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Phase determination by the two-wavelength method of Okaya & Pepinsky. By C. M. MITCHELL, *Physical Metallurgy Research Laboratories, Department of Mines and Technical Surveys, Ottawa, Ontario, Canada*

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In a recent article Okaya & Pepinsky (1956) have treated the problem of phase determination for noncentric crystals in which one or more atoms scatter anomalously. Relations are obtained for the structure factors $|F_{\mathbf{h}}|^2$ and $|F_{-\mathbf{h}}|^2$ which, when the positions of the anomalous atoms are known, reduce to a quadratic equation giving two possible solutions for the components of the structure amplitude, and the phase of the reflection $\mathbf{h}(hkl)$. A number of methods of choosing one solution are proposed, including the use of a second incident wavelength producing normal scattering for all atoms; this will provide a second quadratic equation.

In the present communication the method of using two incident wavelengths is examined. Linear equations in the components of the structure amplitude are obtained which give a single solution when the positions of the anomalously scattering atoms are known. One equation permits the method to be extended to centrosymmetric structures. The relations are derived for the general case in which both radiations produce anomalous scattering. This is necessary, since, with heavy atoms, anomalous scattering occurs for all wavelengths in the normal target range, due to the electrons in L and higher levels. In cases where incident wavelengths can be chosen such that one atom only in the unit cell scatters anomalously, direct phase determination is possible, using only the observed $|F_{\mathbf{h}}|^2$ and $|F_{-\mathbf{h}}|^2$ values.

The atomic scattering factor for anomalous dispersion

$$f_j = f_j^0 + \Delta f_j' + i f_j'' ,$$

where $\Delta f_j'$ and f_j'' are the in-phase and out-of-phase increments to the normal scattering factor f_j^0. The structure amplitude for the reflection $\mathbf{h}(hkl)$ is

$$F_{\mathbf{h}} = A_{\mathbf{h}} + iB_{\mathbf{h}} ,$$

which can be resolved into real and imaginary components as

$$F_{\mathbf{h}} = A_{\mathbf{h}}^{\text{n.s.}} + \Delta A_{\mathbf{h}}' - B_{\mathbf{h}}'' + i(B_{\mathbf{h}}^{\text{n.s.}} + \Delta B_{\mathbf{h}}' + A_{\mathbf{h}}'') ,$$

where

$$A_{\mathbf{h}}^{\text{n.s.}} = \sum_{j=1}^{n} f_j^0 \cos 2\pi(\mathbf{h}.\mathbf{r}_j), \quad B_{\mathbf{h}}^{\text{n.s.}} = \sum_{j=1}^{n} f_j^0 \sin 2\pi(\mathbf{h}.\mathbf{r}_j) ;$$

$$\Delta A_{\mathbf{h}}' = \sum_{j=1}^{n} \Delta f_j' \cos 2\pi(\mathbf{h}.\mathbf{r}_j), \quad \Delta B_{\mathbf{h}}' = \sum_{j=1}^{n} \Delta f_j' \sin 2\pi(\mathbf{h}.\mathbf{r}_j) ;$$

$$A_{\mathbf{h}}'' = \sum_{j=1}^{n} f_j'' \cos 2\pi(\mathbf{h}.\mathbf{r}_j), \quad B_{\mathbf{h}}'' = \sum_{j=1}^{n} f_j'' \sin 2\pi(\mathbf{h}.\mathbf{r}_j) .$$

$\mathbf{r}_j$ is the position vector of atom j in the unit cell. $\Delta A_{\mathbf{h}}'$, $\Delta B_{\mathbf{h}}'$, $A_{\mathbf{h}}''$ and $B_{\mathbf{h}}''$ contain terms dependent only upon the position of the anomalous scattering atoms. The $A_{\mathbf{h}}^{\text{n.s.}}$ and $B_{\mathbf{h}}^{\text{n.s.}}$ terms employed here differ from those used by Okaya & Pepinsky in that here the summation includes the normal scattering contribution of all atoms in the unit cell. For the reflection $-\mathbf{h}(\bar{h}\bar{k}\bar{l})$ the structure amplitude is

$$F_{-\mathbf{h}} = (A_{\mathbf{h}}^{\text{n.s.}} + \Delta A_{\mathbf{h}}' + B_{\mathbf{h}}'') - i(B_{\mathbf{h}}^{\text{n.s.}} + \Delta B_{\mathbf{h}}' - A_{\mathbf{h}}'') .$$

The square of the structure amplitude for $\mathbf{h}(hkl)$ is

$$|F_{\mathbf{h}}|^2 = F_{\mathbf{h}} F_{\mathbf{h}}^* = (A_{\mathbf{h}}^{\text{n.s.}} + \Delta A_{\mathbf{h}}' - B_{\mathbf{h}}'')^2 + (B_{\mathbf{h}}^{\text{n.s.}} + \Delta B_{\mathbf{h}}' + A_{\mathbf{h}}'')^2 ;$$

and for $-\mathbf{h}(\bar{h}\bar{k}\bar{l})$ it is

$$|F_{-\mathbf{h}}|^2 = F_{-\mathbf{h}} F_{-\mathbf{h}}^* = (A_{\mathbf{h}}^{\text{n.s.}} + \Delta A_{\mathbf{h}}' + B_{\mathbf{h}}'')^2 + B_{\mathbf{h}}^{\text{n.s.}} + \Delta B_{\mathbf{h}}' - A_{\mathbf{h}}'')^2 .$$

