The Use of Shorter Wavelengths in X-ray Diffraction in Relation to Scintillation Counting

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After referring to the advantages of scintillation counting discussed in earlier papers, in particular to the high yield it offers in the Mo K range, the conditions are discussed which a crystal-counter powder goniometer must satisfy in order to be adapted to the small deflection angles encountered with short wavelengths and to be free of aberrations which depend on the individual powder specimen and setting and which therefore cannot be allowed for on general terms. Two arrangements complying with these conditions are described.

The use of scintillation counting for X-ray diffraction was reported by Ladany and the writer at the Rochester Meeting of the American Physical Society in 1953 (Brentano & Ladany, 1953, 1954). We then showed that we could suppress the background and obtain a linear response over an extended range down to very low count rates. In the Mo K and Ag K range, where other methods lose efficiency, this requires only very simple instrumentation. Scintillation counting is thus called to make this range of wavelengths accessible to counter techniques.

Compared with, say, Cu K radiation, absorption coefficients for Mo K, outside the range of selective absorption—which can be shifted to a certain extent by substituting Rh K or Ag K—are reduced to about one-eighth, so that eight times greater masses and numbers of electrons can take part in the diffraction. Any intensity gain resulting from this is partly counteracted by other factors and is only of secondary importance. More significant is that by shifting to shorter wavelengths the smaller absorption improves the line contours obtained with the powder rod, that with mixed powders the effect of differential absorption (Brentano, 1935, 1949) is greatly reduced, and that in small-angle diffraction specimens can be made sufficiently thick to present a well defined thickness and density, so that the diffracted intensities can be normalized in terms of the mass of the diffracting material and of the intensity of the incident beam; this greatly enhances the interpretation. Owing to the exponential character of the absorption law this could not be done by averaging over area elements of unequal absorption.

A few points regarding goniometry which arise with shorter wavelengths may be briefly discussed. Assuming that both structure analysis and identifications make use of indices comprising reflections with a greatest $\sin \theta/\lambda = 0.64$, this implies for Cu K deflection angles 2θ extending to 162°, while for Mo K they fall within 54·2°, and for shorter wavelengths within smaller ranges. They fall then within the first quadrant, well below $2\theta = 90°$ and the intensity minimum. This shrinkage makes room for recording reflections with higher indices, although for all but the heavy elements F values become then very small. This reason, the decrease of F with $\sin \theta/\lambda$, limits the use of the high-resolution range $2\theta \sim 180°$ with short wavelengths, which is the main loss they entail.

With shorter wavelengths X-ray diffraction goniometry may thus be considered as confined to a limited angular range within which θ values are more closely proportional to $\sin \theta$. The reduced definition resulting from the angular shrinkage can easily be compensated by projecting to a larger distance; because of the smaller aperture of the diffraction cones this does not entail a proportionate intensity loss.

With the powder rod no difficulties arise although it will in general not be very efficient.

With the flat powder layer the greater penetration and stronger curvature of the toroidal parafocusing surface (Brentano, 1946) in a plane normal to its axis, which arises for small angles, must be considered. It should be pointed out that the flat thick powder layer now commonly used gives correct relative intensities when satisfying the parafocusing condition and this holds good for small angles provided the powder layer receives the full incident beam. The thick layer, however, is not suitable for the exact measurement of diffraction angles because of several aberrations, one of which is the penetration of the beam into the layer, which produce unsymmetrical line broadening. Some of these aberrations depend on the individual layer and its setting: they can thus not be allowed for on the basis of calculated or empirical correction terms.

One way to eliminate these aberrations is to mix the unknown substance with one for which the structure data are known. By determining the line positions by interpolation, errors can be eliminated.

