metric grey part, the symmetry of the former being represented by a certain black-and-white space group. In such a case Friedel's law breaks down.

In a structure as treated in the present paper, the black and white vectors as a whole form a complete 'grey' set as in a centrosymmetric crystal. In fact, if Friedel's law holds, $P_s$ must vanish over the entire range of **u**, and this means that each black vector must have its own white mate with the same magnitude and direction and sense. Such a circumstance can be seen, for example, by inspection of Figs. 1 and 2. In summarizing, Friedel's law holds for any crystal involving two kinds of anomalous scatterers, if the symmetry of a black-and-white vector set as defined above is represented by a certain 'grey' space group.

## Conclusion

It has been shown that Friedel's law may hold in certain non-centrosymmetric structures other than crystals of elements, even with the anomalous dispersion. For such a crystal, if one exists, the absolute configuration cannot be determined by the conventional X-ray absorption-edge techniques. The point group of such a crystal cannot be detected by a statistical treatment of intensity differences between possible Bijvoet pairs (Ibers, 1967). No structure of this type seems so far to have been recorded, though one may be found in future.

It should be noted that the condition (6-3) is always satisfied for reflexions with some special indices, if the *xyz* parameters of all atoms, as well as the three components of **u**, are certain rational fractions of the cell edges. For example, the well known zinc-blende structure (space group $F\bar{4}3m$) consists of two geometrically identical substructures with $\mathbf{u}=(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. Thus, the relation (6-3) holds if indices *hkl* are all even. The centric intensity distribution in these reflexions, in part, arises entirely from the special arrangement of atoms or of substructures. A partial Friedel's law of this type, not as a result of the space-group symmetry, is quite common in a number of crystals of inorganic compounds.

In connexion with this it should be added also that Friedel's law may hold to a very good approximation in several non-centrosymmetric molecular crystals. Practically this problem is sometimes important. Consider a crystal containing atoms of a large atomic number and non-anomalous light atoms. When the heavy atoms are arranged with a certain kind of symmetry higher than that of the crystal, they contribute only to reflexions with certain special indices according to the local symmetry. In such a case, these reflexions often exhibit pseudocentric patterns owing to the large contribution of heavy atoms to diffracted intensities, whereas other reflexions show partially centrosymmetric diffraction patterns. In a 'pseudo-Friedel' case of this type, some difficulties may occur in the determination of the absolute configuration.

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# Systematic Errors in Polarization Corrections for Crystal-Monochromatized Radiation

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The polarization expressions for crystal-monochromatized radiation have been evaluated for both molybdenum and copper radiations under a variety of conditions in order to show the magnitude of the systematic error introduced by the use of an inappropriate expression. The effect of the polarization expression on the extinction correction is also discussed.

The expression for the polarization correction for crystal-monochromatized radiation is well known for the case of the double-crystal spectrometer. In this geometry, hereinafter referred to as 'normal' geometry, the monochromator crystal lies in the equatorial plane of a three- or four-circle diffractometer with its rotation axis perpendicular to the equatorial plane. The beam incident on the monochromator crystal is randomly polarized and thus can be represented as the sum of two equal components polarized parallel ($\chi=90°$) and perpendicular ($\chi=0°$) to the equatorial plane of the diffractometer. The relative intensities of the components are:

$$I_{\parallel}=I_{\perp}=\tfrac{1}{2}I_0 .$$

Since the intensity of radiation diffracted in a particular direction is proportional to $\sin^2\varphi$, where $\varphi$ is the angle between the electric vector and the direction of observation, it follows that the relative intensities of the two components after reflexion at an angle of $\theta_m$ from the monochromator crystal will be $I_\parallel = \frac{1}{2}I_0 \sin^2(90-2\theta_m) = \frac{1}{2}I_0 \cos^2 2\theta_m$ and $I_\perp = \frac{1}{2}I_0 \sin^2 90° = \frac{1}{2}I_0$. In this geometry the component that was attenuated by reflexion from the monochromator crystal is attenuated again by reflexion from the sample crystal so that the polarization correction for the twice-reflected beam becomes

$$p = \frac{1+\cos^2 2\theta_m \cos^2 2\theta}{1+\cos^2 2\theta_m}\,. \tag{1}$$

This expression applies only when the monochromator crystal is mounted with its axis of rotation perpendicular to the equatorial plane of the diffractometer so that the incident beam, the beam reflected by the monochromator and the beam reflected by the sample crystal all lie in the same plane.

