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Phase Determination of the Forbidden Reflection 442 in Silicon and Germanium Using Multiple Bragg Scattering

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Abstract

The sign inversion of the forbidden reflection 442 in silicon between room temperature and 700 K has been verified using multiple beam diffraction and the concept of virtual Bragg scattering. A similar determination in the case of germanium confirms that the 442 is mostly due to anharmonic effects at room temperature.

It is well known that n-beam diffraction can be used, in principle, to determine phases in X-ray or neutron reflections (Colella, 1974; Post, 1977). Progress has been hindered so far by the fact that n-beam dynamical theory, the only one that preserves phase information, is strictly applicable to perfect crystals such as germanium and silicon, and it was not clear how it could be applied to real mosaic crystals. It was proposed (Chapman, Yoder & Colella, 1981), in 1981, that virtual Bragg scattering (VBS), a situation in which all interactions are deliberately kept weak, might provide a way to deal with mosaic crystals.

In practice, a VBS situation is one in which a weak reflection is fully excited and its integrated intensity is measured by varying θ, the angle of incidence on the lattice planes. At the same time one or more extra reflections are excited by choosing a suitable value for φ, the azimuthal angle around the scattering vector, in such a way as to keep the excitation weak. In a plot of R_θ^{hkl} *vs* φ, R_θ^{hkl} being the integrated intensity of the *hkl* reflection integrated with respect to θ at constant φ, a VBS situation corresponds to points on the sides of a strong *Umweganregung* peak, typically 2-4° away from full excitation. It has been proved in our previous work (Chapman, Yoder & Colella, 1981) that the asymmetric pattern observed around a strong *Umweganregung* peak contains phase information.

To test this idea in a very clear cut case, we decided to verify the phase change of the 442 reflection in silicon at two different temperatures.* The forbidden 442 reflection in silicon was measured several years ago (Trucano & Batterman, 1972), and found to

* Since silicon is centrosymmetric, all phases, including those of forbidden reflections, are 0 or π.

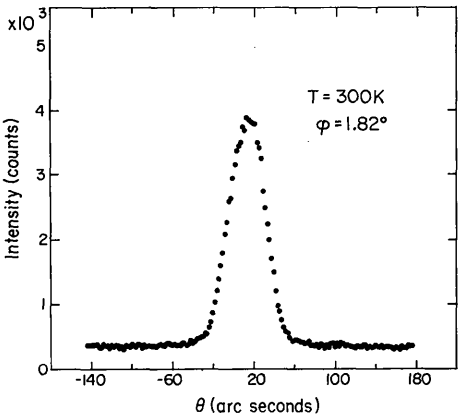

Fig. 1. Typical 442 rocking curve at $T = 300$ K. The zero on the θ scale is arbitrary. Intensity values are referred to a monitor count of 2×10^5, and the average counting time per point is approximately 3 s. At this φ value the 442 is about three times greater than the two-beam value, owing to perturbation effects introduced by the strong $\bar{1}1\bar{1}$ *Umweganregung* peak, centered at about $\varphi = 3{\cdot}00°$.

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decrease with increasing temperature from 300 K up, approach zero value at about 525 K, and then increase again. This temperature dependence was explained by assuming that the 442 arises from two competing effects. At low temperature it is due to the aspherical charge density, also responsible for the other forbidden reflection that has been found in silicon and similar structures, the 222. As temperature is increased, anharmonic effects in thermal vibrations become important, building up a time-averaged charge density along the [111] direction, on the opposite side of the atom from the bonding charge, giving rise to a structure factor F_{442}^{anh} of opposite sign with respect to F_{442}^{bond}.

The 442 in silicon and germanium has been recently remeasured with much greater accuracy using synchrotron radiation (Tischler & Batterman, 1984), and the sign change of the structure factor has been determined using the methods and computational procedures developed by one of us (Colella, 1974), by looking for the best fit between observed and calculated integrated intensities.

In this work we show how the wings of a strong *Umweganregung* reflection change as the temperature is varied between 300 and 700 K. From previous results (Trucano & Batterman, 1972; Tischler & Batterman, 1984) we know that the 442 structure factor has approximately the same magnitude, but opposite signs, at these extreme temperatures.

