Another problem with organic crystals is that the 'size' of the nodes in reciprocal space is very small when the mosaic spread is neglected. In other words, dynamical theory predicts very narrow multiple-diffraction peaks, with asymmetry effects confined to angular regions smaller than, say, 1′ arc, so that the phase information is completely obliterated by the mosaic spread of the crystal. Fig. 1 shows an example of a calculated profile for benzil at $\lambda = 1{\cdot}55$ Å. An experiment performed with a synchrotron beam with $\lambda = 1{\cdot}55$ Å and azimuthal resolution better than 1′ failed to show any asymmetry effect in benzil.

One way to make rocking curves broader is to increase λ. The Darwin width is in fact proportional to $\lambda/\cos\theta$, where θ is the Bragg angle. It is conceivable that at larger λ values the multiple-diffraction peaks may also become broader. A quick calculation confirmed our expectation (Fig. 2).

In this paper we report a successful observation of the asymmetry effects on an organic crystal (benzil) by using 3·5 keV soft X-rays available at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory (BNL). Since benzil is noncentrosymmetric, a possible way to extract any value of the phase triplet will also be discussed.

Experimental

The X-ray storage ring at NSLS of BNL provides a continuous spectrum from below 0·1 keV up to

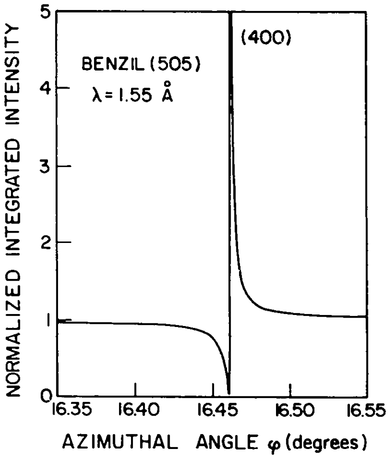

Fig. 1. A three-beam calculation for the benzil 505-400 multiple reflection with $\lambda = 1{\cdot}55$ Å, using Shen's (1986) perturbation theory. Each point in this plot is an integrated intensity with respect to θ, the angle of incidence on the (505) lattice planes. The intensities are for a perpendicularly polarized incident beam and have been normalized to the two-beam value. The zero on the horizontal scale corresponds to the ($\bar{1}20$) reciprocal vector lying in the diffraction plane, mostly antiparallel to $\mathbf{k}_0$, the incident wave vector. It shows that the asymmetry effect is confined within a very small angular region, comparable to the mosaic spread of the crystal. The peak value, corresponding to full excitation of the 400, is not plotted on this graph.

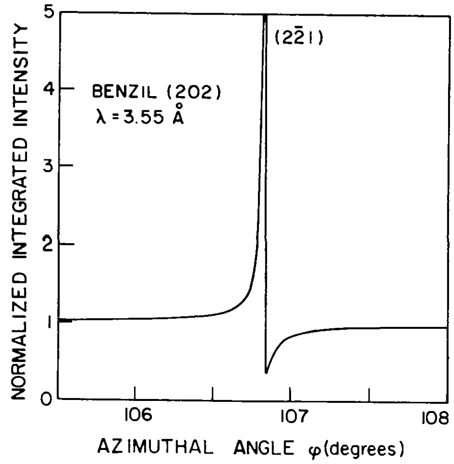

Fig. 2. Same as Fig. 1, except that it is for benzil 202-$2\bar{2}1$ and $\lambda = 3{\cdot}55$ Å. Now the asymmetry effect spans an angular range about ten times wider than the mosaic spread.

20 keV. The experiment was performed on the X-18A beam line. Typical ring current during the experiment was ~60 mA. A double Si(111) perfect-crystal monochromator was used to select the 3·5 keV energy. The third harmonic arising from 333 was greatly attenuated by deliberately offsetting the Bragg angle of the second Si crystal, a method described by Hart & Rodrigues (1978). The beam size used in the experiment was about 2·0 mm horizontal and 1·5 mm vertical at the sample position, with a 21″ arc horizontal divergence and 15″ arc vertical divergence.*

Before the synchrotron experiment, some preliminary measurements had been done of the 505 reflection of the benzil sample using a Cr *Kα* tube. The 505 integrated intensity was measured on an absolute basis. It was found that the lattice parameters of our sample were $a = 8{\cdot}417$ and $c = 13{\cdot}680$ Å, and the 505 structure factor $F_{505} = 1{\cdot}5(1)$, somewhat different from the published values of BS. The structural data recently published by Gabe, Le Page, Lee & Barclay (1981) (GLLB) gave better agreement with our measured values and hence have been used for our structure-factor calculations in this paper.

