$$I_j=(A-g)+(B\delta-k)j+C\delta^2j^2\,, \qquad (151)$$

with its peak displaced from $-B/2\delta C$ to

$$x_m=-(B-k/\delta)/2\delta C\,. \qquad (152)$$

The variance of its position is thus increased by

$$\sigma^2_{\rm ft}(k/2\delta^2C)\sim g/2pR^2\delta^4C^2\tau \qquad (153)$$

for fixed-time counting, and

$$\sigma^2_{\rm fc}(k/2\delta^2C)\sim g^2/2pcR^2\delta^4C^2 \qquad (154)$$

for fixed-count timing.

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A New Method for Obtaining Phase Angles of Structure Factors of Non-Centrosymmetric Structures by the Use of Anomalous Dispersion

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A method is described for finding the phases of structure factors by using the ratio $|F|^2/|\bar{F}|^2$ instead of the Bijvoet difference $|F|^2-|\bar{F}|^2$. The influence of errors of measurement is pointed out and a comparison with the method of Bijvoet differences is made.

Introduction and theory

It is possible to obtain the phases of structure factors by making use of the effects of anomalous dispersion. The method is based on experimental measurements of the Bijvoet differences $|F|^2-|\bar{F}|^2$ between pairs of inverse reflexions hkl and $\bar{h}\bar{k}\bar{l}$ produced by the imaginary component $\Delta f''$ of the scattering factor (Ramachandran, 1964). In order to avoid difficulties and errors of measurement in the determination of the scale factor and the absorption-correction a new method is proposed, which uses the ratios $|F|^2/|\bar{F}|^2$ instead of the differences $|F|^2-|\bar{F}|^2$. If the irradiated volume of the crystal has an inversion centre, there is an immediate connexion between the direct measurable intensities S, $\bar{S}$, and the ratio $|F|^2/|\bar{F}|^2$. This connexion is given by $|F|^2/|\bar{F}|^2=S/\bar{S}$. Supposing the crystal contains only one kind of atom, for which the imaginary component of the scattering factor is significant, whereas for all the other atoms this component is negligible, we get by simple geometrical considerations (Fig. 1) the following equation (Unangst, 1965):

$$\frac{S(\lambda_m)}{\bar{S}(\lambda_m)}=\frac{|F_N(\lambda_m)|^2}{|\bar{F}_N(\lambda_m)|^2}=1-\frac{4\dfrac{|F_P^0|}{|F_N^0|f_P^0}\,\Delta f''(\lambda_m)\sin\alpha}{1+2\dfrac{|F_P^0|}{|F_N^0|f_P^0}\,[\Delta f'(\lambda_m)\cos\alpha+\Delta f''(\lambda_m)\sin\alpha]+\left[\dfrac{|F_P^0|}{|F_N^0|f_P^0}\right]^2[\Delta f'^2(\lambda_m)+\Delta f''^2(\lambda_m)]}\,. \qquad (1)$$

Taking the following abbreviations

$$a_m=\frac{\Delta f''(\lambda_m)}{f_P^0} \qquad b_m=\frac{\Delta f'(\lambda_m)}{f_P^0} \qquad c_m=a_m^2+b_m^2$$

$$f_P(\lambda_m)=f_P^0+\Delta f'(\lambda_m)+i\Delta f''(\lambda_m) \qquad v=\frac{|F_P^0|}{|F_N^0|}$$

$$\eta_m=\frac{|F_N(\lambda_m)|^2+|\bar{F}_N(\lambda_m)|^2}{|F_N(\lambda_m)|^2-|\bar{F}_N(\lambda_m)|^2}=\frac{S(\lambda_m)+\bar{S}(\lambda_m)}{S(\lambda_m)-\bar{S}(\lambda_m)}$$

we get

$$\eta_m=\frac{1+2vb_m\cos\alpha+v^2c_m}{-2va_m\sin\alpha}$$

or

$$v=\frac{-1}{c_m}[a_m\eta_m\sin\alpha+b_m\cos\alpha \pm\sqrt{(a_m\eta_m\sin\alpha+b_m\cos\alpha)^2-c_m}]\,. \qquad (2)$$

The ambiguity in respect of the sign of the square root can be resolved by using the independence of λ of the ratio $v=|F_P^0|/|F_N^0|$. From this it follows that

$$\operatorname{sign}\sqrt{\ }\neq\operatorname{sign}(a_m\eta_m\sin\alpha+b_m\cos\alpha)\,.$$

As α and v are unknowns and equation (2) is quadratic and transcendental, it is necessary to measure the intensities S, $\bar{S}$ at two or more different wave-lengths $(\lambda_m, \lambda_n \ldots)$ within the anomalous-dispersion region. In this way, it is very troublesome to calculate the unknowns α and v unequivocally.