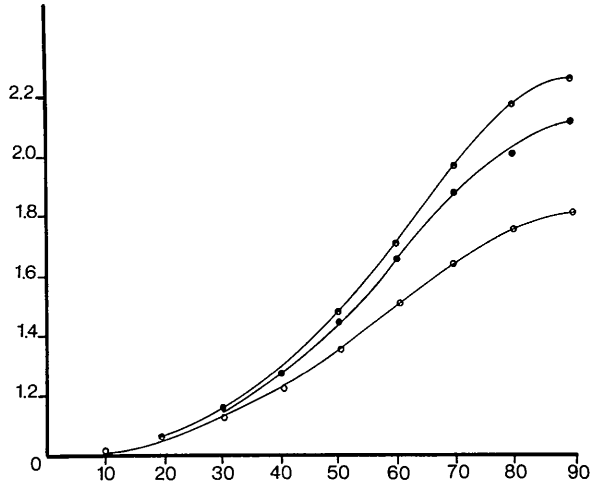

Fig. 1. Plot of $1/p$ for quartz or graphite with Cu radiation. Picker geometry; imperfect crystal —◐—◐—◐. Picker geometry; perfect crystal —●—●—●. 'Normal' geometry; imperfect crystal —○—○—○—.

In many diffractometers, these conditions do not obtain. In one of the more common designs, first available on the Picker diffractometer, the incident-beam monochromator crystal is mounted with its rotation axis parallel to the equatorial plane. The actual radiation source lies above that plane. In the reflexion from the monochromator crystal the component of the beam normal to the equatorial plane ($\chi = 0°$) is attenuated by the factor $\cos^2 2\theta_m$. The parallel ($\chi = 90°$) component is attenuated by reflexion from the sample. For this geometry, hereinafter referred to as Picker geometry, the correct expression for the polarization factor is (Azároff, 1955)

$$p = \frac{\cos^2 2\theta_m + \cos^2 2\theta}{1+\cos^2 2\theta_m}\,. \tag{2}$$

In these two equations for the polarization correction it is assumed that both the monochromator crystal and the sample crystal are ideally imperfect with diffracted intensity proportional to $F^2$. This is probably a reasonable approximation if the monochromator is a single crystal of graphite, but a rather poor approximation in the case of quartz or LiF. When the monochromator crystal approximates to a perfect crystal, a more appropriate expression would be

$$p = \frac{1+|\cos 2\theta_m| \cos^2 2\theta}{1+|\cos 2\theta_m|} \tag{3}$$

for 'normal' geometry, (Arndt & Willis, 1966), or

$$p = \frac{|\cos 2\theta_m| + \cos^2 2\theta}{1+|\cos 2\theta_m|} \tag{4}$$

in the case of the Picker diffractometer.

Table 1 shows the value of $1/p$ as a function of $2\theta$

Table 1. *Values of* $1/p$ *as a function of* $2\theta$ *for* Mo (*upper line*) *and* Cu (*lower line*) *radiations*

