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The Location of Diffuse Maxima in the X-ray Scattering Pattern from Distorted Crystals

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The theory of the modulated diffuse X-ray scattering from crystals containing point centres of dilatation is examined. The usual calculations which predict that the diffuse scattering peaks at the position of the Bragg reflexion are excellent approximations when the distortion involves small atomic displacements. However, in the asymptotic case in which atomic displacements. associated with the defects are large, the maximum in the diffuse scattering occurs between the Bragg position characteristic of the average expanded lattice, and the Bragg position normally expected from a lattice distorted by image forces alone.

Introduction

Many authors (Huang, 1947; Borie, 1957, 1959, 1961) have considered the effect of the presence of isolated point defects on the X-ray scattering pattern from crystals. All conclude that the Bragg reflexions are unbroadened and are shifted to positions characteristic of an average distorted crystal (the distortion which would be measured with a dilatometer); they also conclude that the intensity of the Bragg peaks is reduced, and that modulated diffuse scattering appears. However, the location of the diffuse-scattering maxima is a subject of controversy.

Cochran & Kartha (1956*a*) related the diffuse-scattering intensity to Fourier transforms of the individual defects. They subsequently showed (Cochran & Kartha, 1956*b*) that their theory predicts a peak, in the diffuse scattering, located near a reciprocal point of the average lattice *after* distortion by the defects. Krivoglaz (1959) criticized the theory for its assumption of a Gaussian distribution for the displacements of atoms from their positions in the average lattice.

More recently, Keating (1968) claimed to have shown that the peaks in the diffuse scattering are located at the reciprocal points of the original lattice, before distortion. The Bragg reflexions were again predicted to be at reciprocal points of the average distorted lattice. So Keating's results indicated a shift between the Bragg and the diffuse peaks. Hall (1969) pointed out that Keating's work rests on an inadmissible approximation, but Hall provided no convincing alternative. The Keating–Hall approach is examined in some detail below.

Another theory predicting a shift between Bragg and diffuse peaks is that of Krivoglaz (1969). His approach is asymptotic in that it assumes distortions so great that the Bragg peaks are vanishingly small (although their positions are well defined), and the scattering is almost wholly diffuse. The present work, using much of Krivoglaz's formalism, leads to a quantitatively different result, but it still indicates some shift between Bragg and diffuse peaks.

Formulation of the problem

We denote the location of the sth atom in the undistorted crystal by $\mathbf{R}_s$, and suppose that after distortion the position is $\mathbf{R}_s+\delta\mathbf{R}_s$ and the scattering factor is f_s. Then, the scattered intensity from a crystal of N atoms is

$$\begin{aligned} I &= \left| \sum_{s=1}^{N} f_s \exp\left[i\mathbf{k} \,.\, (\mathbf{R}_s+\delta\mathbf{R}_s)\right] \right|^2 \\ &= \sum_{s,s'=1}^{N} f_s f_{s'}^* \exp\left[i\mathbf{k} \,.\, (\mathbf{R}_s-\mathbf{R}_{s'})\right] \\ &\quad \times \exp\left[i\mathbf{k} \,.\, (\delta\mathbf{R}_s-\delta\mathbf{R}_{s'})\right], \end{aligned} \tag{1}$$

where $\mathbf{k}$ is the scattering vector, of magnitude $4\pi \sin\theta/\lambda$.

Consider identical atoms and identical point defects, and suppose that a defect on the tth site displaces the sth atom by $\mathbf{u}_{st}$ from the undistorted position, leaving the scattering factor f unchanged. Writing $c_t=1$, if there is a defect on the tth site, and $c_t=0$ if not, we get for the total displacement of the sth atom:

$$\delta\mathbf{R}_s = \sum_t c_t \mathbf{u}_{st} ,$$

summed over all possible defect sites in the crystal. Then, expression (1) for the scattered intensity becomes

$$I = ff^* \sum_{s,s'} \exp\left[i\mathbf{k} \,.\, (\mathbf{R}_s-\mathbf{R}_{s'})\right] \prod_t \exp\left[i\mathbf{k} \,.\, (\mathbf{u}_{st}-\mathbf{u}_{s't})c_t\right].$$

