

with  $n$ , as  $n$  becomes large; consequently, it is reasonable to use a finite  $n$ . The second approximation is a linearization which is accomplished by replacing the square-bracketed term in (3) by 1. In order to see that this is justified, consider the exact solution to  $\det(A) = 0$  in the one-beam case ( $n = 1$ ). It is  $\gamma = \chi_z \pm (\chi_z^2 - u_0)^{1/2}$ . We may neglect the plus sign in this equation, since it represents backscattering, and write the solution as  $\gamma = (u_0/2\chi_z)[1 + 0(v_0/E)]$ . Linearization neglects the  $0(v_0/E)$  correction. When  $n > 1$ , linearization is justified for the same reason because the off-diagonal elements  $A$  are of the same magnitude ( $u_g/\chi_z$ ) as the diagonal elements we have just discussed.

These two approximations are well known, but they are usually implemented with the additional restriction  $g_z = 0$ . Our point here is that this latter restriction is not necessary for sufficiently thick specimens. For extremely thin specimens, where the electrostatic potential of the crystal in the  $z$  direction cannot be described by a Fourier series, presumably a Born approximation treatment would be sufficient.

Thus, under these approximations, the dispersion surface is determined by the solution to

$$\det [A' - \gamma(j)I] = 0 \quad (4)$$

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**The relationship between cell volume, mean bond length and effective ionic radius.** By F. C. HAWTHORNE,  
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If ionic radii are calculated so as to predict accurately mean interatomic distances, then the relationship between cell volume and the cube of the cation radius for a series of isotypic compounds is non-linear.

It has been noted by several authors (Shannon & Prewitt, 1969; Shannon, 1975) that in the highly symmetric structure types, such as the rocksalt, fluorite and perovskite structures, the mean bond lengths calculated by summation of the effective ionic radii deviate from the observed values in a systematic manner. In general, the observed bond lengths are significantly greater than the calculated values for small cations; these deviations diminish as the size of the cation decreases, and actually become negative for the oxides EuO, SrO and BaO with the rocksalt structure. Shannon & Prewitt (1969) suggest that these discrepancies may be the result of decreased repulsion effects between nearest-neighbour anions due to the highly symmetric nature of the polyhedra.

Another characteristic of the highly symmetric structure types is their non-linearity on a type I stability diagram (Shannon & Prewitt, 1970a). The majority of plots of unit-cell volume *vs*  $r^3$  (the cube of the cation radius) for isotypic structures are linear to a first approximation, and this has been used both for confirmation of unit-cell volumes and for the calculation of ionic radii (Prewitt & Shannon, 1969; Shannon & Prewitt, 1970b). However, Fukunaga & Fujita (1973) and Shannon (1975) have shown that this type of plot is non-linear for the rocksalt, corundum,  $BaM^{4+}O_3$  and  $SrM^{4+}O_3$  perovskites and  $Sm_2M_2^{4+}O_7$  pyrochlore structures, and we encountered the same non-linearity in an examination of the garnet structures. In addition, Shannon (1975) has

where

$$A'_{gh} = \left[ \frac{K^2 - (\chi + \mathbf{g})^2}{2(\chi + \mathbf{g})_z} \right] \delta_{gh} + (1 - \delta_{gh}) \frac{u_{g-h}}{2(\chi + \mathbf{g})_z}$$

In summary, (4) gives a simple extension of the usual formulation of transmission high-energy electron diffraction (Sturkey, 1962) to higher-order Laue zones. The only difference is that here we allow the vector  $\mathbf{g}$  to range over the Laue zones of interest.

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noted that it is possible that all such plots show this non-linearity, but that it is only noticeable when the structure type is stable for a wide range of cation radii.

With regard to these two points, it is instructive to examine the rocksalt structure in a little more detail. The cation occupies the 4(a) position at 0,0,0 and the anion occupies the 4(b) position at  $\frac{1}{2},0,0$ . Thus the cell edge,  $a$ , may be written in terms of the bond length,  $l$ , as  $a = 2l$ . If ionic radii are calculated so as to reproduce interatomic distances, then

$$l = r_{\text{cation}} + r_{\text{anion}}$$

and the cell volume may be written as

$$v = [2(r_{\text{cation}} + r_{\text{anion}})]^3.$$

Hence the cell volume is not a linear function of the cube of the cation radius. Fig. 1 illustrates this for the  $M^{2+}O$  rocksalt structures, and shows the relationship between cell volume and the cube of the cation radius, where the full line indicates the ideal relationship, the broken line shows the linear relationship indicated by Shannon & Prewitt (1970a) and the data points are plotted using the cation radii of Shannon (1976). As suggested by Shannon (1975), the non-linearity exhibited by Fig. 1 is only apparent over the whole range of cation radius values, and would not be apparent over a reduced range of values.