| | Quartz or graphite | | | | LiF | | | |
|---|---|---|---|---|---|---|---|---|
| $2\theta$(°) | Normal Imperfect | Picker Imperfect | Normal Perfect | Picker Perfect | Normal Imperfect | Picker Imperfect | Normal Perfect | Picker Perfect |
| 10 | 1·014956 | 1·015660 | 1·015132 | 1·015484 | 1·014314 | 1·016303 | 1·014810 | 1·015806 |
| | 1·013581 | 1·017041 | 1·014441 | 1·016176 | 1·010154 | 1·020514 | 1·012649 | 1·017981 |
| 20 | 1·060629 | 1·063620 | 1·061375 | 1·062871 | 1·057917 | 1·066362 | 1·060013 | 1·064240 |
| | 1·054829 | 1·069517 | 1·058452 | 1·065818 | 1·040578 | 1·084578 | 1·050923 | 1·073563 |
| 30 | 1·139169 | 1·146569 | 1·141010 | 1·144710 | 1·132504 | 1·153401 | 1·137652 | 1·148110 |
| | 1·124971 | 1·161321 | 1·133816 | 1·152044 | 1·090917 | 1·199990 | 1·115520 | 1·171568 |
| 40 | 1·252986 | 1·267860 | 1·256671 | 1·264109 | 1·239723 | 1·281736 | 1·249955 | 1·270979 |
| | 1·224883 | 1·297994 | 1·242322 | 1·278969 | 1·159738 | 1·380147 | 1·206490 | 1·319308 |
| 50 | 1·402058 | 1·428696 | 1·408623 | 1·421943 | 1·378618 | 1·453886 | 1·396676 | 1·434329 |
| | 1·352734 | 1·483828 | 1·383190 | 1·448836 | 1·243200 | 1·642576 | 1·321142 | 1·523798 |
| 60 | 1·578537 | 1·622054 | 1·589195 | 1·610953 | 1·540839 | 1·663886 | 1·569832 | 1·631350 |
| | 1·499844 | 1·714489 | 1·548148 | 1·655445 | 1·333370 | 1·999919 | 1·450687 | 1·783576 |
| 70 | 1·759033 | 1·823208 | 1·774647 | 1·806731 | 1·704326 | 1·885954 | 1·746328 | 1·837061 |
| | 1·645746 | 1·963284 | 1·714870 | 1·873209 | 1·417163 | 2·431063 | 1·576722 | 2·071462 |
| 80 | 1·900903 | 1·983780 | 1·920963 | 1·962393 | 1·831138 | 2·065921 | 1·884628 | 2·001820 |
| | 1·757325 | 2·168693 | 1·844522 | 2·049147 | 1·477778 | 2·829156 | 1·671508 | 2·315395 |
| 90 | 1·955682 | 2·046373 | 1·977590 | 2·022924 | 1·879713 | 2·136735 | 1·937930 | 2·066178 |
| | 1·799701 | 2·250467 | 1·894260 | 2·118243 | 1·500061 | 2·999756 | 1·707150 | 2·414127 |

for three different monochromators and two radiations. A comparison of values shows that very large systematic errors can be introduced by using an inappropriate expression for the polarization correction. For instance, if the 'normal' equation (1) were used in place of the Picker expression (2) for Cu $K\alpha$ with a graphite monochromator, the maximum error introduced would be of the order of 20% in $F^2$. This error would be of the order of 10% for a quartz monochromator if equation (3) were used in place of (4). Fig. 1 is a graphical comparison of the expressions for 'normal' and Picker geometry for Cu $K\alpha$ radiation and a monochromator angle of $2\theta_m = 26{\cdot}6°$, typical of graphite or quartz. In the case of a LiF crystal, the larger monochromator angle ($2\theta_m = 45{\cdot}0°$) makes discrepancies between the expressions even larger. As can be seen in Fig. 2, the maximum error introduced by use of the wrong geometry is 50% in $F^2$ for a LiF monochromator.

In these comparisons we have assumed that monochromators diffract as ideal crystals, although the literature clearly shows this assumption to be false (Miyake, Togawa & Hosoya, 1964; Jennings, 1968; Hope, 1971). Fig. 3 shows how important it is to have some information about the actual degree of perfection of the crystal. In the case of LiF and copper radiation, the ratio $p_{\text{perf}}/p_{\text{imp}}$ for a particular reflexion can be as high as 1·24. In the case of quartz or graphite, the effect is substantially smaller, but still significant for copper radiation. However, with molybdenum radiation the effect will be negligible for most experiments since the difference between the polarization corrections at $2\theta = 60°$ is only about 3% for LiF and about 1% for quartz or graphite with Picker geometry.

It should be noted that the calculation of an extinction parameter assumes some functional form for the polarization correction. Zachariasen† (1963) has shown that

$$F_{\text{corr}} = KF_{\text{obs}}[1 + \beta(2\theta)CJ_{\text{obs}}] \qquad (\text{Z. } 14)$$

where $\beta(2\theta)$ is an expression for the angular variation of the extinction parameter and contains the factor $P_2/P_1^2$. This ratio has the form

$$\frac{M + N\cos^2 2\theta}{(M+N)^2}$$

where $M$ is the polarization factor for the component of the beam perpendicular to the equatorial plane of the diffractometer and $N$ is the corresponding factor for the parallel component. For filtered radiation, $M = \frac{1}{2}$ and $N = \frac{1}{2}\cos^2 2\theta$ and

$$\beta(2\theta) = \frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2} \cdot \frac{A^{*\prime}(2\theta)}{A^{*\prime}(0)} \cdot \qquad (\text{Z. } 15)$$

