RHF expressions, can also lead to drastic differences at large thickness and, perhaps, far from the optimum underfocus condition.

To avoid uncertainties in image interpretation, a careful assessment of the scattering factors used should thus be made. When quantitative HREM is used to solve complicated structures, such as extended defects, these considerations will undoubtedly be necessary.

References

CARLSON, T. A., LU, T. T., TUCKER, T. C., NESTOR, C. W. & MALIK, F. B. (1970). Report ORNL-4614. Oak Ridge National Laboratory, Tennessee, USA.

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2*B*, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

DOYLE, P. A. & COWLEY, J. M. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 152–173. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 309–397.

FOX, A. G., O'KEEFE, M. A. & TABBERNOR, M. A. (1989). *Acta Cryst.* A**45**, 768–793.

HYTCH, M. J. & STOBBS, W. M. (1992). Proc. 32nd French Electron Microscopy Society Annual Meeting, Rouen, pp. 28–29.

KILAAS, R. & O'KEEFE, M. A. (1989). *Computer Simulation of Electron Microscope Diffraction and Images*, edited by W. KRAKOW & M. O'KEEFE, pp. 171–183. Warrendale: The Minerals, Metals & Materials Society.

MOTT, N. F. & MASSEY, H. S. W. (1965). *The Theory of Atomic Collisions*, 3rd ed., pp. 86–112. Oxford: Clarendon Press.

PENG, L.-M. & COWLEY, J. M. (1988). *Acta Cryst.* A**44**, 1–5.

SMITH, G. H. & BURGE, R. E. (1962). *Acta Cryst.* **15**, 182–186.

TANG, D., KIRKLAND, A. I. & JEFFERSON, D. A. (1993). *Ultramicroscopy*, **48**, 321–331.

VAND, V., EILAND, T. F. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 303–306.

Acta Cryst. (1994). A**50**, 52–55

Phase Determination from X-ray Powder Diffraction Data. II. Partial Patterson Maps and the Localization of Anomalously Scattering Atoms

BY W. PRANDL

Institut für Kristallographie, Universität Tübingen, Charlottenstrasse 33, D-72070 Tübingen, Germany

(*Received* 22 *March* 1993; *accepted* 8 *June* 1993)

Abstract

Partial Patterson maps containing peaks from anomalous scatterers only can be derived from powder diffraction data. For each anomalous scatterer, three data sets are needed: one off the edge and another two at two wavelengths close to the edge. The method presented is based essentially on the wavelength dependence of the real part of the anomalous scattering factor.

I. Introduction

Because of the high resolution of the X-ray diffractometers that are available now at many synchrotron sources, powder diffraction has become nearly equivalent to single-crystal methods: provided the resolution is high enough, individual intensities $I(\mathbf{H}) = |F(\mathbf{H})|^2 + |F(-\mathbf{H})|^2$ can be measured for a large number of reflections **H** and all the well established methods for the determination of crystal structures can then be used. This statement applies for wavelengths far enough from the absorption edges of atoms in the sample. If anomalous scattering comes into play, the coincidence of Bijvoet pairs in a powder diagram prevents the application of the well known single-crystal techniques, *e.g.* the multiple anomalous dispersion (MAD) method discussed by Karle (1980), for the determination of signs or phases.

In a previous communication (Prandl, 1990, hereinafter paper I), it was shown that, from a simple modification of the single-crystal algorithm, signs or phases can be obtained from powder data also, provided, as usual, the locations of the anomalous scatterers are known. We have demonstrated recently that signs can be determined uniquely in this way (Limper, Prandl & Wroblewski, 1991).

