peratur die Anordnung der PF_6-Baugruppen nicht mehr statistisch erfolgt und vielleicht zu einer Überstruktur mit einer verdoppelten Achse Anlass gibt, doch konnte bisher nichts Dahingehendes beobachtet werden.

Der P–F-Abstand in der Säure beträgt 1,73 Å und ist somit grösser als in den Baugruppen bei den Salzen: beim KPF_6 beträgt dieser Wert nur 1,58 Å. Dieser grössere Abstand zwischen P und F weist darauf hin, dass die Bindung zwischen diesen Atomen geschwächt ist; dadurch lässt sich die leichte Hydrolysierbarkeit dieser Bindung in der Säure verstehen. Dem entspricht, dass allgemein das PF_6-Ion in saurer Lösung zur Zersetzung neigt, während es in alkalischer Lösung bemerkenswert stabil ist.

Diese 'Käfigstruktur' der Säure zeigt keine Analogie zu der Wasserhülle bei den Gashydraten (Stackelberg & Müller, 1951, 1952; Clausen, 1951), bei denen die Wassergerüste aus Fünf- und Sechsringen gebildet werden, wodurch sich andere stöchiometrische Zusammensetzungen ergeben, etwa $X.5\frac{3}{4}H_2O$.

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Factors Determining the Choice of X-ray Reflexions for the Study of the Elastic Properties of Certain Non-cubic Crystals

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The procedure necessary for the determination of the elastic constants of crystals belonging to the orthorhombic system is considered. It is shown that six of the nine elastic constants can be obtained from measurements which depend on only the particular elastic constant under consideration; the remaining constants can be found from measurements which depend on several elastic constants. In the cubic, tetragonal and hexagonal systems the constant c_{12} may be simply determined from a measurement depending only on $(c_{11}-c_{12})$. The relative accuracy with which the constants can be determined is also discussed.

Introduction

There are certain non-cubic crystals which have symmetries sufficiently high to make the determination of the elastic properties by using diffuse X-ray reflexions only slightly more difficult than with cubic crystals. Whereas in cubic crystals the elastic properties are defined by the matrix

$$\begin{array}{cccccc} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ & c_{11} & c_{12} & 0 & 0 & 0 \\ & & c_{11} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & & & & c_{44} & 0 \\ & & & & & c_{44}\,, \end{array}$$

in the orthorhombic system we have

$$\begin{array}{cccccc} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ & c_{22} & c_{23} & 0 & 0 & 0 \\ & & c_{33} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & & & & c_{55} & 0 \\ & & & & & c_{66}\,, \end{array}$$

in the hexagonal system

$$\begin{array}{cccccc} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ & c_{11} & c_{13} & 0 & 0 & 0 \\ & & c_{33} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & & & & c_{44} & 0 \\ & & & & & \frac{1}{2}(c_{11}-c_{12})\,, \end{array}$$

and in the tetragonal system, classes, 42, $\bar{4}2m$, $4mm$, $4/mmm$,

$$\begin{matrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ & c_{11} & c_{13} & 0 & 0 & 0 \\ & & c_{33} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & & & & c_{44} & 0 \\ & & & & & c_{66}\,. \end{matrix}$$

It will be seen that the zero-value elastic constants occur in the same position in each matrix. This fact makes it appropriate to treat all these classes of symmetry together.

The proper choice of diffuse reflexions

In principle any number of observations can be made on the intensity of diffuse X-ray reflexion and each observation depends on one or more elastic constants. It is always possible, therefore, to obtain a sufficient number of equations from which the constants can be determined, provided that the accuracy of observation is high enough. It is because of the limitation on the accuracy that consideration must be given to the choice of reflexion. Ramachandran & Wooster (1951) have pointed out that the optimum experimental conditions are obtained when the Bragg angle of the reflexion lies between 20° and 40° and when the intensity of the Bragg reflexion is large. It often happens that there is no plane of indices such as $h00$ or $0k0$ or $00l$ which satisfies both these conditions and recourse must be had to reflexions of the type $hk0$, $0kl$, $h0l$. Each observation of this kind involves at least two elastic constants, and this may make it more difficult to achieve a specified accuracy in the determination of the constants. Planes of the type hkl are not used because the diffuse reflexions involve such a large number of constants. The results derived in this paper have been used in a study of the elastic properties of tin which will be published later.

