New Formulation and Solution of the Phase Problem in X-Ray Analysis of Noncentric Crystals Containing Anomalous Scatterers*

YOSHIHARU OKAYA AND RAY PEPINSKY
X-Ray and Crystal Structure Laboratory, Department of Physics, The Pennsylvania State University, University Park, Pennsylvania
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Use of anomalous dispersion in x-ray analyses of noncentric crystals reduces the problem of phase determination for any given structure factor to the choice between two possible roots of two simultaneous quadratic equations. This assumes that anomalous scatterer positions have been established by classical techniques. Selection of the correct root is aided by: the $P_s(\mathbf{u})$ function of Okaya, Saito, and Pepinsky; heavy atom or isomorphous replacement techniques; or the linear inequalities of Okaya. Given moderately accurate structure factor amplitudes $|F\mathbf{h}|$ and $|F-\mathbf{h}|$, the phase problem is solved for noncentric crystals containing anomalous scatterers; and the absolute configuration of the structure is obtained as a by-product of the direct analysis.

INTRODUCTION

OKAYA, Saito, and Pepinsky[1] and Pepinsky and Okaya[2] have developed a method for determination of the structures and absolute configuration of noncentrosymmetric crystals, by using the phenomenon of anomalous x-ray dispersion. The imaginary part of the convolution of the density of scattering material (now a complex quantity) is expressed by

$$P_s(\mathbf{u})=\sum_{\mathbf{h}} |F\mathbf{h}|^2 \sin(2\pi\mathbf{h}\cdot\mathbf{u}). \tag{1}$$

This is equivalent to the superposition of all distributions of noncentrically-arranged normal scatterers around each anomalous scatterer; and the superpositions can be unscrambled by image-seeking methods (Takeuchi, Okaya, and Pepinsky[3]).

In the present paper a further method is described, by which the phases of individual structure factors can be directly determined. This has some advantages over the use of the $P_s(\mathbf{u})$ function alone. As in the case of the $P_s(\mathbf{u})$ function, the absolute configuration of the noncentric distribution appears automatically.

NEW FORMULATION OF THE PHASE PROBLEM

Consider the scattered x-ray intensity $I\mathbf{h}$ from a crystallographic plane, of a noncentric crystal, $\mathbf{h}=(h,k,l)$ representing the Miller indices of the plane. $I\mathbf{h}$ is related to the structure factor $F\mathbf{h}$ by

$$I\mathbf{h}=K\cdot F\mathbf{h}\cdot F\mathbf{h}^*=K|F\mathbf{h}|^2, \tag{2}$$

where

$$F\mathbf{h}=A\mathbf{h}+iB\mathbf{h}, \tag{3a}$$

$$F\mathbf{h}^*=A\mathbf{h}-iB\mathbf{h}, \tag{3b}$$

and K is a determinable proportionality constant.

$\rho(\mathbf{r})$ represents the density distribution of scattering material. We consider the crystal to be composed of normal and anomalously scattering atoms and write the structure factor in the discrete atom approximation

$$F\mathbf{h}=\sum_n f_n(\mathbf{h}) \exp(2\pi i\mathbf{h}\cdot\mathbf{r}_n), \tag{4}$$

where $f_n(\mathbf{h})$ is the scattering factor for the nth atom and $\mathbf{r}_n$ is that atom's position.

If the scattered wavelength is close to and just shorter than an absorption edge of a scattering atom $\mathbf{n}$, $f_n(\mathbf{h})$ is complex, because of dispersion:

$$f_n^{\text{a.s.}}(\mathbf{h})=f_n'(\mathbf{h})+if_n''(\mathbf{h}). \tag{5}$$

Otherwise, $f_n(\mathbf{h})$ is real. We can decompose $F\mathbf{h}$ into

$$F\mathbf{h}=F\mathbf{h}^{\text{n.s.}}+F\mathbf{h}^{\text{a.s.}}, \tag{6}$$

where $F\mathbf{h}^{\text{n.s.}}$ is summed over all normal scatterers, and $F\mathbf{h}^{\text{a.s.}}$ over all anomalous scatterers. (For a given incident x-ray wavelength, there will in general be only one type of anomalous scatterer in the crystal.)