The problem is to average this intensity for a random distribution of defects at a concentration $c=\langle c_t \rangle$. For such a distribution

$$\begin{aligned} \overline{\exp\left[i\mathbf{k} \,.\, (\mathbf{u}_{st}-\mathbf{u}_{s't})c_t\right]} &= c \exp\left[i\mathbf{k} \,.\, (\mathbf{u}_{st}-\mathbf{u}_{s't})\right] + 1 - c \\ &= 1 + c\beta_{ss't} , \end{aligned}$$

where

$$\beta_{ss't} = \exp\left[i\mathbf{k} \,.\, (\mathbf{u}_{st}-\mathbf{u}_{s't})\right] - 1 . \tag{2}$$

So the scattered intensity is

$$I=ff^*\sum_{s,s'}\exp\left[i\mathbf{k}\,.\,(\mathbf{R}_s-\mathbf{R}_{s'})\right]\prod_t(1+c\beta_{ss't})\,.$$

In this expression we may replace the scattering vector $\mathbf{k}$ by its difference $\mathbf{k}'$ from any vector of the reciprocal lattice. Then,

$$I=ff^*\sum_{s,s'}\exp\left[i\mathbf{k}'\,.\,(\mathbf{R}_s-\mathbf{R}_{s'})\right]\prod_t(1+c\beta_{ss't})\,. \quad (3)$$

Keating–Hall approach

Both Keating and Hall employ the expansion:

$$\prod_t(1+c\beta_t)=1+c\sum_t\beta_t+\frac{c^2}{2!}\sum_t\sum_{u\neq t}\beta_t\beta_u+\frac{c^3}{3!}\times\sum_t\sum_{u\neq t}\sum_{v\neq t}\beta_t\beta_u\beta_v+\ldots \quad (4)$$

The product and all the sums must run over all the defect sites. Suppose that there are N' such sites. From (2) we can establish only that $|\beta_t|\leq 2$.

Keating has retained only the first two terms in (4). However, each successive term involves a sum that is 'longer' by a factor N' than the previous one, while the sum is multiplied by an additional factor c. So each term could be larger than the previous one by a factor $N'c$, which equals the total number of defects in the crystal.

Hall has shown that retention of the first three terms of expansion (4) leads to results very similar to those of Cochran & Kartha, but the truncation of (4) to just three terms seems equally unjustified.

Krivoglaz approach

The product $\prod_t(1+c\beta_t)$ can be handled in another way; visually:

$$\prod_t(1+c\beta_t)=\exp\left[\sum_t ln\,(1+c\beta_t)\right]\simeq\exp\left(c\sum_t\beta_t\right)=\exp(-T), \quad (5)$$

where

$$T=-c\sum_t\beta_t=c\sum_t\{1-\exp\left[i\mathbf{k}\,.\,(\mathbf{u}_{st}-\mathbf{u}_{s't})\right]\}\,. \quad (6)$$

The approximation is valid for $c|\beta_t|\ll 1$. This is the approach adopted by Krivoglaz. The same quantity T also appears in a treatment by Eisenriegler (unpublished).

In the case of point defects in finite crystals, displacements $\delta\mathbf{R}_s$ comprise homogeneous 'image' displacements due to surface effects (Eshelby, 1954) as well as the displacements expected in an infinite crystal. Subsequently, we allow $\mathbf{R}_s$ to include the homogeneous image displacements, so that for $\delta\mathbf{R}_s$ we can use displacements calculated for an infinite crystal.

We write $\mathbf{R}_s-\mathbf{R}_{s'}=\mathbf{R}_{ss'}$. Clearly, T depends on $R_{ss'}=|\mathbf{R}_{ss'}|$ and we denote this by writing it as $T(R_{ss'})$. Using (5) in (3), and changing from a sum to an integral as follows, we have

$$\begin{aligned}I&=ff^*\sum_{s=1}^{N}\sum_{s'=1}^{N}\exp(i\mathbf{k}'\,.\,\mathbf{R}_{ss'})\exp(-T)\\&\simeq Nff^*\sum_{s'=1}^{N}\exp(i\mathbf{k}'\,.\,\mathbf{R}_{ss'})\exp(-T)\\&\simeq\frac{N}{v}|f|^2\int d\mathbf{R}_{ss'}\exp(i\mathbf{k}'\,.\,\mathbf{R}_{ss'})\exp\left[-T(R_{ss'})\right], \quad (7)\end{aligned}$$

where v is the volume per atom.

