

calculated bond length is obtained by adding the average effective ionic radii. In the NaCl structure there is only one type of bond, between octahedrally coordinated cations and anions and the difference Δx when plotted against the coefficient α (Fig. 2) results in a correlation coefficient equal to 0.90. The equation of the straight line is

$$\alpha = 42.6 + 139.5\Delta x. \quad (2)$$

Equation (1) emphasizes only the effect of radius ratio on the thermal expansion coefficient. Therefore, at large values of r^+/r^- when the anion-anion repulsion effect is small the equation is only approximately true. On the other hand, equation (2) represents the relation between two quantities both of which are likely to have been influenced by the same factors. The correlation coefficient between α and Δx is high and equation (2) may be useful in predicting the coefficient of expansion of an isomorphous alkali halide. The only such compound for which the thermal expansion data are not available in literature is RbF. The reported lattice parameter of this compound (Wyckoff, 1963) gives the Rb-F length as 2.82 Å, identical with the

calculated length. Equation (2) in this case predicts a value of the expansion coefficient as $42.6 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$.

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References

- AHRENS, L. H. (1952). *Geochim. Cosmochim. Acta*, **2**, 155-169.
 DESHPANDE, V. T. (1955). Ph.D. Thesis, Osmania Univ.
 MEGAW, H. D. (1939). *Z. Kristallogr.* **100**, 58-76.
 PAULING, L. (1928). *Z. Kristallogr.* **67**, 377-404.
 PAULING, L. (1929). *J. Amer. Chem. Soc.* **51**, 1010-1026.
 SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925-946.
 SIRDESHMUKH, D. B. (1963). Ph.D. thesis, Osmania Univ.
 SRINIVASAN, R. & KRISHNAN, K. S. (1958), *Progress in Crystal Physics*, Edited by R. S. KRISHNAN. Madras: Viswanathan.
 WYCKOFF, R. W. G. (1963). *Crystal Structures*, Vol. 1, pp. 86-91. New York: Interscience.

Acta Cryst. (1974). **A30**, 106

Elastic and thermoelastic properties of 1,3,5-triphenylbenzene derived from ultrasonic wave velocities.

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All elastic and thermoelastic constants of orthorhombic triphenylbenzene single crystals have been determined from diffraction of light by ultrasonic waves (Schaefer-Bergmann method). These measurements do not agree with the values previously reported by Suresh Chandra & Hemkar [*Acta Cryst.* (1973). **A29**, 25-28] which were derived from thermal diffuse scattering of X-rays and which are not consistent with elastic-stability criteria. This is another example of the great difficulties which still have to be visualized in the quantitative interpretation of thermal-diffuse-scattering intensities by complicated crystal structures.

Recently Suresh Chandra & Hemkar (1973) have published elastic constants of 1,3,5-triphenylbenzene (TPHB) which they had determined from thermal diffuse scattering of X-rays. A first inspection of these values will establish some doubt concerning the errors estimated by the authors because two elastic-stability criteria are violated. The elastic compliance s_{11} turns out to be negative ($-2.4385 \cdot 10^{-11} \text{ cm}^3/\text{erg}$) and also the bulk compressibility $K = -0.293 \cdot 10^{-11} \text{ cm}^3/\text{erg}$. As another peculiar feature of these values should be considered the relatively large shear constants c_{44} and c_{66} . This means that in [010] transverse waves will propagate with higher velocities than longitudinal waves. Such behaviour is extremely rarely observed in crystals. The high elastic anisotropy in longitudinal and in transverse effects, and the large negative value for c_{12} , also suggest a major failure in that investigation.

A similar but less critical situation on benzalazine was clarified earlier (Haussühl, 1965). The constants determined from diffuse scattering of X-rays by Joshi & Kashyap (1964) differed much more from the constants derived by ultrasonic measurements (Haussühl, 1965) than expected from error estimation. In this paper the elastic constants of TPHB are derived from precision ultrasonic measurements in order to find the correct elastic behaviour of this material.

By a thorough comparison of the two sets of constants it should be possible to disclose the major difficulties which still occur in the application of the models describing the diffuse scattering of X-rays in crystals.

Single crystals of TPHB with dimensions of several cm were grown from solutions of *p*-xylene by slow evaporation at about 33 °C. The transparent, pale-yellow crystals grow in an elongated prism {011} which is closed by another prism {120}. A few small faces of the types {010}, {001}, {110} are also formed. The axes of reference are chosen as given by Farag (1954). The crystals used here are metrically identical with the crystals described by Groth (1919) and by Farag. The density for 20 °C as measured by the buoyancy method is 1.205 g cm^{-3} in good agreement with the X-ray value.

From the determination of the elastic constants c_{ij} the propagation velocities of ultrasonic waves travelling in the main directions [100], [010], [001], and in the three median directions of two main directions were measured employing the method of Schaefer-Bergmann (diffraction of light by ultrasonic waves) at about 15 MHz. The specimens were prepared as plane-parallel plates with dimensions of ca. 10 mm. All measured values were controlled independently by observing the eigenfrequencies of such plates in a wider

frequency range. The same method yielded the temperature coefficients of all wave velocities in a temperature range from -20 to 20°C . From these coefficients the thermoelastic constants $T_{ij} = d \log c_{ij}/dT$ were derived. The values of thermal expansion necessary for correction of the thickness and density change of the crystals in that temperature interval were obtained with an optical dilatometer. The problem of sign ambiguity which occurs in evaluating the elastic constants c_{12} , c_{13} , and c_{23} was solved by some static measurements of Young's modulus and Poisson's ratio in some directions also employing the stability criteria which forbid negative values for s_{ii} and K .