The main reflection for the synchrotron experiment was chosen to be the 202, which has a structure factor of $F_{202} = 0{\cdot}42$, from a calculation based on the structural data. The benzil sample, about 12 × 6 mm large and 2 mm thick, was oriented and cut with a wire saw so that both its surfaces were parallel to the 202 planes. No powder grinding was done on the sample because of its brittleness. It was then mounted on an orienting jig and etched and polished with a nylon polishing cloth damped with acetone. Because of its low melting point, the sample was glued on a holder with phenyl salicylate and mounted at the center of a standard Huber four-circle diffractometer.

The *Umweganregung* reflection selected was the $2\bar{2}1$, since the calculation showed that it was fairly isolated at 3·5 keV ($\lambda = 3{\cdot}55$ Å) in the *Umweg* location plot (Fig. 3), and both $2\bar{2}1$ and its cooperating reflection 021 have the strongest structure-factor magnitude $F_{2\bar{2}1} = F_{021} = 82{\cdot}12$ (their phases differing by 120°).

Because of air absorption on the low-energy X-rays, care had to be taken to keep air out of the beam path as much as possible. Two evacuated pipes with 0·025 mm thick Mylar windows were used on the diffractometer, one for the incident and the other for the diffracted beam. An Si(Li) solid-state detector was used to discriminate the fundamental component from its third harmonic because the 202 reflection turned out to be much weaker than expected and was about 100 times weaker than its third-order reflection, 606.

The 101 reflection was used to align the [101] axis parallel to the φ rotation axis on the diffractometer. The χ angle (between the φ and the ω axes) was set to $\chi = 90°$. After the 202 reflection was observed, a quick φ scan was performed to find out the azimuthal orientation of the crystal. The wavelength of the radiation was found to be $\lambda = 3{\cdot}5536$ Å by comparing the φ positions of *Umweg* peaks with the calculated values. Then a series of rocking curves were measured near the $2\bar{2}1$ *Umweg* peak with better statistics. Each rocking curve took about 45 min becuse of the low counting rates. The peak intensity was ~3 counts s^{-1} and the typical background (TDS, Compton scattering, *etc.*) was ~0·5 counts s^{-1}. The widths of the rocking curves were ~2′ arc, which was typical for our benzil crystal.

An oblique reflection, 203, was measured as a reference to the absolute intensity of the 202, because it has a relatively small structure factor, $F_{203} = 2{\cdot}13$, and was considered to be almost extinction free. In fact the calculated dynamical and kinematic values for the integrated intensities only differ by 7% at $\lambda = 3{\cdot}5536$ Å. From this measurement, the magnitude of the 202 structure factor was found to be $F_{202} = 0{\cdot}15\,(2)$, which was about three times smaller than the calculated value from the published structural data. The reason for this large discrepancy is not clear. Most likely it is due to poor refinement of the thermal parameters for weak structure factors. The incident-beam intensity was also estimated from the 203 integrated intensity and found to have a typical value of $I_0 \simeq 1{\cdot}0 \times 10^6$ photons s^{-1} during the experiment.*

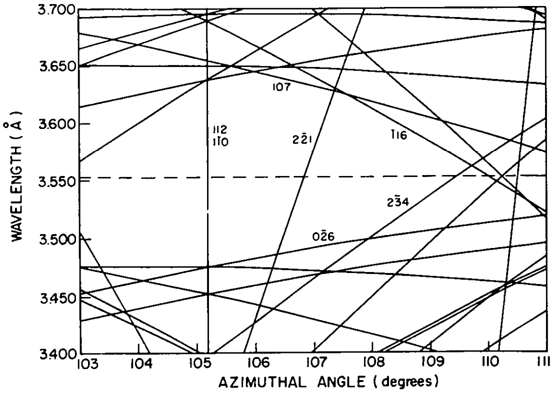

Fig. 3. *Umweganregung* peak location plot for the benzil 202 reflection near 3·5 keV energy. It shows the azimuthal angles of all possible multiple reflections at any given wavelength. The zero on the horizontal scale corresponds to the $\bar{1}20$ lying in the diffraction plane, mostly antiparallel to $\mathbf{k}_0$, the incident wave vector. The dotted horizontal line represents the wavelength used in the experiment ($\lambda = 3{\cdot}5536$ Å).

