

where for the electron case:

$$K^2 = (2m/h^2) [E + V_0]$$

$$U_g = (2m/h^2) V_g,$$

and for the X-ray case:

$$K^2 = c^{-2} [v^2 - 4\pi Q_0 e^2 / m\pi] \quad (8)$$

$$U_g = -e^2 Q_g / (\pi m c^2).$$

Since in the X-ray case η is only very slightly greater than unity, \mathbf{D} can replace ϵ in (6) with negligible error. The solutions of (7), therefore, give the allowed values of the wave vector \mathbf{k} for each Bloch wave excited in the crystal.

Discussion

The above treatment of dynamical theory gives explicitly the close relation between X-ray and electron scattering by crystals and shows in detail why the dispersion equations for the two phenomena have a similar form. The usual treatment of X-ray dynamical theory, following Laue (1931) and James (1958) assumes that the 'polarizability', $(1 - 1/\eta)$, is a periodic function of the lattice and then Bloch wave solutions are inserted into the basic Maxwell equations. As

shown above, however, manipulation of the Maxwell equations gives a 'single photon Schrödinger equation' in which the potential energy term is the fraction of the photon energy stored in the polarized lattice. The Bloch wave solutions and dispersion relationships then follow because of the periodic electron density in the lattice. The mathematical formalism is, thus, somewhat simplified, and the analogy to electron diffraction by a periodic potential is made obvious.

This work was supported by the National Research Council of Canada under grant number A5030.

References

- DITCHBURN, R. W. (1963). *Light*, p. 512. London: Blackie.
 HIRSCH, P. B., HOWIE, A., NICHOLSON, R. B., PASHLEY, D. W. & WHELAN, M. J. (1965). *Electron Microscopy of Thin Crystals*, pp. 197, 209. London: Butterworth.
 JAMES, R. W. (1958). *The Optical Principles of the Diffraction of X-rays*, p. 413. London: Bell.
 LAUE, M. VON (1931). *Ergeb. der Exak. Naturwiss.*, **10**, 133.

Acta Cryst. (1971). **A27**, 677

A note on Cerrini's paper 'Tensor analysis of the harmonic vibrations of atoms in crystals'. By D. W. J. CRUICKSHANK, *Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD, England*

(Received 10 May 1971)

Comments are made on papers by Cerrini, Cruickshank and Scheringer on representations of the harmonic vibration tensor \mathbf{U} with respect to different bases.

The paper by Cerrini (1971) on anisotropic harmonic vibrations in affine (triclinic) coordinate systems is very helpful in clarifying my paper (Cruickshank, 1956) and its relation to the apparently contradictory analysis of Scheringer (1966). The 1956 paper was less explicit than it should have been, and it would have been much better if it had used, as Cerrini has used, the upper- and lower-suffix notation for contravariant and covariant tensor components. The attempt in 1956 to keep the notation simple has led to some confusion, and an indication now of what should have been added to the 1956 paper and of its relation to a 1961 paper may be helpful.

Cerrini uses the following symbols for base axes: \mathbf{a}_i ($i=1,2,3$) are the direct axes, and \mathbf{a}^i are the corresponding reciprocal axes ($\mathbf{a}_i \cdot \mathbf{a}^j = \delta_i^j$). These are called the frame $(\mathbf{a}_i, \mathbf{a}^i)$, and $(\mathbf{e}_i, \mathbf{e}^i)$ is the frame for which \mathbf{e}_i are unit vectors parallel to \mathbf{a}_i ; the \mathbf{e}^i are parallel to \mathbf{a}^i , but are not of unit length for general triclinic direct axes. $(\mathbf{f}_i, \mathbf{f}^i)$ is the frame for which \mathbf{f}^i are unit vectors parallel to \mathbf{a}^i ; the \mathbf{f}_i are parallel to \mathbf{a}_i , but are not of unit length for general triclinic direct axes. Sets $\mathbf{e}_i, \mathbf{e}^i, \mathbf{f}_i, \mathbf{f}^i$ are identical and of unit lengths only when \mathbf{a}_i (hence also \mathbf{a}^i) are an orthogonal set. [The reader should beware of the misprint in the third line of the third paragraph of Cerrini's 'Introduction' where the direct axes are printed \mathbf{a}^i in error for \mathbf{a}_i . A misprint also occurs in the middle of the left-hand column of p. 132 where $U_{ii}(\cos \theta_i)^2$ should read $U^{ii}(\cos \theta_i)^2$.]