From (4),

$$F\mathbf{h}^*=\sum f_n^*(\mathbf{h}) \exp(-2\pi i\mathbf{h}\cdot\mathbf{r}_n). \tag{7}$$

It is obvious that for normal scatterers, since $f_n^{\text{n.s.}}=(f_n^{\text{n.s.}})^*$,

$$(F\mathbf{h}^{\text{n.s.}})^*=F-\mathbf{h}^{\text{n.s.}}, \tag{8}$$

where $-\mathbf{h}=(-h,-k,-l)=(\bar{h},\bar{k},\bar{l})$. Then, from (3a) and (3b),

$$A\mathbf{h}^{\text{n.s.}}=A-\mathbf{h}^{\text{n.s.}} \tag{9a}$$

and

$$B\mathbf{h}^{\text{n.s.}}=-B-\mathbf{h}^{\text{n.s.}}. \tag{9b}$$

The relations (9a) and (9b) do *not* hold for $A\mathbf{h}^{\text{a.s.}}$ and $B\mathbf{h}^{\text{a.s.}}$, because in this case $f_n(\mathbf{h})\neq f_n^*(\mathbf{h})$. It is for this reason that $|F\mathbf{h}|^2\neq|F-\mathbf{h}|^2$.

Using the relations above, we can now write

$$|F\mathbf{h}|^2=(A\mathbf{h}^{\text{a.s.}}+A\mathbf{h}^{\text{n.s.}})^2+(B\mathbf{h}^{\text{a.s.}}+B\mathbf{h}^{\text{n.s.}})^2, \tag{10a}$$

and

$$|F-\mathbf{h}|^2=(A-\mathbf{h}^{\text{a.s.}}+A\mathbf{h}^{\text{n.s.}})^2+(B-\mathbf{h}^{\text{a.s.}}-B\mathbf{h}^{\text{n.s.}})^2. \tag{10b}$$

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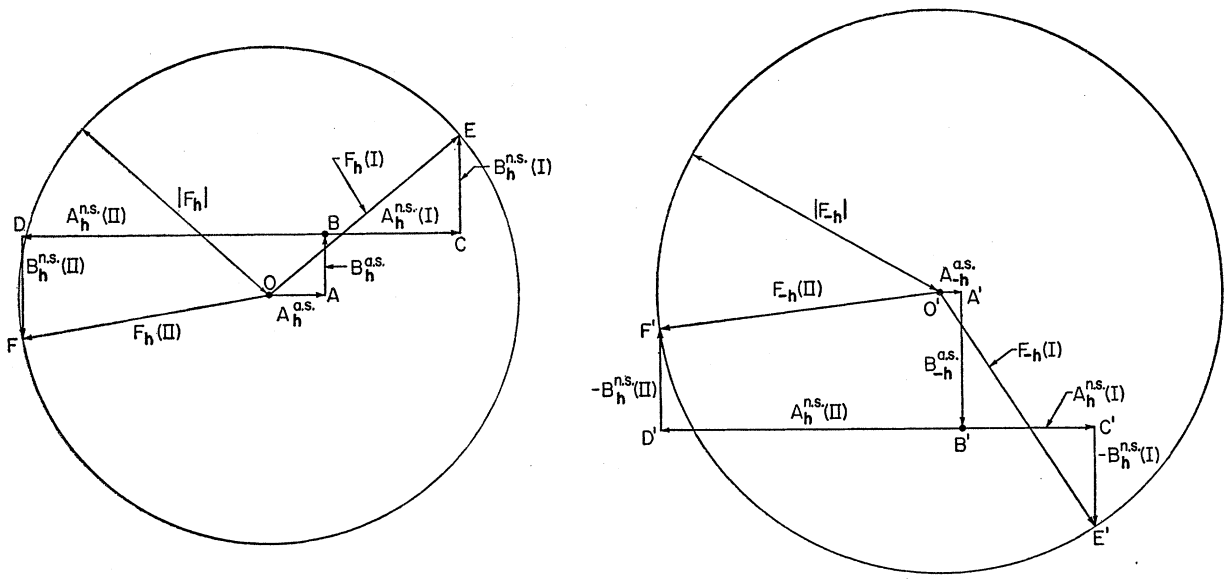
[1] Okaya, Saito, and Pepinsky, Phys. Rev. 98, 1857 (1955).