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* The diffraction plane is vertical, as is usual at a synchrotron site.

* The beam line was not optimized for low-energy photons, and several unnecessary beryllium windows were present, causing a strong reduction of the X-ray intensity.

Results and discussion

The experimental results are shown in Fig. 4, where each data point is an integrated intensity over a rocking curve of the 202 reflection. The solid curve is a six-beam (000-202-$2\bar{2}1$-$1\bar{1}0$-112-$2\bar{3}4$) calculation based on the perturbation theory described by Shen (1986). The absolute value of the two-beam intensity for the 202 and the intensity values on the peak of $2\bar{2}1$ multiple reflection were calculated using the *NBEAM* computer program based on the multi-beam dynamical theory developed by Colella (1974). Such theory is an extension of the standard Ewald-von Laue approach, to include n beams ($n \geq 2$), in the Bragg and Laue geometry of diffraction. The magnitude of F_{202} used in the calculation was $F_{202}=0\cdot15$, as obtained from the 203 reference measurement. All other structure factors, including the phase angle of F_{202}, were calculated from the structural data.

Also included in the calculation was a convolution with a Gaussian mosaic spread function,

$$W(\Delta)=(2\pi\Delta^2)^{-1/2}\exp(-\varphi^2/2\Delta^2),$$

where φ is the azimuthal angle and Δ is the effective mosaic spread of the crystal for the φ rotation. The solid curve in Fig. 4 was obtained using $\Delta=0\cdot05°$. For comparison, the calculation with zero mosaic spread is shown by a dashed curve, which differs from the solid line only in the region that is very close to the *Umweg* peak. From Fig. 4 one can see that the agreement between theory and experiment is very good, despite large statistical errors due to relatively low X-ray intensity combined with a very weak structure factor, five times smaller than expected. The asymmetry effect is clearly apparent, which shows the power of utilizing long-wavelength synchrotron X-rays for this kind of experiment.

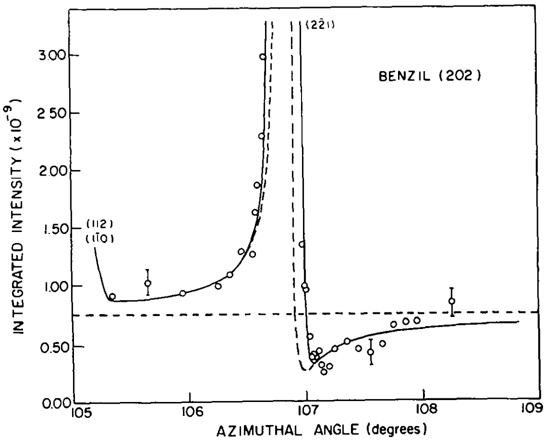

Fig. 4. Integrated intensity of the benzil 202 reflection *vs* azimuthal angle. The experimental data points are shown by circles. The solid curve is a six-beam calculation convoluted by a Gaussian mosaic distribution with a mosaic spread of 3′ (see text). The dashed curve is the same calculation without any mosaic spread. The theoretical 202 two-beam intensity is indicated by the dotted horizontal line.

Since benzil is noncentrosymmetric, an effort to illustrate how to extract arbitrary values of the phase triplet was made with the perturbation theory described by Shen (1986). According to this theory, the normalized intensity of the main reflection **H** near the excitation point of a third reciprocal node **L** is given by

$$I_\perp = 1+\gamma^2A(\varphi)+2\gamma(\cos\delta)(k_L^2-L_\sigma^2)/(k_0^2-k_L^2), \quad (1)$$

where

$$\gamma=\Gamma|F_{H-L}F_L/F_H|, \quad \Gamma=r_e\lambda^2/\pi V_c,$$

$k_0=1/\lambda$, $\mathbf{k}_L=\mathbf{k}_0+\mathbf{L}$, $L_\sigma=\mathbf{L}\cdot\hat{\boldsymbol{\sigma}}$ with $\hat{\boldsymbol{\sigma}}$ being a unit vector perpendicular to the diffraction plane, $\delta=\alpha_L+\alpha_{H-L}-\alpha_H$ is the invariant phase triplet, and $A(\varphi)$ is a function of φ, the azimuthal angle [see equation (23*a*) of Shen (1986)]. We have assumed that the incident beam is polarized normal to the diffraction plane, as is usually the case for synchrotron radiation. If one takes the difference between the intensities of two φ values that are at an equal distance from, but on the opposite sides of, the three-beam point $k_L=k_0$, and plots them against the quantity $(k_L^2-L_\sigma^2)/(k_0^2-k_L^2)$, one obtains a straight line (Fig. 5). This is true because in a small region around the three-beam point the function $A(\varphi)$ can be viewed as a constant. Hence