All values are tabulated in Table 1. The probable errors are within the following limits:

Table 1. *Elastic constants c_{ij} , thermoelastic constants T_{ij} and coefficients of thermal expansion α_i of 1,3,5-triphenylbenzene*

In brackets the values of Suresh Chandra & Hemkar (1973). Units: c_{ij} in 10^{11} erg cm^{-3} , T_{ij} in $10^{-3}/^\circ\text{C}$, α_i in $10^{-6}/^\circ\text{C}$, c_{ij} for 20°C ; T_{ij} and α_i for 0°C .

c_{11}	c_{22}	c_{33}	c_{12}	c_{13}	c_{23}
0.720	1.353	1.433	0.430	0.421	0.468
(0.031)	(0.136)	(0.233)	(-0.178)	(0.092)	(0.080)
c_{44}	c_{55}	c_{66}	α_1	α_2	α_3
0.632	0.097	0.185	125	5	5
(0.502)	(0.034)	(0.369)			
T_{11}	T_{22}	T_{33}	T_{12}	T_{13}	T_{23}
-1.371	-1.504	-1.403	-1.37	-1.33	-2.65
T_{44}	T_{55}	T_{66}			
-1.08	-0.09	-0.75			

Acta Cryst. (1974). **A30**, 107

Conditions for the diffraction enhancement of symmetry of types 1 and 2. By TAKEO MATSUMOTO and KUNIAKI KIHARA, *Department of Earth Sciences, Faculty of Science, Kanazawa University, Kanazawa 920, Japan* and HITOSHI IWASAKI, *The Institute of Physical and Chemical Research, Rikagaku Kenkyusho, Wako-shi, Saitama 351, Japan*

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A re-examination of the conditions for the diffraction enhancement of symmetry for the structures of types 1 and 2 [Iwasaki H. (1972). *Acta Cryst.* **A28**, 253-260] has brought out the existence of some additional solutions. The conditions for these types of structures have been systematically tabulated.

Diffraction enhancement of symmetry, which means the appearance of a higher Laue symmetry than normally expected, has been studied by several authors (Sadanaga & Takeda, 1968; Iwasaki, 1971, 1972; Marumo & Saito, 1972; Ohsumi, Okamura & Sadanaga, 1972). In particular, Iwasaki (1972) has classified the structures into four types, and systematically investigated, using a general expression for the square of the structure amplitude, the necessary conditions of enhancement for each type of structure. By a re-examination of these conditions, we have come across some additional solutions of the equation (12) as given by Iwasaki (1972) for the case of the Laue symmetry $2/m$, mmm , $4/m$ and $4/mmm$ of the structures of types 1 and 2, which are composed of substructures with the same space group.

c_{11}, c_{22}, c_{33} : 0.3%; other c_{ij} : 2%.
 T_{11}, T_{22}, T_{33} : 3%; other T_{ij} except T_{55} : 10%
 For T_{55} the error limit may be larger.

The large discrepancy between the older values published by Suresh Chandra & Hemka (see Table 1) and the values of this paper indicates that only some rough idea of the elastic anisotropy and the order of magnitude of the constants can be derived from thermal diffuse scattering of X-rays. In other cases the discrepancies were not of this magnitude. At the moment one cannot decide whether the experimental procedure of the authors was inadequate or whether the first-order approximation of X-ray scattering by phonons is insufficient. In molecular crystals, such as TPHB, a certain contribution to the background from thermal diffuse scattering by low-frequency internal molecular vibrations and librational movements should be expected. Still other perturbations may originate from stronger deviations of the ideal undisturbed lattice structure.

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References

- FARAG, M. S. (1954). *Acta Cryst.* **7**, 117-121.
 GROTH, P. (1919). *Chemische Kristallographie V*. Leipzig: Engelmann.
 HAUSSÜHL, S. (1965). *Acta Cryst.* **18**, 980.
 JOSHI, S. K. & KASHYAP, B. M. S. (1964). *Acta Cryst.* **17**, 629-632.
 SURESH CHANDRA & HEMKAR, M. P. (1973). *Acta Cryst.* **A29**, 25-28.

For instance, the enhancement condition for monoclinic Laue symmetry $2/m$, unique axis c [equation (18) in Iwasaki (1972)], is given by

$$\cos 2\pi(hu_{pq} + kv_{pq} + lw_{pq}) = \cos 2\pi(hu_{pq} + kv_{pq} - lw_{pq}) \quad (1)$$

for any combination of p and q , where u_{pq} , v_{pq} and w_{pq} are the three components of the difference vector from the origin of the p th substructure to that of the q th substructure, and hkl are the indices of a reflexion. By taking the origin of the crystal coincident with that of an arbitrarily chosen substructure, the solution of equation (1) can be written in the form

$$(u_p, v_p) = (0, 0) \text{ or } (0, \frac{1}{2}) \text{ or } (\frac{1}{2}, 0) \text{ or } (\frac{1}{2}, \frac{1}{2})$$