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Investigations of some Effects of Multiple Diffraction in X-ray Structure Analysis

By Stig Åsbrink

Institute of Inorganic and Physical Chemistry, University of Stockholm, S-113 86 *Stockholm, Sweden*

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The experimental results of some measurements, on an equi-inclination type diffractometer, of the effect of multiple diffraction are reported. Thus, the effect on the extinction correction predicted by Zachariasen is demonstrated. A crystal-size effect is also observed, the theoretical basis for which is derived.

Introduction

The importance of not neglecting the effect of multiple diffraction in X-ray intensity work has recently been stressed by several authors, *e.g.* Zachariasen (1965), Burbank (1965), Jeffery & Whitaker (1965), Santoro & Zocchi (1966), Zocchi & Santoro (1967), Gomes de Mesquita (1967) and Post (1968). In this paper some experimental and theoretical results will be reported, one of which shows the effect of multiple diffraction on the magnitude of the observed extinction and another demonstrates the influence of crystal size on the intensities of the repeated reflexions. The results of two refinements of the monoclinic structure of VO_2 are compared, one being based on data registered under conditions of triple diffraction, the other on data free from systematic multiple diffraction effects.

Experimental work on VO_2

A complete equi-inclination data set (excluding only reflexions corresponding to reciprocal lattice points on, or very close to, the rotation axis) was registered for one single crystal of VO_2 in each of two different orientations on a PAILRED diffractometer.

The intensities were measured out to $2\theta \simeq 100°$ using Mo $K\alpha$ radiation monochromatized by reflexion off the (200) planes of a LiF crystal positioned just outside the X-ray tube. The specimen crystal had the shape of a somewhat elongated octahedron, the volume of which was calculated to be $1{\cdot}14 \times 10^{-7}$ cm^3. (A sphere with the same volume would have a radius of 0·0030 cm.) One data set was obtained with the crystal rotating about [010] (the unique direction) and another with the crystal rotating about [100]. These are referred to below as the *b* and *a* sets respectively. Both sets were corrected for Lorentz–polarization (Lp) and absorption, μ_0 being 81·2 cm^{-1}, ($\mu_0 r \simeq 0{\cdot}25$) and used for least-squares refinements. Starting parameters were those of Longo & Kierkegaard (1970). As it was quite evident that severe extinction affected both data sets, the strong reflexions were excluded in the way presented by Åsbrink & Werner (1966). The final refinements were based on about 70% of the reflexions (*i.e.* the weakest) in each set. The extinction coefficient *g* (*cf.* Zachariasen, 1945, and also the deductions given below) could be determined for each set from the above mentioned strong reflexions using F_{calc} values computed from positional and vibrational parameters obtained in the refinement. The following values were obtained: $g_a = (94 \pm 4) \times 10^2$, $g_b = (165 \pm 6) \times 10^2$. There is thus a highly significant difference between the extinction coefficients for the two data sets. This difference may be explained in the following way.

The observable powers in single and triple diffraction

Zachariasen (1965) has given formulae for the observable incident and diffracted powers in different cases for crystals of mosaic type with moderate or small extinction. The formulae of special interest in this investigation are those given by Zachariasen under the headings 'single diffraction' and 'triple diffraction, case *B*'. These formulae had to be modified, however, since they are valid only for special experimental conditions which were not fulfilled in this work. It was then realized that the way of dealing with these problems used by Moon & Shull (1964), in a paper about the effects of simultaneous reflexions on single-crystal neutron-diffraction intensities, was very useful also for the present investigation as were some of their results.

