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Extinction and Borrmann Effect in a Calcium Fluoride Sphere

BY W. H. ZACHARIASEN

Department of Physics, University of Chicago, Chicago, Illinois 60637, *U.S.A.*

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The theoretical formula for the integrated intensity including extinction and Borrmann effects is tested on observations obtained with a small sphere of calcium fluoride and the use of Mo $K\alpha$ and Cu $K\alpha$ radiations. It is found that a mean domain radius of 3×10^{-4} cm and nearly perfect alignment of the domains give agreement between observed and calculated structure factors corresponding to R values of less than 0·02.

The preceding article (Zachariasen, 1968) described the derivation of a formula for the integrated intensity which includes correction for extinction as well as for the Borrmann effect. In this paper the predictions of the theory are tested experimentally with the use of intensity data obtained with Mo $K\alpha$ and Cu $K\alpha$ radiations and a small sphere of calcium fluoride. Indeed, the theoretical study was prompted by the puzzling nature of the observations for this specimen.

The observations

The nearly perfect sphere of calcium fluoride was supplied by Dr S. C. Abrahams of the Bell Telephone Laboratories. It was one of the many spheres prepared from a synthetic crystal for use in the *ACA Single-Crystal Intensity Project* (Abrahams, Alexander, Furnas, Hamilton, Ladell, Okaya, Young & Zalkin, 1967). The radius was $2{\cdot}20\pm0{\cdot}04\times10^{-2}$ cm, so that $\mu_0R=0{\cdot}72$ for Mo $K\alpha$ and $\mu_0R=6{\cdot}40$ for Cu $K\alpha$ radiation.

The intensities of all reflections (in one hemisphere) with $2\theta<90°$ were measured with Mo $K\alpha$ radiation using a manually operated 'Goniostat' spectrometer, a Zr filter and the stationary counter–crystal technique. A carefully calibrated set of Ni foils was used for beam attenuation to keep the counting rate at a low level for the stronger reflections. Two complete sets of data were taken a few weeks apart. In set I the background correction was made with a balanced Y–Zr filter. In set II the background was measured on both sides of the diffraction peak, and the mean value of the two readings was assumed to give the correct value for the background under the peak. Set I is probably more accurate at small and set II at large scattering angles.

The copper data were taken with a normal beam spectrometer, a Ni filter (and additional calibrated foils for beam attenuation) and stationary counter and crystal. The crystal was mounted with the $[1\bar{1}0]$ axis vertical, and only reflections in the equatorial plane were measured [*i.e.* reflections (HHL)]. The limitation $2\theta<120°$ was imposed to assure that the entire diffracted beam entered the counter. The background was measured at $2\theta\pm2°$.

The results of the measurements, reduced to experimental structure factors F_σ, are shown in Tables 1 and 2.

Table 1. *Calculated and observed structure factors*, Mo $K\alpha$

			F_σ	
HKL	F_c	$F_cy^{1/2}$	I	II
111	62·7	26·9	25·9	25·1
200	2·3	2·2	2·3	2·0
220	96·5	38·5	36·2	35·2
311	45·8	26·2	26·3	26·6
222	7·1	6·7	7·2	7·4
400	71·2	35·6	34·4	34·0
331	36·7	24·2	24·8	25·0
420	8·9	8·3	8·9	9·0
422	56·6	32·6	32·4	32·4
511	31·3	22·7	23·2	23·4
333	31·3	22·7	22·9	23·1
440	47·7	30·3	30·3	30·4
531	27·6	21·2	21·6	21·9
600	10·2	9·6	9·8	9·8
442	10·2	9·6	9·7	9·7
620	41·4	28·5	28·8	29·2
533	24·8	20·3	19·9	20·2
622	10·3	9·8	9·9	10·0
444	36·8	26·9	26·8	27·2
711	22·7	19·2	19·2	19·3
551	22·7	19·2	19·1	19·2
640	10·2	9·7	9·8	9·8
642	33·1	25·3	25·5	25·5
731	20·9	18·1	18·1	18·0
553	20·9	18·1	18·1	17·9
800	30·2	23·8	24·2	24·1
733	19·4	17·0	17·0	17·1
820	9·6	9·2	9·3	9·3
644	9·6	9·2	9·3	9·2
822	27·7	22·3	22·6	22·5
660	27·7	22·3	22·6	22·5
751	18·0	16·0	16·1	16·0
555	18·0	16·0	15·8	15·7
662	9·2	8·9	8·9	8·8
840	25·5	21·1	21·3	21·4
911	16·7	15·1	14·8	15·0
753	16·7	15·1	15·0	15·0
842	8·7	8·4	8·4	8·4
664	23·5	19·8	19·9	20·1
931	15·6	14·4	14·3	14·3
844	21·8	18·7	18·8	18·8
933	14·5	13·4	13·1	13·3
771	14·5	13·4	13·2	13·4
755	14·5	13·4	13·3	13·4

