Concluding remarks

These results indicate that the restrained least-squares refinement method can be successfully adapted to include individual atom weighting from a molecular graphics system. In the early stages, this will be of great benefit in controlling the course of the refinement.

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Applications of High-Order Laue-Case Rocking Curves

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Abstract

Spherical-wave *Pendellösung* fringes have been used for many years to make absolute measurements of X-ray coherent scattering amplitudes. Bonse & Teworte [*J. Appl. Cryst.* (1980), **13**, 410–416] have suggested that the corresponding fringes seen in Laue-case rocking curves between two crystals with almost equal thicknesses might have important applications and they showed that agreement to within $\frac{1}{2}$% could be achieved in structure factor measurements on silicon. Two further applications are demonstrated in this paper. By a simple construction the range of double-crystal topography, using only a Lang camera, has been extended to the region $\delta d/d < 10^{-9}$. In another experiment it is found that the *Pendellösung* method can be extended to very high orders (the 10,10,0 reflection in silicon for example) so that attention can be focused, for the first time with high precision, on the coherent Bragg scattering at very high sin θ/λ.

Introduction

As part of our dispersive double-crystal interferometric spectrometer which is installed at the storage-ring source at Daresbury we required a two-reflection Laue-case silicon monochromator. Since the monochromator was intended for work at short wavelengths and with high orders of Bragg reflection, its testing involved new aspects which we believe have wider application. For example, in the 10,10,0 reflection of Mo $K\alpha_1$ radiation the full width at half height of the reflection curve is only 0·1″ of arc. The stability of our monochromator is better than 0·001″ of arc per day. The gradient of the reflection curve is very steep so that 1% intensity change corresponds to only 0·0005″ of arc in $\delta\theta$ or 9×10^{-10} in $\delta d/d$. For perspective we might note that the reflection widths quoted here are one hundred times narrower than those more commonly used in double-crystal topography (*e.g.* the silicon 440 reflection of Cu $K\alpha_1$) or in double-crystal diffractometry (*e.g.* the 880 reflection of Cu $K\alpha_1$ from gadolinium gallium garnet). The reflection-curve gradients are up to ten times larger than those achieved previously in double-crystal topography (Hart, 1968; Bonse & Hartmann, 1981) using oblique high-order Bragg reflections such as the 880, 844 and 12,0,0 from silicon.

Conventional double-crystal topography with separate reference and sample crystals requires quite complicated goniometers and servo control systems to achieve resolutions of 10^{-8} in $\delta d/d$. Systems with superior resolution have not so far proved feasible and would, in our experience, be extremely difficult to implement in the conventional way.

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Monochromator design

The monolithic Laue-case double-wafer mono-chromator is shown in plan view in Fig. 1. Rotations of one wafer W with respect to the other, about an axis normal to the plane of the figure, are made by bending the spring region S. The necessary force is provided by the electromagnet C and permanent magnet M. Long experience with these elastically deformed monolithic crystal systems (Hart & Rodrigues, 1979; Hart & Siddons, 1980) has shown that long-term stability, to 10^{-12} m in position or $0 \cdot 001''$ of arc in angle, is easily achieved and that these force transducers are quite linear too.

As an extreme example Fig. 2 shows the 10,10,0 Laue-case rocking curve for Mo $K\alpha_1$ from a high-quality monochromator. From preliminary experiments using 220, 440, 660 and 880 reflections of Mo $K\alpha_1$ we were able to establish the wafer thicknesses as $t_1 = 280$ and $t_2 = 270$ μm and the elastic stiffness as $24 \cdot 8$ mA/second of arc by comparing experimental and calculated rocking curves. To emphasize the linearity of the angle drive and the symmetry of the rocking curve it has been reproduced twice in Fig. 2; the rocking curve and its mirror image are superimposed. Since the total counting time was 16 h 40 min it is quite clear that the overall stability is at least $0 \cdot 001''$ of arc per day. The peak intensity is $32 \cdot 8$ s^{-1}. More important for our present purpose the slope of the rocking curve, at A on the central correlation peak, is very high. From detailed measurements at about three times higher angular sensitivity we find that the full width at A is $0 \cdot 0188''$ of arc and the angle change for a 1% intensity change is $0 \cdot 00047''$ of arc ($2 \cdot 28 \times 10^{-9}$ radians). Writing, for the flank of the central peak,

$$\frac{\delta I}{I} = K\left(\frac{\delta d}{d} \tan \theta \pm \delta\theta\right), \tag{1}$$

the corresponding figures are $K = 4 \cdot 39 \times 10^6$ or $\delta d/d = 9 \cdot 47 \times 10^{-10}$. The full width at half height (B) is $0 \cdot 110 \pm 0 \cdot 005''$ of arc.

