This is Cerrini's reciprocal base 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 f^1.

However, for non-orthogonal axes the corresponding direct axes 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 x_C denoted the Å coordinate array x^i with respect to Cerrini's frame (e_i, e^i), while U_C denoted the Å² vibration array U^{ij} with respect to the frame (f_i, f^i). In general, e_i and f^i are not a dual-base pair and, consequently, corresponding to a coordinate transformation to standard orthogonal axes S:

$$x_S = Bx_C,\qquad\text{[1961, (4.4)]}$$

the vibration transformation, has the unusual form

$$U_S = (BD)U_C(BD)',\qquad\text{[1961, (4.5)]}$$

rather than one of the type BU_CB', appropriate to dual bases. Here 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 x and U of that paper are interpreted as the symbols 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 DUD 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 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

$$U_S = (DB)U_C(DB)'$$

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 (f_i, f^i), corresponds to Scheringer's U_R and not to his U_C, which is the contravariant array U^{ij} for the frame (e_i, 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 (e_i, e^i), but which is (f_i, 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.

X-ray diffuse scattering from pentaerythritol.

By Hikaru Terauchi, Hiroshi Okamoto*, Atsushi Tasaka and Tokunosuke Watanabé, Faculty of Science, Kwansei Gakuin Univeristy, Nishinomiya 662, Japan

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, $C(CH_2OH)_4$, 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 $\pm 0 \cdot 1\,^\circ$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

---

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

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 $1\cdot 8,0,0$ and $2,0,0\cdot 2$ 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 $1\cdot 8,0,0$ which

corresponds to the longitudinal acoustic mode travelling in the direction of the hydrogen bond chains parallel to [100], is more sensitive to temperature than the intensity at $2,0,0\cdot2$
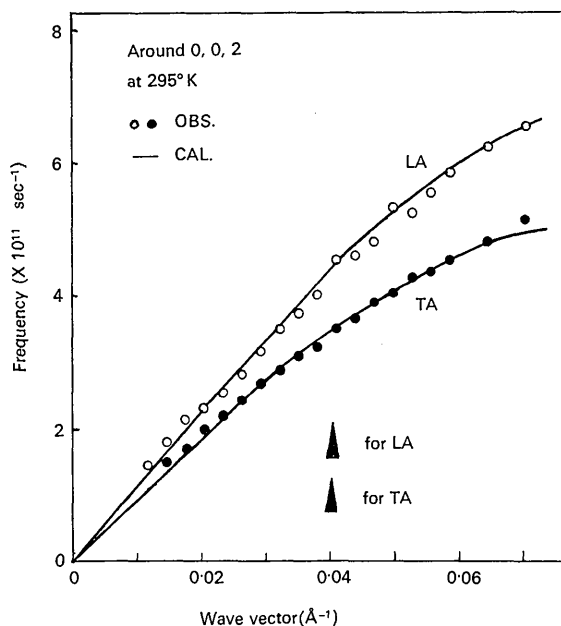

Fig. 1. Typical dispersion relations for pentaerythritol. Observed values are shown by circles and calculated values from equations (4) and (5) are shown by solid curves.
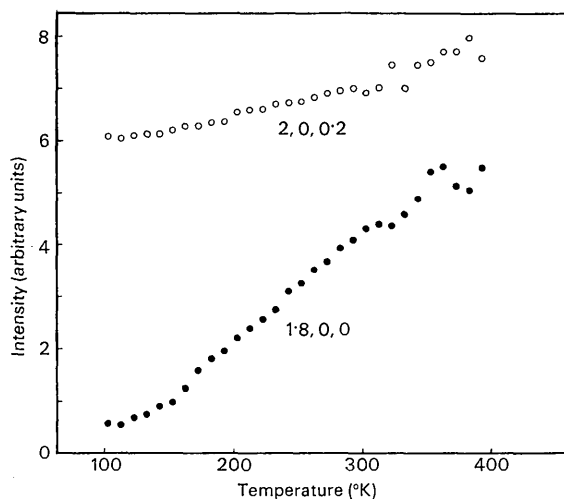

Fig. 2. Temperature dependence of the X-ray diffuse scattering intensity at $1\cdot8,0,0$ and $2,0,0\cdot2$ from pentaerythritol.

which corresponds to the transverse acoustic mode related to the van der Waals force.

The X-ray diffuse scattering for molecular crystals was calculated by Tanaka, Naya & Oda (1969) under a harmonic approximation, assuming the molecules to be rigid bodies. According to their theory, the dispersion relations are written as

$$Z(q_1) \simeq \left\{ \frac{2}{M} \left(2\alpha + \beta_1 + \beta_2 + \frac{8\gamma_2 a^2}{a^2+b^2} \right) (1 - \cos 2\pi q_1 a) \right\}^{1/2},$$
(1)

$$Z(q_2) \simeq \left\{ \frac{2}{M} \left(\beta_1 + \beta_2 + \frac{8\gamma_2 a^2}{a^2+b^2} \right) (1 - \cos 2\pi q_2 a) \right\}^{1/2},$$
(2)

$$Z(q_3) \simeq \left\{ \frac{8}{M} \left(\gamma_1 + \frac{4\gamma_2 c^2}{a^2+c^2} \right) (1 - \cos \pi q_3 c) \right\}^{1/2},$$
(3)

near the 200 reflexion, and

$$Z(q_1) = Z(q_2) \simeq \left\{ \frac{16}{M} \frac{\gamma_2 a^2}{a^2+c^2} (1 - \cos 2\pi q_1 a) \right\}^{1/2},$$
(4)

$$Z(q_3) \simeq \left\{ \frac{8}{M} \left(\gamma_1 + \frac{4\gamma_2 c^2}{a^2+c^2} \right) (1 - \cos \pi q_3 c) \right\}^{1/2}$$
(5)

near the 002 reflexion. In these equations, α represents the force constant for the hydrogen bond, β_1 and β_2 those for the second and third neighbouring oxygen atoms in the (001) plane and γ_1 and γ_2 for the first and second neighbouring oxygen atoms of the adjacent planes parallel to the (001) plane, respectively. Z is the phonon frequency, the wave vector $\mathbf{q} = q_1 \mathbf{a}^* + q_2 \mathbf{b}^* + q_3 \mathbf{c}^*$ is limited within the first Brillouin zone, M is the molecular mass, and a, b and c are the cell dimensions. By comparing the observed dispersion curves with the above relations, the force constants at 295°K are determined as: $\alpha = 9\cdot6 \times 10^2$, $\beta_1 = -3\cdot0 \times 10^2$, $\beta_2 = -3\cdot6 \times 10^2$, $\gamma_1 = -4\cdot7 \times 10^2$, $\gamma_2 = 3\cdot6 \times 10^2$ dyne.cm^{-1}. The results obtained show that the interaction between the oxygen atoms connected by hydrogen bonds is stronger than the van der Waals interactions among other atoms, and is consistent with the elastic properties reported by Srivastava (1962).

References

Amorós, J. L. & Amorós, M. (1968). *Molecular Crystals: their Transforms and Diffuse Scattering.* New York: John Wiley.

Srivastava, R. C. (1962). *Acta Cryst.* **15**, 1306.

Tanaka, S., Naya, S. & Oda, T. (1969). *J. Phys. Soc. Japan*, **27**, 962.