[2] R. Pepinsky and Y. Okaya, Proc. Natl. Acad. Sci. U. S. 42, 286 (1956).

[3] Pepinsky, Takeuchi, and Okaya, presented at the Meeting of the American Crystallographic Association, French Lick, Indiana, June, 1956 (unpublished). See also R. Pepinsky, Record Chem. Progr. (Kresge-Hooker Sci. Lib.) (to be published).



(a) SOLUTIONS FOR **h** (b) SOLUTIONS FOR **-h**

FIG. 1. Geometric representation of solutions for $A_{\mathbf{h}}^{\text{n.s.}}$ and $B_{\mathbf{h}}^{\text{n.s.}}$, from known $|F_{\mathbf{h}}|$, $|F_{-\mathbf{h}}|$, $A_{\mathbf{h}}^{\text{a.s.}}$, $B_{\mathbf{h}}^{\text{a.s.}}$, $A_{-\mathbf{h}}^{\text{a.s.}}$, $B_{-\mathbf{h}}^{\text{a.s.}}$ values.

Let us assume that the positions of the anomalous scatterers have been established by usual methods (e.g., from interpretation of Patterson maps, including if necessary joint Patterson maps obtained by altering the incident x-ray wavelength so that in one case no anomalous scattering occurs).[2] Then $A_{\mathbf{h}}^{\text{a.s.}}$, $B_{\mathbf{h}}^{\text{a.s.}}$, $A_{-\mathbf{h}}^{\text{a.s.}}$, and $B_{-\mathbf{h}}^{\text{a.s.}}$ are known; and of course $|F_{\mathbf{h}}|^2$ and $|F_{-\mathbf{h}}|^2$ are known from the original intensity measurements.

Equations (10a) and (10b) can be regarded as simultaneous quadratic equations with two unknowns $A_{\mathbf{h}}^{\text{n.s.}}$ and $B_{\mathbf{h}}^{\text{n.s.}}$. Each such pair of equations, for a given value of **h**, has two sets of roots:

$$(A_{\mathbf{h}}^{\text{n.s.}})_{\text{I}},\ (B_{\mathbf{h}}^{\text{n.s.}})_{\text{I}},\ \text{and}\ (A_{\mathbf{h}}^{\text{n.s.}})_{\text{II}},\ (B_{\mathbf{h}}^{\text{n.s.}})_{\text{II}}.$$

The phase problem for a noncentric crystal, containing anomalous scatterers in known positions and normal scatterers in unknown positions, has now been reduced to the choice between solutions I and II for the roots of Eqs. (10a) and (10b).

METHODS FOR SOLUTION OF THE PHASE AMBIGUITY

The choice between solutions I and II can be made *via* several approaches. The discussion is clarified by reference to Figs. 1(a) and 1(b). The radius of the circle of Fig. 1(a) corresponds to $|F_{\mathbf{h}}|$, and that of Fig. 1(b) to $|F_{-\mathbf{h}}|$. OA and AB correspond to $A_{\mathbf{h}}^{\text{a.s.}}$ and $B_{\mathbf{h}}^{\text{a.s.}}$, respectively; and $O'A'$ and $O'B'$ correspond to $A_{-\mathbf{h}}^{\text{a.s.}}$ and $B_{-\mathbf{h}}^{\text{a.s.}}$. Solutions I and II correspond respectively to points E and F in Fig. 1(a), and to E' and F' in Fig. 1(b). Equations (9a) and (9b) require that $BC=B'C'[=(A_{\mathbf{h}}^{\text{n.s.}})_{\text{I}}]$, and $BD=B'D'[=(A_{\mathbf{h}}^{\text{n.s.}})_{\text{II}}]$; and, similarly, $CE=-C'E'[=(B_{\mathbf{h}}^{\text{n.s.}})_{\text{I}}]$, and $BD=-B'D'[=(B_{\mathbf{h}}^{\text{n.s.}})_{\text{II}}]$.

