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Ultra-high-angle double-crystal X-ray diffractometry (U-HADOX) for determining a change in the lattice spacing: theory

Atsushi Okazaki* and Yuji Soejima

Department of Physics, Kyushu University, Fukuoka 812-8581, Japan. Correspondence e-mail: hadx6scp@mbox.nc.kyushu-u.ac.jp

Advantages of high-angle double-crystal X-ray diffractometry (HADOX) have been re-examined. It is found that, by extending the Bragg angle θ up to 89.99°, the accuracy of a change in the lattice spacing to one part in 10^9–10^{10} can be attained in proportion to $\tan\theta$. In such a case, the dispersion-free condition is so serious that the spacing of the two crystals should be equal within one part in 10^6. Therefore, this method is appropriate for determining the thermal expansion coefficient in a limited temperature range. To cover a wide temperature range, the temperature of the reference crystal must be adjusted according to the temperature of the specimen crystal; the lattice spacing as a function of temperature can be determined by integrating the temperature derivative of the spacing.

1. Introduction

A number of multiple-crystal diffraction methods have been developed for the accurate determination of the lattice spacing (*International Tables for Crystallography*, 1992). Although they are of highest accuracy, they are applicable only to perfect crystals. For general crystals, in particular, for determining the temperature dependence of the lattice spacing, high-angle double-crystal X-ray diffractometry (HADOX) (Okazaki & Ohama, 1979) is appropriate and gives an accuracy to 10^{-6}–10^{-7} depending on the crystal quality; the accuracy and precision of the method have been analysed in the reference.

At the beginning of the application of HADOX, white X-rays were used to meet Bragg's law at high angles of about 88° (Okazaki & Kawaminami, 1973, 1974). Owing to low intensities of white X-rays from conventional X-ray sources, however, the method was soon coupled with characteristic X-rays; experiments were then carried out at moderately high angles at the expense of accuracy. The method was still useful to trace structural phase transitions in $KMnF_3$ (Sakashita *et al.*, 1981) and in $SrTiO_3$ (Ohama *et al.*, 1984; Sato *et al.*, 1985). Moreover, a modification called the 2θ-resolved HADOX method was developed for crystals of $BaTiO_3$ with grain structures (Tomonaga *et al.*, 1990; Soejima *et al.*, 1991; Onitsuka *et al.*, 1994). The method was applied to investigate the effect of an external electric field on the grain stucture in $BaTiO_3$ near the Curie temperature (Soejima *et al.*, 1995). For crystals with domain structures, like $SrTiO_3$ and $KMnF_3$ in the tetragonal phase, the intensity distribution at a set of equivalent reciprocal-lattice points was simultaneously surveyed; the domain population was determined as a function of temperature (Koga *et al.*, 1995; Hirakawa *et al.*, 1997).

It is obvious that the accuracy that can be attained by the original version of HADOX has been lost, to some extent, in order not to lose the intensity. The purpose of the present paper is to examine HADOX by extending the angular range to ultimately high angles, and to propose a method to fully utilize the inherent advantages. The method is called ultra-high-angle double-crystal X-ray diffractometry (U-HADOX). This is motivated in the circumstances where strong white X-rays of synchrotron radiation are easily available to many crystallographers. The experiment of U-HADOX, however, can be performed even with a conventional X-ray source, with a rotating anode preferably. The results of such an experiment supporting the present proposal will be given in a separate paper, in which technical details will be presented.

2. Fundamentals

The idea of HADOX is to attain high sensitivity for a change in the lattice spacing by high-angle diffraction, and to obtain, simultaneously, high resolution by the dispersion-free arrangement of the coupled crystals. The experimental arrangement shown in Fig. 1 can be classified into two: one is called the *S*–*A* arrangement, which is suitable for measurements with white X-rays as incident beams, and the other *M*–*S* for characteristic X-rays. Here, *S*, *A* and *M* respectively stand for the specimen, analyser and monochromator at the position of the first or second crystal. For example, *S*–*A* means that the first crystal is used as a specimen and the second as an analyser, although in many cases the two crystals are of the same material.