In the present investigation, the reflexions measured by rotation about [100] are obtained under conditions of single diffraction (not taking account of multiple diffraction by chance) while the upper layer reflexions measured by rotation about [010] are obtained under conditions of triple diffraction. The latter case corresponds to Zachariasen's 'triple diffraction, case *B*'. For the two cases the following expressions were derived for the observable power of the primary reflexion (generally but erroneously called the integrated intensity, *cf.* Zachariasen, 1945, p. 104) from a crystal of arbitrary shape and completely bathed in the primary beam.

$$\bar{P}_{a,1} \simeq I_0 v A_a(\mu_0)\,\{Q_{01}K_{a,01}^{-1} - gQ_{01}^2 K_{a,01}^{-1}\bar{T}_a\} \tag{1a}$$

$$\begin{aligned}\bar{P}_{b,1} \simeq I_0 v A_b(\mu_0)\{&Q_{01}K_{b,01}^{-1} + g[Q_{02}Q_{21}(2K_{b,02}^2\\ &+2K_{b,21}^2)^{-1/2} + Q_{03}Q_{31}(2K_{b,03}^2 + 2K_{b,31}^2)^{-1/2}\\ &-Q_{01}^2K_{b,01}^{-1} - Q_{01}Q_{02}(2K_{b,01}^2 + 2K_{b,02}^2)^{-1/2}\end{aligned}$$

$$-Q_{01}Q_{13}(2K^2_{b\,01}+2K^2_{b,13})^{-1/2}-Q_{01}Q_{03}$$
$$(2K^2_{b,01}+2K^2_{b,03})^{-1/2}-Q_{01}Q_{12}$$
$$(2K^2_{b,01}+2K^2_{b,12})^{-1/2}]\bar{T}_b\}\,, \tag{1b}$$

where

$$Q_{ij}=\left[\left(\frac{e^2}{mc^2V}\right)^2\frac{|F|^2\lambda^3}{\sin 2\theta}\right]_{ij},$$

$$K_{ij}=(L\sin 2\theta)^{-1}_{ij}$$

and

$$\bar{T}=A\left(\frac{\mathrm{d}(A^{-1})}{\mathrm{d}\mu}\right)_{\mu=\mu_0}. \tag{2}$$

L is the Lorentz factor, A the transmission factor and μ_0 the linear absorption coefficient (*cf.* also the paper by Zachariasen, 1965). It may easily be shown that $0\le K_{ij}\le 1$.

The double indexing, introduced by Moon & Shull (1964), means that the indexed entity is defined for the process where beam i is diffracted into the direction of beam j.

It is advantageous to change some of the notation to that used by Zachariasen (1965). Employing the following relations which are evident: $Q_{01}=Q_1$, $Q_{02}=Q_{31}=Q_{13}=Q_2$ and $Q_{03}=Q_{21}=Q_{12}=Q_3$, one obtains, after inclusion of polarization effects (Zachariasen, 1965):

$$\bar{P}_{a,1}\simeq I_0vA_a(\mu_0)\{Q_1p_{a,1}K^{-1}_{a,01}-gQ_1^2p_{a,11}(0)K^{-1}_{a,01}\bar{T}_a\}\,, \tag{3a}$$

$$\bar{P}_{b,1}\simeq I_0vA_b(\mu_0)\{Q_1p_{b,1}K^{-1}_{b,01}+g[Q_2Q_3p_{b,23}(1)\sqrt{\tfrac{1}{2}}$$
$$([K^2_{b,02}+K^2_{b,21}]^{-1/2}+[K^2_{b,03}+K^2_{b,31}]^{-1/2})$$
$$-Q_1^2p_{b,11}(0)K^{-1}_{b,01}-Q_1Q_2p_{b,12}(3)\sqrt{\tfrac{1}{2}}([K^2_{b,01}$$
$$+K^2_{b,02}]^{-1/2}+[K^2_{b,01}+K^2_{b,13}]^{-1/2})-Q_1Q_3p_{b,13}(2)\sqrt{\tfrac{1}{2}}$$
$$([K^2_{b,01}+K^2_{b,03}]^{-1/2}+[K^2_{b,01}+K^2_{b,12}]^{-1/2})]\bar{T}_b\}\,. \tag{3b}$$

The entity $p_{ij}(k)$ is the resulting polarization factor for a beam reflected twice, by H_i and H_j into the direction of the singly diffracted beam from H_k.

