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## A New Method for Measuring Integrated Intensities Photographically\*

BY LEONID V. AZÁROFF

*Armour Research Foundation of Illinois Institute of Technology, Technology Center, Chicago, Illinois, U.S.A.*

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A bent-crystal monochromator is used in conjunction with a conventional Buerger precession camera. Each reflection intensity is recorded on the film as a rectangular spot having nearly constant intensity across the long direction and a narrow plateau across the short direction. The integrated intensity is obtained by direct measurement of the height of this plateau with a densitometer. The use of crystal monochromatized X-radiation permits the recording of the direct beam on the same film and the determination of the absolute value of each intensity. The use of crystal monochromatized X-radiation also permits increased exposure times to detect weak intensities owing to the very low background intensity. The accuracy of this method has been tested with a  $\text{CaF}_2$  crystal and the agreement between observed and measured structure factors was better than 2%.

### Introduction

In order to determine the magnitude of structure factors from experimentally observed X-ray diffraction intensities, it is necessary to measure the total X-ray power diffracted by each crystal plane, or, as it is commonly called, the *integrated intensity*. The integrated intensity can be measured directly by an ionization counter (Cochran, 1950) provided that the opening is large enough to admit all characteristic radiation diffracted by the crystal. Alternatively, photographic film can be used. In this case, the area of the film is large enough to intercept all the diffracted radiation; however, to make the blackening on the film proportional to the integrated intensity, it is necessary that a sufficient number of individual grains be exposed for equal increments of time to each equivalent area of the entire diffracted beam. A mechanical device for integrating the intensity on a film during the exposure has been described for the Weissenberg camera (Wiebenga & Smits, 1950) and for the Buerger precession camera (Nordman, Patterson, Weldon & Supper, 1955).

The experimental determination of the magnitude of structure factors has two aspects: the measurement of the integrated intensities, and the detection of

relatively weak intensities. Ionization counters are capable of doing both; however, for reasons of economy of time and cost, film methods are often preferred. The mechanical integrating devices for film methods satisfy the first condition, but actually worsen the second by increasing the background intensity during the increased exposure times.

Although the use of crystal monochromators in X-ray diffraction studies is not new, their use specifically for obtaining accurate diffraction intensities has been overlooked. The arrangement described herein has the advantage that integrated intensities can be determined with an accuracy and sensitivity approaching that of ionization counters while the inherent advantages of film methods (compact permanent records, low equipment costs, etc.) are retained.

### Integrated intensities

The total power diffracted by a set of planes in the specimen crystal is recorded on a photographic film by a blackening of the intersection of the reflected beam and the film. Provided that each and every part of an area large enough to be measured receives a contribution from each equivalent portion of the diffracted beam, the measured intensity is directly proportional to the *integrated intensity*. The necessary conditions for doing this without mechanically displacing the film are:

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(1) The effective X-ray source must be larger than the specimen crystal so that each and every part of the latter is bathed in convergent radiation from each and every part of the effective source.

(2) The specimen-to-film distance must be sufficiently large to produce a measurable area on the film from that portion of the diffracted beam which has been swept (during rotation of the crystal) by rays from every part of the specimen.

(3) The angular range of rotation of the specimen crystal must exceed both its mosaic nature and the convergence angle of the X-ray beam incident on it. The beam convergence in the plane perpendicular to the instantaneous motion axis of the specimen crystal must exceed the mosaic spread of the specimen crystal in that plane.

An experimental arrangement designed to satisfy these conditions is described below. The integral part of this arrangement is a bent-crystal monochromator, which has the added advantage of removing background scattering due to non-characteristic radiation.

#### Experimental arrangement

The arrangement described below resembles conventional arrangements for recording intensities photographically in that a converging beam of X-radiation falls on a crystal which is smaller than the cross-section of the beam. Any of several conventional cameras can be used to record the diffraction spectrum. Because of the advantages inherent in photographing the undistorted reciprocal lattice, a Buerger

precession camera (Buerger, 1944) with  $\text{Ag } K\alpha$  radiation is used in the present arrangement. (With this arrangement, it is possible to record reflections from all planes for which  $\sin \theta/\lambda \lesssim 1.0$ , the approximate limit of other experimental arrangements.) A bent-crystal monochromator, placed between the tube target and the camera, serves to define the incident beam convergence in a vertical plane. A set of slits contained in a collimator following the monochromator limits the divergence in the horizontal plane. The specimen crystal, itself, defines the convergence in this plane. Fig. 1 shows ray diagrams of the con-

