Observation of divergent-beam X-ray diffraction from a crystal of diamond using synchrotron radiation

A. M. Glazer,[a]* S. P. Collins,[b] D. Zekria,[a] J. Liu[c] and M. Golshan[d]

[a]Department of Physics, University of Oxford, Parks Road, Oxford OX1 3PU, UK, [b]Diamond Light Source Ltd, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK, [c]Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, UK, and [d]CCLRC Daresbury Laboratory, Warrington WA4 4AD, UK.
E-mail: glazer@physics.ox.ac.uk

Dedicated to Kathleen Lonsdale, born 28 January 1903, died 1 April 1971

In 1947 Kathleen Lonsdale conducted a series of experiments on X-ray diffraction using a divergent beam external to a crystal sample. Unlike the Kossel technique, where divergent X-rays are excited by the presence of fluorescing atoms within the crystal, the use of an external divergent source made it possible to study non-fluorescing crystals. The resulting photographs not only illustrated the complexity of X-ray diffraction from crystals in a truly beautiful way, but also demonstrated unprecedented experimental precision. This long-forgotten work is repeated here using a synchrotron radiation source and, once again, considerable merit is found in Lonsdale's technique. The results of this experiment suggest that, through the use of modern 'third-generation' synchrotron sources, divergent-beam diffraction could soon enjoy a renaissance for high-precision lattice-parameter determination and the study of crystal perfection.

Keywords: divergent-beam diffraction; Kossel lines; fluorescence.

1. Introduction

In 1914, Rutherford and Andrade observed both reflection and absorption lines photographically, using a point source of divergent gamma rays and a crystal of rock salt. This enabled them to measure the wavelengths of the radiation used. Kossel (1936*a*,*b*) demonstrated the production of black and white conics on a photographic plate by generating the divergent fluorescence X-rays internally within a crystal containing suitable fluorescent atoms. Such lines have subsequently been termed Kossel lines, and are similar to the Kikuchi lines found in electron diffraction. Borrmann (1936) too used fluorescent X-rays from a single crystal as his divergent beam and observed both reflection conics and Laue spots. In addition to exciting the divergent X-rays internally within the crystal, it can also be stimulated externally (sometimes called pseudo-Kossel diffraction), whence the technique can be used on a non-fluorescing crystal. A good example of this was given by Lang (1995), who used an electron beam incident on a Cu film on the surface of a crystal of diamond. In this paper, he pointed out that the divergent-beam technique is important also for observation of the 'enhanced Borrmann effect', since at the crossing points of the conics multiple diffraction occurs and this can lead to an enhanced transmitted intensity at such points. Pseudo-Kossel lines using synchrotron radiation have been proposed as a precise technique for studying the quality of non-fluorescing X-ray monochromators (Lin *et al.*, 2000).

The inherently high sensitivity of the divergent-beam technique to the study of lattice parameters, and small changes thereof, arises from the extended lines of diffraction. This means that there are many places where such lines cross, giving well defined points of intersection. The distance between nearby intersections can be determined very precisely, and are found to be extremely sensitive to small changes in lattice parameters. Moreover, these distances are relatively insensitive to modest misalignments of the sample and detector.

Lonsdale (1947) showed in a classic paper that, if one uses such a highly divergent X-ray beam incident on a crystal, the continuous conic lines observed on a photographic plate could be used to obtain information about the texture and perfection of the crystal. In addition, she was able to make precise measurements of lattice constants or wavelength by considering coincident crossings of various conics. In particular, she observed that for Cu $K\alpha_1$ radiation the 311 conics intersected precisely with the 022 and 004 conics, but not for Cu $K\alpha_2$, Cu $K\beta$ or Zn $K\alpha$. Using this change in coincidence, she was able to measure the lattice parameters, and hence the C—C distance in individual diamonds to seven significant figures! Her divergent beam photographs also showed that many crystals of organic compounds are quite perfect, and that type-I diamond and natural ice, even near to its melting point, possess a high degree of perfection.

Because of its rather specialized nature, and general difficulty to perform (Lonsdale used a special X-ray tube capable of producing about 180° of divergence) and analyse, the technique has not been generally pursued with conventional sources, and so has largely been forgotten. However, it has occurred to us that, if one could use this technique using synchrotron radiation, the high tunability and brilliance would enable it to be used more generally and with even more precision. Applications of this technique that can be envisaged include texture and strain studies of materials, accurate lattice-parameter measurement as a function of temperature and other variables for the study of phase transitions and in the assessment of crystal quality. It is possible that the development of this technique applied to synchrotron radiation may well lead to applications so far not considered. In addition, the fact that today we have computing power that was unimaginable in the 1940s means that the analysis of the divergent beam conics is now much simpler.