The *K* values for particular rekhas and relps

The intensity of diffuse X-ray scattering from a small element of volume lying along a line (rekha) passing through a given reciprocal-lattice point (relp) is proportional to the K value. The general expression for the K value has been given by Ramachandran & Wooster (1951) as follows:

$$\begin{aligned} K[ABC]_{hkl} = {} & P^2(A^{-1})_{11}+Q^2(A^{-1})_{22}+R^2(A^{-1})_{33} \\ & +2PQ(A^{-1})_{12}+2PR(A^{-1})_{13}+2QR(A^{-1})_{23}\,, \quad (1) \end{aligned}$$

where P, Q, R are the direction cosines of the rel-vector, hkl, with respect to the orthogonal coordinates used to define the rekha, and $(A^{-1})_{ij}$ are the elements of the matrix, A^{-1}, inverse to the matrix A_{ij}, whose elements are given by

$$\begin{aligned} A_{11} &= c_{11}u^2+c_{66}v^2+c_{55}w^2+2c_{56}vw+2c_{15}wu+2c_{16}uv\,, \\ A_{22} &= c_{66}u^2+c_{22}v^2+c_{44}w^2+2c_{24}vw+2c_{46}wu+2c_{26}uv\,, \\ A_{33} &= c_{55}u^2+c_{44}v^2+c_{33}w^2+2c_{34}vw+2c_{35}wu+2c_{45}uv\,, \\ A_{12} &= c_{16}u^2+c_{26}v^2+c_{45}w^2+(c_{25}+c_{46})vw+(c_{14}+c_{56})wu \\ &\quad +(c_{12}+c_{66})uv\,, \\ A_{13} &= c_{15}u^2+c_{46}v^2+c_{35}w^2+(c_{36}+c_{45})vw+(c_{13}+c_{55})wu \\ &\quad +(c_{14}+c_{56})uv\,, \\ A_{23} &= c_{56}u^2+c_{24}v^2+c_{34}w^2+(c_{23}+c_{44})vw+(c_{36}+c_{45})wu \\ &\quad +(c_{25}+c_{46})uv\,. \end{aligned}$$

In the orthorhombic system, using the matrix for c_{ik} given above, the evaluation of the A_{ik} leads to the following expressions:

$$\begin{aligned} A_{11} &= c_{11}u^2+c_{66}v^2+c_{55}w^2\,, \\ A_{22} &= c_{66}u^2+c_{22}v^2+c_{44}w^2\,, \\ A_{33} &= c_{55}u^2+c_{44}v^2+c_{33}w^2\,, \\ A_{12} &= (c_{12}+c_{66})uv\,, \\ A_{13} &= (c_{13}+c_{55})wu\,, \\ A_{23} &= (c_{23}+c_{44})vw\,. \end{aligned}$$

For the direction [100] we have

$$u = 1,\quad v = w = 0\,;$$

the components of the reciprocal matrix are

$$\begin{matrix} 1/c_{11} & 0 & 0 \\ & 1/c_{66} & 0 \\ & & 1/c_{55}\,. \end{matrix}$$

For the relps having indices $hk0$, which correspond to direction cosines P, Q, R, of the rel-vector, the K value is, from equation (1),

$$K[100]_{hk0} = P^2/c_{11}+Q^2/c_{66}\,.$$

When this method is applied to the most suitable relps and rekhas we obtain the values shown in Table 1. In the first half of the table the conditions for determining the c_{ik}'s for which $i = k$ are set out and in the second half the conditions for determining the c_{ik}'s for which $i \neq k$ are given.

In the second half of the table the K values are given for planes of the type $h00$, $0k0$, $00l$ only. The expressions for K values of $hk0$, $0kl$, $h0l$ planes are more involved, though the same elastic constants are present. These planes can be used when no suitable planes of indices $h00$, $0k0$, $00l$ are available. However, with an appropriate choice of wavelength it will seldom happen that planes of the type $hk0$, $0kl$, $h0l$ must be used.

The corresponding values in the hexagonal and tetragonal systems of symmetry may be obtained from Table 1 by substituting the appropriate suffixes to the c_{ik}'s. Thus, for instance, in the tetragonal system c_{22}, c_{23} and c_{55} must be replaced by c_{11}, c_{13} and c_{44} respectively, as is shown in the matrix in the first paragraph of this paper.

In the same tetragonal and hexagonal classes of

Table 1. *K values in the orthorhombic system*

Direction cosines of rekha (uvw)	Indices of relp hkl: $h00$	$0k0$	$00l$	$hk0$	$0kl$	$h0l$
100	$\frac{1}{c_{11}}$	$\frac{1}{c_{66}}$	$\frac{1}{c_{55}}$	$\frac{P^2}{c_{11}}+\frac{Q^2}{c_{66}}$	$\frac{Q^2}{c_{66}}+\frac{R^2}{c_{55}}$	$\frac{P^2}{c_{11}}+\frac{R^2}{c_{55}}$
010	$\frac{1}{c_{66}}$	$\frac{1}{c_{22}}$	$\frac{1}{c_{44}}$	$\frac{P^2}{c_{66}}+\frac{Q^2}{c_{22}}$	$\frac{Q^2}{c_{22}}+\frac{R^2}{c_{44}}$	$\frac{P^2}{c_{66}}+\frac{R^2}{c_{44}}$
001	$\frac{1}{c_{55}}$	$\frac{1}{c_{44}}$	$\frac{1}{c_{33}}$	$\frac{P^2}{c_{55}}+\frac{Q^2}{c_{44}}$	$\frac{Q^2}{c_{44}}+\frac{P^2}{c_{33}}$	$\frac{P^2}{c_{55}}+\frac{R^2}{c_{33}}$