Similar arguments may be developed for other cubic

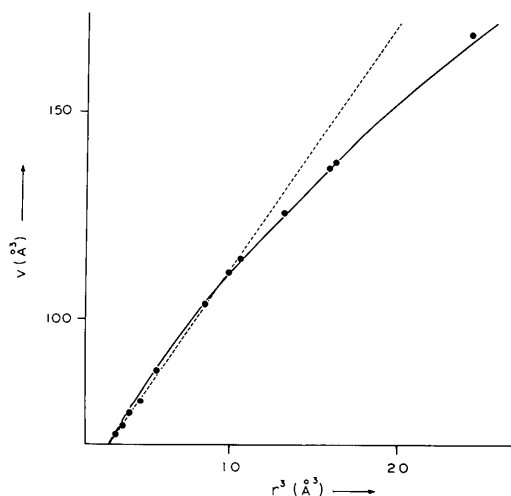


Fig. 1. Cell volume *vs* cube of cation radius for the  $M^{2+}O$  structures. The full line indicates the ideal relationship, the broken line shows the linear relationship indicated by Shannon & Prewitt (1970a) and the data points are plotted using the radii of Shannon (1976).

structure types (e.g.  $M^{2+}F_2$  fluorites) to illustrate this point. Thus if cation radii are calculated to reproduce mean interatomic distances, the relationship between cell volume and the cube of the cation radius is non-linear. This factor should be taken into account both in the use of type I stability diagrams (Shannon & Prewitt, 1970) and the prediction of mean interatomic distances using cation radii that have been derived from  $V$  *vs*  $r^3$  plots.

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### An X-ray determination of the thermal expansion of silver and copper-base alloys at high temperatures.

**III. Ag–Ge and Cu–Ge.** BY S. K. PAL, S. K. HALDER and S. P. SEN GUPTA, *Department of General Physics and X-rays, Indian Association for the Cultivation of Science, Calcutta 700 032, India*

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X-ray measurements of the lattice spacings in three Ag–Ge alloys in the temperature interval 30–595°C and in two Cu–Ge alloys in the temperature interval 25–611°C, in the solid-solution range, have been made with a Unicam 19 cm high-temperature camera. The measured lattice spacings have been found to increase non-linearly with temperature, this non-linearity being slightly enhanced for Cu–9.25 at.% Ge alloy. The dependence of the measured lattice spacings on temperature has been expressed in an analytical form (polynomial of second degree) from least-squares fitting of the data. The thermal expansion coefficient,  $\alpha$ , for the alloys considered, in general, has been found to decrease linearly with increasing temperature (from  $\sim 25$  to  $\sim 17 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ ), except for the greater germanium concentration (9.25 at.%) in copper solvent where the tendency is reversed.

X-ray measurements of lattice spacing in the temperature interval 26–522°C for four Ag–Ga alloys, and in the temperature interval 30–514°C for four Cu–Ga alloys have been reported earlier in parts I and II, respectively, by Halder & Sen Gupta (1974, 1975). The present investigation, referred to as III, reports the X-ray measurement of lattice expansion on three Ag–Ge alloys from 30 to 595°C and two Cu–Ge alloys from 25 to 611°C, all the alloys being in the solid-solution range. The purpose of the present programme has already been emphasized earlier in I (Halder & Sen Gupta, 1974).

The preparation of three Ag–Ge alloys containing 1.48, 4.51 and 7.51 at.% Ge (Halder & Sen Gupta, 1977) and two Cu–Ge alloys containing 3.05 and 9.25 at.% Ge was made by placing suitable amounts of spectroscopically pure silver, copper and germanium material, obtained from Messrs Johnson, Mathey & Co. Ltd, London, in evacuated and

sealed quartz capsules and by melting the elements in a temperature-controlled furnace. The homogenization treatment for Cu–Ge and Ag–Ge alloys was made at temperatures of 750 and 650°C respectively for 10 d. The actual compositions were determined in the same way as described earlier in I after comparison of the powder photographs and diffractometer (Philips model 1050, 51) data with those of Hume-Rothery, Lewin & Reynolds (1936) for Cu–Ge and Owen & Rolands (1940) for Ag–Ge alloys, and this was further confirmed from chemical analyses which did not show appreciable change. X-ray photographs at different temperatures were taken with powder samples in thin-walled quartz capillaries of inner diameter 0.3 mm in the standard Unicam (19 cm) high-temperature powder camera, with Cu  $K\alpha$  radiation. Powder samples were made 'strainfree' by annealing the Ag–Ge samples at 600°C for 6 h and the Cu–Ge sample at 620°C for 8 h inside the