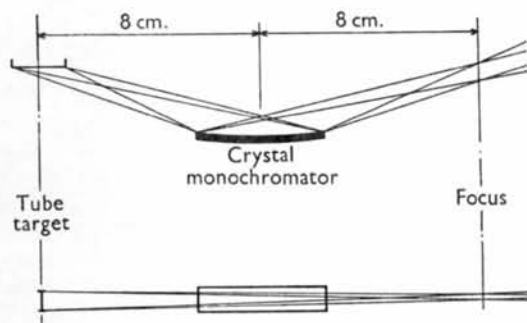


Fig. 1. Ray diagram of the crystal-monochromatized beam. The top drawing shows the focusing condition of the bent crystal. The bottom drawing illustrates the natural convergence in a plane normal to the above plane. In order that each point in the focus receives radiation converging from every point of the monochromator it is necessary that there be a sufficient mosaic spread in the monochromator crystal. This specifically excludes perfect monochromator crystals with polished and etched surfaces.

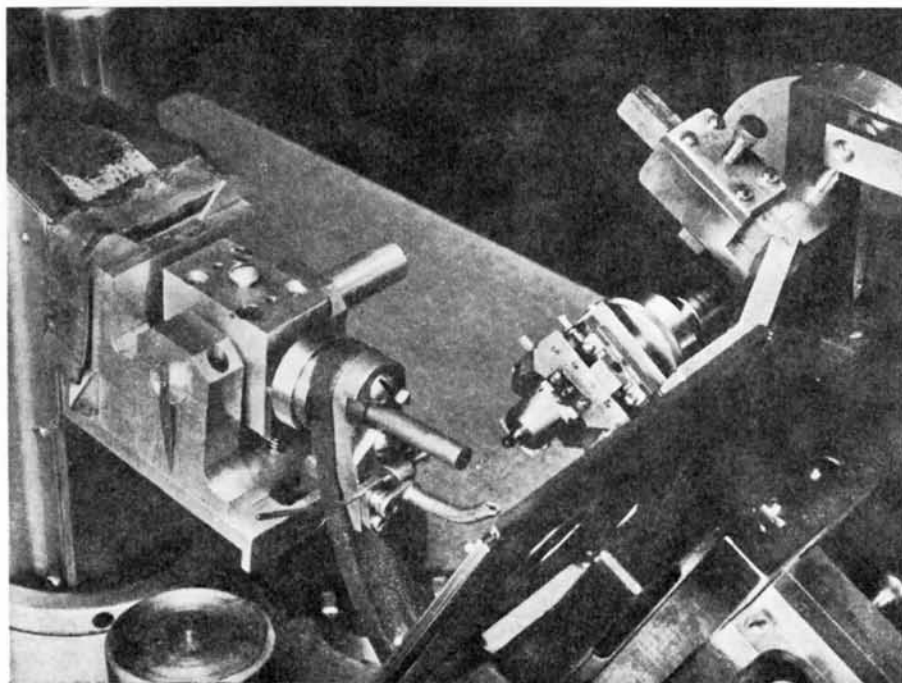


Fig. 2. Monochromator mounted for use with a Buerger precession camera.