Another way is to use a thin transparent layer; by observing reflections to both sides and with the layer
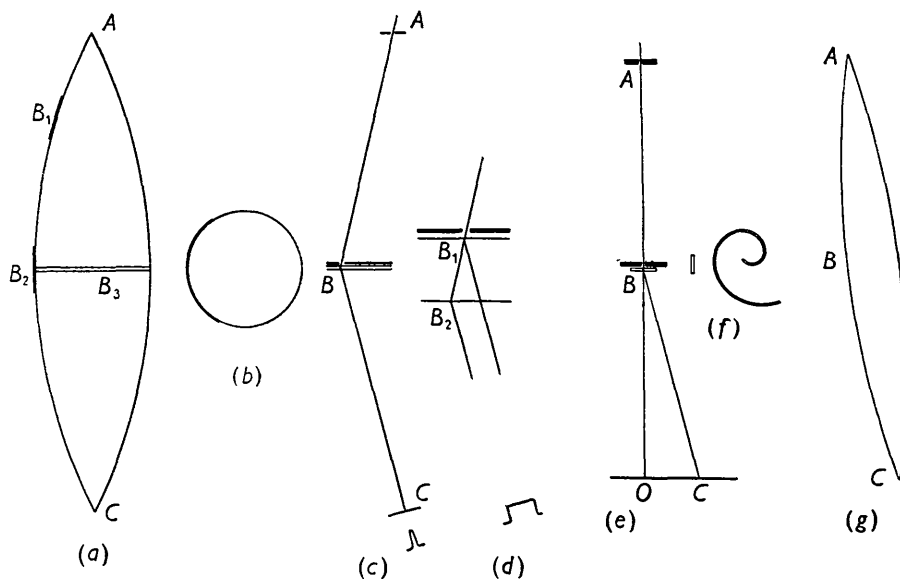
Fig. 1. (a, b) Parafocusing surface drawn for a small deflection angle. (c) Transmission method adapted for scintillation counting. (d) Characteristic aberration for narrow beams leading to a rectangular line contour. (e, g) Variation of transmission method for very small angles and corresponding parafocusing surface. (f) Two shapes of slits, rectangular and spiral, used in transmission methods.

rotated through 180° some of the aberrations, notably penetration and eccentricity of mounting, can be eliminated. The method (Brentano, 1925) is primarily suitable for photographic recording.

With short wavelengths a transmission method can be used adapted to the small absorption coefficients and to the limited angular range. Fig. 1(a, b) characterizes the elongated parafocusing surface for small deflection angles. Fig. 1(c) shows in B a powder slab of such thickness that the intensity of the beam incident from A is reduced to about 1/e. The diffracted intensity is recorded with the small crystal in C placed behind a narrow scanning slit. If the incident radiation is confined to a parallel beam in the plane of drawing, defined by narrow short slits in A and B, a diffraction line assumes a rectangular contour (Fig. 1(d)), which shows that all diffracted rays suffer the same intensity loss so long as the angles of incidence and diffraction with regard to the layer can be taken as equal. If now we increase the angular width of the incident beam by increasing the width of slit B this gives rise to a diffracted beam of similar aperture and to a broadening of the line in C. No gain in specific intensity results from increasing the angular broadening beyond the rectangular line width discussed above. The superposition of the two aberrations gives a line with a central peak which is easy to interpret. It depends only on the thickness of the layer, on the aperture of the incident beam and on the angles, parameters which are well defined. It is independent of the absorption in the layer and insensitive to small deviations in setting.

If we extend the length of slit B in a direction normal to the plane of drawing it will be seen that for small angles the curvature of the toroidal surface (Fig. 1(a, b)) has a much smaller radius in the plane normal to its axis (b) than in the plane containing the axis (a). The departure of the straight slit from the toroidal surface gives rise to an aberration which, in distinction from the aberrations with a linear character discussed before, is more difficult to allow for: it increases with the square of the slit length and increases rapidly for smaller diffraction angles. It can be suppressed by reducing the slit length; a shorter slit is imposed for smaller angles. This can be achieved by a movable cross slit, which reduces the slit length for smaller angles as discussed in earlier papers. At the same time this equalizes line intensities.