Table 1 (*cont.*)

			F_σ	
HKL	F_c	$F_cy^{1/2}$	I	II
10.0.0	7·8	7·6	7·6	7·6
860	7·8	7·6	7·6	7·6
10.2.0	20.2	17·6	17·6	17·7
862	20·2	17·6	17·7	17·7
951	13·5	12·6	12·4	12·5
773	13·5	12·6	12·6	12·6
10.2.2	7·3	7·2	7·1	7·1
666	7·3	7·2	7·0	7·2

Table 2. *Structure factors*, Cu *Kα*

		$F_cy^{1/2}$ Borrmann effect		
HKL	F_c	neglected	included	F_σ
111	63·4	28·9	41·5	40·5
002	5·0	4·9	4·9	4·8
220	97·4	44·3	55·9	56·5
113	46·6	31·0	35·6	35·3
222	8·3	8·0	8·0	8·6
004	72·2	41·7	48·8	48·9
331	37·4	27·6	30·3	29·0
224	57·5	35·6	40·3	41·3
115	32·0	24·9	26·4	26·2
333	32·0	24·9	26·4	26·2
440	48·5	33·4	36·4	36·5
006	10·9	10·4	10·4	10·6
442	10·9	10·4	10·4	10·6

The standard fluorite sphere used in the *Intensity Project* was of nearly identical size ($R=2{\cdot}22\times10^{-2}$ cm) with the one used in the present study, and the F_σ^2 values obtained by the various participating laboratories have been reported (Abrahams *et al.*, 1967). The F_σ values for the standard sphere, when adjusted to agree with the data of Table 1 for weak reflections at large scattering angles, are generally lower than those of the present study at small scattering angles for the stronger reflections. It is thus indicated that the extinction effects were somewhat larger for the standard sphere, possibly because it was prepared from a smaller crystal fragment which needed shorter grinding time.

Cromer & Waber's (1964) theoretical f_0 curves for ionized atoms and Cromer's (1965) values for the real part of the dispersion correction were adopted. However, the imaginary parts were computed from the experimental atomic absorption coefficients with the aid of equation (12) of the preceding article. The values used for the anomalous dispersion corrections are accordingly

	Mo *Kα*		Cu *Kα*	
	Δ'	Δ''	Δ'	Δ''
Ca	0·24	0·30	0·36	1·25
F	0·02	0·014	0·06	0·06 .

The results

The theoretical results of the preceding paper show that, for a given wave length, extinction and Borrmann effects introduce a single adjustable parameter into the problem, namely the quantity r^*. The obvious procedure for the determination of r^* is thus to include this parameter with the scale factor C and the positional and thermal parameters in a least-square refinement which minimizes the differences between the observed set of structure factor F_σ and the calculated set $CF_cy^{1/2}$, where y is given by equation (24)–(26) of the preceding article. However, such a refinement program is not yet available.

The only adjustable parameters for the crystal under study are the scale factor C, the thermal parameters $B_{\rm Ca}$ and $B_{\rm F}$, and the quantity r^*. In the absence of a computer program the approximate values of these parameters were obtained by means of a crude refinement carried out by trial and error hand calculations. The expression for r^* is

$$r^*=r[1+(r/\lambda g)^2]^{-1/2}$$

where r is the mean domain radius and g the quantity introduced in the preceding paper. In order to find both r and g, which characterize the mosaic crystal specimen, it is thus necessary to determine r^* independently for the two radiations, *i.e.* $r^*_{\rm Mo}$ and $r^*_{\rm Cu}$. Theoretically one must have $r\ge r^*_{\rm Cu}\ge r^*_{\rm Mo}$.

Since $\mu_0R=0{\cdot}72$ for the molybdenum data it was assumed as a first approximation that the Borrmann effect would be negligible, *i.e.* that the expression for y given in equation (1)–(2) of the preceding paper could be used. With $r^*_{\rm Mo}=2{\cdot}2\times10^{-4}$ cm an R value of 0·013 was obtained for the data of set I of Table 1, and the corresponding values of the thermal factors were $B_{\rm Ca}=0{\cdot}60\pm0{\cdot}01$ Å^2 and $B_{\rm F}=0{\cdot}80\pm0{\cdot}02$ Å^2.

