Table 8. *Sulphur–oxygen bond lengths for M*14 *and M*21

Bond lengths are in Å. Errors × 10^3 are given in brackets.

*M*14					
S(1)$^+$–O(1)$^+$	══	S(1)$^-$–O(1)$^-$	1·432 (1)	S(2)–O(5)	1·443 (1)
S(1)$^+$–O(2)$^+$		S(1)$^-$–O(2)$^-$		S(2)–O(6)	
S(1)$^+$–O(3)$^+$		S(1)$^-$–O(3)$^-$		S(2)–O(8)	
S(1)$^+$–O(4)$^+$	1·534 (8)	S(1)$^-$–O(4)$^-$	1·585 (8)	S(2)–O(7)	1·560 (2)
*M*21					
S(1)$^+$–O(1)$^+$	1·42 (11)	S(1)$^-$–O(1)$^-$	1·44 (10)	S(2)–O(5)	1·435 (1)
S(1)$^+$–O(2)$^+$	1·38 (8)	S(1)$^-$–O(2)$^-$	1·48 (8)	S(2)–O(6)	1·440 (1)
S(1)$^+$–O(3)$^+$	1·46 (8)	S(1)$^-$–O(3)$^-$	1·42 (9)	S(2)–O(8)	1·455 (2)
S(1)$^+$–O(4)$^+$	1·56 (11)	S(1)$^-$–O(4)$^-$	1·57 (11)	S(2)–O(7)	1·564 (2)

positional parameters – which accept the probability that H(9) is disordered. More complete and accurate information on this important feature of the structure should emerge from a full three-dimensional neutron structural study of ND_4DSO_4 currently being pursued by Mr K. D. Rouse at A.E.R.E., Harwell.

6. Conclusion

The techniques, value and application of a moderately straightforward extension of usual least-squares procedures have been illustrated. Some remaining difficulties have been outlined and a few possible improvements suggested. These techniques applied to AHS have led most importantly to the conclusion that in the phase above the ferroelectric transition the *S*1 sulphate group is disordered (equally) between two sites. The results of a recent study of the structure in the ferroelectric phase indicate that this feature plays an important role in the transition to the ferroelectric phase (Nelmes, 1972). The nature of the room-temperature disorder – principally its time scale – remains as an interesting problem for investigation by dynamical techniques. Advances in this direction are expected from some light-scattering experiments currently being performed in this Department.

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X-ray Diffraction from Materials Containing Anti-Phase Domains

BY R. W. CHEARY AND N. W. GRIMES

Physics Department, University of Aston, Birmingham, England

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A theory of X-ray diffraction from materials containing anti-phase domains is developed in terms of the characteristic function of the domain thickness distribution and the function J_p which is defined as the mean value of FF^* for cells separated by p domain boundaries. Also, an expression is derived for the domain thickness distribution which may be applied to the analysis of experimental data from any system in which the sizes of adjacent domains are uncorrelated.

Introduction

In certain order–disorder materials, Cu_3Au being the classic example, the transformation from the disordered to the ordered state is associated with the formation of anti-phase domains. When the domains in such a material are small the X-ray diffraction pattern exhibits broadened superlattice lines and lattice lines whose breadths remain sharp and substantially independent of the state of order. The first quantitative theory of this diffraction behaviour was developed by Wilson (1943) on the basis that the mechanism for the formation of the domains is that of growth with occasional mistakes [*i.e.* a domain thickness distribution $f(t)=(1/D)\,.\exp(-t/D)$ where D is the mean domain thickness]. Although this theory accounts for the first-order features of the line broadening it does not account satisfactorily for the domain thickness distribution (Edmunds & Hinde, 1952; Steeple & Edmunds, 1956). Unfortunately, the development of diffraction theories based on other mechanisms of domain formation, such as multiple nucleation and growth till domains meet (Lifschitz, 1937), or increase in local order through atomic rearrangement (Taylor, Hinde & Lipson, 1951), is not a simple matter and thus Wilson's theory remains the only one applicable to three-dimensional growth which may be compared with experiment.