Synchrotron radiation is of course closely parallel, and even the use of focusing optics does not provide very much of a divergent beam. Despite this, the use of crystals containing fluorescent atoms to generate Kossel lines has been successfully demonstrated with synchrotron radiation, first in 1992 at HASYLAB (Ullrich *et al.*, 1994). This has been used, for instance, to measure residual stresses in micrometre regions (Brechbühl *et al.*, 1999) and in a study of fluorescent quasicrystals (Schetelich *et al.*, 1998), again at HASYLAB. The standard Kossel method, however, suffers from the disadvantage that it can only be applied to crystals containing suitable fluorescent atoms. To overcome this limitation, we have been able reproduce Lonsdale's original method applied to a diamond crystal using synchrotron radiation and externally generated fluorescent X-rays from a metal foil, thus opening up this technique to a large range of crystals.

2. Experiment

The experiment was carried out at CCLRC Daresbury on station 16.3 (Collins *et al.*, 1998), a wavelength-shifter beamline with a critical energy of around 16 keV. A white beam of X-rays was directed onto a 15 μm-thick niobium metal foil, on the opposite side of which was

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mounted a brilliant-cut diamond (approximately 1.5 mm thick and about 1.5 mm across). The beam cross section was set at a height of 200 μm and a width of 200 μm. An A3-size image plate was used to obtain the diffraction patterns: this was placed at a distance of 125 mm from the sample. Experiments were carried out with the image plate mounted directly perpendicular to the incident beam and with the diamond crystal aligned with its [001] direction also along the beam. This resulted in good divergent beam patterns plus Laue spots in 30 s of exposure, with a storage-ring current of approximately 150 mA [Schetelich *et al.* (1998), like us, also used white radiation and obtained simultaneous Laue spots and Kossel lines, but with internal fluorescence]. However, this did mean that the central region of the image was overexposed by the incident beam despite the use of a lead beam trap. We found it better to rotate the image plate in the vertical plane to an angle of approximately 40° to the incident beam to avoid the incident beam intensity. At the same time the diamond crystal was rotated through the same angle so that its [001] direction still pointed perpendicular to the image plate (Fig. 1).

A small portion at the centre of the resulting photograph is illustrated in Fig. 2. As the conic lines are weak, for the sake of publication we have computer-enhanced the image by varying the contrast and gamma function, followed by an embossing filter. The Laue spots can clearly be seen and, because the crystal is now tilted with respect to the incident beam, the pattern corresponds to a direction approximately 40° from [001]. However, the divergent beam conics, because they are produced by fluorescent X-rays at the surface of the diamond, still show the symmetry expected for [001] perpendicular to the image plate. Attempts at repeating this type of experiment using a monochromatic beam tuned to the correct energy failed, principally because of the dominance of the background radiation over the modest (attenuated) X-ray fluorescence intensity. While the monochromatic beam approach would, undoubtedly, become feasible with an optimized beamline on a modern synchrotron source, there is clearly considerable advantage in exciting fluorescence with an incident beam of broad bandwidth.

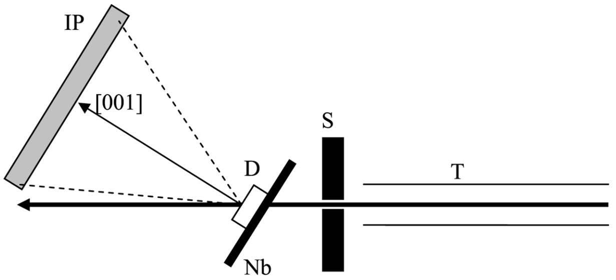

Figure 1
Schematic drawing of the experimental arrangement. IP: image plate, D: diamond crystal, Nb: niobium foil, S: slits, T: metal tube to screen background radiation.

In order to demonstrate that these observed conics can be interpreted and that our observed pattern is meaningful, Fig. 3 shows a simulation based on the known crystal structure and symmetry of diamond. The figure is in the form of a stereographic projection (only the central region is shown in order to compare with Fig. 2), and was computed by the method given by Lonsdale. Strictly speaking, a gnomonic projection is the exact way to simulate the divergent-beam pattern when the film is set perpendicular to a defined direction, but for lines not too far from the centre, as shown here, the stereographic construction is sufficiently precise, and as explained by Lonsdale, because the conics can be drawn as circles it has advantages of simplicity. The program *Crystallographica* (Oxford Cryosystems, UK) was first used to generate a list of the observable X-ray reflections for Nb $K\alpha$ radiation (0.747567 Å) plus the angles φ, ω and θ. θ is the Bragg angle for an *hkl* reflection, φ is the angle between the [001] direction (corresponding to the axis perpendicular to the stereographic projection) and any particular (*hkl*) plane normal, and ω is the angle to this plane normal measured from the [100] direction. These latter two angles then determine the direction of the (*hkl*) normal projected onto the stereographic plane, given by the angle α to the [100] direction, where

$$\cos\alpha = \cos\omega / \sin\varphi.$$

Lonsdale showed that the distance *CT* from the centre of the stereographic projection to the centre of the divergent beam circle corresponding to *hkl* is given by