The large value found for $r^*_{\rm Mo}$ showed that the initial assumption of negligible Borrmann effect is not truly valid for the strongest reflections, and that hence equations (24)–(26) rather than equations (1)–(2) should have been used. The inclusion of the Borrmann effect will primarily affect the r^* value, and it was assumed that the B values would remain unchanged. On this basis a revised value of $r^*_{\rm Mo}=2{\cdot}5\times10^{-4}$ cm was obtained.

The trial and error analysis of the copper data in terms of equations (24)–(26) (with $B_{\rm Ca}=0{\cdot}60$ Å^2 and $B_{\rm F}=0{\cdot}80$ Å^2) gave as result $r^*_{\rm Cu}=3{\cdot}0\times10^{-4}$ cm.

The two values obtained for $r^*_{\rm Mo}$ and $r^*_{\rm Cu}$ give $r=3{\cdot}2\times10^{-4}$ cm and $g=5{\cdot}7\times10^4$, showing that the domains are in nearly perfect alignment.

The calculated values of F_c per unit cell and of $F_cy^{1/2}$ (with the scale factor adjusted to unity) are listed in Tables 1 and 2. It is seen that the agreement between the sets F_σ and $F_cy^{1/2}$ corresponds to R values of less than 0·02 for both radiations.

A refinement, properly carried out, will no doubt lead to some revision of the B and r^* values given above, and to a further reduction of the R index for the molybdenum data.

The Borrmann effect amounts to a correction of only eight per cent for the largest structure factor of the molybdenum data. However, as shown in Table 2, the correction for the Borrmann effect is 44% for the (111) and 26% for the (220) structure factors of the copper data. Because of the restriction $r^*_{\text{Cu}} \geq r^*_{\text{Mo}}$ it is clearly impossible to obtain a self-consistent interpretation of the combined copper and molybdenum data without taking the Borrmann effect into account.

It is a most surprising result to find such a high degree of perfection (as illustrated by the large values for r and g) for a crystal which has been ground into a sphere. The pure extinction effect is very great for both radiations firstly because r^* is large, and secondly because of the simplicity of the structure which allows F_c/V to be very large for many reflections. For the same two reasons, with the additional condition $\mu_0 R \gg 1$, the Borrmann effect becomes very great for the copper data.

The good agreement between theory and experiment suggests that the intensity formula presented in the preceding paper is satisfactory even for extreme conditions of extinction. However, further experimental tests of the theory are needed.

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Diffraction of Light by Opals

BY J. V. SANDERS

Commonwealth Scientific and Industrial Research Organization, Division of Tribophysics, University of Melbourne, Australia

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Gem opals were examined in an optical diffractometer and found to give several types of diffraction pattern which are interpreted by analogy with conventional three-dimensional X-ray theory to give the structure of the opal. The results show that the spherical silica particles in opals are arranged hexagonally in layers which are usually stacked randomly. In some specimens there are parallel domains of ordered packing, commonly in a f.c.c. sequence and sometimes in a h.c.p. sequence. Although the silica particles cannot be resolved by optical microscopy, bands parallel to the layers and fringes across the bands can be seen in images with the diffracted light.

Introduction

Precious opal is an unusual form of silica and is valued as a gemstone because it exhibits intense colours which come and go or change in wavelength as the gemstone is viewed at various angles in white light. It is this effect of the play of colours which gives opals their distinctive appearance.

This property has not been well understood (Leechman, 1961). Baier (1932) made extensive optical measurements on opals, and suggested that opal was a pseudomorph of calcite (Baier, 1966) and that the colours arose by diffraction from regularly spaced sets of planes which originated in the twinned structure of the calcite. Raman & Jayaraman (1953) as well as Baier (1932) noted the high degree of monochromatism in the colour; they realized that this must be due to diffraction, and suggested an arrangement of equally spaced parallel plates of two forms of silica of different refractive indices.

It has recently been shown by Jones, Sanders & Segnit (1964) that precious opals are composed of spherical particles of amorphous silica whose size (1500–3500 Å) is too small for their resolution in an optical microscope, but large enough for them to be easily visible in an electron microscope. In gem quality opal the particles are remarkably uniform in size and they were therefore able to pack together regularly to form a pseudo-crystal. The particles of silica are transparent to light, but the unfilled voids between them scatter light because of the change of refractive index at their interfaces. This arrangement makes a three-dimensional grating which can give diffracted beams of light in the visible range when the particles of silica are larger than about 1500 Å in diameter (Sanders, 1964).

Electron microscopy clearly reveals the ordered arrangement of voids at the surface of opals, but the technique is not very suitable for investigating the packing arrangement of the particles of silica, because