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An Absolute Measurement of the Lattice Parameter of Germanium Using Multiple-Beam X-ray Diffractometry

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The d spacing of the 355 reflexion in silicon has been compared with the d spacing of the 800 reflexion in germanium using pseudo non-dispersive multiple-beam X-ray diffractometry with Mo $K\alpha_1$ radiation. This technique gives the ratio of the two lattice parameters without the need for a precise knowledge of the X-ray wavelength. Symmetric transmission geometry was used to eliminate the refractive index correction. The results were:

$$\frac{d(800\text{ Ge})}{d(355\text{ Si})} = 1{\cdot}0002348\ (\pm 0{\cdot}0000006)\text{ at }22{\cdot}5\,^\circ\text{C}$$

and

$$\frac{d(800\text{ Ge})}{d(355\text{ Si})} = 1{\cdot}0002458\ (\pm 0{\cdot}0000016)\text{ at }25\,^\circ\text{C}.$$

By using the known lattice parameter of silicon obtained by X-ray and optical interferometry it was found that the lattice parameter of germanium at 25°C is $5{\cdot}6579060 \pm 0{\cdot}0000092$ Å.

Introduction

In traditional measurements of interplanar spacings the Bragg angle for an X-ray emission line is measured and Bragg's law, corrected for refractive index if necessary, is used to obtain d. The resulting value of d depends on the wavelength, which is not known to better than a few p.p.m. on an absolute scale, and on the Bragg angle, θ_B, which is measured. The measurement of θ_B requires the accurate location of single-crystal reflexion peaks which are the convolution of the intrinsic single-crystal reflexion curve with the spectral profile of the X-ray source and with the angular intensity distribution of the incident beam. Conventional X-ray sources of characteristic radiation have a line width $\Delta\lambda/\lambda$ of about 5×10^{-4} and this appears to set the random-error limit to about one in 10^7 (Baker, George, Bellamy & Causer, 1966).

Hart (1969) introduced the technique of multiple-beam diffractometry which measures the d spacing of one crystal relative to that of a second crystal pseudo-non-dispersively and so avoids the error due to the uncertainty in X-ray wavelengths. We have used this technique to compare the lattice parameters of good-quality silicon and germanium.

Deslattes & Henins (1973) have used optical and X-ray interferometry to measure the absolute lattice parameter of silicon. Using this value for silicon we obtained the *absolute* lattice parameter of germanium. In these experiments the results were drift-limited to about 0·6 p.p.m. If a silicon crystal with lattice spacing calibrated to 1 part in 10^8 had been available, our technique could have been improved to give the lattice parameter of germanium to the same precision.

The experiment

(*a*) *Perfect alignment*

The experimental arrangement is shown in Fig. 1. Symmetric Laue-case reflexions in parallel-sided crystals are used and the reflexions are chosen so that the two Bragg angles are as nearly equal as possible. The X-ray sources were positioned with respect to the first crystal so that the crystal Bragg reflects the beams from both sources simultaneously. It is convenient but not essential to limit the divergence of these beams so that only one characteristic emission line is diffracted. As the second crystal is rotated a double-crystal rocking curve is recorded first in one detector and then in the other. The angle of crystal rotation between these rocking curves, $2\Delta\theta$, is twice the difference in Bragg angle between the two crystals, so that using Bragg's law we obtain

$$\Delta\theta = (\theta_1 - \theta_2) = \tan\theta\Delta d/d$$

or

$$\Delta d/d = \cot\theta\,.\,\Delta\theta\,. \qquad (1)$$

We used a silicon crystal with a 355 reflexion in the first position and a germanium crystal with an 800 reflexion in the second position. With Mo $K\alpha$ radiation the Bragg angles are about 30·1° and $\Delta\theta$ is about 30″. Because the Bragg angles are nearly equal the arrangement is almost non-dispersive and the rocking curves are symmetrical and extremely narrow. The full widths at half-peak intensity were approximately 1″.

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(*b*) *Alignment errors*

If there were no errors of alignment the two sources, the pinhole and the two diffraction vectors would all lie in one plane. It has been shown (Hart, 1969) that relative tilts between the diffraction vectors for the crystals would change the measured value of $2\Delta\theta$ and could be a major source of error in this type of experiment. Larson (1974) has produced a general theory of misalignment.