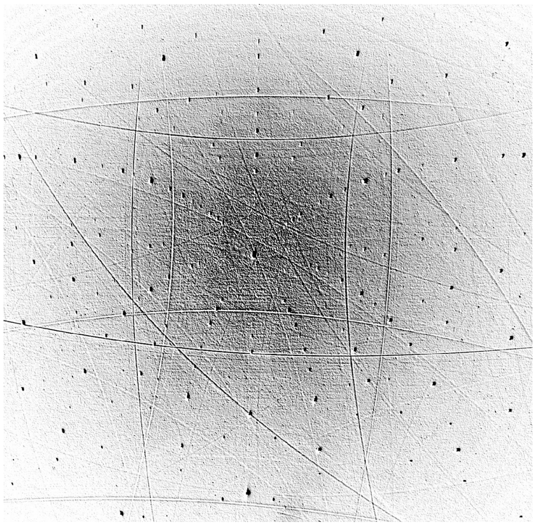

Figure 2
Central portion of a divergent-beam X-ray photograph of a brilliant-cut diamond, [001] direction perpendicular to film. The image has been computer-enhanced.

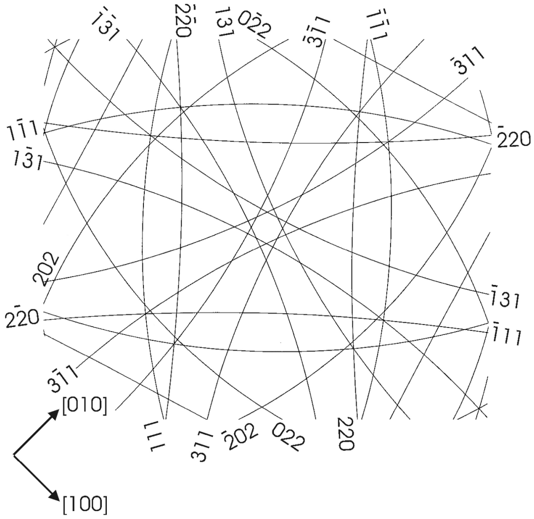

Figure 3
Computer simulation of divergent-beam conics seen in Fig. 2. There are many more lines observable on the original image, but here we show just the first few low-angle lines.

$$CT = \tfrac{1}{2}\left[\tan\tfrac{1}{2}(\varphi + \theta - 90^\circ) + \tan\tfrac{1}{2}(\varphi - \theta + 90^\circ)\right].$$

The radius MT of this circle is given by

$$MT = \tfrac{1}{2}\left[\tan\tfrac{1}{2}(\varphi - \theta + 90^\circ) - \tan\tfrac{1}{2}(\varphi + \theta - 90^\circ)\right].$$

These formulae then allow one to trace the conics directly onto the stereographic projection.

It can be seen that Fig. 3 is in very close agreement with the observed pattern in Fig. 2, thus showing that the method has indeed worked well, and from such a diagram it is then easy to identify the *hkl* indices of the planes giving rise to the conics. This demonstration now opens up the possibility of carrying out divergent-beam experiments using synchrotron sources on many materials and with a very large range of X-ray wavelengths available, much more than can be obtained with conventional targets or by using the standard Kossel method.

3. Conclusion

There are many advantages, and potential applications, of combining divergent-beam diffraction with synchrotron radiation. Experiments could easily be performed with a range of wavelengths, simply by changing the fluorescent foil, and one could even employ divergent-beam diffraction as a spectrometer for fluorescence radiation, much as Rutherford did with a gamma-ray source. The use of an external source, as demonstrated here, allows divergent-beam photography to be carried out on most crystals, including organic or biological crystals, provided that the crystal is neither too perfect nor too imperfect. The external fluorescent source can take many forms including liquids and gels, rather than metal foils as used here, in order to avoid contamination by powder diffraction rings. The fluorescent material could then either be placed close to the crystal sample or even just painted onto its surface. A particularly intriguing possibility is to focus the intense X-ray beam from a third-generation synchrotron radiation source to a micrometre-scale spot, allowing a precise determination of the strains in individual crystallites of granular materials such as in CVD diamond and in large-grain metals. Moreover, this technique could be also applied to the study of strain in many other areas, such as that found in ferroelastic domains and across domain walls.

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