A confusion in notation that can occur is that the symbol \mathbf{x} may be used to denote either a vector or a set of vector components. Of itself, the vector has no algebraic form, but when a frame $(\mathbf{a}_i, \mathbf{a}^i)$ is defined, we write

$$\mathbf{x} = x^1 \mathbf{a}_1 + x^2 \mathbf{a}_2 + x^3 \mathbf{a}_3$$

$$= x_1 \mathbf{a}^1 + x_2 \mathbf{a}^2 + x_3 \mathbf{a}^3.$$

The point to be watched comes if the component array (x^1, x^2, x^3) is called \mathbf{x} . In tensor language both (x^1, x^2, x^3) and (x_1, x_2, x_3) , together with an infinity of arrays for other frames, are all representations of the vector \mathbf{x} . Similarly, symbol \mathbf{U} , according to context, may denote either the vibration tensor \mathbf{U} or one of the 3×3 matrix arrays U^{ij} and U_{ij} , which are the contravariant and covariant representations of the tensor with respect to the frame $(\mathbf{a}_i, \mathbf{a}^i)$.

Cerrini's discussion shows that in equations (1.5)–(1.7) and the Appendix of my 1956 paper symbols \mathbf{x} and \mathbf{U} are the contravariant arrays x^i and U^{ij} , and the 1956 symbols ' x_i ' and ' U_{ij} ' are also these contravariant arrays, while the symbols s and s_i are the covariant array s_i . The 1956 symbol \mathbf{U}^{-1} is Cerrini's covariant array V_{ij} . With these interpretations, equations (1.5)–(1.7) and the Appendix are true for any frame $(\mathbf{a}_i, \mathbf{a}^i)$.

In equations (2.1) and (2.2), a particular choice of reciprocal base is implicit in the exponential term

$$\exp [-2\pi^2 (h^2 a^{*2c} U_{11} + \dots)].$$

This is Cerrini's reciprocal base \mathbf{f}^i , which has axes of unit length parallel to the crystal reciprocal axes. Further, as Cerrini shows, ' U_{11} ', which is U^{11} in tensor notation, is the mean-square displacement in the direction \mathbf{f}^1 .

However, for non-orthogonal axes the corresponding direct axes \mathbf{f}_i are not of unit length. It was for this reason that additional formulae for computational purposes were given by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961). In the computational scheme it was desired to output coordinates in Å and vibration mean-square amplitudes in Å². With the Å as the unit of length, the 1961 symbol \mathbf{x}_C denoted the Å coordinate array x^i with respect to Cerrini's frame ($\mathbf{e}_i, \mathbf{e}^i$), while U_C denoted the Å² vibration array U^{ij} with respect to the frame ($\mathbf{f}_i, \mathbf{f}^i$). In general, \mathbf{e}_i and \mathbf{f}^i are not a dual-base pair and, consequently, corresponding to a coordinate transformation to standard orthogonal axes S :

$$\mathbf{x}_S = \mathbf{B}\mathbf{x}_C, \quad [1961, (4.4)]$$

the vibration transformation, has the unusual form

$$U_S = (\mathbf{B}\mathbf{D})U_C(\mathbf{B}\mathbf{D})', \quad [1961, (4.5)]$$

rather than one of the type $\mathbf{B}U_C\mathbf{B}'$, appropriate to dual bases. Here \mathbf{D} is a diagonal matrix with diagonal elements $a_i a^i$, where a_i and a^i are the lengths of the axes.

