

With the d spacing data and an IBM 1620 computer we have refined the lattice parameters of α -MoO₃, and the values obtained are tabulated in Table 2.

A probable explanation for the transformation may be that the sulphur and chlorine decomposed from MoSCl and, on taking oxygen from the air, the compound α -MoO₃ was formed.

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A description of electron diffraction from higher-order Laue zones. By ALAN L. LEWIS, *Physics Department, Natural Sciences II, Santa Cruz, California 95064, USA*, ROBERT E. VILLAGRANA, *General Atomic Company, PO Box 91608, San Diego, California 92138, USA* and ALLEN J. F. METHERELL, *Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, England*

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The usual Bloch wave description of electron diffraction from higher-order Laue zones requires the solution of a quadratic eigenvalue equation. In this note we show that in the high-energy case this eigenvalue equation reduces to linear form.

Recently there has been interest in the theoretical description of high-energy electron diffraction, in the Laue geometry, from higher-order Laue zones. For instance, Buxton (1976) has used perturbation methods to study diffraction effects from non-zero Laue zones. In this note we demonstrate that the quadratic eigenvalue problem one obtains in Bloch wave descriptions of high-energy electron diffraction from higher Laue zones can be reduced to a linear eigenvalue problem. Before doing this we will comment on the validity of the Bloch formalism.

Consider a planar crystal with a coordinate system such that the z axis is normal to the crystal surface and the xy plane is coplanar with the zero Laue zone. If this crystal is now assumed to be infinite in the xy plane, then the electrostatic potential in this plane can be expanded as a Fourier series. If we now restrict ourselves to a discussion of diffraction maxima that lie on the zero Laue zone then the Bloch formalism is rigorous. However, when we consider diffraction from higher-order Laue zones, problems arise since the crystal is finite in the z direction. Expressing the potential in this direction as a Fourier series introduces an error whose magnitude is of the order of an atomic spacing divided by the thickness of the crystal. Keeping this fact in mind, we will proceed in the assumption that the crystal potential has a Fourier series and that the Bloch formalism is valid.

We begin with the general eigenvalue equation of high-energy electron diffraction (Colella, 1972) which we write as $\det(A) = 0$. The elements of A are written

$$A_{gh} = \{K^2 - [\mathbf{k}(j) + \mathbf{g}]^2\} \delta_{gh} + (1 - \delta_{gh}) u_{g-h} \quad (1)$$

where the $\mathbf{k}(j)$ are the unknown Bloch wave vectors, \mathbf{g} is the reciprocal-lattice vector, and δ_{gh} is the Kronecker delta

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function. The coefficients u_g are related to the Fourier coefficients of the crystal potential by $u_g = 2mev_g/h^2$, and $K^2 = 2meE/h^2 - e^2E^2/c^2h^2 + u_0$, where E is the potential difference through which the electron was initially accelerated prior to its incidence upon the crystal. Now let us transform (1) into a more convenient form by defining

$$\mathbf{k}(j) = \boldsymbol{\chi} + \gamma(j)\hat{\mathbf{z}} \quad (2)$$

where $\boldsymbol{\chi}$ is the wave vector of the electron in vacuum and $|\boldsymbol{\chi}| = (2meE - e^2E^2/c^2)^{1/2}/h$. Then, substituting (2) into (1) gives us

$$A_{gh} = \left\{ \frac{K^2 - (\boldsymbol{\chi} + \mathbf{g})^2}{2(\boldsymbol{\chi} + \mathbf{g})_z} - \gamma(j) \left[1 + \frac{\gamma(j)}{2(\boldsymbol{\chi} + \mathbf{g})_z} \right] \right\} \delta_{gh} + (1 - \delta_{gh}) \frac{u_{g-h}}{2(\boldsymbol{\chi} + \mathbf{g})_z} \quad (3)$$

In principle, construction of the dispersion surface $\gamma(j)$, as a function of $\boldsymbol{\chi}$ for a given crystal potential, is straightforward. First, one selects n beams with the only restriction being that $n > j$. Then one solves $\det(A) = 0$, where A is an $n \times n$ matrix. The process is repeated, letting $n \rightarrow \infty$, until the eigenvalue converges. In practice, because $v_0/E \approx 10^{-4}$ for 100 keV electrons, and v_g/E is even smaller for the other Fourier coefficients, two approximations are justified which simplify the dispersion-surface construction. The first is the n -beam approximation in which one takes a finite number of beams, thereby restricting A to $n \times n$, and one avoids taking the limit $n \rightarrow \infty$. The important beams are determined by the usual Ewald-sphere construction. Once any and all strongly diffracted beams are included, there is rapid convergence of the non-negligible beam intensities

with n , as n becomes large; consequently, it is reasonable to use a finite n . The second approximation is a linearization which is accomplished by replacing the square-bracketed term in (3) by 1. In order to see that this is justified, consider the exact solution to $\det(A) = 0$ in the one-beam case ($n = 1$). It is $\gamma = \chi_z \pm (\chi_z^2 - u_0)^{1/2}$. We may neglect the plus sign in this equation, since it represents backscattering, and write the solution as $\gamma = (u_0/2\chi_z)[1 + 0(v_0/E)]$. Linearization neglects the $0(v_0/E)$ correction. When $n > 1$, linearization is justified for the same reason because the off-diagonal elements A are of the same magnitude (u_g/χ_z) as the diagonal elements we have just discussed.