A more effective way is a slit which approximates the curvature of the parafocusing surface. Fig. 1(f) shows to the right of the rectangular slit a spiral slit. Placed in B a superposed auxiliary slit (not shown) restricts its aperture so that only a small fraction of one turn of the spiral passes X-rays. By turning the spiral in a correlated way while scanning a certain angular range, those parts are used in succession which approximate the sections of the toroidal surface for the particular angles. In this way beams with larger apertures giving higher intensities can be used. Slit A and the crystal with its covering slit in C are always small so as to conform with the parafocusing property of the toroid and the desideratum of small scintillating crystals.

The powder layers in Fig. 1 are rapidly rocked through a small angular range so as to increase the number of crystallites taking part in the reflection. This rocking is not correlated to the scanning.

Higher intensities are obtained with an annular surface in the form of a single bent crystal or powder layer acting as monochromator or goniometer (Brentano 1917, 1919). For small angles its resolution is limited.

The use of short wavelengths for small-angle diffraction does not need any special discussion: it only requires sufficiently extended cameras. We found it essential to operate with evacuated instruments in order to avoid disturbance by air scatter.

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The Crystal and Molecular Structure of Orthorhombic Sulfur*

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The lattice constants of orthorhombic sulfur have been determined as $a = 10\cdot437\pm0\cdot010$, $b = 12\cdot845\pm0\cdot010$, $c = 24\cdot369\pm0\cdot010$ Å. Using Mo $K\alpha$ radiation, and both Weissenberg and precession cameras, 669 out of a possible 1046 structure factors have been measured. Warren & Burwell's approximation to the structure was refined first by double Fourier series, and then by repeated least-squares analyses, using all the measured structure factors. The coordinates thus obtained, after the least-squares method had completely converged, were used in evaluating a triple Fourier series. The arithmetic mean of the coordinates obtained by the triple-Fourier-series method corrected for series-termination errors, and the final least-squares analysis, correspond to an S_8 molecule in which the mean S–S bond length is $2\cdot037\pm0\cdot005$ Å, the mean S–S–S bond angle is $107° 48'\pm25'$ and the mean dihedral angle is $99° 16'\pm31'$. There are no unusual intermolecular contacts. The dimensions in the S_8 molecule are briefly discussed in terms of other recent determinations on sulfur compounds.

1. Introduction

The crystal structure of orthorhombic sulfur was first determined by Warren & Burwell (1935) and found to consist of symmetrically puckered S_8 ring molecules. Using an elegantly simple method for reducing the number of positional parameters in the problem from 12 to 2, these parameters were refined by the trial-and-error method until satisfactory agreement was obtained between the 42 observed and calculated intensity amplitudes. The resulting arrangement led to an average S–S bond length of 2·12 Å and a S–S–S bond angle of 105·4°.

A re-examination of Warren & Burwell's structure was made by Ventriglia (1951), who confirmed the original solution to be correct by the use of double Patterson series. He also suggested that the S–S bond distances are about 2·1 Å and the S–S–S bond angles about 105°.

The importance of an accurate knowledge of this S–S bond distance to current discussion concerning the presence of double-bond character in similar bonds, suggested that a new investigation be undertaken. Accordingly, all the reflections observable with molybdenum radiation have been measured, and the resulting 669 structure factors were used in three-dimensional least-squares analyses and triple Fourier series to determine the positional parameters.

2. Crystal data

Orthorhombic sulfur, S_8; mol. wt. 256·53; transforms at 95·5° C. to monoclinic sulfur and melts at 118·95° C.; $D_{obs.}=2\cdot069$ g.cm.$^{-3}$ (Batuecas & Losa, 1951); $D_{calc.}= 2\cdot085$ g.cm.$^{-3}$. The lattice constants were redetermined using precession photographs corrected for film shrinkage; the orthorhombic unit cell had

$$a = 10\cdot437\pm0\cdot010, \quad b = 12\cdot845\pm0\cdot010 \text{ and}$$
$$c = 24\cdot369\pm0\cdot010 \text{ Å}$$

(Warren & Burwell's values were 10·48, 12·92 and 24·55 Å); (hkl) present only when $h+k$, $k+l$, $l+h=2n$;