Now

$$|a_m\eta_m \sin\alpha + b_m \cos\alpha| \gg c_m \tag{3}$$

except for a small region in the neighbourhood of $\alpha = n\pi$. However, in such a case the anomalous-dispersion method is anyhow not useful. With the condition (3) equation (2) reduces to

$$v = -(a_m\eta_m \sin\alpha + b_m \cos\alpha)^{-1}$$

and

$$\tan\alpha = \frac{\Delta f'(\lambda_n) - \Delta f'(\lambda_m)}{\Delta f''(\lambda_m)\eta_m - \Delta f''(\lambda_n)\eta_n}$$

The ambiguity in respect of α yields two values of $v = |F_P^0|/|F_N^0|$. These two values differ only in the sign of v; thus the attribute $v > 0$ leads to a unique solution.

As the contributions of the L-, M-... shells generally are not negligible, there are often anomalous scatterers of different atomic numbers in the unit cell. If the positions of the anomalous scatterers are known, similar considerations as above for anomalous scatterers of two different kinds give an analogous expression (Müller, 1966):

$$\tan\alpha = \frac{e_n - e_m}{g_n - g_m}$$

where (Fig. 2)

$$e_i = |F'_R(\lambda_i)| + |F'_P(\lambda_i)| \cos\varphi + |F''_P(\lambda_i)|\eta_i \sin\varphi$$
$$g_i = |F'_P(\lambda_i)| \sin\varphi - |F''_R(\lambda_i)|\eta_i - |F''_P(\lambda_i)|\eta_i \cos\varphi\,.$$

The ambiguity of α can be resolved in the same manner as above. For example, the calculated phase-angles of some structure factors of cadmium sulphide ($P6_3mc$) were in a good agreement with the measured values. The deviations of about 6·5° lay within the error of measurement of about ±20°. These values were obtained by using film and Cr $K\alpha$, Fe $K\alpha$, Cu $K\alpha$ and Cu $K\beta$ radiation (Müller, 1966).

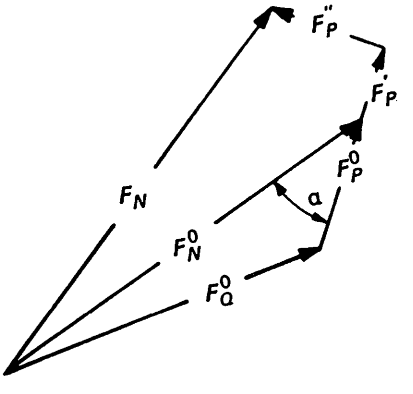

Fig. 1. Vector components of the structure factor in the case of anomalous scatterers of the same atomic number. $F_Q{}^0$: non-anomalous vector (Raman, 1960) (arises from the non-anomalous scatterers). $F_P{}^0$: normal vector (arises from the normal scattering of the anomalous scatterers). F_P': anomalous real vector (arises from the real part correction of the atomic scattering factor of the anomalous scatterers). F_P'': anomalous imaginary vector (arises from the imaginary component of the atomic scattering factor). $F_N{}^0$: normal structure factor. F_N: anomalous structure factor.

Influence of errors of measurement

In connexion with measurements it is important to know in which way the errors of measurement operate with regard to the accuracy of the phase-angle α. Though in products and sums

$$S(\lambda_m) \simeq S(\lambda_n) \simeq \bar{S}(\lambda_m) \simeq S$$

and in differences

$$S(\lambda_m) - \bar{S}(\lambda_m) \simeq 4Sv \sin\alpha \,.\, \Delta f''(\lambda_m)/f_P^0$$

is used a circumstantially applicable expression arises, even in the case of one kind of anomalous scatterer:

$$|\Delta\alpha| \simeq \frac{\frac{1}{4}\left|\frac{\Delta S}{S}\right| \left(\frac{|F_N^0| f_P^0}{|F_P^0|}\right)^2 |\Delta_1(f',f'')|}{1 + \frac{|F_P^0|}{|F_N^0| f_P^0}\Delta_2(f',f'')\cos\alpha + \frac{1}{4}\left[\frac{|F_P^0|}{|F_N^0| f_P^0}\Delta_2(f',f'')\right]^2} \tag{4}$$

