

SHORT COMMUNICATIONS

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Thermal expansion and phase separation of MoSCl. By J. SADANANDAM and S. V. SURYANARAYANA, *Department of Physics, University College of Science, Osmania University, Hyderabad-500007, India*

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The lattice parameter of MoSCl was determined at different temperatures from 30 to 437°C with X-ray diffraction methods. The coefficient of thermal expansion of this cubic compound was determined from the above data. At 550°C it was found that the compound irreversibly transforms to α -MoO₃, which belongs to the orthorhombic system.

Recently, Perrin, Cherrell & Sergent (1975) prepared new thiohalides of the type MoSX ($X = \text{Cl, Br, I}$). These compounds crystallize in the cubic system with the space group $F43m$. The thiohalides are diamagnetic.

The specimen used in the present investigation was prepared by Dr Perrin. The starting mixtures (MoCl₂ + Mo + 2S) were put in an evacuated and sealed quartz ampoule, and heated at 1000°C for about 24 h. The compound is dark in colour and reported to be stable in air.

The specimen was annealed for 20 h at 400°C, and gave a good X-ray powder photograph at room temperature. A Unicam 19 cm diameter was employed to collect the experimental data at high temperatures. The experimental details for collecting X-ray data and the method of calculating the lattice parameter at different temperatures were described in an earlier publication from this laboratory (Deshpande & Ram Rao Pawar, 1962). All the diffraction lines on the photograph, taken at room temperature, were indexed with the d spacings as calculated from the values of the lattice parameter (9.68 Å) reported by Perrin *et al.* (1975), and in conformity with the space-group extinctions of $F43m$.

The reflexions measured and used in the calculation of the a parameter were 951(α_1), 955(α_1), 10,6,0(α_1), 937(α_1), 12,0,0(α_1), 11,5,1(α_1) and 12,2,2(α_1, α_2) recorded in the

Bragg-angle region 55 to 79°. The values of the lattice parameter at different temperatures are given in Table 1.

The standard error in the value of a is ± 0.001 Å as calculated by the method of Jette & Foote (1935). From a plot of the temperature *vs* lattice parameters with the graphical method suggested by Deshpande & Mudholkar (1961), the coefficient of thermal expansion of MoSCl was evaluated. The data were subjected to least-squares analysis and can be represented by the following expression:

$$\alpha_t (\text{°C}^{-1}) = 7.985 \times 10^{-6} + 4.06 \times 10^{-9} T + 4.28 \times 10^{-12} T^2$$

where T is the temperature in °C.

In Fig. 1 the observed and calculated values of α are shown as a function of temperature. The mean value of α in the temperature range 30 to 437°C is $\bar{\alpha} = 9.34 \times 10^{-6} \text{°C}^{-1}$.

After 437°C, the next X-ray photograph was taken at 550°C. It was quite different in comparison with the earlier photographs. The number of lines which appeared on the photograph indicated that the specimen had transformed to a system of lower symmetry. The sample, which had been black in colour, became pale yellow.

A comparison of the observed d spacings with those quoted by Swanson & Fuyat (1953) indicated that the specimen transformed to α -MoO₃. The colour of the transformed specimen also conforms with that of α -MoO₃ (Wells, 1962).

Table 1. *Lattice parameters of MoSCl at different temperatures*

No.	Temperature (°C)	a -lattice parameter (Å)
1	30	9.6777
2	109	9.6815
3	201	9.6941
4	325	9.7035
5	437	9.7146

Table 2. *Lattice parameters of α -MoO₃*

No.	a (Å)	b (Å)	c (Å)	References
1	3.92	13.94	3.66	Anderson & Magnéli (1950)
2	3.962	13.858	3.697	Swanson & Fuyat (1953)
3	4.101	13.865	3.693	Present study

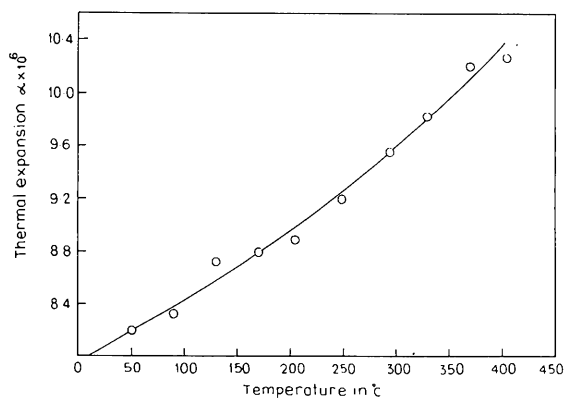


Fig. 1. Temperature variation of the coefficient of thermal expansion of MoSCl.

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