The difference of squares gives the relation

$$|F_{\mathbf{h}}|^2 - |F_{-\mathbf{h}}|^2 = 4\{(A_{\mathbf{h}}'' B_{\mathbf{h}}^{\text{n.s.}} - B_{\mathbf{h}}'' A_{\mathbf{h}}^{\text{n.s.}}) + (A_{\mathbf{h}}'' \Delta B_{\mathbf{h}}' - B_{\mathbf{h}}'' \Delta A_{\mathbf{h}}')\} \quad (1)$$

This equation, which is linear in $A_{\mathbf{h}}^{\text{n.s.}}$ and $B_{\mathbf{h}}^{\text{n.s.}}$, has been discussed by Okaya & Pepinsky, and in a recent article by Peerdeman & Bijvoet (1956).

In order to obtain a second linear equation in $A_{\mathbf{h}}^{\text{n.s.}}$ and $B_{\mathbf{h}}^{\text{n.s.}}$, consider the case where two incident wavelengths λ_1 and λ_2 have been used. The mean square value for reflections $\mathbf{h}(hkl)$ and $-\mathbf{h}(\bar{h}\bar{k}\bar{l})$ is

$$\mathscr{F}_{\mathbf{h}}^2 = \tfrac{1}{2}\{|F_{\mathbf{h}}|^2 + |F_{-\mathbf{h}}|^2\} = (A_{\mathbf{h}}^{\text{n.s.}})^2 + (B_{\mathbf{h}}^{\text{n.s.}})^2 + \alpha_{\mathbf{h}}^2 + \beta_{\mathbf{h}}^2 + 2(\Delta A_{\mathbf{h}}' A_{\mathbf{h}}^{\text{n.s.}} + \Delta B_{\mathbf{h}}' B_{\mathbf{h}}^{\text{n.s.}}) , \quad (2)$$

where

$$\alpha_{\mathbf{h}}^2 = \Delta A_{\mathbf{h}}'^2 + A_{\mathbf{h}}''^2, \quad \beta_{\mathbf{h}}^2 = \Delta B_{\mathbf{h}}'^2 + B_{\mathbf{h}}''^2 .$$

Subtracting the two equations of type (2), we have

$$\tfrac{1}{2}\left\{\mathscr{F}_{\mathbf{h}_{\lambda_1}}^2 - \mathscr{F}_{\mathbf{h}_{\lambda_2}}^2 + \left(\alpha_{\mathbf{h}_{\lambda_2}}^2 - \alpha_{\mathbf{h}_{\lambda_1}}^2\right) + \left(\beta_{\mathbf{h}_{\lambda_2}}^2 - \beta_{\mathbf{h}_{\lambda_1}}^2\right)\right\} = \left(\Delta A_{\mathbf{h}_{\lambda_1}}' - \Delta A_{\mathbf{h}_{\lambda_2}}'\right) A_{\mathbf{h}}^{\text{n.s.}} + \left(\Delta B_{\mathbf{h}_{\lambda_1}}' - \Delta B_{\mathbf{h}_{\lambda_2}}'\right) B_{\mathbf{h}}^{\text{n.s.}} . \quad (3)$$

It is evident that, where the positions of the anomalous scatters are known, (1) and (3) give the values of $A_{\mathbf{h}}^{\text{n.s.}}$ and $B_{\mathbf{h}}^{\text{n.s.}}$ and thus the phase of the reflection $\mathbf{h}(hkl)$.

The two-wavelength relation, equation (3), has certain interesting features which have not been previously noted in connection with anomalous dispersion. The first is that this relation alone can be used to determine the sign of the phase in centrosymmetric structures, where the positions of the anomalous scattering atoms are known; here $B_{\mathbf{h}}^{\text{n.s.}} = 0$ and the relation gives magnitude and sign of $A_{\mathbf{h}}^{\text{n.s.}}$. The second is that, since only the mean square values $\mathscr{F}_{\mathbf{h}}^2$ appear, the relation can be evaluated from intensity measurements on powder specimens; this will enable such effects as primary and secondary extinction and accidental inequalities of reflection from equivalent faces in single crystal specimens to be avoided.