Recently, Roessler & Flinn (1967) have taken an alternative approach to the problem in that they assumed a general domain thickness distribution $f(t)$ as a basis for calculation, as opposed to a model of domain growth. In particular they showed that $f(t)=(9D/16)\,.\,J''(t)/J(0)$, where $J(t)$ is the Fourier transform of a superlattice line profile, provided that a series expansion for $J''(t)$ may be terminated at the second term. This result must be of limited application, however, in view of the very restrictive approximation used in its derivation. It does not hold, for example, for Wilson's model in which all types of adjacent domain are equally probable, for this case leads to $f(t)=\{(9D^{2/3}/16)\,.\,[J''(t)/J(0)]\}^{3/4}$, *i.e.* $J(t)=J(0)\exp(-4t/3D)$.

In the present work, we present a derivation of the intensity distribution across a line profile in terms of a general domain thickness distribution $f(t)$, by a method similar to that of Landau (1937) and Lifschitz (1937), in which the structure amplitude scattered from a crystallite is calculated as the sum of the structure amplitudes scattered by the individual domains. The domain thickness distribution derived from this result retains the property of access from experimental data sought by Roessler & Flinn (1967), but should be applicable to a wider range of circumstances.

Derivation of the intensity distribution

The intensity distribution across an X-ray diffraction line profile is given, within a scale factor by

$$I(s)=2\int_0^\infty [J(t)\cos 2\pi st-K(t)\sin 2\pi st]\mathrm{d}t$$

(Wilson, 1962)

where t is a vector length parallel to the $[hkl]$ direction, $s=2\sin\theta/\lambda-1/d$ and $J(t)-jK(t)$ is the Fourier transform of $I(s)$ which in physical terms is the mean value of FF^* for cells separated by a distance t in the $[hkl]$ direction. As a consequence of the latter definition the derivation of an intensity distribution reduces to a one-dimensional problem in relation to the crystal structure.

Consider therefore, a columnar section of unit cells parallel to the $[hkl]$ direction, from a crystallite containing anti-phase domains. Let the boundaries of the nth domain be y_n and y_{n+1}, and the structure factor of the unit cells in that domain be F_n (see Fig. 1).

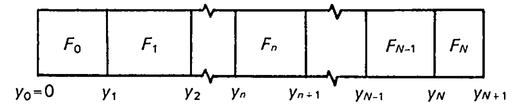

Fig. 1. Columnar section of crystal with antiphase domains

By analogy with the general equation for $I(s)$, the amplitude $A(s)$ contributed by the (hkl) planes may be expressed as

$$A(s)=\int_0^\infty F(t)\exp(2\pi jst)\mathrm{d}t \tag{1}$$

where $F(t)$ is the structure factor of the cell at distance t from the origin which in this instance is chosen to correspond to $t=y_0=0$. For the domain structure defined in Fig. 1,

$$\begin{aligned}A(s)&=\sum_{n=0}^{N}F_n\int_{y_n}^{y_{n+1}}\exp(2\pi jst)\mathrm{d}t\\&=\sum_{n=0}^{N}\frac{F_n}{2\pi js}[\exp(2\pi jsy_{n+1})-\exp(2\pi jsy_n)]\,.\end{aligned}\tag{2}$$

The intensity function is therefore given by

$$\begin{aligned}I(s)&=A(s)A^*(s)\\&=\sum_{n=0}^{N}\sum_{m=0}^{N}\frac{F_nF_m^*}{(2\pi s)^2}[\exp(2\pi jsy_{n+1})-\exp(2\pi jsy_n)]\\&\quad\times[\exp(-2\pi jsy_{m+1})-\exp(-2\pi jsy_m)]\\&=\sum_{n=0}^{N}\sum_{m=0}^{N}\frac{F_nF_m^*}{(2\pi s)^2}\{\exp[-2\pi js(y_{m+1}-y_{n+1})]\\&\quad-\exp[-2\pi js(y_m-y_{n+1})]\\&\quad-\exp[-2\pi js(y_{m+1}-y_n)]+\exp[-2\pi js(y_m-y_n)]\}\,.\end{aligned}\tag{3}$$