To proceed further we must specify the type of defect and the displacements $\mathbf{u}_{st}$. In the case of isolated interstitials or vacancies in an infinite elastically isotropic medium,

$$\mathbf{u}_{st}=C\frac{\mathbf{r}_{ts}}{r_{ts}^3}, \quad (8)$$

where $\mathbf{r}_{ts}$ is the vector from the defect site t to the normal atom s (before distortion). In general, C is positive for interstitials and negative for vacancies. The elastic solution given above is expected to fail very close to the defect where r_{ts} is less than some critical distance r_0, but we assume the solution valid for $r_{ts}>r_0$. The value of r_0 is expected to be about one interatomic distance. With the expression (8) for $\mathbf{u}_{st}$ it is possible, at least in principle, to determine T from equation (6) and the scattered intensity I from (7).

Eisenriegler evaluates T when small displacements allow the approximation:

$$\sin\left[\mathbf{k}\,.\,(\mathbf{u}_{st}-\mathbf{u}_{s't})\right]\simeq\mathbf{k}\,.\,(\mathbf{u}_{st}-\mathbf{u}_{s't})\,.$$

Under these circumstances no displacement is expected between Bragg and diffuse peaks.

Krivoglaz's theory is appropriate for larger displacements. He predicts the location of the scattering peak by concluding that $T(R_{ss'})$ has no significant imaginary part, and that it increases with $R_{ss'}$ to a large value. Under these circumstances the Bragg peak is severely attenuated, and I has a maximum at $\mathbf{k}'=0$, *i.e.*, at a position corresponding to the lattice as distorted by image terms only. The Bragg peak would appear at a position corresponding to an average lattice after the total distortion is included.

Evaluation of T

The primary purpose of this paper is to give a new estimate of the imaginary part of T, for this is evidently crucial in determining the location of the scattering maxima.

First, note that the real part of T is given from (6), by

$$\mathscr{R}e(T)=c\sum_t\{1-\cos\left[\mathbf{k}\,.\,(\mathbf{u}_{st}-\mathbf{u}_{s't})\right]\}\,. \quad (9)$$

For large values of $R_{ss'}$, t can be close to only one of s, s', so only one of the displacements $\mathbf{u}_{st}$ and $\mathbf{u}_{s't}$ can be appreciable, and the asymptotic value is

$$\mathscr{R}e(T)_\infty=2c\sum_t(1-\cos\mathbf{k}\,.\,\mathbf{u}_{st})$$

$$\simeq \frac{2c}{v}\int(1-\cos \mathbf{k}\,.\,\mathbf{u}_{st})\mathrm{d}\mathbf{r}_{ts}$$

$$= \frac{2c}{v}\int_{4\pi}\mathrm{d}\Omega\int_{r_0}^{\infty} r^2\left(1-\cos C\frac{\mathbf{k}\,.\,\hat{\mathbf{r}}}{r^2}\right)\mathrm{d}r$$

$$= \frac{2c}{v}\int_{4\pi}\mathrm{d}\Omega\int_{r_0}^{\infty} 2\sin^2\left(\frac{C\mathbf{k}\,.\,\hat{\mathbf{r}}}{2r^2}\right)r^2\mathrm{d}r\,,$$

where we have used expression (8) for $\mathbf{u}_{st}$, and the integral approximation (omitting $r_{ts}<r_0$). In the above expressions $r=|\mathbf{r}_{ts}|$ and $\hat{\mathbf{r}}$ is a unit vector in the direction of $\mathbf{r}_{ts}$, while $\mathrm{d}\Omega$ is an element of solid angle.

Substituting u for $\frac{C\mathbf{k}\,.\,\hat{\mathbf{r}}}{r^2}$ gives

$$\mathscr{R}e(T)_\infty \simeq \frac{2c}{v}\int_{4\pi}\mathrm{d}\Omega(C\mathbf{k}\,.\,\hat{\mathbf{r}})^{3/2}\int_0^{Ck.\hat{\mathbf{r}}/r_0^2}\frac{\sin^2(u/2)}{u^{5/2}}\,\mathrm{d}u\,.$$

Supposing $\frac{C\mathbf{k}\,.\,\hat{\mathbf{r}}}{r_0^2}\gg 1$, then we have

$$\int_0^{Ck.\hat{\mathbf{r}}/r_0^2}\frac{\sin^2(u/2)}{u^{5/2}}\,\mathrm{d}u \simeq \int_0^{\infty}\frac{\sin^2(u/2)}{u^{5/2}}\,\mathrm{d}u = \frac{\sqrt{2\pi}}{3}$$

and

$$\mathscr{R}e(T)_\infty \simeq \frac{2\sqrt{2\pi}}{3}\frac{c}{v}\int_{4\pi}(C\mathbf{k}\,.\,\hat{\mathbf{r}})^{3/2}\mathrm{d}\Omega$$