For these arrangements, Bragg's law can be given by

$$d_S \sin\theta_S = d_A \sin\theta_A \qquad (1)$$

and

$$d_M \sin\theta_M = d_S \sin\theta_S, \qquad (2)$$

where d and θ, respectively, denote the lattice spacing and the Bragg angle. Both the equations result from Bragg's law for the first and second crystals for a common wavelength. In the experiment, the quantities θ_S and d_A in (1) and d_M and θ_M in (2) are kept constant. That is, in either arrangement the orientation of the first crystal is fixed; the change in d_S, *i.e.* the change in the lattice spacing of the specimen, can be determined from the change in θ of the second crystal. The requirement that d_S is equal (or nearly equal) to d_A or that d_M is equal (or nearly equal) to d_S is essential for the dispersion-free condition.

Measurements are made by scanning, stepwise, the angular position of the second crystal; we then observe the rocking curve at the position corresponding to the lattice spacing of the specimen crystal. The detector is fixed and is open so that the aperture is much wider than the diffracted beam.

3. Examination of the method

3.1. High-angle diffraction for high sensitivity

The main factor that determines the accuracy of HADOX in the *S–A* arrangement is the sensitivity $\Delta\theta_A/\Delta d_S$: *i.e.* the change in θ of the second crystal associated with the unit change in d_S, the spacing of the first crystal. The sensitivity that is relevant to the *M–S* arrangement is $\Delta\theta_S/\Delta d_S$. In both the arrangements, the sensitivity for a given diffraction is proportional to $\tan\theta$, which acceleratively increases when θ approaches 90°. Therefore, measurements at highest angles are advantageous. Values of $\tan\theta$ are given in Table 1 for some typical values of θ; the peak shift at $\theta = 80, 89.0, 89.9$ and $89.99°$ will be in the ratio $1 : 10 : 10^2 : 10^3$.

It has been shown for silicon that by HADOX at $\theta = 79°$ we attain a relative accuracy of a change in the lattice spacing of the order of 10^{-7}; therefore, the accuracy to be attained by U-HADOX at $\theta = 89.99°$ will be one part in 10^{10}. The peak width (FWHM) observed for most other crystals so far investigated is about one order of magnitude larger than that of silicon. Consequently, the precision for these crystals will be lower by a factor of ten.

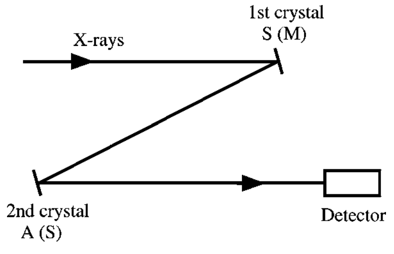

Figure 1
The beam path of X-rays in the *S–A* or *M–S* arrangement of HADOX; the deviation from $\theta = 90°$ is exaggerated.

Table 1
Values of $\tan\theta$ and $(1 - \sin\theta)$ at high angles.

For $(1 - \sin\theta)$, 1.5 (−8), for example, means 1.5×10^{-8}.

θ (°)	$\tan\theta$	$1 - \sin\theta$
89.99	5730	1.5 (−8)
89.95	1150	3.8 (−7)
89.90	573	1.5 (−6)
89.50	115	3.8 (−5)
89.00	57	1.5 (−4)
85.00	11.4	3.8 (−3)
80.00	5.7	1.5 (−2)

3.2. Double-crystal arrangement for the dispersion-free condition

In the history of HADOX, it has been recognized that the advantage of the double-crystal arrangement remains, though not fully, even when the combination of two slightly different lattice spacings is adopted. Therefore, the use of a reference crystal, namely the analyser or monochromator, of higher quality can be advantageous owing to smaller FWHM and higher intensity. This is true for HADOX at moderately high angles. For example, the combination of 400 of $SrTiO_3$ (a monochromator, $\theta \sim 82.5°$) and 400 of $BaTiO_3$ (a specimen, $\theta \sim 74°$) has successfully been used with Fe $K\alpha_1$ radiation in the experiment by Irie *et al.* (1987) and in the later experi-