Direction cosines of rekha (uvw)	Indices of relp hkl: $h00$	$0k0$	$00l$
$1/\sqrt{2}, 1/\sqrt{2}, 0$	$\frac{2(c_{22}+c_{66})}{\{c_{11}(c_{22}+c_{66})+c_{22}c_{66}-2c_{12}c_{66}-c_{12}^2\}}$	$\frac{2(c_{11}+c_{66})}{\{c_{11}(c_{22}+c_{66})+c_{22}c_{66}-2c_{12}c_{66}-c_{12}^2\}}$	$\frac{2}{c_{44}+c_{55}}$
$0, 1/\sqrt{2}, 1/\sqrt{2}$	$\frac{2}{c_{55}+c_{66}}$	$\frac{2(c_{33}+c_{44})}{\{c_{22}(c_{33}+c_{44})+c_{33}c_{44}-2c_{23}c_{44}-c_{23}^2\}}$,	$\frac{2(c_{22}+c_{44})}{\{c_{22}(c_{33}+c_{44})+c_{33}c_{44}-2c_{23}c_{44}-c_{23}^2\}}$
$1/\sqrt{2}, 0, 1/\sqrt{2}$	$\frac{2(c_{33}+c_{55})}{\{c_{11}(c_{33}+c_{55})+c_{33}c_{55}-2c_{13}c_{55}-c_{13}^2\}}$	$\frac{2}{c_{44}+c_{66}}$	$\frac{2(c_{11}+c_{55})}{\{c_{11}(c_{33}+c_{55})+c_{33}c_{55}-2c_{13}c_{55}-c_{13}^2\}}$

symmetry it is possible to find c_{12} very simply. On applying the usual formulae it will be found that the value of $K[1/\sqrt{2}, -1/\sqrt{2}, 0]_{hh0}$ is given by $2/(c_{11}-c_{12})$. The same result also occurs in the cubic system. This K value is, therefore, well suited to the determination of c_{12}.

The accuracy with which the elastic constants may be determined

It will be seen from Table 1 that the six constants for which the suffixes are equal, namely c_{11}, c_{22}, c_{33}, c_{44}, c_{55} and c_{66}, may be determined independently of one another. For this, however, an absolute measurement of the intensity of diffuse reflexion must be made and for such measurements the accuracy is lower than for relative measurements. From relp $h00$ the ratios c_{55}/c_{11} and c_{66}/c_{11} may be found; from relp $0k0$ c_{44}/c_{22} and c_{66}/c_{22}; the ratio c_{22}/c_{11} may be found from the two ratios c_{66}/c_{11} and c_{66}/c_{22}. Finally from the relp $00l$ the ratios c_{44}/c_{33} and c_{55}/c_{33} may be determined. In this way the five ratios c_{22}/c_{11}, c_{33}/c_{11}, c_{44}/c_{11}, c_{55}/c_{11} and c_{66}/c_{11} may be measured. A single absolute measurement suffices to put all of these constants on an absolute scale.

After determining the constants c_{ik} for which $i = k$ it is possible to determine the three for which $i \neq k$, namely c_{12}, c_{13} and c_{23}. The expression for $K[1/\sqrt{2}, 1/\sqrt{2}, 0]_{h00}$ in Table 1 shows the way in which c_{12} can be found. The following relation holds:

$$c_{11}(c_{22}+c_{66})+c_{22}c_{66}-2c_{12}c_{66}-c_{12}^2 = 2(c_{22}+c_{66})/K[1/\sqrt{2}, 1/\sqrt{2}, 0]_{h00}\,.$$

From this equation we obtain

$$c_{12} = -c_{66}\pm\sqrt{[c_{66}^2 + \{c_{22}c_{66}+(c_{22}+c_{66})(c_{11}-2/K[1/\sqrt{2}, 1/\sqrt{2}, 0]_{h00})\}]} \quad (2)$$

(the negative sign before the root is never applicable).

The accuracy with which the constants c_{12}, c_{23} and c_{13} can be determined is generally less than that of the c_{ii} constants. This is in part due to the way in which they occur in the formulae for $K[1/\sqrt{2}, 1/\sqrt{2}, 0]_{h00}$ etc., and also to the fact that they involve several other constants.

However, a study of a number of actual examples shows that the accuracy of c_{12}, c_{23} and c_{13} need not be much lower than that of the other constants.

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