These two approximations are well known, but they are usually implemented with the additional restriction $g_z = 0$. Our point here is that this latter restriction is not necessary for sufficiently thick specimens. For extremely thin specimens, where the electrostatic potential of the crystal in the z direction cannot be described by a Fourier series, presumably a Born approximation treatment would be sufficient.

Thus, under these approximations, the dispersion surface is determined by the solution to

$$\det [A' - \gamma(j)I] = 0 \quad (4)$$

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The relationship between cell volume, mean bond length and effective ionic radius. By F. C. HAWTHORNE,
Department of Earth Sciences, University of Manitoba, Winnipeg, Manitoba, Canada, R3T 2N2

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If ionic radii are calculated so as to predict accurately mean interatomic distances, then the relationship between cell volume and the cube of the cation radius for a series of isotypic compounds is non-linear.

It has been noted by several authors (Shannon & Prewitt, 1969; Shannon, 1975) that in the highly symmetric structure types, such as the rocksalt, fluorite and perovskite structures, the mean bond lengths calculated by summation of the effective ionic radii deviate from the observed values in a systematic manner. In general, the observed bond lengths are significantly greater than the calculated values for small cations; these deviations diminish as the size of the cation decreases, and actually become negative for the oxides EuO, SrO and BaO with the rocksalt structure. Shannon & Prewitt (1969) suggest that these discrepancies may be the result of decreased repulsion effects between nearest-neighbour anions due to the highly symmetric nature of the polyhedra.

Another characteristic of the highly symmetric structure types is their non-linearity on a type I stability diagram (Shannon & Prewitt, 1970a). The majority of plots of unit-cell volume *vs* r^3 (the cube of the cation radius) for isotypic structures are linear to a first approximation, and this has been used both for confirmation of unit-cell volumes and for the calculation of ionic radii (Prewitt & Shannon, 1969; Shannon & Prewitt, 1970b). However, Fukunaga & Fujita (1973) and Shannon (1975) have shown that this type of plot is non-linear for the rocksalt, corundum, $BaM^{4+}O_3$ and $SrM^{4+}O_3$ perovskites and $Sm_2M_2^{4+}O_7$ pyrochlore structures, and we encountered the same non-linearity in an examination of the garnet structures. In addition, Shannon (1975) has

where

$$A'_{gh} = \left[\frac{K^2 - (\chi + \mathbf{g})^2}{2(\chi + \mathbf{g})_z} \right] \delta_{gh} + (1 - \delta_{gh}) \frac{u_{g-h}}{2(\chi + \mathbf{g})_z}$$

In summary, (4) gives a simple extension of the usual formulation of transmission high-energy electron diffraction (Sturkey, 1962) to higher-order Laue zones. The only difference is that here we allow the vector \mathbf{g} to range over the Laue zones of interest.

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noted that it is possible that all such plots show this non-linearity, but that it is only noticeable when the structure type is stable for a wide range of cation radii.

With regard to these two points, it is instructive to examine the rocksalt structure in a little more detail. The cation occupies the 4(a) position at 0,0,0 and the anion occupies the 4(b) position at $\frac{1}{2},0,0$. Thus the cell edge, a , may be written in terms of the bond length, l , as $a = 2l$. If ionic radii are calculated so as to reproduce interatomic distances, then

$$l = r_{\text{cation}} + r_{\text{anion}}$$

and the cell volume may be written as

$$v = [2(r_{\text{cation}} + r_{\text{anion}})]^3.$$

Hence the cell volume is not a linear function of the cube of the cation radius. Fig. 1 illustrates this for the $M^{2+}O$ rocksalt structures, and shows the relationship between cell volume and the cube of the cation radius, where the full line indicates the ideal relationship, the broken line shows the linear relationship indicated by Shannon & Prewitt (1970a) and the data points are plotted using the cation radii of Shannon (1976). As suggested by Shannon (1975), the non-linearity exhibited by Fig. 1 is only apparent over the whole range of cation radius values, and would not be apparent over a reduced range of values.

Similar arguments may be developed for other cubic