Approaches to choice between I and II for each **h** can be categorized as follows:

1. If $F_{\mathbf{h}}^{\text{a.s.}}$ is sufficiently large (e.g., for a heavy atom), one or the other solution may perhaps be excluded because an unreasonable value of $|F_{\mathbf{h}}^{\text{n.s.}}|$ is required.

2. Another pair of Eqs. (10a) and (10b) can be achieved by altering the incident x-ray wavelength so that anomalous scattering is avoided. $A_{\mathbf{h}}^{\text{n.s.}}$ and $B_{\mathbf{h}}^{\text{n.s.}}$ are then unchanged, but $A_{\mathbf{h}}^{\text{a.s.}}$ and $B_{\mathbf{h}}^{\text{a.s.}}$ now become $A_{\mathbf{h}}^{\text{h.a.}}$ and $B_{\mathbf{h}}^{\text{h.a.}}$ where h.a. indicates a heavy atom *without* dispersion. This then adds a third quadratic equation to (10a) and (10b), which suffices to exclude one or the other of former solutions I and II.

3. A method related to method 2 above is to replace the anomalous scatterer isomorphously with an atom of quite different normal scattering power. This may or may not be possible chemically; and one must depend upon fairly strict isomorphism: i.e., $\mathbf{r}'_n$ for the replaceable scatterers are essentially identical, and this replacement does not alter the coordinates and hence the $F_{\mathbf{h}}^{\text{n.s.}}$ contributions from the original normal scatterers. Such isomorphous replacement has of course often been very helpful in classical phase analysis; so it can be expected often to be useful here. Analytically, this procedure also adds a third equation to (10a) and (10b).

4. The *most* useful technique is likely to be application of the deconvoluted $P_s(\mathbf{u})$ function of Okaya *et al.*[1]

and Pepinsky and Okaya.[2] This directly provides knowledge of the noncentric dispositions of normal scatterers about the anomalous scatterers, and hence should give the general if not the correct direction and magnitude of $F_{\mathbf{h}}^{\text{n.s.}}$. If the correct direction and magnitude is immediately given by $P_s(\mathbf{u})$, then of course the entire analysis presented above is unnecessary. Situations can conceivably arise, however, where a considerable amount of the scattering material is centrosymmetrically disposed about the anomalous scatterer. The disposition of this material will *not* be centrically arranged around a second anomalous scatterer (of the same atomic species) in the same cell, if more than one such scatterer is present per cell; and this condition will aid in location of the centrically-disposed atoms.

The analysis of this paper is quite independent of such accidental partially-centric distributions. Any centric distributions will not contribute to $(B_{\mathbf{h}}^{\text{n.s.}})_{\text{I}}$ or $(B_{\mathbf{h}}^{\text{n.s.}})_{\text{II}}$; and in general they are not likely to change the direction of $(A_{\mathbf{h}}^{\text{n.s.}})_{\text{I}}$ or $(A_{\mathbf{h}}^{\text{n.s.}})_{\text{II}}$.

5. The linear inequalities of Okaya[4] for the noncentric case may also be useful in distinguishing between solutions I and II.