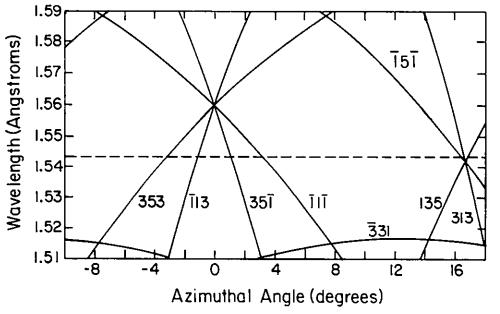

Fig. 2. This plot shows the φ values of all possible *Umweganregung* reflections at any given wavelength. The zero on the φ axis corresponds to a [$\bar{1}$10] lying in the diffraction plane, mostly antiparallel to the incident beam. The dotted horizontal line corresponds to the wavelength used in this experiment. (λ = 1·54335 Å.)

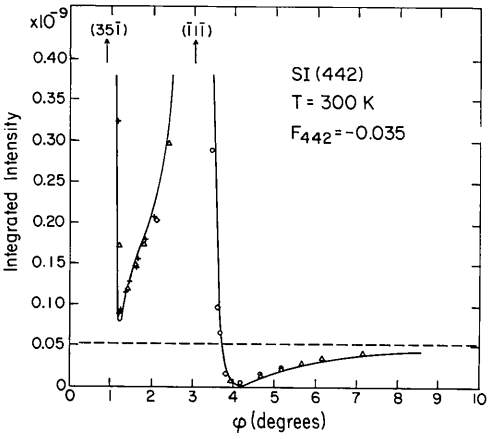

Fig. 3. Integrated intensity (with respect to the angle of incidence θ) of the 442 reflection *vs* φ, azimuthal angle, at 300 K. The horizontal dotted line corresponds to the two-beam intensity, which has been used for standardizing all points on an absolute basis. The zero on the φ axis is defined in the caption to Fig. 2. The ordinate values become very large near two φ values, around 1 and 3°, corresponding to two strong *Umweganregung* reflections, the $35\bar{1}$ and $\bar{1}1\bar{1}$ respectively. The continuous solid line is calculated from theory, using ten beams, as explained in the text, and with $F_{442} = -0{\cdot}035$. Different symbols correspond to separate runs. Note how the integrated intensity almost vanishes at $\varphi \simeq 4{\cdot}2°$.

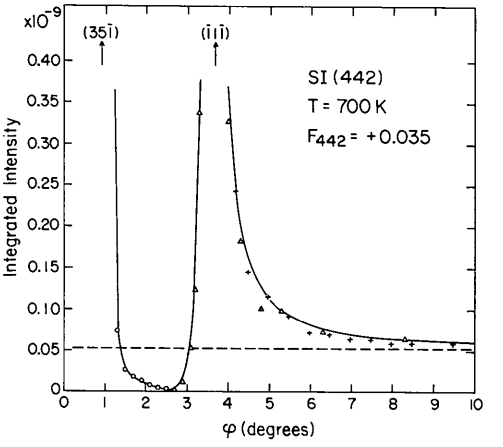

Fig. 4. Same as Fig. 3, except for $T = 700$ *K*, and $F_{442} = +0{\cdot}035$ in the calculated profile.

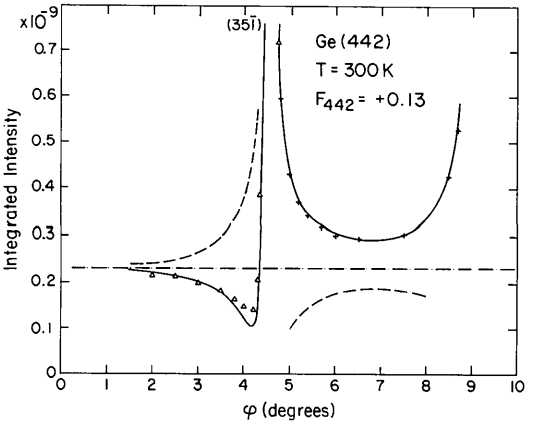

Fig. 5. Similar to Fig. 3, but for the Ge 442 reflection. The solid curve is calculated using a positive value for F_{442}, and the dashed curve using a negative value. Ten beams are included in the calculations: 000, 442, $35\bar{1}$, $3\bar{3}1$, 135, $\bar{1}1\bar{1}$, $\bar{3}51$, $5\bar{3}1$, $22\bar{2}$ and 224, among which the $35\bar{1}$ is strongly excited.