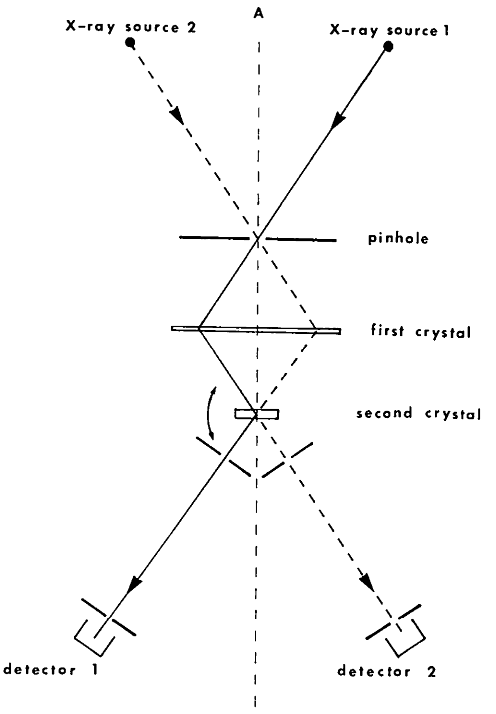

Fig. 1. Experimental arrangement used to record double-crystal rocking curves (not to scale).

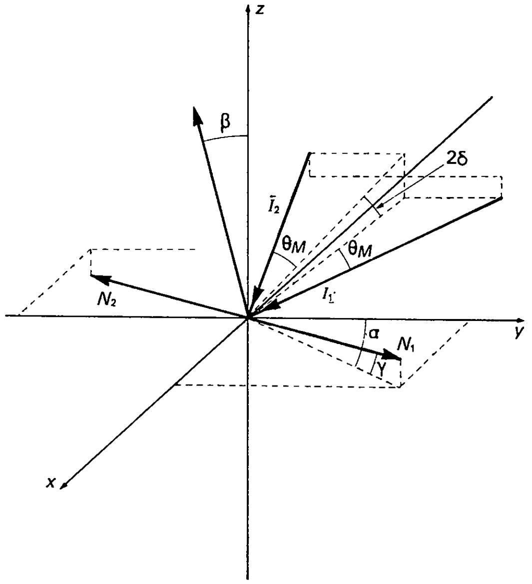

Fig. 2. Geometry of misalignments in two-source diffractometry (after Larson, 1974).

In our experiment the first crystal was rotated about line *AA* in Fig. 1 so that the two diffracted beams were parallel with the plane defined by the two sources and the pinhole to within 8′. Relative tilts between the two crystals increase the width of the crystal rocking curve and decrease its peak intensity. The second crystal was adjusted to maximize the intensity of the peak recorded while using a beam effectively 20 times higher than that used to measure the separation of the peaks. In practice this adjustment was made with three separate beams, all in the same vertical plane. The central beam was that drawn in Fig. 1 coming from source 1 and lying in the plane of the paper. The other two beams came from the same source but one lay above and one below the plane of the paper. The vertical angle between these two alignment beams was 2·6°, equivalent to a vertical separation of 8 mm at the crystals. After the adjustment of the second crystal had been completed the two alignment beams were blocked off. Using this technique the two diffraction vectors could be set parallel to within 5″ and from Larson's (1974) theory it is possible to estimate the maximum effect of this misalignment.

The essential geometry of Larson's theory is shown in Fig. 2. The two beams I_1 and I_2 are those Bragg reflected by the first crystal and incident on the second crystal. The *xz* plane is parallel to the diffracting planes of the first crystal and the *xy* plane is taken to bisect the angle 2δ between the 'planes of diffraction' of I_1 and I_2. The second crystal rotates about an axis making an angle β with the *z* axis and the tilting of this crystal out of perfect alignment is such that the normals to the reflecting planes N_1 and N_2 make an angle γ with the *xy* plane.

Larson assumes that all misorientations are less than ± 2° (which is certainly the case in our experiments) and that $\Delta d/d < 10^{-3}$. He obtains (equation 21: Larson, 1974):

$$\Delta\alpha = 2\Delta\theta + \gamma^2 \tan\theta + 2\gamma\delta \qquad (2)$$

where $\Delta\alpha$ is the measured rotation between the two peaks.

Substituting $\gamma = 5''$ and $\delta = 8'$, we calculate that the effect of misalignments on the measured value of $\Delta d/d$ is approximately 4×10^{-8}.