DISCUSSION

It should be remarked that phase determination could be accomplished, except for determination of absolute configuration, *if* three crystals were available which were precisely isomorphous but contained different heavy atoms. This condition is very difficult to satisfy, as every investigator who has attempted to prepare such an isomorphous series can testify. Not only are the heavy atoms likely to be slightly displaced, but the organic constituents (or inorganic constituents other than the replaceable heavy atom) are likely to rearrange slightly due to the unequal radii and thermal oscillations of the replaced heavy atoms. Use of anomalous dispersion, plus measurements with a change in wavelength such that dispersion is avoided, guarantees precise isomorphism, since one single crystal is used throughout.

Use of the "crystal engineering" technique of Pepinsky[5] is the only method known to the authors which is likely to provide a very closely isomorphous series of structures. In this technique, organic ions are crystallized with complex ions, and the size of the latter tends to control the molecular packing, with the resulting structures generally very amenable to x-ray examination. Central atoms of the complex ion can generally be replaced with chemically-similar atoms, without significant change in the size of the complex. These central atoms are also generally very useful as anomalous scatterers.

It is interesting that although noncentric structures were very much more difficult to solve than centrosymmetric crystals, before introduction of the $P_s(\mathbf{u})$ function, the latter plus the present approach utilizing anomalous dispersion now provide an essentially direct route to the solution of noncentric structures containing anomalous scatterers. As already stated, the absolute configuration results automatically. An examination of Eqs. (10a) and (10b) reveals the importance of anomalous dispersion. Without that phenomenon, the two equations would reduce to a single one, with $F_{\mathbf{h}}^{\text{h.a.}} = A_{\mathbf{h}}^{\text{h.a.}} + iB_{\mathbf{h}}^{\text{h.a.}}$ replacing $F_{\mathbf{h}}^{\text{a.s.}}$; and rather than only two possible solutions for these equations, with straightforward procedures available for selecting the correct root, the phase of $F_{\mathbf{h}}^{\text{n.s.}}$ is entirely uncontrolled. The technique of triple isomorphism without dispersion, as discussed above, will *not* establish absolute configurations; this is because, without anomalous scattering, $|F_{\mathbf{h}}|^2 = |F_{-\mathbf{h}}|^2$.

Utilizing $A_{\mathbf{h}} = A_{\mathbf{h}}^{\text{a.s.}} + A_{\mathbf{h}}^{\text{n.s.}}$ and $B_{\mathbf{h}} = B_{\mathbf{h}}^{\text{a.s.}} + B_{\mathbf{h}}^{\text{n.s.}}$ as determined by our procedure, we can compute the electron density function $\rho(\mathbf{r})$:

$$\rho(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{h}} (A_{\mathbf{h}} \cos 2\pi\mathbf{h}\cdot\mathbf{r} + B_{\mathbf{h}} \sin 2\pi\mathbf{h}\cdot\mathbf{r}) - \frac{i}{V}\sum_{\mathbf{h}} (A_{\mathbf{h}}^{\text{a.s.}} \sin 2\pi\mathbf{h}\cdot\mathbf{r} - B_{\mathbf{h}}^{\text{a.s.}} \cos 2\pi\mathbf{h}\cdot\mathbf{r}).$$

The real part of this function reveals the real part of the scattering power of the anomalous scatterers, plus all the normal scatterers. The imaginary part of $\rho(\mathbf{r})$ gives the imaginary part of the scattering power associated with the anomalous scatterers; the disappearance of coefficients $A_{\mathbf{h}}^{\text{n.s.}}$ and $B_{\mathbf{h}}^{\text{n.s.}}$ from this imaginary part follows because of Eqs. (9a) and (9b). We need compute only the real part of $\rho(\mathbf{r})$ for a structure determination.

Experience to date indicates that the multifilm photographic method of intensity recording, with visual estimation, can provide sufficiently accurate intensity data for determination of moderately complex structures by the methods discussed in the preceding sections. Use of counter recording instruments is preferable, however, and will no doubt be required for quite complex structures. With the solution of the phase problem now dependent only upon instrumental measurements, it is obvious that efforts to obtain adequate accuracy are justified.

[4] Y. Okaya, Acta Cryst. (to be published).
[5] R. Pepinsky, Phys. Rev. **100**, 971 (1955).