Discussion of equations

Equation (3*b*) is valid for the upper level reflexions in the equi-inclination experiment with the rotation axis parallel to [010]. Q_1 is the integrated reflectivity per unit volume of a small crystallite for the reflexion *HKL*. Let Q_2 refer to 0*K*0, then Q_3 refers to *H*0*L*. Then, obviously $K_{b,02}=0$.

One observes that, if every K_{ij} were unity, the expressions given above are identical with those given by Zachariasen (1965) provided that Zachariasen defines his entity L_j, the Lorentz factor, as $(\sin 2\theta)^{-1}_j$. With any other definition the expressions never agree. However, K_{ij} is unity only when the crystal is rotated about an axis normal to the ith and the jth beams which is normally not the case in this experiment. The Zachariasen equations are of course more convenient for qualitative discussions than the present ones. However, there is at least one case of practical importance where the quantitative use of the former leads to an erroneous result, *viz.* in the extinction correction of intensities registered with an equi-inclination instrument.

Extinction correction influenced by multiple diffraction

A first order approximation formula for extinction correction valid for any diffraction geometry provided only that the conditions for single diffraction are fulfilled, can be derived from equation (3*a*) *via* the relation

$$|F_{\text{obs}}|^2=(\text{Lp}A)^{-1}\bar{P} \tag{4}$$

as

$$|F_{\text{obs}}|^2\simeq 2c'I_0v\left\{|F_{\text{cor}}|^2-2c'g|F_{\text{cor}}|^4\,\frac{p_{11}(0)}{p_1}\,\frac{1}{\sin 2\theta}\,\bar{T}\right\}. \tag{5}$$

This equation may be solved for $|F_{\text{cor}}|$:

$$|F_{\text{cor}}|\simeq|F_{\text{obs}}|\left\{1+gc'\,\frac{p_{11}(0)}{p_1}\,\frac{1}{\sin 2\theta}\,\bar{T}|F_{\text{obs}}|^2\right\}. \tag{6}$$

For equi-inclination geometry

$$\frac{p_{11}(0)}{p_1}=\frac{a+b\cos^4 2\theta}{a+b\cos^2 2\theta}$$

with

$$a=\tan^2\theta-\tan^2\nu+\cos^2 2\theta_0\tan^2\nu$$

$$b=\tan^2\nu+\cos^2 2\theta_0(\tan^2\theta-\tan^2\nu)\,.$$

θ_0 is the Bragg angle for the monochromator, ν the equi-inclination angle and

$$c'=\frac{\lambda^3}{2}\left(\frac{e^2}{mc^2V}\right)^2$$

(*cf.* Gomes de Mesquita, 1967).

If the extinction coefficient g is determined from a number of appropriately chosen strong reflexions according to equation (6), in which $|F_{\text{calc}}|$ is substituted for $|F_{\text{cor}}|$, (*cf.* Åsbrink & Werner, 1966), it should be expected that the g value calculated from the b set is larger than the one calculated from the a set. This statement is based on the fact that the major difference between the values of $\bar{P}_a$ and $\bar{P}_b$, and thus also between the corresponding F_{obs} values, lies in the multiple diffraction terms containing the factors Q_iQ_j, $i\neq j$, in the formula (3*b*). In the present case, $\bar{P}_b$ should in general be less than $\bar{P}_a$ since terms containing the large factor Q_1 have negative signs.

As mentioned above, the following values were obtained for g_a and g_b:

$$g_a=(94\pm 4)\times 10^2$$
$$g_b=(165\pm 6)\times 10^2\,.$$

While g_a thus should be a pure extinction coefficient, multiple diffraction by chance being of minor importance, g_b takes account of multiple diffraction effects as well.