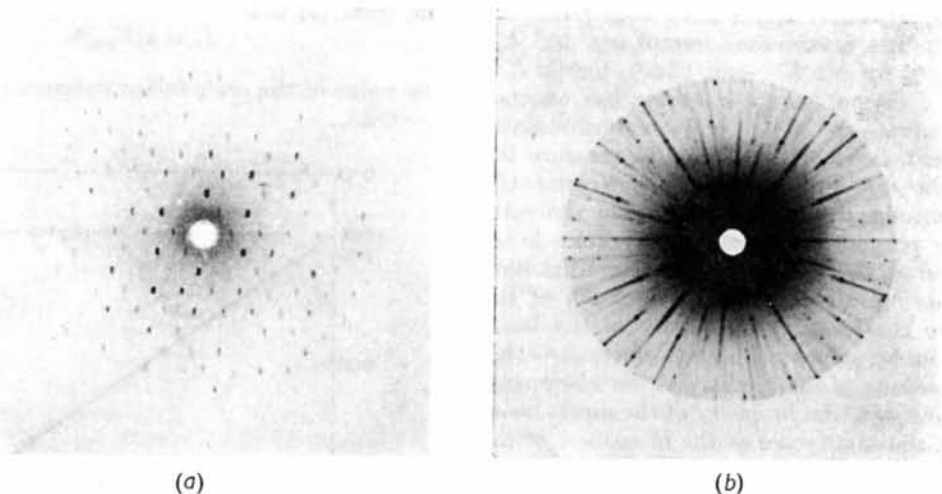


Fig. 3. Fairfieldite,  $(0kl)$  level,  $\mu = 21^\circ$ , Ag  $K\alpha$ , 35 kV., 15 mA., 10 hr. (a) Prepared with monochromator. (b) Prepared with conventional arrangement.

vergence conditions in these two planes. The convergence of the beam in one plane, combined with the crossfire of the incident beam in the other plane, produces a direct beam that effectively converges in all planes.

The design and construction details of a bent-crystal monochromator are well known (see, for instance, Guinier, 1952, or Wilsdorf, 1951) and will not be discussed here. There are a finite number of suitable crystals that can be used as monochromators, the choice depending primarily on the wavelength of the radiation used. A monochromator built by the author employs a 4 cm.-long quartz plate, cut parallel to  $(10\bar{1}1)$  and bent to a radius of 95.4 cm. placed so that the target is viewed at an angle of approximately  $5^\circ$ . The convergence angle of the beam is approximately  $2\frac{1}{2}^\circ$  and the target-to-monochromator and monochromator-to-specimen distances are 8 cm. Fig. 2 shows the actual equipment used in the author's laboratory.

The exposure times necessary to achieve intensities comparable to standard photographic techniques are approximately of the same duration. This is due to the fact that the virtual elimination of the background decreases the total blackening necessary to achieve the same signal-to-noise ratio. Longer exposure can be used successfully, however, to bring out the weaker reflections. Figs. 3(a) and 3(b) show the same zero-level photograph prepared with this arrangement and an ordinary pinhole collimator under identical exposure conditions, i.e. the tube voltage and current, as well as the exposure time, were the same.

#### Intensity measurement

Fig. 3(a) clearly shows the rectangular shape of each reflection spot. A microphotometer trace across the

long direction of the spot shows a uniform density with a rapid decline at both edges of the spot. A trace across the short direction shows a more narrow plateau which is uniform over approximately one third of the total width of the spot. The total uniform area of each spot, however, is large enough to be measured with a microphotometer. If a recording microphotometer is used, each reflection can be scanned automatically, substituting paper for operator time. In this case, the integrated intensity is proportional to the height of the plateau less the height of the background.

If a recording microphotometer is used, the use of the Buerger precession camera gives an advantage by recording the undistorted reciprocal lattice so that the spots fall on straight lines, and each reciprocal-lattice row can be scanned automatically. After the integrated intensity has been determined, the magnitude of the structure factors can be determined from the relation

$$|F|^2 = \frac{1}{Lp} I, \quad (1)$$

where  $Lp$  is the Lorentz and polarization correction. The X-ray beam irradiating the specimen crystal is partially polarized by the monochromator. It is necessary, therefore, to use an expression for the polarization correction different from the standard  $\frac{1}{2}(1 + \cos^2 2\theta)$  relation. Since standard charts for making this correction include the expression for the Lorentz factor, it is suggested that the new polarization correction be made a second step in converting  $I$  to  $|F|^2$ . Thus:

$$|F|^2 = \frac{1}{Lp} I \times \frac{p}{p'}, \quad (2)$$

where  $p'$  is the polarization correction for a partially polarized beam. Tables listing this correction as a

function of the reflection angles have been published (Azároff, 1955). The maximum value of  $p/p'$  is 1.4% for Ag  $K\alpha$ , 2.4% for Mo  $K\alpha$ , and 12.5% for Cu  $K\alpha$ .