where

$$\Delta_1(f',f'') = \frac{\Delta f''(\lambda_n) + \Delta f''(\lambda_m)}{\Delta f''(\lambda_n)\Delta f''(\lambda_m)[\Delta f'(\lambda_m) - \Delta f'(\lambda_n)]}$$

and

$$\Delta_2(f',f'') = \frac{\Delta f'^2(\lambda_m) - \Delta f'^2(\lambda_n) + \Delta f''^2(\lambda_m) - \Delta f''^2(\lambda_n)}{\Delta f'(\lambda_n) - \Delta f'(\lambda_m)}.$$

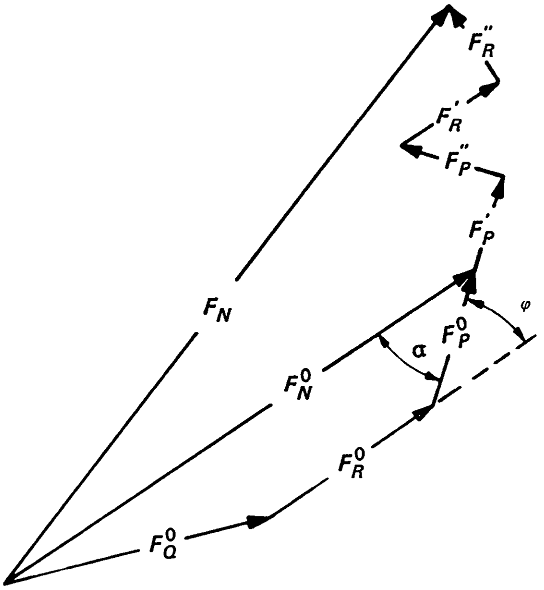

Fig. 2. Vector components of the structure factor in the case of anomalous scatterers of two different atomic numbers. The indices P and R designate the corresponding terms of the two kinds of anomalous scatterer (Fig. 1).

To get an idea of the magnitude of $\Delta\alpha$, the terms $\Delta_1(f',f'')$ and $\Delta_2(f',f'')$ were computed for some atomic numbers, using the results of Saravia & Caticha-Ellis (1966) and the formulae of Parrat & Hempstead (1954). The results are presented as contour maps in Figs. 3 and 4. For example, these contour maps show for Zn ($Z=30$) and $\lambda_n=0{\cdot}71$ Å (Mo $K\alpha$), $\lambda_m=1{\cdot}54$ Å (Cu $K\alpha$) the values $\Delta_1(f',f'')\simeq 0{\cdot}9$ and $\Delta_2(f'f'')\simeq 0{\cdot}9$. So we get for the 533 reflexion of zinc sulphide ($F\bar{4}3m$) $|\Delta\alpha|\simeq 0{\cdot}8$, accepting an error of measurement of $|\Delta S/S|=0{\cdot}02$.

If $|F_N^0|f_P^0/|F_P^0|\gg 1$ or $\ll 1$ the difficultly usable expression (4) may be reduced as follows

$$|\Delta\alpha|<\tfrac{1}{4}\left|\frac{\Delta S}{S}\right|\left(\frac{|F_N^0|f_P^0}{|F_P^0|}\right)^2|\Delta_1(f',f'')|\ ;\quad \frac{|F_N^0|f_P^0}{|F_P^0|}\gg 1. \quad (5)$$

or

$$|\Delta\alpha|<\left|\frac{\Delta S}{S}\right|\left(\frac{|F_N^0|f_P^0}{|F_P^0|}\right)^4\left|\frac{\Delta_1(f',f'')}{\Delta_2^2(f',f'')}\right|\ ;\quad \frac{|F_N^0|f_P^0}{|F_P^0|}\ll 1. \quad (6)$$

These expressions consist of three terms. The first term depends on the error of measurement, the second term shows the influence of structure, and the third term states the dependence on the two wave-lengths utilized. With this the value of $|\Delta\alpha|$ of the mentioned 533 reflexion is about 0·85, in good agreement with the result obtained by formula (4). Especially in some cases, it is possible to use the $K\alpha$ and $K\beta$ radiation of the same element. For instance, the 135 reflexion of potassium bromate ($R3m$) with Mo $K\alpha$ and Mo $K\beta$ radiation (anomalous scatterer: Br, $|F_N^0|f_P^0/|F_P^0|=6{\cdot}8$, $\Delta_1(f',f'')=2{\cdot}7$) yields $|\Delta\alpha|<0{\cdot}6$.