By making the substitution $p=m-n$ and $q=n$, $I(s)$ may be expressed by the single summation

$$\begin{aligned}I(s)=\sum_{p=-n}^{N}&\frac{(N+1-|p|)}{(2\pi s)^2}\\&\times(2J_p-J_{p+1}-J_{p-1})\,.\,\langle\exp(-2\pi jsx_p)\rangle\end{aligned}\tag{4}$$

where J_p is the mean value of FF^* for cells separated by p domain boundaries,

i.e.

$$J_p=\frac{\sum_{q=0}^{N-p}(F_qF_{q+p}^*)}{(N+1-|p|)}\quad\text{for } p\geq 0\,.$$

x_p is the column length of p adjoining domains and $\langle \exp(-2\pi jsx_p)\rangle$ is the mean value of $\exp(-2\pi jsx_p)$, *i.e.*

$$\langle \exp(-2\pi jsx_p)\rangle = \int_0^\infty f_p(x) \exp(-2\pi jsx_p)\mathrm{d}x_p \quad (5)$$

where $f_p(x)$ is the thickness distribution of p adjoining domains.

If the number of domains N in a column is large, equation (4) may be written as

$$I(s) = N \sum_{p=-N}^{N} \frac{(2J_p - J_{p+1} - J_{p-1})}{(2\pi s)^2} \langle \exp(-2\pi jsx_p)\rangle \quad (6)$$

since the terms of the form J_p tend to decay far more rapidly to zero with respect to p, than $(N+1-|p|)$. In principle this expression should be summed over all columnar sections of the crystallite, but if it is assumed that particle size effects are negligible or if the crystallite is of uniform thickness in the $[hkl]$ direction then N will be the same for each columnar section. This assumption is not expected to restrict the general usefulness of our result. For example, it may be shown that the application of equation (6) leads directly to an expression for truncated variance equivalent to that obtained by Wilson (1963) (see Appendix).

If the thickness of the ith domain is t_i then x_p may be expressed as the sum, $x_p = \sum_{i=1}^{p} t_i$ and $x_0 = 0$. Thus for the situation in which the sizes of the domains are uncorrelated

$$\langle \exp(-2\pi jsx_p)\rangle = \langle \exp(-2\pi jst_i)\rangle^p = m^p \quad (7)$$

where m is the characteristic function of the domain thickness distribution $f(t)$, *i.e.*

$$m = \int_0^\infty f(t) \exp(-2\pi jst)\mathrm{d}t\,. \quad (8)$$

In the following text, the assumption that the sizes of domains are uncorrelated is retained. This would not appear to be a serious approximation as a necessary condition for correlated domain sizes is the interaction of next-but-one boundaries. Wilson's model and the model due to Lifschitz (1937) should satisfy the approximation.

Calculation of J_p

For an anti-phase domain structure based on the transition from a face-centred to a primitive lattice there are four possible structural arrangements. Two of these lead to a structure factor $+F$ for a superlattice line whilst the other two have the structure factor $-F$ (see Wilson, 1943). When each type of adjacent domain structure is equally probable the difference equation defining the probability Q_p of two domains separated by p boundaries being similar is given by

$$Q_{p+1} = \tfrac{1}{3}\,.\,(1-Q_p)$$

which from the condition $Q_0 = 1$ gives

$$Q_p = \tfrac{1}{4}[1 + 3(-\tfrac{1}{3})^p]\,. \quad (9)$$

The function J_p is therefore given by

$$\begin{aligned} J_p = {} & 2\,.\,\tfrac{1}{4}(+F)\,[Q_pF^* + \tfrac{1}{3}\,.\,(1-Q_p)\,(-F^*)] \\ & +2\,.\,\tfrac{1}{4}(-F)\,[Q_p(-F^*) + \tfrac{1}{3}(1-Q_p)F^*] \\ & = FF^*(-\tfrac{1}{3})^p\,. \end{aligned} \quad (10)$$