The main results of paper I may be summed up as follows. For the determination of signs, for centrosymmetric structures, a single anomalous scatterer is sufficient. Two data sets are needed, one with intensities $I_\sigma(\mathbf{H})$ close to the absorption edge of the atom σ and a second one with intensities $I_o(\mathbf{H})$ sufficiently far from the edge. In the acentric case, two different anomalous scatterers must be available in the structure. Three data sets are needed: one off all edges, $I_o(H)$, and another two close to the edges of the atoms σ_1 and σ_2, $I_{\sigma 1}(\mathbf{H})$ and $I_{\sigma 2}(\mathbf{H})$, respectively. The structure of the anomalous scatterers can, in principle, be determined from difference Patterson maps using $I_\sigma(\mathbf{H}) - I_o(\mathbf{H})$ in the case of centrosymmetry and $I_{\sigma 1}(\mathbf{H}) - I_o(\mathbf{H})$ and $I_{\sigma 2}(\mathbf{H}) - I_o(\mathbf{H})$, respectively, in the acentric case. In any of these cases, however, the difference Patterson map will contain peaks not only from interatomic distances between the anomalous scatterers but also from those between anomalous scatterers and normal atoms.

It is the purpose of the present paper to show that, from a minor variation of the data sets taken and a new algorithm, a partial Patterson map $P_\sigma(\mathbf{u})$, containing peaks from anomalous scatterers only, can be determined. The procedure suggested is specific to individual kinds of anomalous scatterers: different elements can be analysed/located separately.

II. Analytic procedure and selection of data

As in paper I, we write the atomic form factor

$$f_s = f_{os} \tag{1a}$$

for normal scattering and

$$f_\sigma = f_{o\sigma} + \Delta'_\sigma + i\Delta''_\sigma \tag{1b}$$

for the anomalous scatterer σ, where the f_{os} and $f_{o\sigma}$ depend only on $\sin\theta/\lambda$ and the Δ'_σ, Δ''_σ vary with the wavelength. Δ'_σ and Δ''_σ are expected to depend only slightly, if at all, on the scattering angle and for the present discussion they are taken as scalar quantities [the general tensorial form factor has been discussed recently by Kirfel, Petcov & Eichhorn (1991)]. Far from the absorption edge, the structure factor is

$$F_{o\pm} \equiv F(\pm\mathbf{H}) = \textstyle\sum \hat{f}_{os} \exp(\pm 2i\pi \mathbf{H}\mathbf{r}_s) = |F_o| \exp(\pm i\Phi), \tag{2}$$

where $\hat{f}_{os}$ is the product of the form factor f_{os} with the appropriate isotropic temperature factor and $\Phi \equiv \Phi(\mathbf{H})$ is the unknown phase. Close to an absorption edge of the atoms σ, we obtain, with the shorthand notation a_σ,

$$a_\sigma = (\Delta'_\sigma + i\Delta''_\sigma)/f_{o\sigma} = (\delta_\sigma/f_{o\sigma}) \exp i\alpha_\sigma \tag{3}$$

$$\delta_\sigma = (\Delta'^2_\sigma + \Delta''^2_\sigma)^{1/2} \tag{4}$$

$$\alpha_\sigma = \arctan(\Delta''_\sigma/\Delta'_\sigma) \tag{5}$$

$$\begin{aligned} F_{\sigma\pm} \equiv F_\sigma(\pm\mathbf{H}) &= F_{o\pm} + a_\sigma F^\sigma_o(\pm\mathbf{H}) \\ &= |F_o| \exp(\pm i\Phi) \\ &\quad + |a_\sigma||F^\sigma_o| \exp i(\alpha_\sigma \pm \Psi_\sigma). \end{aligned} \tag{6}$$

Here, $F_\sigma(\pm\mathbf{H})$ is the actual structure factor of the crystal and $F^\sigma_o(\pm\mathbf{H})$ is the normal (*i.e.* nonanomalous) part of the structure factor, pertaining only to the anomalous scatterer σ with its phase angle $\Psi_\sigma = \Psi_\sigma(\mathbf{H})$. Equations (3)–(6) are a correct formulation if all the anomalous scatterers σ are equivalent. If the atoms of type σ occur at different lattice sites and/or in different valency states, then (6) is only approximately valid. The present procedure may become less reliable quite close (say within ±20eV) to the absorption edge, because the chemical environment may change the position of the edge: chemical shifts of the absorption edge have been reported by, for instance, Wong, Lytle, Messmer & Maylotte (1984).