Scheringer's (1966) criticism of the 1956 paper is valid, if symbols \mathbf{x} and U of that paper are interpreted as the symbols \mathbf{x}_C and U_C of the 1961 paper. (Scheringer intended his criticism to apply only in this case.) With such an interpretation, though (1.7) retains U , equation (1.6) must involve $\mathbf{D}\mathbf{U}\mathbf{D}$ in place of U , and some corresponding changes are needed in the Appendix. However, as shown by Cerrini's discussion summarized above, such an interpretation of the 1956 paper is not necessary, and the paper is in order

provided \mathbf{x} and U are defined with respect to the same frame.

Scheringer also stated that equation (4.5) of the 1961 paper ought to have appeared as now given above and not as

$$U_S = (\mathbf{D}\mathbf{B})U_C(\mathbf{D}\mathbf{B})'$$

which was printed originally. This criticism is correct and is not affected by Cerrini's analysis. I regret the error, which was due to carelessness in matrix manipulation and not to any confusion between representations. With the particular choice (4.1) of standard orthogonal axes S in the 1961 paper, the error in fact affects only triclinic and not monoclinic calculations (for which the formula had been cross-checked). It should be added that the 1961 symbol U_C , which represents the contravariant array U^{ij} for the frame ($\mathbf{f}_i, \mathbf{f}^i$), corresponds to Scheringer's U_R and not to his U_C , which is the contravariant array U^{ij} for the frame ($\mathbf{e}_i, \mathbf{e}^i$).

In my paper (Cruickshank, 1970) on the least-squares refinement of atomic parameters, vibration parameters are written in the contravariant style U^{ij} and are defined with respect to a frame there called ($\mathbf{e}_i, \mathbf{e}^i$), but which is ($\mathbf{f}_i, \mathbf{f}^i$) in Cerrini's notation.

References

- CERRINI, S. (1971). *Acta Cryst.* **A27**, 130.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747.
 CRUICKSHANK, D. W. J. (1970). *Crystallographic Computing*, p. 187. Copenhagen: Munksgaard.
 CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 32. Oxford: Pergamon Press.
 SCHERINGER, C. (1966). *Acta Cryst.* **20**, 316.

Acta Cryst. (1971). **A27**, 678

X-ray diffuse scattering from pentaerythritol. By HIKARU TERAUCHI, HIROSHI OKAMOTO*, ATSUSHI TASAKA and TOKUNOSUKE WATANABÉ, *Faculty of Science, Kwansai Gakuin University, Nishinomiya 662, Japan*

(Received 27 July 1971)

The X-ray diffuse scattering from pentaerythritol is measured at various temperatures. By taking account of five intermolecular force parameters, the dispersion relations are calculated and compared with the observed data. It is found that the interaction between the oxygen atoms connected by the hydrogen bond is stronger and more sensitive to temperature than other interactions.

In order to elucidate the nature of hydrogen bonds in pentaerythritol, $C(\text{CH}_2\text{OH})_4$, the intensity distribution and temperature dependence of the X-ray diffuse scattering from this substance were studied. The specimen crystal was a rod which was cut out from a single crystal grown by the sublimation method, and was set in a small glass cryostat with a Mylar window. The temperature was indicated by a Cu-CuNi thermocouple placed at the top of the specimen and was controlled automatically to within $\pm 0.1^\circ\text{K}$. A parallel narrow beam of Mo $K\alpha$ radiation monochromated by a graphite crystal was used.

The intensity distributions of the X-ray diffuse scattering

in the vicinity of the 002 and 200 reflexions about the [010] axis of rotation were observed, and five dispersion relations for the principal axes were obtained. The intensities of scattered X-rays were normalized by referring to the diffuse scattering from paraffin (Amorós & Amorós, 1968). In Fig. 1, typical dispersion curves of the transverse acoustic (TA) and longitudinal acoustic (LA) phonons polarized in the [001] direction are shown, where the small triangles indicate the estimated angular resolutions for the different directions. The temperature dependence of the intensities of the diffuse scattering near the 200 reflexion are plotted in Fig. 2. Both the intensities at 1.8,0,0 and 2,0,0.2 increase linearly with temperature. The fluctuation of intensities in the temperature range above 350°K seems to be due to decomposition of the crystal. The intensity at 1.8,0,0 which

* Present address: Japan Catalytic Chemical Industry, Suita 564, Japan.