Data were collected by fixed-time counting while step-scanning the second crystal angle. Since symmetric profiles were obtained most methods of peak location are practicable and lead to the same result. In practice, centroids were found by using Simpson's rule on profiles truncated at about 1 % of the peak intensity with Thomsen & Yap's (1968) skew-truncation correction. Over wide limits (0·1 to 10 % peak intensity) of truncation the same centroid position was found.

The area surrounding the two crystals was totally enclosed in a thermostatic chamber. This gave temperature stability within the enclosure to better than 0·05°C but limited the minimum temperature attainable to about 22·2°C. The temperature was monitored with a mercury-in-glass thermometer checked against an N.P.L. calibrated thermometer.

In this experiment small drifts in angle limited the final accuracy to about $\frac{1}{2}$ p.p.m. The rate which data were recorded was set so that the uncertainty in peak positions due to counting statistics equalled the uncertainty due to drift. The effect of a constant rate of drift on $\Delta\alpha$ should be equal and opposite when rotating the axis clockwise (c.w.) and counterclockwise (c.c.w.). Accordingly, the mean value of measurements made in the c.w. and c.c.w. directions was used. Fig. 3 shows the pair of rocking curves obtained in a typical experiment.

The samples

The silicon was grown in the [111] direction by Haldor Topsøe of Denmark. Double-crystal topographs showed it to contain fluctuations in lattice parameter of less than one in 10^7. The germanium was grown in the [111] direction by Hoboken of Belgium and was of comparable quality. The two slices of crystal were oriented by the Bond (1961) technique and cut on a high-speed diamond saw. After grinding on plate glass with fine carborundum powder and water, the surface damage was removed with a chemical polish. The final thicknesses, estimated by X-ray absorption, were approximately 300 μm for the silicon and 90 μm for the germanium slice.

To ensure that the crystals used in the experiment were free from strain we took double-crystal topographs of the two slices after they had been mounted using the same reflecting planes and the same transmission geometry as were used in the actual experiment. In each case the double-crystal rocking curve from the whole specimen area had a width of less than 1″ and the double-crystal topographs showed that mounting strains were smaller than 3×10^{-7}. A small pillar of soft wax proved to be the only method of mounting which did not distort the thin germanium crystal.

Results

Measurements of $\Delta\alpha$ were made at 22·5 and 25°C but when the temperature was raised to 27·5°C the drifts became so large that further measurements were impossible. It is probable that the soft wax mounting of the germanium crystal was becoming unstable.

The results were

$$22{\cdot}5^\circ\mathrm{C}:\quad \frac{d(800\mathrm{Ge})-d(355\mathrm{Si})}{\frac{1}{2}[d(800\mathrm{Ge}+d(355\mathrm{Si})]}=234{\cdot}8\pm0{\cdot}6\ \text{p.p.m.}$$

$$25^\circ\mathrm{C}:\quad \frac{d(800\mathrm{Ge})-d(355\mathrm{Si})}{\frac{1}{2}[d(800\mathrm{Ge})+d(355\mathrm{Si})]}=245{\cdot}8\pm1{\cdot}6\ \text{p.p.m.}$$

Errors are standard errors of the mean for ten measurements at each temperature.

Using Deslattes & Henins (1973) value for the lattice parameter of silicon at 25°C (5·431065 Å) we obtain the lattice parameter of germanium as

$$5{\cdot}6578437\pm0{\cdot}0000035\ \text{Å at } 22{\cdot}5^\circ\mathrm{C}$$

and

$$5{\cdot}6579060\pm0{\cdot}0000092\ \text{Å at } 25^\circ\mathrm{C}\,.$$

Dr T. W. Baker of A. E. R. E., Harwell, used the Bond (1960) method to measure the Bragg angle for the symmetric 444 reflexion of Cu $K\alpha_1$ for good quality silicon as 79°18′46″ and the equivalent Bragg angle for a piece of germanium physically close to our slice in the original boule as 70°36′37″ (Baker, 1974, private communication). After correction for refractive index using the zero-absorption dynamical theory, but including the real part of the dispersion corrections, this gives

$$25^\circ\mathrm{C}:\quad d(800\mathrm{Ge})-d(355\mathrm{Si})=244\ \text{p.p.m.}\,,$$

which is in good agreement with our result.