In a powder diagram, one obtains the off-edge intensities

$$I_o = 2|F_o|^2 \tag{7}$$

and, near the edges,

$$I_\sigma = |F_{\sigma+}|^2 + |F_{\sigma-}|^2. \tag{8}$$

We define an intensity ratio r_σ that depends, *via* a_σ, on the wavelength

$$\begin{aligned} r_\sigma &= I_\sigma/I_\sigma \\ &= 1 + |a_\sigma|^2(|F^\sigma_o|^2/|F_o|^2) \\ &\quad + 2|a_\sigma| \cos\alpha_\sigma(|F^\sigma_o|/|F_o|) \cos(\Phi - \Psi_\sigma). \end{aligned} \tag{9}$$

In paper I, it was suggested that, for the determination of phases in the acentric case, two different anomalous scatterers σ_1 and σ_2 should be chosen and data should be taken at λ_o, $\lambda_{\sigma 1}$ and $\lambda_{\sigma 2}$, where the latter two wavelengths are close to resonances of the atoms σ_1 and σ_2. Under these conditions, the two resulting equations (9) for $r_{\sigma 1}$ and $r_{\sigma 2}$ can be solved uniquely for $\sin\Phi$ and $\cos\Phi$ and, therefore, also for Φ, provided the $F^\sigma_o = |F^\sigma_o| \exp(i\Psi_\sigma)$ are known.

Here, we show that (9) can be used to find $|F^\sigma_o|^2$, the 'intensities of the anomalous scatterers', directly. For this purpose, we now assume that three data sets specified in the following way are available: $I_o(\mathbf{H})$ at λ_o (off edge) and $I_\sigma(\mathbf{H},\lambda_1)$ and $I_\sigma(\mathbf{H},\lambda_2)$, where λ_1 and $\lambda_2 \neq \lambda_1$ are both close to an edge of atoms σ. Under these conditions, the normalized anomalous scattering factors a_σ can be calculated, *e.g.* by the program distributed by Cromer (1983; see also Cromer & Liberman, 1970, 1981). The $|F_o|$, Φ, $|F^\sigma_o|$ and Ψ_σ in (9) do not depend on the wavelength. Let us define

$$\mathbf{M} = \begin{vmatrix} |a_\sigma(\lambda_1)|^2 & 2|a_\sigma(\lambda_1)| \cos\alpha_\sigma(\lambda_1) \\ |a_\sigma(\lambda_2)|^2 & 2|a_\sigma(\lambda_2)| \cos\alpha_\sigma(\lambda_2) \end{vmatrix} \tag{10}$$

$$\mathbf{Y} = \begin{vmatrix} |F^\sigma_o|^2/|F_o|^2 \\ (|F^\sigma_o|/|F_o|) \cos(\Phi - \Psi_\sigma) \end{vmatrix} \tag{11}$$

$$\mathbf{V} = \begin{vmatrix} r_\sigma(\lambda_1) - 1 \\ r_\sigma(\lambda_2) - 1 \end{vmatrix}. \tag{12}$$

Then, the two versions of (9) corresponding to λ_1 and λ_2 may be written as

$$\mathbf{MY} = \mathbf{V} \tag{13}$$

and (13) can be inverted if the matrix **M** is nonsingular.

In the approximation chosen, the matrix elements of **M** depend only on the X-ray resonance properties of the atoms σ and not on their positions. **M** will be singular if

$$|a_\sigma(\lambda_1)|/|a_\sigma(\lambda_2)| = \cos\alpha_\sigma(\lambda_1)/\cos\alpha_\sigma(\lambda_2). \tag{14}$$

For λ_1, $\Delta'_\sigma(\lambda_1)$, $\Delta''_\sigma(\lambda_1)$ and $\delta_\sigma(\lambda_1)$ given, all the vectors $\Delta'_\sigma(\lambda_2^*) + i\Delta''_\sigma(\lambda_2^*)$ obeying (14) lie on a circle with the radius

$$R = \delta^2_\sigma(\lambda_1)/2\Delta'_\sigma(\lambda_1), \tag{15}$$

which passes through the origin as shown in Fig. 1. By a proper selection of $\lambda_2 \neq \lambda_2^*$, one can always avoid this condition and then **M** can be inverted. In Fig. 2, this construction is demonstrated for copper as the anomalous scatterer. The anomalous contributions have been calculated by the Cromer–Liberman program. It is evident from Fig. 2 that the restriction (14) becomes irrelevant, if one chooses $\lambda_1 > \lambda_{\text{edge}}$ and $\lambda_2 > \lambda_{\text{edge}}$.