The experiment has been done at the Cornell High Energy Synchrotron Source, using a standard four-circle diffractometer equipped with an electric furnace. The crystal was in the form of a circular slice, about 1 mm thick, 38 mm diameter, polished and etched, with the plane of the slice parallel to the (442) planes. The beam was monochromatized by a channel-cut silicon crystal followed by a flat glass mirror, which eliminated harmonics. The beam impinging on the crystal had a rectangular cross section of $1\times$ 20 mm.

The mirror could be temporarily removed to pass $\lambda/2$ corresponding to the allowed 884 reflection, for easy orientation and adjustment of the counter and slit system.

The peak intensity of the two-beam value 442, with the mirror inserted, was about 4000 counts s^{-1}. Fig. 1 shows a typical 442 rocking curve at room temperature, which was measured in 8 min. In Fig. 2 we show a plot in which all intersections with a horizontal straight line (the dashed line corresponds to the wavelength used in the experiment, $\lambda = 1{\cdot}54335$ Å) give the φ values of nodes other than the 000 and 442 lying on the Ewald sphere. The wavelength measurement was refined from the φ values at which the *Umweganregung* peaks were found. The azimuthal values chosen for our experiment are in the range of the φ values shown in Fig. 2. Since the 442 is an exceedingly weak reflection, and n-beam perturbation effects may be important even when the relevant nodes in reciprocal space are at some distance from the Ewald sphere, as a consequence of VBS effects (Chapman, Yoder & Colella, 1981), ten beams were considered in the computations: 000, 442, 353, $\bar{1}13$, $35\bar{1}$, $\bar{1}1\bar{1}$, $\bar{3}31$, 135, $\bar{1}5\bar{1}$ and 313. The n-beam integrated intensities were evaluated using the procedures and ideas described in a separate reference (Colella, 1974). Temperature effects were included in all structure factors involved.

The results are shown in Figs. 3 and 4. The structure factor F_{442} was taken to be $-0{\cdot}035$ at 300 K and $+0{\cdot}035$ at 700 K (Trucano & Batterman, 1972). Figs. 3 and 4 show how the integrated intensities of the 442 vary with φ at two different temperatures, and how they compare with the calculated values for two different choices of the signs of the structure factor. The result is unmistakable; the sign inversion between 300 and 700 K is perfectly confirmed. The fine structure for $\varphi = 1°$ at 300 K is well reproduced by the experimental points, owing to the high resolution in φ available at a synchrotron source. At both temperatures the 442 almost vanishes for particular values of φ.

The $\bar{1}1\bar{1}$ peak values around $\varphi = 3°$, at 300 K, and 4°, at 700 K, were also measured and compared with theory.* No useful information could be extracted from this part of the experiment, however, because, to three significant digits, the calculated peak intensities were found to be independent of sign at both temperatures. It is therefore confirmed that strong *Umweganregung* reflections are less useful for phase determinations than the details on the wings of the *Umweganregung* peaks (Chapman, Yoder & Colella, 1981).

As a further test, we examined the germanium 442 reflection at room temperature. While the bonding charge in germanium is about the same as that in silicon, the structure factor $F_{442}^{\rm anh}$ is certainly larger, owing to the greater number of core electrons. Therefore, F_{442} is positive in germanium. The measured integrated intensities shown in Fig. 5 clearly fit the calculation using $F_{442} = +0{\cdot}13$ (Tischler & Batterman, 1984) much better than does the calculation using $F_{442} = -0{\cdot}13$.

This work confirms the soundness of our procedures in using VBS for phase determination of structure factors in diffraction experiments and shows the capability and advantages of using synchrotron radiation X-rays in dealing with extremely weak reflections whose phases are being probed.

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* The difference in φ values is due to a change in lattice parameter resulting from thermal expansion.