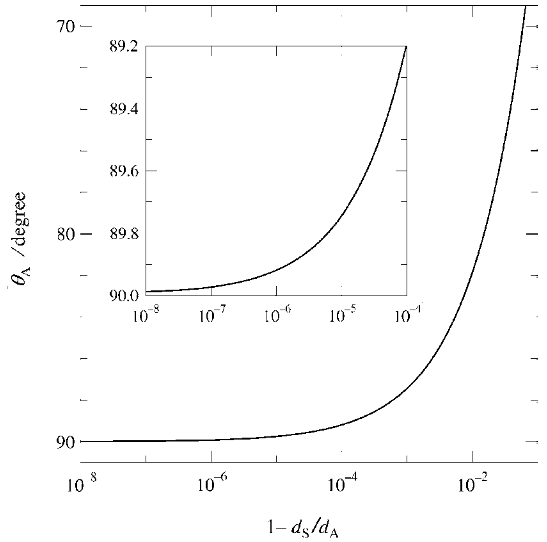

Figure 2
The relation between θ_A *vs* mismatch $(1 - d_S/d_A)$ for $\theta_S = 89.99°$ on a semilogarithmic scale. The region of highest angle is expanded in the inset.

ments mentioned previously; the mismatch in the lattice spacing is about 2.5% at room temperature. At ultra-high angles, however, we find a different situation. For the combination mentioned above, for example, θ_S is 76° for $\theta_M = 89.99°$; by the mismatch we lose sensitivity by a factor of more than 10^3 in comparison with the case where $\theta_S = \theta_M = 89.99°$. The loss in sensitivity outweighs the gain in resolution to be attained by using a reference crystal of higher quality. Let us quantitatively examine the effect of the mismatch in the *S*–*A* arrangement.

We define the mismatch by

$$1 - d_S/d_A = 1 - \sin\theta_A/\sin\theta_S \sim 1 - \sin\theta_A. \qquad (3)$$

The value of $(1 - \sin\theta)$ is also shown in Table 1; it should be noted there that $(1 - \sin\theta)$ varies even faster than $\tan\theta$. In Fig. 2, the relation between θ_A and the mismatch $(1 - d_S/d_A)$ is given for $\theta_S = 89.99°$. It is clear that the difference $(\theta_S - \theta_A)$ acceleratively increases with increasing mismatch. The figure is also valid for lower θ_S's provided that only the region with $\theta_A \leq \theta_S$ is concerned. From this figure and Table 1, we can estimate that the sensitivity will decrease by a factor of ten for the mismatch of 1.5×10^{-6} for $(\theta_S - \theta_A) = 0.09°$. If we come down to $\theta = 89.00°$, we lose sensitivity by a factor of 10^2; the mismatch of 1.5×10^{-2} will be allowed for further losing the sensitivity by a factor of ten. This corresponds to the case of $SrTiO_3$–$BaTiO_3$ mentioned above. In general, it will not be practicable to keep a mismatch as small as 10^{-6} with a combination of different materials.

The argument is also applicable to the mismatch of the lattice spacing due to the temperature difference of the two crystals of the same material; for silicon at room temperature, the mismatch of 1.5×10^{-6} corresponds to a temperature difference of 0.4 K of the *S* and *A* crystals. For many crystals, the temperature difference that corresponds to the same mismatch will even be smaller by a factor of ten owing to larger thermal expansivity.

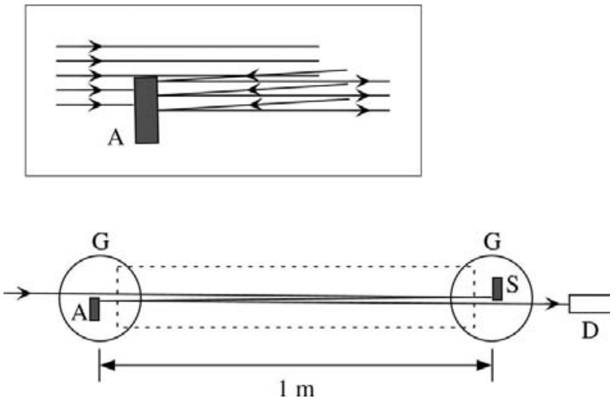

Figure 3
Lay-out of the diffractometer; *S*, *A*, *D* and *G* stand for specimen, analyser, detector and goniometer, respectively. Dotted lines indicate an evacuated tube. The inset schematically shows X-ray beams around the analyser crystal; the angle between the beams *S* to *A* and *A* to *D* is enlarged.

