X-ray measurement of the thermal expansion of ammonium chloride.
By D. B. SIRDESHMUKH* and V. T. DESHPANDE, *Physics Department, Osmania University, Hyderabad-7, India*

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 $58·5 \times 10^{-6}\,°C^{-1}$.

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 $48 \times 10^{-6}\,°C^{-1}$. 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

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on ammonium bromide (Deshpande & Sirdeshmukh, 1961). The main results are given below.

$$a_{31·5} = 3·8771 \pm 0·0002\ \text{Å}$$
$$a_{54·0} = 3·8822 \pm 0·0002\ \text{Å}$$
$$\alpha = 58·5 \times 10^{-6}\,°C^{-1}$$

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.

References

DESHPANDE, V. T. & SIRDESHMUKH, D. B. (1961). *Acta Cryst.* 14, 353.
FIZEAU, H. (1867). *C.R. Acad. Sci. Paris*, 64, 314, 771.
HAUSSÜHL, S. (1960). *Acta Cryst.* 13, 685.
SHARMA, S. S. (1950). *Proc. Ind. Acad. Sci.* A31, 339.

A least-squares method for the determination of the orientation matrix in single-crystal diffractometry.
By K. TICHÝ,* *Physics Department, University College, Cardiff, Wales*

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)

$$\mathbf{X} = \mathbf{UBh} = \mathbf{Qh} \ . \tag{1}$$

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

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ameters. 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 $\mathbf{Q} = \mathbf{UB}$ 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 $\mathbf{U}$ 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

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

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 $X_i^{(q)}(\text{obs})$ are calculated from measured diffractometer angles.

Using equation (1) re-written in the index notation

$$X_i{}^{(q)} = \sum_k Q_{ik} h_k{}^{(q)} \qquad (1a)$$

we introduce the required elements Q_{ij} into equation (2)

$$S = \sum_q \sum_i w^{(q)} [\sum_k Q_{ik} h_k{}^{(q)} - X_i{}^{(q)}(\text{obs})]^2 \qquad (2a)$$

and from the conditions

$$\frac{\partial S}{\partial Q_{ml}} = 0, \quad m, l = 1, 2, 3, \qquad (3)$$

we obtain three systems of three linear normal equations for the nine matrix elements Q_{ml}

$$\sum_q w^{(q)} \sum_k \{Q_{mk} h_k{}^{(q)}\} h_l{}^{(q)} = \sum_q w^{(q)} X_m{}^{(q)}(\text{obs}) h_l{}^{(q)},$$

$$l = 1, 2, 3 \quad \text{for} \quad m = 1, 2, 3. \qquad (4)$$

The estimated standard deviations can be calculated in the usual way (*International Tables for X-ray Crystallography*, 1959)

$$s^2(Q_{ml}) = a^{ll} \sum_q w^{(q)} (\Delta_m{}^{(q)})^2 / (N_q - N) \qquad (5)$$

where

$s(Q_{ml})$ is the estimated standard deviation of the matrix element Q_{ml},

a^{ll} is the diagonal matrix element of the matrix a inverse to the matrix of the normal equations in (4),

$$\Delta_m{}^{(q)} = X_m{}^{(q)}(\text{calc}) - X_m{}^{(q)}(\text{obs}) = \sum_k Q_{mk} h_k{}^{(q)} - X_m{}^{(q)}(\text{obs})$$

is the difference between the observed and the calculated value of the mth component of the vector $X^{(q)}$ of the qth setting reflexion,

N_q is the number of setting reflexions used,

$N = 3$ is the number of parameters determined (N is not equal to 9 as there are three systems of three normal equations, each of them for the determination of three parameters Q_{ml}, $l = 1, 2, 3$).

The whole problem of accuracy and in particular the assignment of correct weights clearly requires further attention.

My thanks to Dr J. P. G. Richards for valuable discussion.

References

BUSING, W. R. & LEVY, H. A. (1967). *Acta Cryst.* **22**, 457.
International Tables for X-ray Crystallography (1959). Vol. II, p.330. Birmingham: Kynoch Press.
SHOEMAKER, D. P. (1969). *Acta Cryst.* **A25**, 575.

International Union of Crystallography

Opening of new Union office

The President of the Union, Professor A. Guinier, together with the Chairman of the Commission on Journals, the General Secretary, the Treasurer, employees of the Union and guests, attended a luncheon in Chester on 7 January to mark the opening of the new Union office. This office, incorporating the office of the Technical Editor and the office of the Executive Secretary, is at 13 White Friars, Chester CH1 1NZ, England. All correspondence for the Technical Editor, Mr S. A. Bryant, and the Executive Secretary, Dr J. N. King, should be sent to this address. Dr King has now taken over the day-to-day business of the Union from the General Secretary and the Treasurer.

Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the Executive Secretary of the International Union of Crystallography (J. N. King, 13 White Friars, Chester CH1 1NZ, England). Publication of an item in a particular issue cannot be guaranteed unless the draft is received 8 weeks before the date of publication.

Third International Conference of Crystal Growth (I.C.C.G.–3)
Marseille, France, 5–9 July 1971

The programme planned for the Conference includes the theory of crystal growth; the characterization of crystals in relation to their way of growing; fundamental experimental work dealing with growth from the vapour phase, from the melt and from aqueous solution, growth at high pressures or temperatures, transformations in the solid phase and recrystallization, crystallization of big polymers and biological crystals. Sessions will also be held on new techniques for the production of single crystals and on crystallization on an industrial basis.

Parallel sessions are planned and a film show and an exhibition will be held.

For further information apply to:
General Secretary of the I. C. C. G.-3
B. Mutaftschiev

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Second International Conference on Small-Angle X-ray Scattering
Graz, Austria, 26-29 August 1970

The Second International Conference on Small-Angle X-ray Scattering will be held on 26–29 August, 1970 at Graz, Austria. Further information may be obtained from:

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