The so-called extinction correction applied to the reflexions in the *b* set is thus not a mere extinction correction but also a correction for repeated reflexion which, however, is likely to be correct only for the strong reflexions, *i.e.* the reflexions which have most probably suffered a net loss of power in the triple diffraction process. The majority of medium and weak reflexions on the other hand, which often increase their power by that process, tend to become overcorrected. However, the magnitude of the corrections decreases rapidly with the magnitude of F_{obs} and will be insignificant for the medium and weak reflexions. This is strikingly demonstrated by the circumstance that, for the reflexions in the *b* set with $F_{\text{obs}} \lesssim 14$ (70% of all reflexions; $F_{\max} = 70$; see above) the *maximum* relative correction, $(|F_{\text{cor}}| - |F_{\text{obs}}|)/|F_{\text{obs}}|$, was only 1·8%. In general, for such reflexions the correction is considerably less than the statistical error of F_{obs}.

Another question is how the triple diffraction processes directly influence the intensities of these non-strong reflexions of the *b* set. Consider again equation (3*b*), now letting the index 1 refer to a medium or weak reflexion. One observes that the second term within the brackets, $g[---]\bar{T}_b$, can only be significant relative to the first term, $Q_1 p_{b,1} K_{b,01}^{-1}$, if the two other reflexions in the triple diffraction process are both rather strong. (*N.B.* $\bar{T}_b g \simeq 0{\cdot}004 \,.\, 10^4 = 40$ and $Q_1 \simeq 10^{-3} - 10^{-4}$ for a medium or weak reflexion.) In the diffraction geometry employed, one of these is a 0*k*0 reflexion, the other is an *h*0*l* reflexion. Since the symmetry of VO_2 is $P2_1/c$, 0*k*0 reflexions with $k \neq 2n$ and *h*0*l* reflexions with $l \neq 2n$ are forbidden. Therefore, only *hkl* reflexions with *k* and *l* even may obtain considerable positive contributions from systematic triple diffraction processes.

Effect on refined structural parameters

The possible effect of the triple diffraction processes on the finally obtained structural parameters and their estimated standard deviations was investigated in the following way. Least-squares structure refinements were performed using the two sets of data, equivalent after being limited to the 799 reflexions present in both materials. Both sets had been corrected for extinction according to equation (6). The results, which are presented in Table 1, show that all the positional parameters agree between the two sets within a maximum difference of less than 2 e.s.d.'s. The vibrational parameters similarly agree within a maximum difference of 3·5 e.s.d.'s. Thus, the two results scarcely differ significantly from each other. The magnitudes of the e.s.d.'s do not differ appreciably either. Note especially that the e.s.d.'s of the *b* set are not larger than those of the *a* set though they might have been expected to be so from the possible presence of multiple diffraction errors in the former set.

Table 1. *Comparison between the results from the refinement of the crystal structure of monoclinic* VO_2 *using the a set and the b set*

Each set contained 799 crystallographically independent reflexions. The unit-cell dimensions are $a = 5{\cdot}75_2$, $b = 4{\cdot}52_8$, $c = 5{\cdot}38_3$ Å and $\beta = 122{\cdot}6_5°$.

	a set	*b* set
x_{V}	0·239450 ± 46	0·239421 ± 43
y_{V}	0·978892 ± 49	0·978962 ± 43
z_{V}	0·026283 ± 57	0·026369 ± 53
B_{V}	0·293 ± 5	0·308 ± 5
$x_{\text{O(1)}}$	0·10605 ± 21	0·10633 ± 21
$y_{\text{O(1)}}$	0·21162 ± 24	0·21204 ± 20
$z_{\text{O(1)}}$	0·20869 ± 27	0·20872 ± 26
$B_{\text{O(1)}}$	0·351 ± 12	0·391 ± 11
$x_{\text{O(2)}}$	0·40024 ± 22	0·40061 ± 21
$y_{\text{O(2)}}$	0·70268 ± 24	0·70264 ± 20
$z_{\text{O(2)}}$	0·29862 ± 27	0·29869 ± 26
$B_{\text{O(2)}}$	0·381 ± 12	0·397 ± 12
Scale factor	0·4298 ± 24	0·4248 ± 28
R	0·032	0·030