From the inversion of (13), one arrives at

$$|F^\sigma_o|^2 = |F_o|^2(\mathbf{M}^{-1}\mathbf{V})_1 \tag{16}$$

$$|F^\sigma_o|\cos(\Phi - \Psi_\sigma) = |F_o|(\mathbf{M}^{-1}\mathbf{V})_2. \tag{17}$$

The solution (16) is the quantity we look for: from $|F^\sigma_o|^2$ we may immediately compute the partial Patterson function $P_\sigma(\mathbf{u})$.

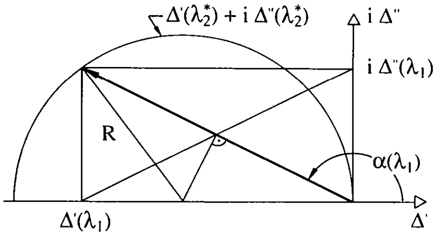

Fig. 1. For λ_1 given, the circle with the radius R represents the conditions [(14)] under which the matrix **M** becomes singular. Details are given in the text.

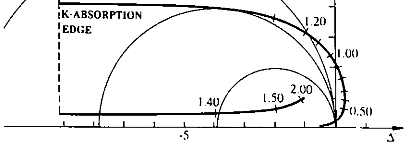

Fig. 2. The circle construction (14)/Fig. 1 applied to copper as the anomalous scatterer. Δ'_{Cu} and Δ''_{Cu} in electron units.

For centrosymmetric structures, (17) is reduced to

$$|F^\sigma_o|s(\mathbf{H})s_\sigma(\mathbf{H}) = |F^\sigma_o|(\mathbf{M}^{-1}\mathbf{V})_2, \tag{18}$$

where $s(\mathbf{H})$ and $s_\sigma(\mathbf{H})$ are the signs of $F_o(\mathbf{H})$ and $F^\sigma_o(\mathbf{H})$, respectively. Since, at this stage of the analysis, the localization of the anomalous scatterers may be taken as being known from $P_\sigma(\mathbf{u})$, the signs $s_\sigma(\mathbf{H})$ are known also and (18) solves the sign problem for $s(\mathbf{H})$ with a single anomalous scatterer.

For acentric structures, the Ψ_σ are known with one restriction: densities $\rho_\sigma(\mathbf{r})$ and inverted densities $\rho_\sigma(-\mathbf{r})$ cannot be discriminated. In other words, powder diffraction cannot, in fact, be used to derive absolute configurations. In the acentric case, one set of equations (16) and (17) is not sufficient to determine the phases $\Phi(\mathbf{H})$ uniquely, as discussed earlier (paper I); a second anomalous scatterer is needed for this purpose.

The considerations given so far rely on perfect resolution in the powder diagram; overlap and coincidences of nonequivalent reflections have been excluded. Limitations owing to these two effects will be treated elsewhere.

III. Discussion

The main purpose of this communication is to point out that, using anomalous scattering, the partial Patterson function $P_\sigma(\mathbf{u})$ is accessible not only from single-crystal but also from powder data. With the localization of the anomalous scatterers at hand, the phase problem can be solved. One may, however, put aside the structure problem and ask whether a partial Patterson function $P_\sigma(\mathbf{u})$, being an autocorrelation function, has a value in itself. This is indeed the case in many problems of disorder. Examples are substitution in garnets or spinels and the partial autocorrelation functions in quasicrystals.

In a more speculative manner, one might also consider using the present method to solve the problem of site occupancies of and correlations between less concentrated defects at unknown lattice sites, *e.g.* interstitials, which very often give rise to appreciable changes in the physical properties of technical materials. Data of very high accuracy are required in this case. They may be attained under the conditions shown in Fig. 1: if the wavelengths are chosen on the low absorption side of an edge [$\lambda_i > \lambda_\sigma(K, L$ edges), $i = 1, 2$], then the absorption and experimental conditions, for instance, counter efficiency and reflection positions, remain nearly constant for the two measurements close to the edge. If the $|F^\sigma_o|^2$ could be measured, then major complementary information beyond extended X-ray absorption fine-structure spectroscopy would be accessible for the defect problem by powder diffraction.