$$= \frac{16\pi\sqrt{2\pi}}{15}\frac{c}{v}(Ck)^{3/2}\,.$$

Krivoglaz suggests that even at small concentrations, $|C|$ is large enough to make $\mathscr{R}e(T)_\infty \gg 1$. (For MgO, *e.g.*, Hickman & Walker (1965) estimate volume changes of $3v$ and $-0{\cdot}2v$ per interstitial or vacancy, respectively. This means (Eshelby, 1954) that $|C|$ is about $3v/4\pi$ for an interstitial and $0{\cdot}2v/4\pi$ for a vacancy. Taking the average atomic volume as 9·3 Å^3, and considering the 200 reflexion with $k=3{\cdot}0$ Å^{-1}, we get

$$\mathscr{R}e(T)_\infty \sim 15c \text{ or } 0{\cdot}27c\,,$$

for interstitials and vacancies, respectively. Thus, the Krivoglaz criterion is unlikely to be attained, but the theory is still useful as an asymptotic case. Following Krivoglaz's method, we assume $\mathscr{R}e(T)\gg 1$ for large values of $R_{ss'}$, whereas for $R_{ss'}=0$ ($s=s'$) it is evident from (9) that $\mathscr{R}e(T)=0$. In these circumstances, the main contribution to the integral (7) is from the region of small $R_{ss'}$.

The imaginary part of T is given by

$$\mathscr{I}mT = -c\sum_t \sin[\mathbf{k}\,.\,(\mathbf{u}_{st}-\mathbf{u}_{s't})]$$

$$\simeq -\frac{c}{v}\int \mathrm{d}\mathbf{r}_t \sin[\mathbf{k}\,.\,(\mathbf{u}_{st}-\mathbf{u}_{s't})] = X\,, \qquad (10)$$

in the integral approximation. We now evaluate this integral for small values of $R_{ss'}$. To first order in $R_{ss'}$,

$$\mathbf{k}\,.\,(\mathbf{u}_{st}-\mathbf{u}_{s't}) = \frac{3CkR_{ss'}}{r^3}\psi\,, \qquad (11)$$

where $\psi=\frac{1}{3}\cos\gamma-\cos\theta\cos\chi$, $\mathbf{r}$ is a vector drawn to the site t from a point halfway between s and s', and θ, χ, and γ are the angles between $\mathbf{r}$ and $\mathbf{R}_{ss'}$, $\mathbf{k}$ and $\mathbf{r}$, $\mathbf{k}$ and $\mathbf{R}_{ss'}$ respectively.

The approximation (11) holds for $r\geq R_0$, where $R_0\gg R_{ss'}$, $R_0\gg r_0$.

Omitting the sphere of radius R_0, we find from (10) and (11) that

$$X = -\frac{c}{v}\int_{R_0}^{\infty} r^2\mathrm{d}r\int_{4\pi}\sin\left(\frac{3CkR_{ss'}}{r^3}\psi\right)\mathrm{d}\Omega\,. \qquad (12)$$

At first sight it seems that the r integral may be divergent, because when $r^3\gg 3CkR_{ss'}\,\psi$, the leading term in the integrand, is

$$\int_{4\pi}\frac{3CkR_{ss'}}{r}\psi\mathrm{d}\Omega \propto \frac{1}{r}\,.$$

However, $\int\psi\mathrm{d}\Omega=0$, the leading non-zero term, is proportional to r^{-7}, and the convergence of the integral is established.

The integral (12) can be transformed, as shown in the Appendix, with the result:

$$X = -\frac{4\pi c}{3v}CkR_{ss'} \times\int_0^{CkR_{ss'}/R_0^3}\frac{\mathrm{d}u}{u^2}\int_0^{\frac{\pi}{2}}\sin[u\cos\gamma(1-3\sin^2\xi)] \times J_0\left(-\frac{3u}{2}\sin\gamma\sin 2\xi\right)\cos\xi\,\mathrm{d}\xi\,. \qquad (13)$$

For the special case $\gamma=\pi/2$ the integral X vanishes; it is otherwise intractable. However, we can attempt an approximate evaluation. If we follow Krivoglaz's method in assuming C is so large that

$$\frac{CkR_{ss'}}{R_0^3}\gg 1\,,$$

then

$$\mathscr{I}m(T)\simeq X\simeq -\frac{4\pi c}{3v}CkR_{ss'}Y\,, \qquad (14)$$

where

$$Y = \int_0^{\infty}\frac{\mathrm{d}u}{u^2}\int_0^{\frac{\pi}{2}}\sin[u\cos\gamma(1-3\sin^2\xi)] \times J_0(-\frac{3u}{2}\sin\gamma\sin 2\xi)\cos\xi\,\mathrm{d}\xi\,. \qquad (15)$$

This result is interesting in that $\mathscr{I}m(T)$ depends linearly on $R_{ss'}$, in contrast with the Krivoglaz (1969) result. The radius R_0 of the omitted sphere does not appear, provided $R_0^3\ll CkR_{ss'}$.