This seems somewhat unexpected even if one reason for it may be the non-existence of odd 0*k*0 reflexions and the relative weakness of the rest of them. A further explanation was eventually tried along the following lines of reasoning: if the observable power (integrated intensity) of a single reflexion is proportional to the volume *v* of the diffracting crystal, should not then the observable power of a double reflexion be proportional to v^2/S, where *S* is an average crystal cross section seen by the primarily reflected beam? *i.e.* The 'intensity' of a double reflexion should be proportional to $v^{4/3}$. Thus, the double reflexion contributions should be relatively less important for a small crystal than for a bigger crystal of the same compound. The VO_2 crystal used was indeed very small, as mentioned at the beginning of the paper.

Investigation of the dependency of crystal size

Experiment

The hypothesis presented above was tested on crystals of the cubic spinels $FeCr_2O_4$ and $CoCr_2O_4$ with the unit cell edge $a = 8{\cdot}379$ and 8·331 Å respectively. These compounds were chosen partly because of the ease with which similar, regularly shaped crystals of different sizes could be grown. Furthermore, the axis reflexions *h*00 with $h = 4n + 2$, $n = 0, 1, 2, \ldots$ are absent in the spinel diffraction pattern. This means that by rotating the crystal an angle ω around [100], with the inclination angle μ of the PAILRED-diffractometer set for the $h = 4n + 2$ level and with the detector positioned at $\Upsilon = 0°$ and $\nu = \theta_{h00}$ to register the *h*00 reflexion, one could observe pure double reflexions and measure their intensities. Pairs of crystals different in size but similar in shape and selected from the same batch were studied for each of the two spinel compounds. Azimuthal scans, from $\omega = 0°$ to $\omega = 360°$, were performed for the 200, 600 and 10,0,0 reflexions using Mo $K\alpha$ radiation (LiF monochromatized). The intensities of the strongest double reflexions observed were carefully measured by the conventional ω-scan method. (It should be mentioned that the intensity of the strongest double reflexion observed was of the order of one per cent of the strongest observable single reflexion intensity from the same crystal.) Furthermore, for each of the crystals, all $0kl$ reflexions within a semicircle of the reciprocal lattice out to $2\theta \simeq 100°$ were measured. From these reflexions which should be free from any systematic double reflexion contributions, weak, but not very weak ones, were selected, as they should be only slightly affected by extinction and not impaired by too large statistical errors. The average ratios, $(\bar{P}_{1,A}/\bar{P}_{1,B})_{\rm sgl}$, between the observable powers of corresponding single reflexions for the pairs of crystals of the two spinels are given in Table 2. In the same Table are listed the mean values of the corresponding ratios of the observable powers of chosen double reflexions denoted by $(\bar{P}_{1,A}/\bar{P}_{1,B})_{\rm dbl}$. The results from both investigations indicate that the intensity of a double reflexion increases faster with the size of the crystal than that of a single reflexion. This result evidently supports the hypothesis presented above. Further studies on this matter are in progress.

Table 2. *Mean values of the ratios between the observable powers of a number of chosen single reflexions and double reflexions respectively registered partly from the bigger crystal A and partly from the smaller crystal B of the spinels* $FeCr_2O_4$ *and* $CoCr_2O_4$

	$\left(\frac{\bar{P}_{1,A}}{\bar{P}_{1,B}}\right)_{\rm sgl}$	Number of reflexions	$\left(\frac{\bar{P}_{1,A}}{\bar{P}_{1,B}}\right)_{\rm dbl}$	Number of reflexions
$FeCr_2O_4$	1·98 ± 2	64	2·22 ± 2	22
$CoCr_2O_4$	3·23 ± 3	62	4·81 ± 13	12