The use of a crystal monochromator has another very distinct advantage. When truly monochromatic radiation is used, it becomes possible to measure the intensity of the direct beam and to determine the absolute magnitude of each intensity from the ratio of  $I/I_0$ . In the present arrangement, the direct beam can be recorded on the same film with the diffraction diagram by placing an absorber in the path of the direct beam to cut down the intensity of the beam reaching the film by a known amount. After correcting the measured density of the central spot for absorption by the absorbing well, the intensity of the direct beam is obtained on the same scale as the intensities of the crystal reflections.

### Accuracy

A single crystal of  $\text{CaF}_2$  was ground to a spherical shape (approximately  $\frac{1}{8}$  mm. diameter) and used to test the accuracy attainable with this arrangement. The [100] and [111] zones of fluorite were photographed using Ag  $K\alpha$  radiation, and each intensity was measured by recording the density with a recording microphotometer. A 0.02 cm.-thick sheet of copper was used to attenuate the direct beam whose trace was recorded on the same film. The high symmetry of fluorite allowed each intensity to be measured four or more times and the averages of these readings were used to determine  $|F|^2$  according to (1). The additional polarization correction in (2) was not made since it differed from the conventional correction by less than 1% within the range recorded by the precession camera.

The measured structure factors were assumed to be related to the calculated structure factors according to:

$$|F|_o^2 = k|F|_c^2 \exp[-2B \sin^2 \theta / \lambda^2], \quad (3)$$

where  $k$  is the scale factor, and the exponential term relates the usual temperature factor. Ratios of  $|F|_o^2/|F|_c^2$  were plotted as a function of  $\sin^2 \theta / \lambda^2$  on semilogarithmic paper in order to determine the scale factor,  $k$ . As can be seen in this plot, Fig. 4, the value of the scale factor is  $k = 0.32$ . The temperature factor is  $2B = 1.62 \text{ \AA}^2$ . After correcting the calculated structure factors for temperature motion of the atoms, and after dividing the observed structure factors by the scale factor  $k$ , the largest difference between observed and calculated structure factors was 1.4%.

In order to determine the scale factor directly, the density of the direct beam trace was first measured in the same way as that used for measuring the reflection intensities and then corrected for absorption by the copper sheet. The intensity of the direct beam was determined by assuming that

$$I_0/|F_{000}|^2 = |F_{hkl}|_o^2/|F_{hkl}|_c^2 \quad (4)$$

and from (3) that

$$I_0 = k|F_{000}|^2. \quad (5)$$

The value of the scale factor determined from (5) was  $k = 0.29$ .

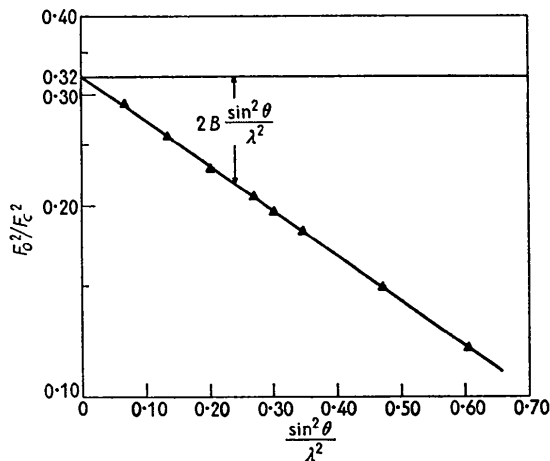


Fig. 4. Determination of temperature factor and absolute scale.

The above agreement between observed and calculated structure factors is somewhat amazing. It is not intended as proof that such accuracy can always be attained with this arrangement but rather as an indication of what can be done under optimum conditions. On the other hand, the disagreement between the scale factors determined directly from the direct-beam intensity and from the use of (3) can be attributed to uncertainties in the true absorption coefficient of the absorbing material used. These uncertainties are caused by impurities in the material used and by the inability to determine its thickness precisely. It is suggested, therefore, that after a suitable absorbing well is fashioned its absorption coefficient be determined empirically.

### Discussion

The above described arrangement has several distinct advantages over film methods currently in use. These are: (1) The *integrated* intensity of each reflection is recorded on a film. (2) The sensitivity of the film is increased by virtually eliminating the background. (3) The absolute scale of the observed intensities can be determined directly. (4) The accuracy is improved over that attainable by conventional film methods.

In conclusion, it should be pointed out that some of these advantages apply also to ionization-type detectors if crystal monochromatized X-radiation is used.