Finally we can test the internal consistency of our results using measured values of the thermal expansion coefficients of silicon and germanium. For example, Gibbons (1958) measured the thermal expansion coefficients of both silicon and germanium The difference between his results was $\alpha_{\mathrm{Ge}}-\alpha_{\mathrm{Si}}=3{\cdot}4\times10^{-6}{}^\circ\mathrm{C}^{-1}$, in good agreement with the value $4{\cdot}4\pm1{\cdot}7\times10^{-6}{}^\circ\mathrm{C}^{-1}$ required by our results.

At the temperature (about −50°C) where the 800 Ge and 355 Si lattice spacings are identical, such equality is measurable without any knowledge whatsoever of the X-ray wavelength.

Conclusions

We have shown that starting from an interferometric standard, atomic spacings can be determined without any precise knowledge of X-ray wavelengths. It is

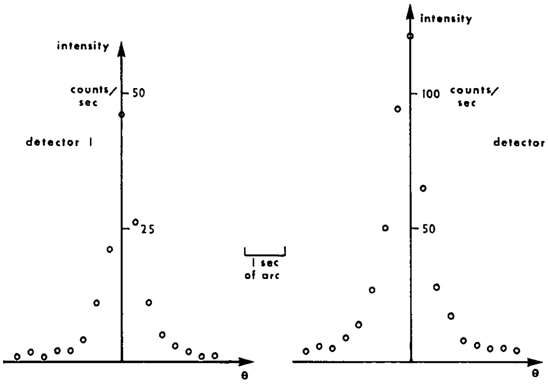

Fig. 3. Rocking curves recorded with Mo $K\alpha_1$ radiation. The two Bragg angles differ by $\Delta\theta\simeq30''$ but the full width of the rocking curve is only 1″. Different source intensities in the two channels result in different peak intensities. First crystal Si 355, second crystal Ge 800.

clear that provided problems of specimen mounting can be overcome, the Bragg angles of any two crystals can be compared to about 0·1% of the width of the pseudo non-dispersive double-crystal rocking curve. Since at exact equality the rocking curves are symmetric, there is no limit in principle other than that set by counting statistics on the precision with which lattice parameters can be compared.

Finally we should point out that it is not a 'lucky chance' which makes these measurements possible. By using sufficiently high orders of Bragg reflexions it is inevitable that lattice-parameter matches occur in different materials at some accessible temperature.

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On the Application of Phase Relationships to Complex Structures. VIII. An Extension of the Magic-Integer Approach

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A magic-integer approach, called the *P–S* set method is described. A primary (*P*) set of reflexions contains some which fix the origin and enantiomorph and others expressed symbolically in magic-integer form. Probable phases for a secondary (*S*) set of reflexions are derived, also in symbolic form, from single triple-phase relationships containing a pair of *P* reflexions. Relationships which link the combined *P* and *S* sets give rise to the terms of a Fourier map, the peaks of which indicate likely sets of phases for all the reflexions under consideration. These sets of phases are used as starting points for the computer program *MULTAN*. The process is completely automated and is illustrated by the solution of the structure of cephalotaxine, $C_{18}H_{21}O_4N$, the space group of which is $C2$ with two molecules in the asymmetric unit.

Introduction

In a recent paper White & Woolfson (1975) described a technique whereby phases may be represented to a sufficient degree of approximation in a symbolic form such that a single symbol may be used to represent several phases. Thus for a suitable set of m integers – $n_1, n_2, \ldots, n_m$ – one may write

$$\varphi_r = n_r x \bmod (1), \quad r = 1 \text{ to } m, \qquad (1)$$

where the phase angles, φ, are expressed in cycles and the set of equations is approximately satisfied for some value of x in the range $0 \le x < 1$.

Trials by White & Woolfson (1975) showed that a simple application of magic integers, in a way which is a blend of the symbolic-addition and multiple-solution approaches, could lead to complete and straightforward solutions of structures which had been solved rather tortuously from E maps given by the *MULTAN* computer package. The extension of the magic-integer approach which is described in this paper is even more powerful and has solved a number of known test structures for which the automatic *MULTAN* procedure had failed completely.

The *P-S* sets method

In explaining the new magic-integer approach we shall use as an example the structure of cephalotaxine, $C_{18}H_{21}O_4N$, the form of the molecule of which is shown in Fig. 1. The space group is $C2$ with $a = 22{\cdot}84$, $b = 8{\cdot}15$, $c = 19{\cdot}54$ Å and $\beta = 117{\cdot}7°$. There are two mole-