When a monochromator is used with 'normal' geometry

$$M = \frac{\cos^2 2\theta_m \cos^2 2\theta}{(1+\cos^2 2\theta_m)}\ ; \quad N = \frac{1}{1+\cos^2 2\theta_m}\ ;$$

and

$$\beta(2\theta) = \frac{(1+\cos^2 2\theta_m)\,(1+\cos^2 2\theta_m \cos^4 2\theta)}{(1+\cos^2 2\theta_m \cos^2 2\theta)^2} \cdot \frac{A^{*\prime}(2\theta)}{A^{*\prime}(0)} \cdot \qquad (\text{Z. } 15a)$$

In these expressions $A^{*\prime}(2\theta)$ is the value of $\mathrm{d}A^*/\mathrm{d}\mu$ at $2\theta$, $A^{*\prime}(0)$ is the value at $2\theta = 0$ and $A^*$ is the absorption factor, $A^{-1}$.

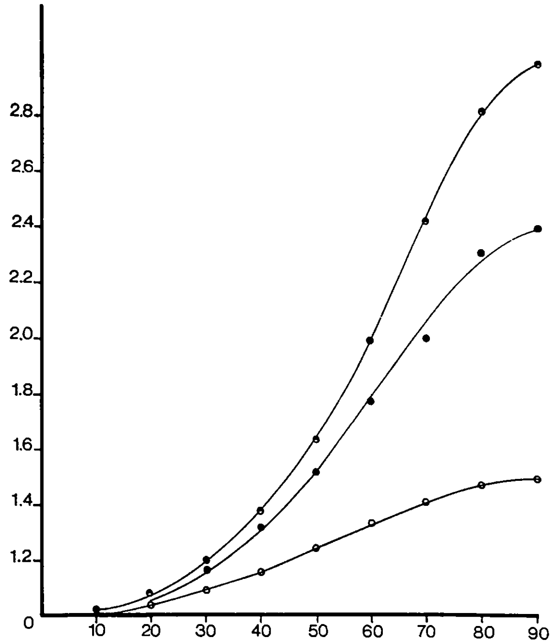

Fig. 2. Plot of $1/p$ for LiF with Cu radiation. Picker geometry; imperfect crystal —◓—◓—◓. Picker geometry; perfect crystal —●—●—●—. 'Normal' geometry; imperfect crystal —○—○—○.

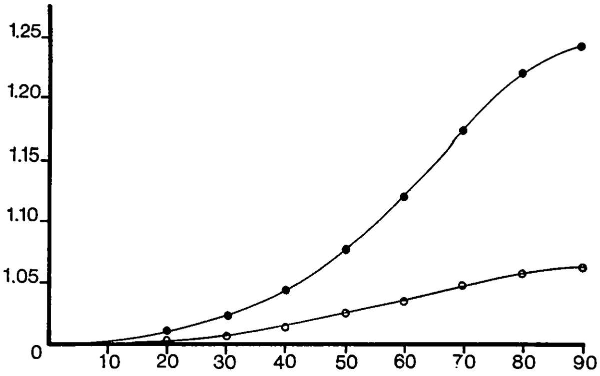

Fig. 3. The ratio of polarization factors for Picker geometry $P^{-1}$ imperfect/$P^{-1}$ perfect. LiF and Cu radiation —●—●—. Quartz or graphite and Cu radiation —○—○—.

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† Equations taken from Zachariasen (1963) are indicated by the letter Z preceeding the equation number used in that paper.

Table 2. *A comparison of the various functional forms of* $\beta(2\theta)$ *for both* Mo (*upper line*) *and* Cu (*lower line*) *radiations*