On substituting for J_p, the expression for $I(s)$ now becomes

$$\begin{aligned} I(s) &= \frac{8NFF^*}{3(2\pi s)^2} + \frac{16NFF^*}{3(2\pi s)^2} \sum_{p=1}^{N} (-\tfrac{1}{3})^p\,.\,(m^{*p} + m^p) \\ &= \frac{8NFF^*}{3(2\pi s)^2} + \frac{16NFF^*}{3(2\pi s)^2} \left[\frac{m^*}{3+m^*} + \frac{m}{3+m}\right] \end{aligned} \quad (11)$$

which is an even function of s [*i.e* $K(t) = 0$]. Thus we have an equation for the intensity distribution across a line profile, the form of which may be calculated from the domain thickness distribution. Some modification of this result is necessary however, if all types of adjacent domain are not equally probable as in Cu_3Au alloy, but this only requires that J_p be recalculated.

Evaluation of domain thickness distribution

To obtain an expression for the domain thickness distribution, consider the Fourier transform of $(2\pi s)^2 I(s)$ which is given by

$$\begin{aligned} & \int_{-\infty}^{+\infty} (2\pi s)^2 I(s) \exp(2\pi jst)\mathrm{d}s \\ & = \frac{8NFF^*}{3} \int_{-\infty}^{+\infty} \exp(2\pi jst)\mathrm{d}s + \frac{16NFF^*}{3} \\ & \times \sum_{p=1}^{N} (-\tfrac{1}{3})^p\,.\int_{-\infty}^{+\infty} \exp(2\pi jst)\,(m^{*p} + m^p)\mathrm{d}s \\ & = \frac{8NFF^*}{3}\,\delta(t) + \frac{16NFF^*}{3} \\ & \times \sum_{p=1}^{N} (-\tfrac{1}{3})^p\,.\int_0^\infty f_p(t)[\delta(x+t) + \delta(x-t)]\mathrm{d}x \\ & = \frac{8NFF^*}{3}\,\delta(t) + \frac{16NFF^*}{3} \sum_{p=1}^{N} (-\tfrac{1}{3})^p\,.\,f_p(t) \end{aligned} \quad (12)$$

where the terms of the form $\delta(x+t)$ are Dirac delta functions [for the properties of these functions see Irving & Mullineux (1966)].

If the formulation $I(s) = 2\int_0^\infty J(t) \cos 2\pi st\ \mathrm{d}t$ is substituted into the left hand side of equation (12) and NFF^* is replaced by $J(0)/D$, where D is the mean domain thickness, it is possible to show by comparing each side of the resultant equation that

$$J'(0) = -4J(0)/3D$$

and

$$J''(t) = -\frac{16J(0)}{3D} \sum_{p=1}^{N} (-\tfrac{1}{3})^p f_p(t) .$$

Let

$$Z(s) = \int_0^\infty \frac{J''(t)}{J(0)} \exp(-2\pi jst)\mathrm{d}t = H(s) - jG(s) \quad (13)$$

so that on substituting for $J''(t)/J(0)$,

$$Z(s) = -\frac{16}{3D} \sum_{p=1}^{N} \left(-\frac{m}{3}\right)^p = \frac{16m}{3D(3+m)}$$

or,

$$m = \frac{3Z(s)}{\left[\frac{16}{3D} - Z(s)\right]} . \quad (14)$$

The expression for the domain thickness distribution is therefore given by performing a cosine transform on $m + m^*$,

i.e.