3.3. Procedure for determining *d*(*T*)

What we directly determine by U-HADOX is $\alpha(T)$, the thermal expansion coefficient as a function of temperature. As mentioned in the preceding section, the mismatch of the lattice spacing significantly reduces the accuracy. Therefore, measurements of $\alpha(T)$ should be made by keeping the difference between the temperature of the two crystals within a limit that is relevant to the accuracy to be aimed, and to the thermal-expansion coefficient of the crystal. Consequently, the temperature of the reference crystal, the analyser crystal in this case, must be adjusted according to the temperature of the specimen crystal if we need to cover a wider temperature range. The temperature dependence of the lattice spacing $d(T)$ can be determined by integrating $\alpha(T)$:

$$d(T) = \text{constant}[1 + \textstyle\int \alpha(T)\,\mathrm{d}T]. \qquad (4)$$

The constant can be determined with knowledge of the lattice constant value at the relevant temperature.

4. Design of the diffractometer

The basic design is shown in the schematic lay-out in Fig. 3. We have two requirements: First, the Bragg angle must be as high as 89.95° and, second, the temperature must be controlled within ±1 mK in order to be compatible with the accuracy of the lattice spacing. By allowing a horizontal width of the X-ray beams of 2 mm and the distance between the two crystals of 1 m, $\theta = 89.95°$ will be reached in laboratory experiments; the beam width can be reduced if more intensity is available. For limiting the beam width, as shown in the inset of Fig. 3, the edge of each crystal can be used. X-ray beams penetrate the window of the specimen chamber of a cryostat or a thermostat.

The dynamical theory shows that the peak width (FWHM) of a perfect crystal is proportional to $(1 + |\cos 2\theta|)/\sin 2\theta$. Therefore, with increasing θ at high angles, the peak width of any *hkl* increases in proportion to $\tan\theta$, as in the increase of the peak shift. Consequently, a ratio of the peak shift to the width does not change much with θ. For example, the FWHM of 555 of silicon will increase, corresponding to a change in θ from 79.00 to 89.95°, from 2×10^{-4} to $3 \times 10^{-2\circ}$. At higher angles, with the same goniometer, we can attain higher accuracy in peak shifts relative to the width; the minimum steps of 10^{-4} and $10^{-3\circ}$ will be appropriate for perfect and non-perfect crystals, respectively. The diffractometer will thus consist of commercially available instruments only.

5. Systematic errors

Several systematic errors of U-HADOX are discussed here following the discussion by Okazaki & Ohama (1979) for HADOX. The refraction error is negligible at very high angles, the Lp error not being significant for high-quality crystals.

5.1. Crystal tilt error

For a horizontal diffractometer, the contribution of the vertical component of the scattering vector to the error of the lattice spacing will increasingly be significant when θ approaches 90°. The error due to a crystal tilt can be minimized by keeping the height of the beam path constant over the whole path length. At present, the minimum vertical shift is estimated to be 0.1 mm. For a horizontal shift of 2 mm, corresponding to $\theta = 89.95^\circ$ at the distance *S–A* equal to 1.15 m, the number of significant digits in the thermal expansion coefficient α may be three.

5.2. Temperature error

For silicon, the coefficient α is larger than $10^{-6}\,\mathrm{K}^{-1}$ except at low temperatures. Therefore, the temperature error allowed for the accuracy of the lattice spacing to 10^{-9} is smaller than 1 mK. For larger values of α, the smaller temperature error is required. For many crystals with α larger than that of silicon, however, the FWHM of HADOX peaks is larger than that of silicon by one order of magnitude. Therefore, the precision to 1 mK will be the requirement at the moment, this not being difficult to reach by the present technique. It should be noted that one of the advantages of HADOX is that good thermal insulation is easily attainable; the main item affecting the insulation is two small windows for the X-rays.

5.3. Crystal displacement error

In the conventional HADOX experiment, it was important to minimize the effect of a spurious angular shift in θ, owing to a twist of the crystal holder and the cryostat/thermostat; this was particularly important when the experiment covered a wide temperature range over a long period as in the study of structural phase transitions.

In U-HADOX, in contrast, an individual series of measurements will be made in a narrow temperature range. Moreover, the relative contribution of such a spurious shift to the observed peak shift is smaller at higher θ's. Therefore, the effect of the spurious shift can generally be neglected. To be more careful about such an effect, we may use a second analyser crystal on the opposite side of the incident beam. If a change in θ_A due to a change in d_S is the same on each analyser, we may assume that the spurious shift is negligible; if not, there must be a spurious shift in either, or both, of θ_A. The spurious shift about θ_S is also a nuisance, but can be followed by the scan of θ_S.