| | Quartz or graphite | | | | | LiF | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $2\theta$(°) | Filter | Normal Imperfect | Picker Imperfect | Normal Perfect | Picker Perfect | Filter | Normal Imperfect | Picker Imperfect | Normal Perfect | Picker Perfect |
| 10 | 1·000234 | 1·000234 | 1·000234 | 1·000234 | 1·000234 | 1·000234 | 1·000233 | 1·000234 | 1·000234 | 1·000234 |
| | 1·000234 | 1·000231 | 1·000232 | 1·000233 | 1·000234 | 1·000234 | 1·000206 | 1·000210 | 1·000226 | 1·000229 |
| 20 | 1·003859 | 1·003846 | 1·003868 | 1·003853 | 1·003864 | 1·003859 | 1·003813 | 1·003874 | 1·003840 | 1·003871 |
| | 1·003859 | 1·003759 | 1·003865 | 1·003821 | 1·003874 | 1·003859 | 1·003293 | 1·003577 | 1·003667 | 1·003827 |
| 30 | 1·020408 | 1·020266 | 1·020530 | 1·020340 | 1·020472 | 1·020408 | 1·019958 | 1·020701 | 1·020202 | 1·020575 |
| | 1·020408 | 1·019529 | 1·020812 | 1·020024 | 1·020673 | 1·020408 | 1·016530 | 1·020000 | 1·018871 | 1·020815 |
| 40 | 1·067797 | 1·066970 | 1·068569 | 1·067390 | 1·068190 | 1·067797 | 1·065325 | 1·069827 | 1·066612 | 1·068872 |
| | 1·067797 | 1·063239 | 1·071014 | 1·065663 | 1·069594 | 1·067797 | 1·051026 | 1·072265 | 1·060296 | 1·072099 |
| 50 | 1·172434 | 1·169147 | 1·175636 | 1·170801 | 1·174046 | 1·172434 | 1·162953 | 1·181232 | 1·167765 | 1·176932 |
| | 1·172434 | 1·155585 | 1·187202 | 1·164196 | 1·180152 | 1·172434 | 1·118278 | 1·206477 | 1·145842 | 1·194016 |
| 60 | 1·360000 | 1·350227 | 1·369803 | 1·355108 | 1·364899 | 1·360000 | 1·332502 | 1·387728 | 1·346197 | 1·373862 |
| | 1·360000 | 1·312422 | 1·408243 | 1·335995 | 1·384182 | 1·360000 | 1·222243 | 1·499980 | 1·287235 | 1·434184 |
| 70 | 1·624962 | 1·602848 | 1·647638 | 1·613835 | 1·636230 | 1·624962 | 1·563905 | 1·690499 | 1·593867 | 1·657180 |
| | 1·624962 | 1·521429 | 1·742055 | 1·571465 | 1·681868 | 1·624962 | 1·348007 | 2·024096 | 1·470350 | 1·811830 |
| 80 | 1·886342 | 1·849263 | 1·924931 | 1·867617 | 1·905445 | 1·886342 | 1·785246 | 1·999519 | 1·834356 | 1·941347 |
| | 1·886342 | 1·717194 | 2·092267 | 1·797549 | 1·984320 | 1·886342 | 1·456488 | 2·673110 | 1·637662 | 2·223556 |
| 90 | 2·000000 | 1·955682 | 2·046373 | 1·977590 | 2·022924 | 2·000000 | 1·879713 | 2·136735 | 1·937930 | 2·066178 |
| | 2·000000 | 1·799701 | 2·250467 | 1·894260 | 2·118243 | 2·000000 | 1·500061 | 2·999756 | 1·707150 | 2·414127 |

In the case of the Picker monochromator

$$M=\frac{\cos^2 2\theta_m}{1+\cos^2 2\theta_m}\,;\quad N=\frac{\cos^2 2\theta}{1+\cos^2 2\theta_m}\,;$$

and

$$\beta(2\theta)=\frac{(1+\cos^2 2\theta_m)\,(\cos^2 2\theta_m+\cos^4 2\theta)}{(\cos^2 2\theta_m+\cos^2 2\theta)^2}\cdot\frac{A^{*\prime}(2\theta)}{A^{*\prime}(0)}\,. \quad (5)$$

The corresponding expressions for a perfect monochromator crystal can be obtained by substituting $|\cos 2\theta_m|$ for $\cos^2 2\theta_m$.

The angular parts of these expressions have been evaluated. The results are presented in Table 2. It is clear that the differences are small for a graphite or quartz monochromator, but can become quite large in the case of copper radiation and a LiF crystal.

In summary, we have shown that very large systematic errors can arise through failure to consider the geometry of the monochromator or the state of perfection of the monochromator crystal. For molybdenum radiation and a monochromator with a small diffraction angle, $\theta_m$, the magnitude of the errors is small. However, if copper radiation is used, or if the monochromator has a large diffraction angle, as in the case of LiF, the error introduced by use of an inappropriate expression is too large to be ignored.

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