$$f(t) = \int_{-\infty}^{\infty} (m + m^*) \cos 2\pi st \,\mathrm{d}s$$

$$= \int_{-\infty}^{\infty} \left[\frac{3Z(s)}{(\gamma - Z(s)} + \frac{3Z^*(s)}{(\gamma - Z^*(s)}\right] \cos 2\pi st \,\mathrm{d}s \quad (15)$$

where $\gamma = 16/3D$. Utilizing the symmetry of this integrand about $s = 0$ and substituting $Z(s) = H(s) - jG(s)$,

$$f(t) = 12 \int_0^\infty \frac{\{\gamma H(s) - [G^2(s) + H^2(s)]\}}{\{G^2(s) + [H(s) - \gamma]^2\}} . \cos 2\pi st \,\mathrm{d}s . \quad (16)$$

We observe finally that this result is consistent with Wilson's model, for in this case
$J(t) = J(0) \exp(-4t/3D)$, so that

$$Z(s) = \frac{16\left(\frac{4}{3D} - 2\pi js\right)}{9D^2[(\frac{4}{3})^2 + (2\pi s)^2]} \quad (17)$$

and consequently

$$(m + m^*) = \frac{2}{[1 + (2\pi sD)^2]} .$$

The domain thickness distribution is therefore

$$f(t) = \mathrm{Re}\left[\int_{-\infty}^{\infty} \frac{2 \exp(2\pi jst)\mathrm{d}s}{[1 + (2\pi sD)^2]}\right] \quad (18)$$

which after integration around an infinite semi-circle in the upper half of the complex plane gives $f(t) = (1/D) . \exp(-t/D)$, as expected.

Summary

Two results have been derived:

(i) the intensity distribution $I(s)$ in terms of the domain-thickness distribution,

(ii) the domain-thickness distribution in terms of parameters which can be obtained from experimental data.

It should be emphasized that unless experimental results are accurate and reliable the application of the latter will serve little purpose. If the operation of one Fourier transform on an intensity profile leads to errors in the $J(t)$ characteristic, which is frequently the case (see for instance Young, Gerdes & Wilson, 1967), further transform operations together with a double differentiation procedure must result in much larger errors in the final domain-thickness distribution. Even reliable crystallite-size distributions have proved difficult to determine, because of systematic errors (see, for instance, Langford, 1968), and they only require the second derivative of the Fourier transform of the intensity profile for their evaluation.

It is a pleasure to acknowledge useful comments made to us by Professor A. J. C Wilson, F.R.S., concerning equation (6). One of us (R.W.C.), is also indebted to the Science Research Council for financial support.

APPENDIX

To derive the expression for variance corresponding to equation (6) we recall that for the range σ_1 to σ_2,

$$W_s = \frac{\int_{-\sigma_1}^{\sigma_2} s^2 I(s)\mathrm{d}s}{\int_{-\infty}^{\infty} I(s)\mathrm{d}s} \quad (19)$$

where, in our nomenclature,

$$\int_{-\infty}^{\infty} I(s)\mathrm{d}s = N\langle x_1\rangle J_0 \quad (20)$$

and

$$\int_{-\sigma_1}^{\sigma_2} s^2 I(s)\mathrm{d}s = N \sum_{p=-N}^{N} (2J_p - J_{p+1} - J_{p-1})$$

$$\times \int_{-\sigma_1}^{\sigma_2} \frac{1}{(2\pi)^2} \langle\exp(-2\pi jx_p s)\rangle \mathrm{d}s . \quad (21)$$

Now when $p = 0$, $\langle\exp(-2\pi jx_p s)\rangle = 1$, therefore since $J_1 = J_{-1}$, the contribution made to the variance before normalizing will be

$$\frac{N}{2\pi^2} . (J_0 - J_1)(\sigma_1 + \sigma_2) . \quad (22)$$

When $p = 1$, $\langle\exp(-2\pi jx_1 s)\rangle = \int_0^\infty f_1(x) \exp(-2\pi jx_1 s)\mathrm{d}x_1$ and the contribution to variance is

$$= -\frac{N}{4\pi^2}(J_0 - 2J_1 + J_2)\int_0^\infty f_1(x)\mathrm{d}x_1$$

$$\times \int_{-\sigma_1}^{\sigma_2} \exp(-2\pi jsx_1)\mathrm{d}s .$$

If σ_1 and σ_2 are sufficiently large the double integral in this expression is approximately

$$= \int_0^\infty f_1(x) . \delta(x_1)\mathrm{d}x_1 = \tfrac{1}{2} . f_1(0) . \quad (23)$$