The value of Y has been determined by numerical integration for various angles γ. The results are listed in Table 1.

Table 1. *Calculated values of Y*

$\cos\gamma$	Y	$Y/\cos\gamma = Z$
0	0	-
0·2	0·057	0·286
0·4	0·099	0·247
0·6	0·128	0·214
0·8	0·148	0·185
1·0	0·160	0·160

With the listed values, little direct progress can be made in evaluating the scattered intensity. However, to the extent that we can consider $Y/\cos\gamma = Z$ approximately constant we have

$$\mathscr{I}m(T) \simeq -\frac{4\pi c}{3v} CkR_{ss'} Z\cos\gamma$$
$$= -\frac{4\pi c}{3v} C\mathbf{k}\,.\,\mathbf{R}_{ss'} Z\,. \qquad (16)$$

Then, the substitution of (16) into integral (7) indicates a scattering peak located at

$$\mathbf{k}' - \frac{4\pi c}{3} C\mathbf{k}Z = 0\,.$$

$Z=0$ would locate the maximum at $\mathbf{k}'=0$, while $Z=1$ would locate it at the position expected for the Bragg peak. From Table 1 it would seem reasonable to take $Z\simeq 0{\cdot}2$. So the diffuse maximum is shifted from the position as distorted by image terms only, towards the Bragg positions, by about 20% of the separation of these two positions. This result has recently been confirmed in a private communication from Krivoglaz.

Conclusion

Calculations of the X-ray diffraction pattern from crystals containing point centres of dilatation are now available for two asymptotic cases.

When the defects do not cause severe local distortions, use of the acceptable approximation

$$\sin[\mathbf{k}\,.\,(\mathbf{u}_{st} - \mathbf{u}_{s't})] = \mathbf{k}\,.\,(\mathbf{u}_{st} - \mathbf{u}_{s't})$$

allows no displacement between Bragg and diffuse peaks.

For defects giving rise to large atomic displacements, the Krivoglaz formalism predicts that the maximum in the diffuse scattering occurs between the Bragg peaks characteristic of the average expanded lattice and those of a lattice distorted by image forces alone. In this approximation the Bragg peaks have been completely attenuated.

Observations of neutron irradiated beryllium oxide (Hickman, Sabine & Coyle, 1962; Walker, Mayer & Hickman, 1964; Austerman & Miller, 1965) show the intermediate case of a Bragg peak and a diffuse maximum well separated from the Bragg position. Calculations for this case are in progress.

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APPENDIX

To evaluate integral (12) we evaluate the Ω integral through spherical polar coordinates, $\mathbf{k}$ defining the pole. If the azimuthal angle φ is measured from the plane containing $\mathbf{k}$ and $\mathbf{R}_{ss'}$ it can be shown that

$$\cos\chi = \sin\gamma\sin\theta\cos\varphi + \cos\theta\cos\gamma$$

and, hence, that

$$\psi = \tfrac{1}{3}\cos\gamma(1-3\cos^2\theta) - \tfrac{1}{2}\sin\gamma\sin 2\theta\cos\varphi\,.$$

Then,

$$\int_{4\pi} \sin\left(\frac{3CkR_{ss'}}{r^3}\psi\right) d\Omega$$
$$= \int_{4\pi} \sin(A\psi)\,d\Omega, \text{ where } A = \frac{3CkR_{ss'}}{r^3},$$
$$= \int_0^{2\pi}\int_0^{\pi} \sin\left[\frac{A}{3}\cos\gamma(1-3\cos^2\theta)\right.$$
$$\left. -\frac{A}{2}\sin\gamma\sin 2\theta\cos\varphi\right]\sin\theta\,d\theta d\varphi$$
$$= \int_0^{2\pi}\int_0^{\pi} \sin\left[\frac{A}{3}\cos\gamma(1-3\cos^2\theta)\right]$$
$$\times\cos\left[\frac{A}{2}\sin\gamma\sin 2\theta\cos\varphi\right]\sin\theta\,d\theta d\varphi$$
$$-\int_0^{2\pi}\int_0^{\pi} \cos\left[\frac{A}{3}\cos\gamma(1-3\cos^2\theta)\right]$$
$$\times\sin\left[\frac{A}{2}\sin\gamma\sin 2\theta\cos\varphi\right]\sin\theta\,d\theta d\varphi\,.$$