$$I_+-I_-\simeq4\gamma(\cos\delta)(k_L^2-L_\sigma^2)/(k_0^2-k_L^2). \quad (2)$$

Here we have named the intensities I_+ when **L** is inside the Ewald sphere and I_- when **L** is outside. Equation (2) indicates that the slope of the straight line is proportional to the cosine of the phase triplet δ. Therefore, $\cos\delta$ can be computed from the plot if the magnitudes of the structure factors are known.

In Fig. 5 we plot the situation for benzil 202-$2\bar{2}1$, for which $\gamma=6\cdot08\times10^{-3}$. Seven straight lines are shown corresponding to different δ values so one can see the sensitivity of this method. Eight experimental data points are also plotted in the same figure. Because of poor statistics there is some scatter among the data points, but the line corresponding to $\delta=180°$ is obviously a good choice to fit the data (with probably ±20° uncertainty); this is also the value calculated from the structural data. A value for the phase triplet invariant $\delta=180°$ results in a phase value $\alpha_{202}=-60°$, which agrees with the value calculated from the structural data of BS, but disagrees with that obtained from GLLB, which is 120°. Neither of the two papers lists the 202, which is a very weak reflection owing to cancellation effects among the atoms. In such a situation small differences in the structural data may result in large discrepancies on the phases. While GLLB data provide in general better values for the magnitudes of the structure factors than BS, our experiment clearly demonstrates that the correct phase for the 202 is consistent with the BS data.

The accuracy can be easily improved with better experimental statistics. The effect of mosaic spread is not too important if the measurements are not too close to the *Umweg* peak, as the difference between the dashed and the solid curves in Fig. 4 suggests. So we believe that this method provides a practical approach to deducing values for the phase triplets of a noncentrosymmetric crystal.

Concluding remarks

The long-wavelength X-radiation available at synchrotron-radiation sites can be used in a diffraction experiment to observe the phase-sensitive asymmetry effects for organic crystals like benzil with relatively large unit-cell dimensions. The polarization of the synchrotron beam also helps in obtaining arbitrary values of the cosines of the phase triplets in noncentrosymmetric crystals if the statistics is sufficiently good in such an experiment. A synchrotron beam line that is optimized for brightness in the low-energy region is particularly suitable for multi-beam experiments designed to phase structure factors of organic crystals.

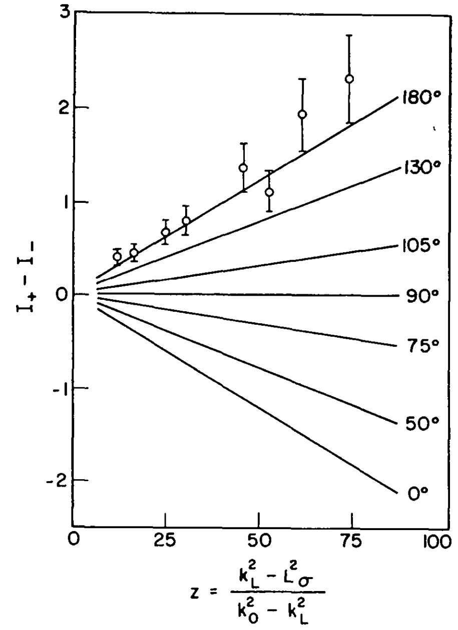

Fig. 5. Intensity difference $I_+ - I_-$ *vs* z [$=(k_L^2 - L_\sigma^2)/(k_0^2 - k_L^2)$], which is a function of φ, the azimuthal angle. I_+ and I_- are the intensities (divided by the two-beam value) at two φ angles that are at an equal distance from the three-beam point $k_L = k_0$, but on the opposite sides of it. The straight lines are calculations for benzil 202-2$\bar{2}$1, and the circles are data points taken from the experiment. The slope of each straight line is proportional to the cosine of the invariant phase triplet δ. The seven lines that are shown correspond to $\delta = 180$, 130, 105, 90, 75, 50 and 0° respectively.