In this connexion it is also interesting to compare the ratio method with the technique of Bijvoet differences. In this case the same simplifications as above yield

$$|\Delta\alpha|=\left(\left|\frac{\Delta\sigma}{\sigma}\right|+\left|\frac{\Delta S}{S}\right|\right)\times\left[\frac{|F_N^0|f_P^0}{|F_P^0|}\,\frac{1}{|\Delta f'(\lambda_m)\sin\alpha|}+\frac{|\cot\alpha|}{2}\right] \quad (7)$$

for the equation for $|F|^2+|\bar{F}|^2$ and $\cos\alpha$ (Raman, 1960, equation 12) and

$$|\Delta\alpha|=\left(\left|\frac{\Delta\sigma}{\sigma}\right|+\left|\frac{\Delta S}{S}\right|\right)\times\left[\frac{|F_N^0|f_P^0}{|F_P^0|}\,\frac{1}{|\Delta f''(\lambda_m)\,.\,2\cos\alpha|}+|\tan\alpha|\right] \quad (8)$$

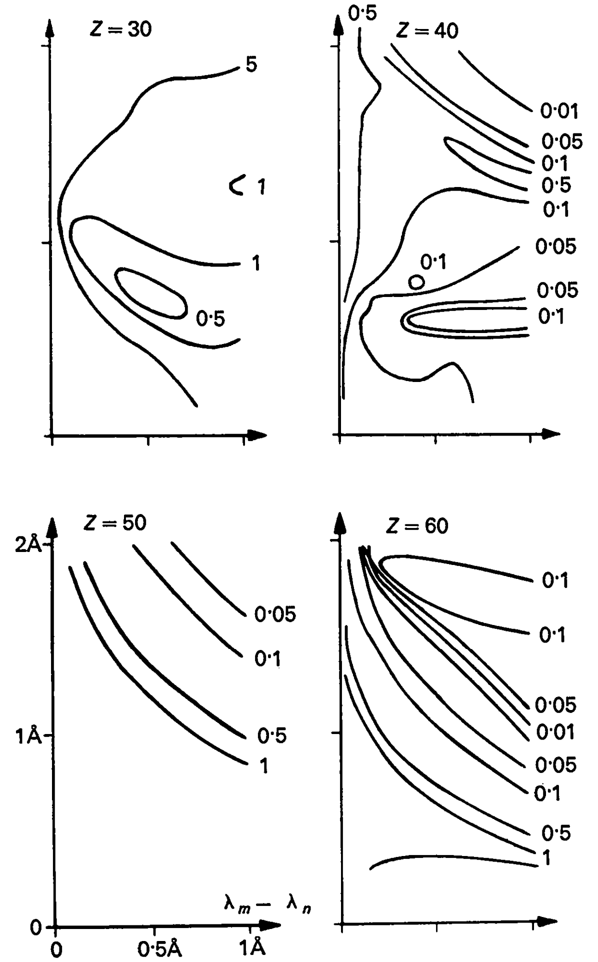

Fig. 3. Contour maps of $\Delta_1(f',f'')$ for some atomic numbers Z.