We can now perform the φ integrations. This means, in effect, evaluating the integrals

$$\int_0^{2\pi} \begin{matrix}\cos\\ \sin\end{matrix} (B\cos\varphi)d\varphi\,, \quad \text{where} \quad B = \frac{A}{2}\sin\gamma\sin 2\theta\,.$$

Through changing the variable to $\cos\varphi$ we obtain

$$\int_0^{2\pi} \cos(B\cos\varphi)d\varphi = 4\int_0^1 \frac{\cos Bx}{\sqrt{1-x^2}}\,dx = 2\pi J_0(B),$$

and

$$\int_0^{2\pi} \sin(B\cos\varphi)d\varphi = 0\,.$$

So

$$\int_{4\pi} \sin\left(\frac{3CkR_{ss'}}{r^3}\psi\right) d\Omega$$
$$= 2\pi\int_0^{\pi} \sin\left[\frac{A}{3}\cos\gamma(1-3\cos^2\theta)\right] J_0(B)\sin\theta\,d\theta$$

$$= 4\pi \int_0^{\frac{\pi}{2}} \sin\left[\frac{A}{3}\cos\gamma\,(1-3\sin^2\xi)\right] \times J_0\left(-\frac{A}{2}\sin\gamma\sin 2\xi\right)\cos\xi\,\mathrm{d}\xi\,.$$

Substituting in (12) gives

$$X = -4\pi\frac{c}{v}\int_{R0}^{\infty} r^2\mathrm{d}r \int_0^{\frac{\pi}{2}} \sin\left[\frac{A}{3}\cos\gamma\,(1-3\sin^2\xi)\right] \times J_0\left(-\frac{A}{2}\sin\gamma\sin 2\xi\right)\cos\xi\,\mathrm{d}\xi\,.$$

Finally, a change in variable from r to $u = \frac{CkR_{ss'}}{r^3} = \frac{A}{3}$ gives the expression in (13).

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Crystallographic Shear Relations between the Structure Types α-UO_3, CaF_2, La_2O_3 and NaCl and a Correlation of some Lanthanide and Actinide Oxide Structures

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When the α-UO_3, La_2O_3 and NaCl structure types are idealized by a topological distortion involving only an extension or contraction of the hexagonal *c* axis (cubic [111]) it is clear that they are related to each other, and to the CaF_2 type, by *crystallographic shear*. A number of lanthanide and actinide oxide structures are of these types, or derived superstructure types containing ordered anion 'vacancies' or 'interstitial' anions. The structural relations suggest possible reduction mechanisms.

Introduction

A multitude of actinide and lanthanide oxides may be regarded as deriving from a very few basic structural types. The derived structures are superstructures of some of these parent types, containing ordered arrangements of 'point defects' – anion vacancies or interstitial anions. Although the structural details of many of the phases are still unknown the broad picture is quite firmly and clearly established. The basic structure types are α-UO_3, CaF_2 (fluorite type), La_2O_3 (*A*-type rare earth sesquioxide) and NaCl. The derived structures are related to the first two and are summarized in Table 1. The purpose of this paper is to examine the structural relations between the basic types, and thus between the derived types also.

Previous papers (Anderson & Hyde, 1965, 1967) have discussed structural relations within various families of 'Magnéli phases', whose members are related by so-called crystallographic shear (CS) (Wadsley, 1955). The families concerned are 'homologous series' (Magnéli, 1953) of various outer transition metal oxides in which the metal ion is octahedrally coordinated by oxygen; *e.g.* tungsten, molybdenum and mixed tungsten+molybdenum oxides of general formulae M_nO_{3n-1} and M_nO_{3n-2} derived from the ReO_3 structure type, and titanium and vanadium oxides M_nO_{2n-1} derived from the rutile type.

A plausible dislocation mechanism was described for producing the derived phases from the parent. In reduction it involves the aggregation of anion vacancies into a disc across which the crystal then collapses and shears (the CS operation) so that the vacant sites are eliminated and the previous cation coordination [MO_6] is restored. In oxidation a new anion plane is nucleated by aggregation of interstitial anions. Either process produces a dislocation ring which then expands by the accretion of point defects until a complete