When a pair of wavelengths are chosen such that one atom only in the unit cell scatters anomalously, then, considering this atom as the cell origin, equation (3) reduces to

$$A_{\mathbf{h}}^{\text{n.s.}} = \frac{\mathscr{F}_{\mathbf{h}_{\lambda_1}}^2 - \mathscr{F}_{\mathbf{h}_{\lambda_2}}^2 + (\Delta f_a')_{\lambda_2}^2 - (\Delta f_a')_{\lambda_1}^2 + (f_a'')_{\lambda_2}^2 - (f_a'')_{\lambda_1}^2}{2(\Delta f_{a\lambda_1}' - \Delta f_{a\lambda_2}')} , \quad (4)$$

and equation (1) reduces to

$$B^{\text{n.s.}}_{\mathbf{h}} = \frac{|F_{\mathbf{h}}|^2-|F_{-\mathbf{h}}|^2}{4f''_a}\,. \qquad (5)$$

The criteria for optimum wavelengths for phase determination are found in the denominators of equations (4) and (5); first, that one radiation gives a large value of the out-of-phase component f''_a, for one or more atoms, which will give a large difference in the observed reflections $F^2_{\mathbf{h}}$ and $F^2_{-\mathbf{h}}$; secondly, that the difference of the in-phase components of anomalous scattering for the two radiations, $(\Delta f'_{a_{\lambda_1}}-\Delta f'_{a_{\lambda_2}})$, be as large as possible to produce a large difference in the observed mean square values $\mathscr{F}^2_{\mathbf{h}\lambda_1}$ and $\mathscr{F}^2_{\mathbf{h}\lambda_2}$.

The accuracy of the method is dependent upon an exact knowledge of the anomalous scattering increments $\Delta f'$ and f'' to the atomic scattering factor. The table of these values calculated by Dauben & Templeton (1955) for $Z \gtrsim 20$ is for three radiations Cr $K\alpha$, Cu $K\alpha$ and Mo $K\alpha$ only. Values for intermediate radiations can be estimated by interpolation, but for general application of this method of calculation of exact values, or their experimental measurement, a full range of radiations would be of great assistance.

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The crystal structures of thorium bismuthides.

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The diagram of the thorium–bismuth alloys, obtained *in vacuo* by direct synthesis from the elements, has been studied by means of X-rays; the examination was performed by the powder method using Cu $K\alpha$ radiation (λ(Cu $K\alpha_1$) = 1·540500 Å). The only impurity in the thorium used (prepared by reduction of ThO_2 with Ca) was about 0·3% oxygen, mainly as ThO_2; the bismuth had a purity higher than 99·9%, with traces of lead.

In the part of the diagram richer in bismuth the alloys show the existence of the compounds Th_3Bi_4 and $ThBi_2$. No other compounds having higher quantities of bismuth have been observed, as alloys of a composition of around 80% Bi (both quenched from 1000° C. or annealed up to 400° C.) showed only the Debye reflexions of $ThBi_2$ and elementary bismuth.

The X-ray examination of the central part of the diagram shows the possible existence of two phases of a composition near to ThBi; however, it was not possible (with several thermal treatments, including also annealing and heating to higher temperatures) to obtain a cubic phase of the NaCl- or CsCl-type, as might expected by comparison with similar systems of thorium and uranium with other metalloids. With regard to these alloys it must be remarked that, if heated *in vacuo* at approximately 1500° C., they undergo alteration by bismuth distillation.

Finally, the alloys with a low bismuth content have not shown (after heating at a high temperature and cooling) the formation of other compounds: samples which on analysis had a composition around 30% Bi show mainly the reflexions of elementary thorium.

As with bismuth and the intermediary phases, the photographs exclude the formation of appreciable solid solution for thorium. All the alloys are fairly pyrophoric.

Th_3Bi_4

The compound Th_3Bi_4 (45·44% Th) is body-centred cubic with

$$a_0 = 9{\cdot}559 \text{ Å},\ Z = 4,\ \varrho = 11{\cdot}65 \text{ g.cm.}^{-3}.$$

The structure is of the Th_3P_4 type (Meisel, 1939), $D7_3$ type (*Strukturbericht*, 1943) with:

Space group No. 220 (*International Tables*, 1952): $I\bar{4}3d$.

Atomic positions:

12 Th in (a) $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}) + \frac{3}{8},0,\frac{1}{4};\ \circlearrowleft$.
16 Bi in (c) $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}) + x,x,x;$
$\circlearrowleft$ with $x = \frac{1}{12}$.

Each thorium atom is thus bound to 8 bismuth atoms at the distance of 3·32 Å.

$ThBi_2$

The compound $ThBi_2$ (35·70% Th) is tetragonal with

$$a_1 = 4{\cdot}492,\ a_3 = 9{\cdot}298 \text{ Å},\ a_3/a_1 = 2{\cdot}070,\ Z = 2,\ \varrho = 11{\cdot}50 \text{ g.cm.}^{-3}.$$

The structure corresponds to the $C38$ type (*Strukturbericht*, 1937) with:

Space group No. 129 (*International Tables*, 1952): $P4/nmm$.

Atomic positions:

2 Bi_I in (a) $0,0,0;\ \frac{1}{2},\frac{1}{2},0$.
2 Bi_{II} in (c) $0,\frac{1}{2},x;\ \frac{1}{2},0,\bar{x}$ with $x = 0{\cdot}63$.
2 Th in (c') $0,\frac{1}{2},t;\ \frac{1}{2},0,\bar{t}$ with $t = 0{\cdot}28$.