Theory

Could this result also have been foreseen from the formulae presented at the beginning of the paper? Let us consider the following two relations holding for a reflexion free from extinction and double reflexion contributions, equation (7), and for a pure double reflexion, *i.e.* one with $Q_1=0$, equation (8):

$$\bar{P}_1 \simeq I_0 v A_1(\mu_0) Q_1 p_1 K_{01}^{-1} \qquad (7)$$

$$\bar{P}_{1'} \simeq I_0 v A_{1'}(\mu_0) g \bar{T} Q_2 Q_3 p_{23}(1) \sqrt{\tfrac{1}{2}} \left(K_{21}^{-1} + [K_{03}^2 + K_{31}^2]^{-1/2}\right) . \qquad (8)$$

The observable power of a single 'extinction-free' reflexion should thus be proportional to the crystal volume v while the corresponding entity of a pure double reflexion should be proportional to $v\bar{T}$, $\bar{T}$ being the effective path length. The hypothesis discussed above was that $\bar{P}_{1'}$ is proportional to $v^{4/3}$. It thus remained to investigate the relation between $\bar{T}$ and v. This was done quite generally by calculating $\bar{T}$ for a number of reflexions of each of several model crystals with varying values for $\mu_0 l$, l being the linear dimension of the crystal. For the sake of convenience the model crystals were given cubic shape. The result of these calculations is presented in Table 3. It is found that for not too large values of the product mentioned, *viz.* for $\mu_0 l \lesssim 1$, $\bar{T}$ may be approximated as $v^{1/3}$. For moderately absorbing crystals of not too extreme shape one can thus set $\bar{P}_{1'} \propto v^{4/3}$. When the absorption is higher, due to larger μ_0 or crystal size, $\bar{T}$ increases slower than $v^{1/3}$ and the exponent used above decreases from 4/3.

Table 3. *Results of calculations of the effective path length, $\bar{T}$, for some chosen reflexions ($\lambda = 0·71069$ Å) from a number of model crystals of cubic shape with different values of the product $\mu_0 l$, l being the cube edge*

For crystal A, $l = 0·005$ cm and for crystal B, $l = 0·015$ cm. The cubic unit cell edge is assumed equal to 8·38 Å.

μ_0(cm^{-1})	h	k	l	$\bar{T}_A$ ($\times 10^3$ cm) (l_A = 0·005 cm)	$\bar{T}_B$ ($\times 10^3$ cm) (l_B = 0·015 cm)	$\bar{T}_B/\bar{T}_A$
10	2	0	0	4·9	14·6	3·0
	2	2	0	4·7	14·0	3·0
	4	0	0	4·8	14·3	3·0
	4	4	0	4·7	13·9	3·0
	6	0	0	4·7	14·1	3·0
	8	0	0	4·7	13·9	3·0
	6	6	0	4·6	13·9	3·0
	10	0	0	4·6	13·9	3·0
	8	8	0	4·7	14·0	3·0
	10	10	0	4·8	14·3	3·0
100	2	0	0	4·9	14·4	2·9
	2	2	0	4·6	12·8	2·8
	4	0	0	4·7	13·8	2·9
	4	4	0	4·5	12·7	2·8
	6	0	0	4·6	13·4	2·9
	8	0	0	4·6	13·0	2·8
	6	6	0	4·5	12·7	2·8
	10	0	0	4·5	12·7	2·8
	8	8	0	4·6	12·8	2·8
	10	10	0	4·6	12·9	2·8
300	2	0	0	4·8	13·0	2·7
	2	2	0	4·3	10·1	2·3
	4	0	0	4·6	11·5	2·5
	4	4	0	4·2	10·1	2·4
	6	0	0	4·5	10·6	2·4
	8	0	0	4·3	9·9	2·3
	6	6	0	4·2	10·1	2·4
	10	0	0	4·2	9·4	2·2
	8	8	0	4·3	10·1	2·3
	10	10	0	4·3	10·1	2·3
500	2	0	0	4·7	10·0	2·1
	2	2	0	3·9	8·1	2·1
	4	0	0	4·4	8·7	2·0
	4	4	0	3·9	8·1	2·1
	6	0	0	4·2	7·9	1·9
	8	0	0	4·0	7·3	1·7
	6	6	0	3·9	8·1	2·1
	10	0	0	3·9	6·9	1·8
	8	8	0	3·9	8·1	2·1
	10	10	0	4·0	8·1	2·0