This investigation was supported financially by the Bundesministerium für Forschung und Technologie under project numbers 03-PR2TUE3 and 05-5VTIXB.

References

CROMER, D. T. (1983). *J. Appl. Cryst.* **16**, 437.
CROMER, D. T. & LIBERMAN, D. J. (1970). *J. Chem. Phys.* **53**, 1891–1898.
CROMER, D. T. & LIBERMAN, D. J. (1981). *Acta Cryst.* A**37**, 267–268.
KARLE, J. (1980). *Int. J. Quant. Chem. Symp.* **7**, 356–367.
KIRFEL, A., PETCOV, A. & EICHHORN, K. (1991). *Acta Cryst.* A**47**, 180–195.
LIMPER, W., PRANDL, W. & WROBLEWSKI, T. (1991). *Mater. Sci. Forum*, **79–82**, 221–226.
PRANDL, W. (1990). *Acta Cryst.* A**46**, 988–992.
WONG, J., LYTLE, F. W., MESSMER, R. P. & MAYLOTTE, D. H. (1984). *Phys. Rev. B*, **30**, 5596–5610.

Acta Cryst. (1994). A**50**, 55–57

Enantiomorphism and Multiple-Beam X-ray Diffraction

BY ROBERTO COLELLA

Purdue University, Physics Department, West Lafayette, Indiana 47907, *USA*

(*Received* 27 *January* 1993; *accepted* 10 *June* 1993)

Abstract

It is shown that multiple-beam X-ray diffraction does not provide a means of distinguishing between the two enantiomorphic forms of the same crystal. A detailed proof is presented for the case of benzil. It is also shown that, without anomalous dispersion, multiple-beam diffraction is equally incapable of determining the polarity of acentric crystals. Applications are presented to results published in recent literature.

It is well known that multiple Bragg scattering, a situation in which two or more Bragg reflections are excited simultaneously, can be used to determine the phases of structure factors. It is also well known that enantiomorphic forms of the same structure cannot be distinguished in ordinary X-ray experiments since the diffraction patterns are identical. Only when anomalous scattering occurs (*i.e.* the X-ray energy is not too far from the absorption edge of one atomic species present in the crystal) are certain Bragg reflections, otherwise identical in the two enantiomorphic forms, slightly strengthened or weakened, depending on the space group, thereby making it possible to distinguish between the two enantiomorphic forms.

Such has been the case, for example, for α-quartz, which is found with either the $P3_12$ or $P3_22$ space group. It has been shown (De Vries, 1958) that anomalous scattering can indeed be used to determine the absolute configuration, or handedness, of α-quartz.

Since the determination of handedness ultimately reduces to a phase determination, it would seem that multiple Bragg scattering could be fruitfully applied to the solution of the enantiomorphism problem. Such a proposition was seriously considered recently (Shen, 1984) and looked very attractive because it seemed that it could be used with organic crystals containing light atoms, such as C, O and H atoms, for which anomalous scattering is not feasible. However, it was soon realized that even multiple Bragg scattering could not solve the enantiomorphism problem in the absence of anomalous scattering and this conclusion was reported in a review paper (Shen & Colella, 1986) in which the case of benzil (isomorphous with quartz) was considered. The explanation given in the paper was essentially based on the fact that our initial inability to distinguish between left- and right-handedness prevents us from determining the orientation of the crystal and, therefore, drawing conclusions from any conceivable multibeam experiment.

Since then, a number of papers have appeared in the literature in which this conclusion is either openly rejected or ignored and cases have been reported in which multiple-beam diffraction has been used to solve the enantiomorphism problem. Such is the case, for example, for the experiment on benzil described by Hümmer, Weckert & Bondza (1989), in which it is claimed that the handedness of the sample used in the experiment was unambiguously determined by comparing *Umweganregung* peaks with different intensities.

Another case in point is the paper by Chang, King, Huang & Gao (1991), in which some multi-