# Ionic size effects on the thermal expansion coefficient in NaCl-type alkali halides. By Aijaz A. Khan, *Department of Geological Sciences, University of Illinois – Chicago, Chicago, Illinois* 60680, *U.S.A.*

Relations are observed in NaCl-type crystals between the coefficient of thermal expansion, $\alpha$, and (1) the radius ratio $r^+/r^-$, and (2) the difference, $\Delta x$, between the observed and calculated bond length when the calculated bond length is obtained by adding the average effective ionic radii.

The coefficient of thermal expansion of a crystal depends to a large extent on its atomic structure type. Megaw (1939) has shown for ionic crystals that the average coefficient of expansion, $\alpha$, is inversely proportional to the square of the electrostatic valency defined by Pauling (1929) as ($Z$/C.N.), where $Z$ is the valency and C.N. is the coordination number of an ion. This relation is true to a considerable degree and the product $\alpha \times (Z/C.N.)^2 \times 10^6$ is approximately equal to unity in many ionic structures. However, many isomorphous crystal structures have different expansion coefficients. For example, LiF and LiI, both with the NaCl structure, have coefficients $33 \cdot 8 \times 10^{-6} {}^\circ C^{-1}$ and $55 \cdot 7 \times 10^{-6} {}^\circ C^{-1}$ respectively (see Fig. 1). In these cases, other factors such as the ionic-size effect, electronegativities and polarizabilities of

atoms may show their influence. In NaCl-type structures the effect of radius ratio on thermal expansion appears to be important. Pauling (1928) has emphasized the anion–anion repulsion effect in alkali halide structures at small $r^+/r^-$ values. The thermal expansion coefficients and the radius ratios of several alkali halides with the NaCl structure are plotted against each other in Fig. 1. Many of the points lie on a smooth curve, the coefficient $\alpha$ increasing rapidly at smaller values of $r^+/r^-$. The coefficients for LiF and NaF are much too small to lie on this curve and probably are to be attributed to the high electronegativity of fluorine and to the closer anion–cation approach in the structure. The equation of the curve excluding these two points is

$$\alpha = 113 \cdot 4 - 290 \cdot 9(r^+/r^-) + 379 \cdot 8(r^+/r^-)^2$$
$$- 166 \cdot 6(r^+/r^-)^3 . \quad (1)$$

The same factors which may influence the coefficient of expansion may also affect the length of an ionic bond. In other words, the effective size of an ion may differ slightly for different members of an isomorphous series. The difference, $\Delta x$, between the observed and calculated bond length may reflect the influence of these factors when the
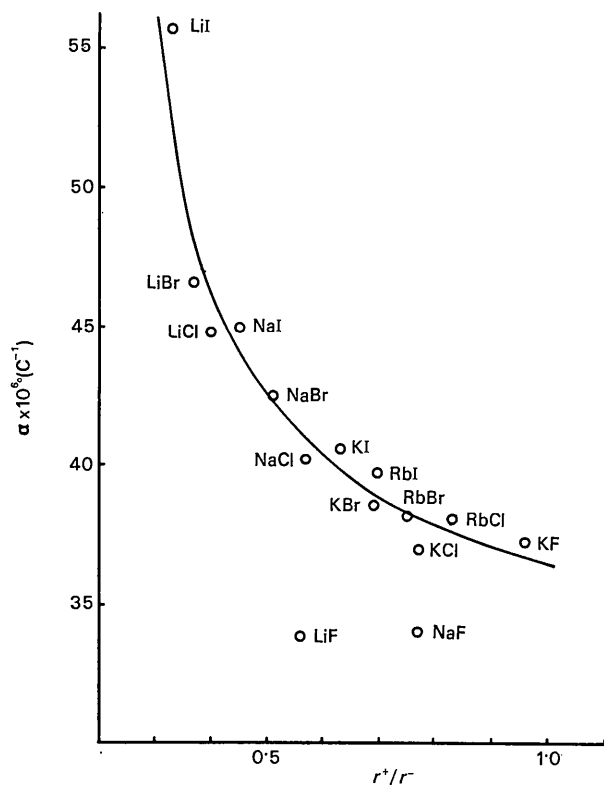


Fig. 1. Coefficient of thermal expansion $\alpha$ *vs.* radius ratio $r^+/r^-$. Expansion coefficients for NaF and KF from Deshpande (1955), for RbCl, RbBr and RbI from Sirdeshmuk (1963) and for the rest as listed by Srinivasan & Krishnan (1958). Effective ionic radii for the cations are from Shannon & Prewitt (1969) and for the anions from Ahrens (1952). For KF the radius ratio $r^-/r^+$ is used instead of $r^+/r^-$.
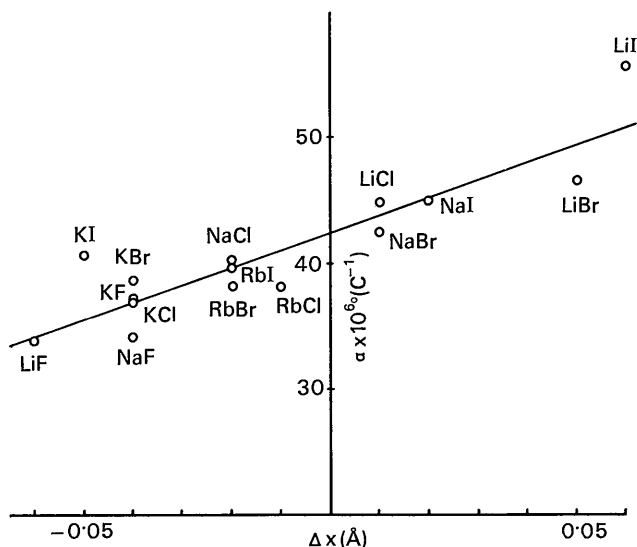


Fig. 2. Coefficient of thermal expansion $\alpha$ *vs.* the difference, $\Delta x$, between the observed and the calculated bond length ($r^+ + r^-$). Observed bond length based on the lattice parameters listed in Wyckoff (1963). See Fig. 1 for other references.

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 $\Delta x$ when plotted against the coefficient $\alpha$ (Fig. 2) results in a correlation coefficient equal to 0·90. The equation of the straight line is

$$\alpha = 42 \cdot 6 + 139 \cdot 5 \Delta x . \qquad (2)$$

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 $\alpha$ and $\Delta x$ 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 $42 \cdot 6 \times 10^{-6} {}^{\circ}C^{-1}$.

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# 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). A**29**, 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 ($-2 \cdot 4385 . 10^{-11}$ cm³/erg) and also the bulk compressibility $K = -0 \cdot 293 . 10^{-11}$ cm³/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