Application to X-ray diffraction topography

In studying the performance of our two-reflection monochromators we quickly became aware that the shape of the higher-order (harmonic) rocking curves was crucially dependent upon the position of the X-ray beam. Since the crystal performance depends not only on intrinsic crystal perfection but also on the flatness of the crystal surfaces and their freedom from surface damage, there is a clear need for a new high-resolution diffraction topographic technique. A simple-to-implement response involves mounting the entire two-wafer assembly on a Lang-type camera (Fig. 1) in which images of the entire wafer are obtained by traversing crystal and film together while the two wafers are offset, for example to the point A in Fig. 2. Clearly, from equation (1), such diffraction topographs contain information about both wafers, about $\delta d/d$ and $\delta\theta$ with unprecedented sensitivity, and about thickness variations in the two wafers (Bonse & Teworte, 1980).

The most sensitive oblique double-crystal topographs have achieved sensitivities around one part in 10^8 of lattice parameter as Table 1 shows for 1% contrast.

Fig. 3 shows double-crystal topographs of a monochromator obtained as indicated in Fig. 1 using a Lang camera and Mo $K\alpha_1$ radiation. In each case the topograph was taken with the offset angle adjusted to the flank of the central correlation peak as indicated by the arrow in Fig. 2, typical offsets being between $0 \cdot 01$ and $0 \cdot 1''$ of arc. In the least sensitive 220 topograph the sensitivity to lattice-parameter variations is about the same as that available in the 844 Bragg-case reflection (Table 1) and the sensitivity is ten times higher in the 660 topograph.
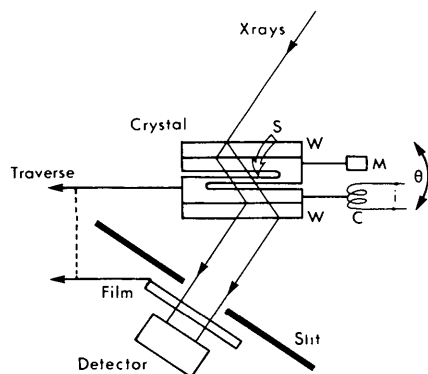

Fig. 1. Monolithic double-wafer Laue-case monochromator arranged for diffraction topographs on a standard Lang camera. Double-crystal rocking curves are obtained by driving the coil C from a computer-controlled current source i. The force on the permanent magnet M bends the spring S through an angle θ.
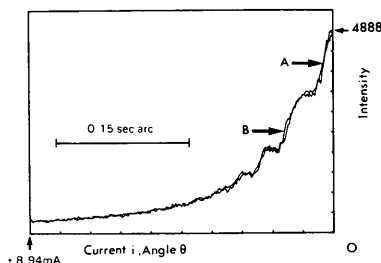

Fig. 2. 10,10,0 rocking curve (both flanks superimposed) obtained with Mo $K\alpha_1$ radiation. Wafer thicknesses 280 ± 5 μm and 270 ± 5 μm determined from low-order rocking curves.

Table 1. *Sensitivities of double-crystal topographs*

	Radiation	$h\,k\,l$	K |equation (1)|	$\delta d/d$	$\delta\theta$ (milliseconds of arc)
(a)	Mo $K\bar{\alpha}$	8 4 4	$6\cdot3 \times 10^5$	$1\cdot6 \times 10^{-8}$	3·3
(a)	Mo $K\bar{\alpha}$	8 8 0	$6\cdot8 \times 10^5$	$1\cdot3 \times 10^{-8}$	3·0
(b)	Mo $K\alpha$	8 8 0	$2\cdot6 \times 10^6$	$3\cdot5 \times 10^{-9}$	0·80
(b)	Mo $K\alpha$	884/12,0,0	$2\cdot9 \times 10^6$	$2\cdot7 \times 10^{-9}$	0·70
Present experiments	Mo $K\alpha_1$	10,10,0	$4\cdot4 \times 10^6$	$9\cdot5 \times 10^{-10}$	0·47
Present experiments*	Mo $K\alpha_1$	8 8 0	$7\cdot9 \times 10^6$	$1\cdot2 \times 10^{-9}$	0·26
	Mo $K\alpha_1$	6 6 0	$6\cdot7 \times 10^6$	$2\cdot3 \times 10^{-9}$	0·31
	Mo $K\alpha_1$	4 4 0	$3\cdot4 \times 10^6$	$7\cdot4 \times 10^{-9}$	0·61
	Mo $K\alpha_1$	2 2 0	$2\cdot2 \times 10^6$	$2\cdot5 \times 10^{-8}$	0·95

(a) Hart (1968). (b) Bonse & Hartmann (1981).

