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X-ray measurement of the thermal expansion of ammonium chloride.

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The lattice parameters of ammonium chloride have been measured at 31·5 and 54·0°C. The coefficient of linear expansion is found to be $58{\cdot}5\times10^{-6}\,°C^{-1}$.

The thermal expansion of ammonium chloride (CsCl structure) has been measured by Fizeau (1867) and Sharma (1950). The values reported by them for the coefficient of linear expansion near room temperature are 62·5 and 59·9 (in units of $10^{-6}\,°C^{-1}$) respectively. Haussühl (1960) has quoted a very much lower value of $48\times10^{-6}\,°C^{-1}$. In view of these differences, an accurate X-ray determination of the coefficient of thermal expansion was undertaken.

A flat-faced powder sample was prepared with Analar grade B.D.H. material. X-ray powder photographs were taken with a flat-film back-reflexion camera. With filtered copper radiation, the camera could record three $\alpha_1\alpha_2$ doublets at high angles. Photographs were taken at 31·5 and at 54·0°C. The procedure for the precision determination of the lattice parameter was the same as in our earlier work on ammonium bromide (Deshpande & Sirdeshmukh, 1961). The main results are given below.

$$a_{31\cdot5}=3{\cdot}8771\pm0{\cdot}0002\ \text{Å}$$
$$a_{54\cdot0}=3{\cdot}8822\pm0{\cdot}0002\ \text{Å}$$
$$\alpha\quad=58{\cdot}5\times10^{-6}\,°C^{-1}$$

It can be seen that the value of the coefficient of expansion obtained in this investigation by the X-ray method agrees very well with the value obtained by Sharma (1950) by the optical interferometric method.

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A least-squares method for the determination of the orientation matrix in single-crystal diffractometry.

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An appropriate choice of the function minimized permits linearization of the least-squares determination of the matrix which transforms the diffraction indices into the components of the reciprocal vector in the diffractometer φ-axis system of coordinates. The coefficients of the least-squares equations are based on diffraction indices and measured diffractometer angles of three or more non-coplanar setting reflexions.

In order to bring a reciprocal lattice vector into a reflexion position on the Ewald sphere, it is necessary to know its components in the φ-axis system of coordinates. The components can be calculated from the equation (Busing & Levy, 1967)

$$\mathbf{X}=\mathbf{UBh}=\mathbf{Qh}\,. \qquad (1)$$

In this matrix equation **X** represents the column vector of components of a reciprocal lattice vector $\mathbf{r}^*_{hkl}$ in the φ-axis system of coordinates and **h** is the column vector for the diffraction indices *hkl*. The **B** matrix transforms **h** into the reciprocal crystal cartesian system of axes and **U** is the unitary orientation matrix, which transforms the vector components in the crystal system into the φ-axis system of coordinates.

Several methods for determining the orientation matrix **U** have been published. Busing & Levy (1967) describe methods using two or three setting reflexions and mention an iterative numerical method for the least-squares determination of the orientation matrix and the unit-cell parameters. Their approach enables one to refine the unit-cell parameters both with and without the constraints imposed by the symmetry of the crystal to three axial lengths and three interaxial angles. Shoemaker (1969) proposed an alternative to the unit-cell determination from the **Q**=**UB** matrix.

In this paper a straightforward non-iterative least-squares method is given which enables one to calculate nine matrix elements Q_{ij} directly from linear equations, the coefficients of which are evaluated according to the analytical formula (4) given below. The orientation matrix **U** and the lattice parameters can then be derived according to the method of Shoemaker (1969) based on a knowledge of the matrix elements Q_{ij} only.

The nine elements Q_{ij} must meet the condition that the components of the vectors $\mathbf{X}^{(q)}$ based on them, according to the equation (1), are the closest to those observed. The function minimized is chosen to be of the form

$$S=\sum_q\sum_i w^{(q)}[X_i^{(q)}(\text{calc})-X_i^{(q)}(\text{obs})]^2 \qquad (2)$$

where the superscript q denotes the summation over all setting reflexions considered and the index $i=1, 2, 3$ ranges over x, y and z components. The values of $X_i^{(q)}$(obs) are calculated from measured diffractometer angles.

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