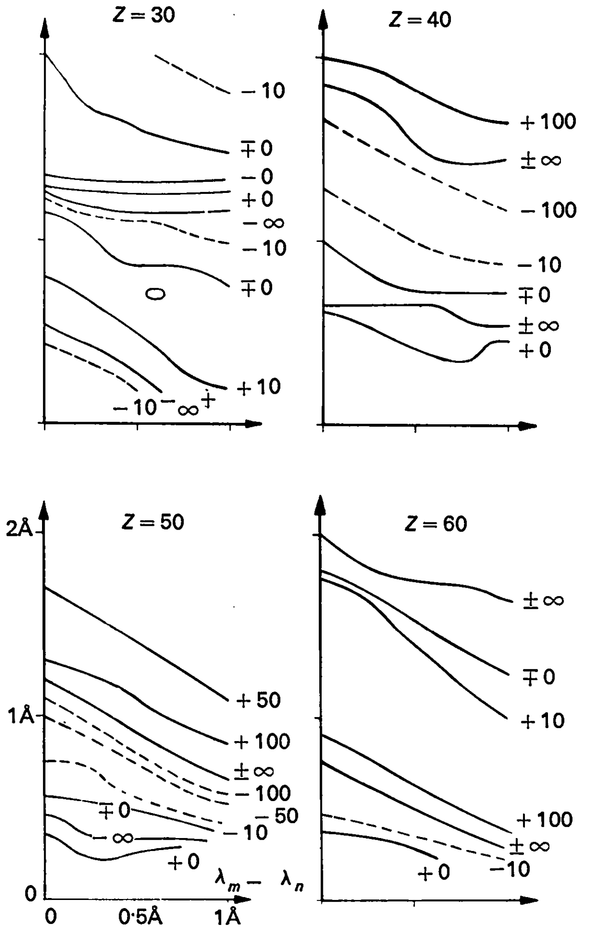

Fig. 4. Contour maps of $\Delta_2(f',f'')$ for some atomic numbers Z.

for the expression for $|F|^2-|\bar{F}|^2$ and $\sin\alpha$ (Raman, 1960, equation 11). $\sigma=|F|^2/S$ is the factor including the absorption correction, scale factor *etc.*

Comparison of equations (7) and (8) with equations (5) and (6) shows the superiority of the ratio method except for values of $|F_N^0|f_P^0/|F_P^0|$ which are very much greater than 1. Frequently $|F_N^0|f_P^0/|F_P^0|$ is less than or of the order of 1, if there are many normal scatterers and only few anomalous scatterers in the molecule, as for example in organic molecules with 'heavy atoms'.

Moreover, comparison of equation (7) with equation (8) suggests that preference should be given to the results obtained by Raman's equation (12) (Raman, 1960) if $\alpha\simeq(2n+1)\pi/2$, and Raman's equation (11) if $\alpha\simeq n\pi$.

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High-Temperature Phase Transitions in $SrZrO_3$

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Differential thermal analysis of samples of strontium zirconate up to 1000°C shows peaks which indicate phase transitions during heating at 730 and 860°C. A high-temperature X-ray investigation revealed that the peaks correspond to crystallographic transformations. The orthorhombic form found at room temperature exists up to 700°C, at which temperature a tetragonal modification with $c/a<1$ is formed. At 830°C another tetragonal modification is formed but with $c/a>1$. This exists up to 1170°C where it transforms to a cubic form. A few very faint 'extra' lines in the diffraction patterns are observed even at the highest temperatures where the structure is cubic. This indicates that the true unit cells of the zirconate in the high-temperature phases are multiples of the simple small-cell perovskite. It is found that the 'extra' lines could be satisfactorily indexed on the basis of a unit cell containing 8 formula units where the axes of the true unit cell are twice the cell-edges of the ideal small-cell.

Introduction

Strontium zirconate is a ceramic substance which belongs to the group of perovskites and has a melting point of *ca.* 2800°C. Funk, Nemeth & Tinklepaugh (1964) found that polycrystalline specimens of $SrZrO_3$ exhibited a measurable amount of mechanical yield or deformation at room temperature. They therefore investigated its thermal behaviour by dilatometry and X-ray analysis; the results were interpreted as indicating a possible phase transition between 850 and 1000°C. Krainik (1958) examined the dielectric constant for the system $PbZrO_3$–$SrZrO_3$ from room temperature up to 450°C. He did not investigate higher molecular concentrations of $SrZrO_3$ than 30% and found that there existed five different phases for concentrations above 10%, one of which disappeared at about 30% $SrZrO_3$ at room temperature. Krainik considered it possible to extrapolate the phase diagram to higher molecular concentrations of $SrZrO_3$ and suggested that two high-temperature transitions would be found for pure $SrZrO_3$, one of them at *ca.* 700°C.

Our attempts to grow single crystals of $SrZrO_3$ both by a flux-method and the Verneuil method with plasma heating, proved it to be difficult to obtain crystals larger than of millimetre dimensions. These were also of poor quality and showed a high degree of twinning which may indicate phase transitions during cooling. An investigation with differential thermal analysis showed two peaks between room temperature and 1000°C which suggested the occurrence of phase transitions. It was therefore decided to carry out high-temperature investigations up to 1300°C, this being the highest temperature at which available equipment could be used.

Structure

At room temperature the structure of $SrZrO_3$ is orthorhombic, as Roth (1957) was the first to point out. Earlier publications by *e.g.* Zachariasen (1928), Hoffman (1935) and Megaw (1946) considered the structure to be cubic with one formula unit per unit cell and with a unit-cell edge of *ca.* 4·09 Å. The orthorhombic structure was verified by Swanson, Cook, Isaacs &