* These values, quoted for the present experiments, are theoretical for wafers each 500 μm thick and, as such, are expected to be upper bounds since both variations in thickness and strain gradients will tend to reduce the sharpness of the central correlation peak.
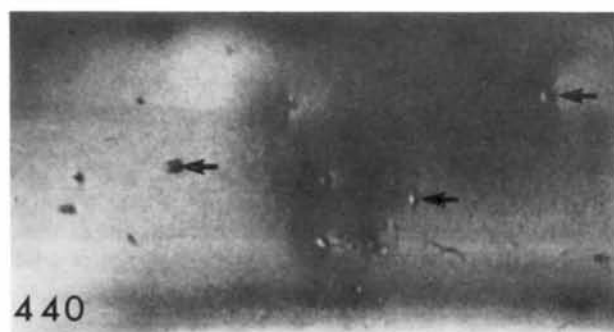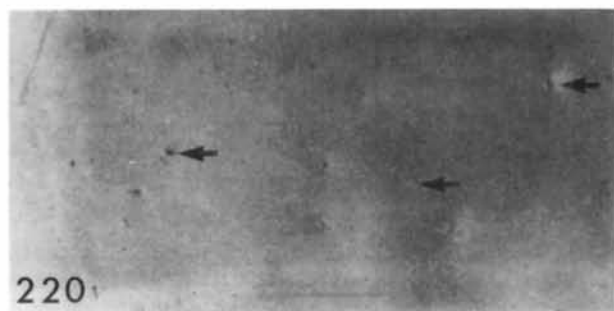

Fig. 3. Lang-type topographs of a monochromator with 500 μm thick wafers and Mo $K\alpha_1$ radiation. The θ-offset was to half-height on the central double-crystal rocking-curve correlation peak in each case. Field 12 × 6 mm.

Since the extinction distance is very much smaller for the low-order Bragg reflections than for high-order reflections at the same X-ray wavelength, area contrast which is highest in the lowest-order topograph can be ascribed to local variations in one or other of the wafer thicknesses. For example, a thickness variation in one crystal might easily lead to 20% contrast in the 220 Bragg reflection whereas much less contrast would be observed in the 660 topograph. A good indication of the sensitivity to thickness variations is given in Fig. 6 of Bonse, Graeff, Teworte & Rauch (1977).

In our diffraction topographs the long-range area contrast increases with diffraction order, as required if the images indicate variations in strain. As Table 1 shows, the inverse strain sensitivities obtained in the 220, 440 and 660 topographs would be in the ratio 95:61:31 (for $\delta\theta$) or 25:7·4:2·3 (for $\delta d/d$). Area-contrast ratios roughly follow these ratios in Fig. 3 if account is taken of the fact that the 660 topograph was taken on the opposite rocking-curve flank from that used in the 220 and 440. In that case we expect the contrast from strain fields to be reversed, as shown. These topographs were obtained on an imperfectly polished monochromator containing several regions of surface damage, indicated by arrows in Fig. 3. The images of these strain centres increase in size in the higher-order Bragg reflections as expected. The interest in this new topographic method stems from its very high sensitivity to strain and the ease with which topographs can be obtained compared with conventional double-crystal methods.

Application to structure amplitude measurements

The advantages and disadvantages of the conventional *Pendellösung* method for measuring coherent scattering amplitudes are well known (Kato & Lang, 1959; Tanemura & Kato, 1972; Aldred & Hart, 1973a,b). The coherent scattering amplitude has not been studied before with adequate precision to detect the effect of relativistic corrections to core-electron wavefunctions.

Preliminary analysis of the 10,10,0 rocking curve shown in Fig. 2 indicates a scattering factor per atom of 0·83 ± 0·02 e. At present the precision of measurement is not limited by the 10,10,0 measurement itself but by small, and so far unexplained, deviations between theoretical and experimental rocking curves for the lower-order Bragg reflections which we use to determine the crystal thickness using the known values of the X-ray optical constants (Tanemura & Kato, 1972; Aldred & Hart, 1973a,b). When this problem has been resolved we anticipate that the high-order scattering factors will be determined to 0·1% or so. At that precision not only the core scattering itself but also the temperature variation of the Debye–Waller factor becomes theoretically interesting. Further work is in progress.

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The Consequences of the Neglect of TDS Correction for Temperature Parameters

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Abstract

The importance of carrying out TDS corrections is emphasized. Their relative effect on the derived temperature parameter values is discussed and shown to rely primarily on the experimental conditions and not on the softness of the crystal.

1. Introduction

In accurate analyses of charge density distributions from X-ray diffraction data there has recently been a tendency to utilize shorter wavelengths of X-rays such as Ag Kα radiation to improve the resolution of charge density maps synthesized by Fourier methods from observed X-ray data. Such studies clearly require correction for thermal diffuse scattering (TDS) contributions to the Bragg peaks since these often amount to more than 35%.

The consequences of the neglect of TDS correction on structure analysis have been discussed by Harada & Sakata (1974) on the basis of their general formalism of TDS correction. They predicted that while the position parameters are little affected, thermal parameters are modified in such a way that the principal axes of the thermal ellipsoids change their directions. Furthermore, it was emphasized that TDS correction was particularly important for soft materials because in this case the correction factor is larger. This statement, however, was not intended to imply that it is unnecessary to correct for possible TDS if the crystal is sufficiently hard. It will in fact be shown that the relative reduction of the temperature parameters due to neglect of TDS correction is almost the same for any crystal, largely independent of its hardness and depending mainly on the experimental conditions under which the Bragg intensities were measured: the size and shape of the counter aperture, the scan width, the wavelength of the radiation used and the unit-cell dimension of the crystal.

In this paper we discuss this problem theoretically on the basis of the formalism of Harada & Sakata (1973, 1974) and then endeavour to test our findings in four different cases.

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