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## The Crystal Structure of Diphenyl Sulfoxide\*

BY S. C. ABRAHAMST†

*Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge,  
 Massachusetts, U.S.A.*

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Diphenyl sulfoxide forms monoclinic crystals, space group  $P2_1/n$ , in a cell with  $a = 8.90 \pm 0.02$ ,  $b = 14.08 \pm 0.03$ ,  $c = 8.32 \pm 0.02$  Å,  $\beta = 101^\circ 7' \pm 10'$ , containing four molecules. The crystal structure has been solved by a combination of isomorphous-replacement and trial-and-error methods. Refinement of the atomic parameters was effected by the use of double Fourier series, followed by least-squares analysis of a set of 664 independent structure factors. This partially complete set of three-dimensional structure factors was derived by visual intensity measurement. The final coordinates lead to the bond lengths: S-O,  $1.47 \pm 0.016$  Å; S-C,  $1.76 \pm 0.015$  Å; C-C,  $1.40 \pm 0.008$  Å; and the bond angles: C-S-O,  $106^\circ 10' \pm 40'$ ; C-S-C,  $97^\circ 19' \pm 58'$ ; S-C-C,  $119^\circ 27' \pm 34'$ , corresponding to a pyramidal arrangement of the three bonds about the sulfur atom. The dihedral angle between the normals to the planes of the aromatic rings is  $75^\circ 50' \pm 68'$ , and between the plane of each ring and the common C-S-C plane is  $81^\circ 57' \pm 49'$ .

## Introduction

In considering the stereochemistry of subgroup VIb of the periodic table, there is a special importance in a study of these atoms when chemically linked to three other atoms. The early debates on the possibility of planarity in the three sulfur bonds in the sulfoxide group were largely ended by the optical resolution of unsymmetrical sulfoxides by Harrison, Kenyon & Phillips (1926). This work clearly demonstrated that the three bonds could not be coplanar, but left the precise arrangement undetermined. Recent studies of the molecular constants of several simple sulfoxides have entirely confirmed the pyramidal form of these bonds. The present study of the simplest aromatic sulfoxide was undertaken in order to throw further light on the stereochemistry of the sulfoxide group.

A survey of the general stereochemistry of oxygen, sulfur, selenium, tellurium and polonium has now been given (Abrahams, 1956).

## Crystal data

Diphenyl sulfoxide,  $(C_6H_5)_2SO$ ; m. p.,  $70.5^\circ$  C.;  $D_m = 1.276$  g.cm.<sup>-3</sup>,  $D_x = 1.313$  g.cm.<sup>-3</sup>. Monoclinic, with  $a = 8.90 \pm 0.02$ ,  $b = 14.08 \pm 0.03$ ,  $c = 8.32 \pm 0.02$  Å,  $\beta = 101^\circ 7' \pm 10'$ . Four molecules per unit cell;  $(hkl)$  present in all orders;  $(h0l)$  present only when  $h+l=2n$  and  $(0k0)$  only when  $k=2n$ . Space group  $C_{2h}^5-P2_1/n$ . No molecular symmetry required. Absorption coefficient for Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å),  $3.1$  cm.<sup>-1</sup>. Volume of the unit cell,  $1023.3$  Å<sup>3</sup>. Total number of electrons per cell,  $F(000) = 424$ . Dipole moment, 4.44D (Jensen, 1943). The magnetic anisotropy, measured through the courtesy of Dame Kathleen Lonsdale (Toor, 1952) is  $\chi_1 = -69 \times 10^{-6}$ ,  $\chi_2 = -117 \times 10^{-6}$  and  $\chi_3 = -126 \times 10^{-6}$  c.g.s.e.s.u., where  $\chi_1$  is about  $30^\circ$  to  $a$  in acute  $\beta$ ,  $\chi_2$  is about  $60^\circ$  to  $a$  in obtuse  $\beta$  and  $\chi_3$  is along  $b$ .

## Analysis of the structure

The position of the sulfur atom in diphenyl sulfoxide was not apparent from an examination of the Patterson function projected along the crystal axes. A model based upon a poorly resolved peak taken as the

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† Present address: Bell Telephone Laboratories Incorporated, Murray Hill, New Jersey, U.S.A.