Conclusions

Both experiment and theory show that, with decreasing crystal size, the intensity of a double reflexion diminishes faster than that of a single reflexion. Referring to equation (3*b*), this result may also be formulated in the following way. The combined relative errors due to extinction and simultaneous reflexion decrease when the size of the crystal decreases. Even though it is often possible to eliminate systematic multiple diffraction effects by a rational choice of rotation axis or, in an equi-inclination experiment, by a slight missetting of the inclination angle μ (*cf.* Jeffery & Whitaker, 1965; Åsbrink, Brandt & Kierkegaard, 1969) one is still left with multiple diffraction by chance. Rather lengthy computations are required to detect and avoid this phenomenon. The procedure is eminently practicable with a tape- or computer-steered diffractometer. However, one can evidently always reduce the effects of both systematic and unsystematic multiple diffraction, as well as of extinction, by the use of as small a crystal as possible. There are doubtless numerous other good reasons for using small crystals in X-ray single-crystal work to get intensities as free from *systematic errors* as possible. Only one more will be mentioned here: the difficulty in making exact absorption corrections partly due to the uncertainty in the X-ray attenuation coefficients published (Deslattes, 1969) and partly to unavoidable errors in the geometrical description of the crystal.

Finally, one further conclusion can be drawn from relations (3*a*) and (3*b*). A higher 'average atomic number' of the atoms constituting a crystal will mean a relatively higher effect of both extinction and multiple diffraction, since these phenomena give rise to second-degree Q terms.

The data reduction, including Lorentz and polarization corrections, of the PAILRED data was performed with a program obtained from the Philips Company, Eindhoven. The absorption and extinction calculations were performed with the program *DATAP*2 originally written by Coppens, Leiserowitz & Rabinovich (1965), modified and adapted to CD 3600 by Olofsson & Elfström, University of Uppsala and modified for extinction calculations by Brandt & Åsbrink, University of Stockholm. The $\bar{T}$ values presented in Table 3 were obtained with the program *DATAPH* which is the above mentioned program by Coppens, Leiserowitz & Rabinovich modified by Hamilton, Brookhaven National Laboratory. It was adapted to IBM 360/75 by Carlbom, University of Stockholm. The least-squares refinements were performed with the program *LALS* originally written by Gantzel, Sparks & Trueblood (1966), modified by Zalkin, University of California, extended and adapted to CD 3600 by Lundgren, Liminga, University of Uppsala & Brändén, Agricultural College of Sweden, Uppsala and further extended and adapted to IBM 360/75 by Brandt & Nord, University of Stockholm.

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APPENDIX

The *g* value in the VO_2 investigation

The quantity g is defined as (Zachariasen, 1945, p. 168)

$$g=\int W^2 \mathrm{d}(\theta-\theta_B)=\frac{1}{2\sqrt{\pi}\eta}$$

where $W(\theta-\theta_B)$ is the Gaussian distribution function which describes the orientation of the mosaic blocks around the Bragg angle θ_B.η is the standard deviation of the distribution.

A condition which must be fulfilled in using the first order approximation formula (3*a*) is that $gQ_1\bar{T}\ll 1$. However, with the large g value determined from the a set, $g\simeq 10^4$, $gQ_1\bar{T}$ will be close to 1 for the strongest reflexions. For these, one might not expect the approximation to be a good one. It does work acceptably, notwithstanding, as observed and reported, for two similar cases, by Zachariasen (1963) and Zachariasen & Plettinger (1965) respectively.