5.4. Radiation damage error

As mentioned by Okazaki & Ohama (1979), the effect of X-radiation on the lattice spacing was not detected with X-rays from a conventional source. For synchrotron X-rays, however, care must be taken not to irradiate with an unnecessary dose. The best way to reduce the incident intensity will be the use of attenuators coupled with heat sinks. Evacuation of the beam paths will be required to reduce the intensity loss of diffracted beams due to absorption by air; this can be achieved by placing a single tube between the crystals, as shown by the dotted lines in Fig. 3.

6. Discussion

From Table 1, we find that most of the HADOX measurements were made in a region where the value of $\tan\theta$ was between five and ten. Therefore, we realize that the main advantages of these measurements are the high resolution due to the double-crystal arrangement, but not the high sensitivity due to high-angle diffraction. In U-HADOX, in contrast, we can use the full advantage of sensitivity two or three orders of magnitude higher than that of HADOX. It is difficult to predict what U-HADOX will give us.

As for the application of U-HADOX, the experiment aiming at the ultimate accuracy of the temperature derivative of the lattice constant will be important for crystals of standard types of materials, such as those used in the semiconductor industry. The accuracy of the thermal-expansion coefficient attained by thermal-expansion experiment for bulk specimens has been better than that attained by X-ray diffraction. For example, Lyon *et al.* (1977) attained, by the three terminal capacitance method, the accuracy of a change in the length of the bulk specimen to one part in 10^9. We are now overtaking this level of accuracy using U-HADOX. If we consider that the specimen used by Lyon *et al.* (1977) was 10 cm long and that the measurement was based on a sophisticated technique, the method is not at all general. For U-HADOX, in contrast, we need only a couple of tiny crystals of normal quality; the experimental procedure is simple. Moreover, what we obtain by X-ray diffraction is the interatomic distance through measuring the lattice constant. Therefore, it is obvious that U-HADOX will be the best method to determine the thermal expansivity, as far as crystalline materials are concerned.

Extending the Bragg angle up to 89.99°, we have found quite different features of HADOX; it should be emphasized that the dispersion-free condition has a major effect on determining $d(T)$ only at ultra-high angles. To meet this condition, the mismatch of the lattice spacing of the two crystals should be as small as one part in 10^6; this results in the situation where the difference between the *S–A* and *M–S* arrangements is not very meaningful. In other words, the diffractions at the two crystals must be highly symmetrical.

If we wish, we can reach the region of θ higher than 89.99° by expanding the distance between the two crystals, getting even larger values of $\tan\theta$. As shown by Shvyd'ko & Gerdau (1999), however, the angular profile of the diffracted beams at $\theta \geq 89.995^\circ$ can be complicated owing to multiple-beam diffraction. Therefore, the discussion given in this paper may not directly be applicable to the region of θ higher than 89.995°. On the other hand, if we do not try to approach higher than 89.50°, the experiment will be much easier at the expense of the accuracy of one to two orders of magnitude. Even at this level of experiment, a new field will be explored in phase transitions. The geometry of U-HADOX is suitable for experiments at high pressures, provided that the pressure can be accurately controlled.

7. Conclusions

By U-HADOX at $\theta \sim 89.99^\circ$, we can attain an accuracy to one part in 10^9–10^{10} for a change in the lattice spacing; the mismatch between the lattice spacing of the coupled crystals is crucial. For this accuracy, the temperature of the crystals should be controlled within ±1 mK. The highest barrier that prevents us from attaining the ultimate accuracy is the crystal tilt error, which will be more serious when θ approaches 90°. The way to avoid this problem is to have more finely collimated beams and/or to have a longer distance between the crystals. The highest accuracy of the data together with highest efficiency to get them will be obtained for high-quality crystals when U-HADOX is combined with synchrotron X-rays. For less perfect crystals with FWHM larger than that of silicon by a factor of ten, U-HADOX at $\theta \sim 89.50^\circ$ with an accuracy to one part in 10^8 will still be useful for investigating structural phase transitions; the experiment will then be easy to carry out.

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