The contribution from $p=1$ is therefore

$$= -\frac{N}{8\pi^2}(J_0-2J_1+J_2)\,.\,f_1(0) \tag{24}$$

and there will be a corresponding contribution from $p=-1$. Similarly when $|p|>1$ the contribution is

$$\frac{N}{8\pi^2}(2J_p-J_{p+1}-J_{p-1})\,.\,f_p(0)$$

but this is identically zero since by definition $f_p(0)=0$ in this case.

Summing over all p and normalizing we obtain

$$W_s=\frac{(\sigma_1+\sigma_2)}{2\pi^2}\cdot\frac{(J_0-J_1)}{\langle x_1\rangle J_0}-\frac{1}{4\pi^2}\cdot\frac{(J_0-2J_1+J_2)\,.\,f_1(0)}{\langle x_1\rangle J_0} \tag{25}$$

in agreement with Wilson (1963).

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Application de la Notion de Groupe Rigide à la Détermination de Structures Cristallines Simples

Par Daniel André, Roger Fourme et Michel Renaud

Laboratoire de Chimie-Physique, Matière et Rayonnements, de l'Université Paris VI, associé au C.N.R.S., Bâtiment 350, 91-*Orsay, France*

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An algorithm is given which is suitable for solving molecular structures when the shape of the whole molecular skeleton, or at least the main part of it, can be assumed. The molecular parameters, *i.e.* three rotations and three translations in the general case, are randomly generated by a Monte-Carlo method. The packing thus obtained is group-refined using only a few selected strong reflexions, then kept or rejected according to several tests on the weighted reliability index; the best structures are furtherly group-refined using an increasing number of reflexions up to a given limit. The whole program has been arranged to be as fast as possible and fully automatic. Such a method is helpful when the experimental data are poor or restricted to some extent (high-pressure single-crystal data, unstable crystals, ...) or in cases of static or dynamic disorder (plastic crystals). Even when accurate three-dimensional data are available, it may be of value and possibly faster than other methods, if one or several molecular parameters are *a priori* fixed from symmetry considerations or one atom located (heavy atom). Several typical examples of structures which have been solved or redetermined are given.

Les méthodes de recherche de structures cristallines pouvent être classées en trois catégories principales:

(1) les méthodes 'directes' permettant d'obtenir les phases des facteurs de structure à partir de l'information contenue dans le réseau réciproque R;*

(2) les méthodes utilisant la distribution de Patterson;

(3) les méthodes opérant dans l'espace direct R et permettant de 'mesurer' l'accord entre les résultats expérimentaux et ceux obtenus à partir d'un modèle structural déterminé; ceci est réalisé en considérant une fonction G des n paramètres structuraux décrivant les positions atomiques dans la maille élémentaire. Si elles sont moins générales et moins efficaces que les précédentes, leur intérêt est évident, notamment quand l'information obtenue par diffraction X est qualitativement ou quantitativement appauvrie.

La méthode décrite ici relève de cette dernière catégorie.† Après en avoir décrit le principe, nous donnons quelques exemples caractéristiques de son application à la recherche des structures de composés organiques simples.

Rappel sur les méthodes de recherche dans l'espace réel

Les méthodes permettant de trouver les extremums des fonctions peuvent être réparties dans trois rubri-

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* Le programme de calcul correspondant, baptisé *PYTHIE*, est écrit en Fortran V pour UNIVAC 1106/1108. Les temps de calculs donnés ci-après sont relatifs à l'ordinateur UNIVAC 1108.