Another problem in this connexion is brought to light in the paper by Zachariasen (1967) where a new formula for the integrated intensity of X-ray diffraction from real crystals was derived. There Zachariasen discusses real crystals of two types with negligible primary extinction. They are characterized in the following way: 'In type I crystals the distribution function W is much wider than the diffraction pattern from a single domain, whereas the reverse situation is true in type II crystals.' The theoretical relations presented in this paper are first order approximation formulae for type I crystals. By everywhere substituting $r\lambda^{-1}$ for g, r being the mean radius of the perfect crystal domains, formulae valid for type II crystals would be obtained. The question, then, is whether the VO_2 crystal used is type I or type II and whether the quantity called g is g or $r\lambda^{-1}$. With the assumption that primary extinction is negligible, Zachariasen found that g for type I crystals is of the order of 10^{+3} or smaller. The g value determined for the VO_2 crystal was, as mentioned, about 10^{+4}, which fact strongly points to the crystal being of type II. This result does not, however, in any way affect the conclusions reached in this paper.

From $r\lambda^{-1}=94\,.\,10^2$ the value of r could be determined as $r=0{\cdot}67\,.\,10^{-4}$ cm. It remains to be proved that the basic condition of negligible primary extinction is fulfilled. In his paper, Zachariasen (1967) shows that, if $r\lambda^{-1}Q\bar{t}<0{\cdot}02$, the primary extinction becomes negligible. The only *a* set reflexions not satisfying this inequality are 011 and 022, for which the left hand side is calculated equal to 0·055 and 0·023 respectively using $\bar{t}=\frac{3}{2}r=1{\cdot}0\,.\,10^{-4}$ cm. Since it can therefore be concluded that the large majority of reflexions from which *g* was determined satisfy the above mentioned inequality very well, it may be stated that the primary extinction is really negligible.

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Quelques Cas d' Orthogonalité d' Ondes se Propageant dans des Milieux Non-Absorbants

PAR A. LEVELUT

Laboratoire d'Ultrasons, Faculté des Sciences, Tour* 13, 9 *quai Saint Bernard, Paris* 5*e, France*

ET J. BILLARD

Laboratoire de Physique des Milieux Cristallins† *attaché à la Chaire de Physique Théorique du Collège de France, place Marcelin Berthelot, Paris* 5*e, France, et Département de Physique, Faculté des Sciences de Lille, BP* 36, 59 *Lille, France*

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For transparent media (homogeneous and twisted), orthogonality of the eigen-waves (elastic and electromagnetic) is examined. Particular attention is given to media with characteristic constants independent of frequency and to waves with the same wave-vector. Occurences of orthogonality are presented.

1. Introduction

Dans les milieux homogènes, sauf cas exceptionnels (Khapalyuk, 1963), il existe des vibrations privilégiées qui se propagent en restant identiques à elles-mêmes. Et le problème de la propagation d'une onde plane homogène est résolu lorsque l'on connait les vibrations privilégiées et leurs vitesses de propagation dans la direction considérée: il suffit de décomposer la vibration de l'onde plane sur les vibrations privilégiées. Ces dernières sont au nombre de deux pour les ondes électromagnétiques et de trois pour les ondes élastiques; dans le cas le moins restrictif (milieu anisotrope et actif), elles sont elliptiques.

Pour les ondes électromagnétiques, Airy (1831) posa l'hypothèse suivante, relative aux composantes transversales du champ électrique des vibrations privilégiées de *même fréquence:*

- leurs axes principaux de même nom sont perpendiculaires,
- leurs sens de parcours sont opposés,
- leurs ellipticités sont égales.

De telles vibrations sont dites orthogonales.

Cette hypothèse est encore généralement admise. Elle n'est pas remise en cause par les mesures insuffisamment fines effectuées jusqu'à ce jour sur les cristaux. Toutefois, quelques auteurs (de Mallemann, 1924; Bil-

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* Equipe associée au CNRS.

† Laboratoire associé au CNRS.