The results described in this paper have been obtained using a large flat crystal slab, completely intercepting the X-ray beam. The interesting question for crystallographers is whether or not the same kind of asymmetry effects might be visible with small spheres or crystalline fragments of irregular shapes. Since the diffraction process operating on the wings of a Renninger peak is kinematic, because the cross section for scattering is weak, we do not expect shape effects to be important. A formal demonstration of this statement can be obtained from Shen's (1986) theory, in which no use is made of boundary conditions. Plans are under way to verify this point by experiment.

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Multiple Scattering and the 200 Reflection in Silicon and Germanium*

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Abstract

Absolute measurements of the 200 reflection in Si and Ge at various azimuthal orientations are compared with *N*-beam calculations of the integrated intensity. All of the non-zero integrated intensity is accounted for by multiple-beam scattering. The measurements match the calculations on the assumption that $F_{200}=0$.

I. Introduction

Recent indications of a possible non-zero structure factor for the silicon 200 reflection (Post & Ladell, 1987) pose an interesting question since, for reasons of symmetry, the 200 structure factor F_{200} in diamond-structure materials should be exactly zero (Henry & Lonsdale, 1952). To investigate this problem we have made measurements of the 200 reflection in silicon and germanium using the ORNL X-ray beam line (X-14) at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.

Silicon and germanium 200 rocking curves were measured at various azimuthal orientations and analyzed using dynamical-theory multiple-beam calculations. The multiple-beam calculations included hundreds of extra reciprocal-lattice points to ensure that all multiple-beam effects were included. In this paper the measured rocking curves are completely accounted for by multiple-beam diffraction with a null 200 structure factor.

II. Multiple-beam scattering

The 200 reflection for the diamond structure is a basis-forbidden reflection. Most basis-forbidden reflections do not have precisely zero intensity owing to the existence of non-centrosymmetric parts in the atomic charge distribution; the atoms are not perfect spheres. These non-centrosymmetric parts, arising from the tetrahedrally oriented lobes of bonding electrons and the anharmonic core vibrations, produce a non-zero structure factor F_{hkl} for the 222, 442, 622 and other basis-forbidden reflections (Dawson, 1967). On the other hand, for any atomic charge distribution that is consistent with the tetrahedral site symmetry, the 200 structure factor is exactly zero. The null value of F_{200} is not the low-order result of an expansion; it is correct for all atomic charge distributions that are consistent with the atomic site symmetry. This is shown by the selection rules listed for the diamond cubic space group in *International Tables for X-ray Crystallography* (Henry & Lonsdale, 1952). If h, k or l are zero and $h+k+l$ is not evenly divisible by four, then $F_{hkl}=0$. If F_{200} were found to be non-zero, then the material could not truly have the diamond cubic structure. Such a finding would, of course, affect many of the fundamental studies of silicon and germanium.

In general, the width of a reflection from a perfect crystal of material such as silicon and germanium is governed by the conservation of energy and the conservation of crystal momentum. The latter condition requires that the wave vector of the scattered beam be near a reciprocal-lattice point, and the former condition that the wave vector lie on the Ewald sphere.

Consider the situation shown in Fig. 1 where $\mathbf{k}_f-\mathbf{k}_0$ is exactly $\mathbf{H}=(hkl)$, and there is another reciprocal-lattice point $\mathbf{H}'=(h'k'l')$ off the Ewald sphere. H'' is a third reciprocal-lattice vector which is $\mathbf{H}-\mathbf{H}'$. We know from the definition of a lattice that if $\mathbf{H}$ and $\mathbf{H}'$ are reciprocal-lattice vectors then $\mathbf{H}''$ must also be one.

A reflection with final wave vector $\mathbf{k}'$ is clearly forbidden since $\mathbf{k}'$ is off the Ewald sphere and so the process does not conserve energy. However, the double process $\mathbf{k}_0\rightarrow\mathbf{k}'\rightarrow\mathbf{k}_f$ is possible since $\mathbf{H}'+\mathbf{H}''=\mathbf{H}=\mathbf{k}_f-\mathbf{k}_0$, and $\mathbf{k}_f$ is on the Ewald sphere. Note that the scattering is not a sequential process; there is no photon with wave vector $\mathbf{k}'$. The incident beam

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