

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, α , for the alloys considered, in general, has been found to decrease linearly with increasing temperature (from ~ 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

chamber of the high-temperature camera. The lattice parameters were determined to an accuracy of $\pm 0.0004 \text{ \AA}$ with the same procedure as adopted earlier in I and II.

Figs. 1 and 2 show the dependence of lattice spacing, obtained from the measurements of two sets of photographs, on temperature. This dependence may be analytically expressed by relations of the form: $a_T = a_0 + a_1T + a_2T^2$ (T in $^\circ\text{C}$) derived from a least-squares fit (on an IBM 1130 computer) of experimental data, the best fit being obtained with a polynomial of second degree.

(a) Ag-Ge alloys

(i) Ag-1.48 at.% Ge

$$a_T(\text{\AA}) = 4.0831 + 1.0585 \times 10^{-4}T - 2.5956 \times 10^{-8}T^2.$$

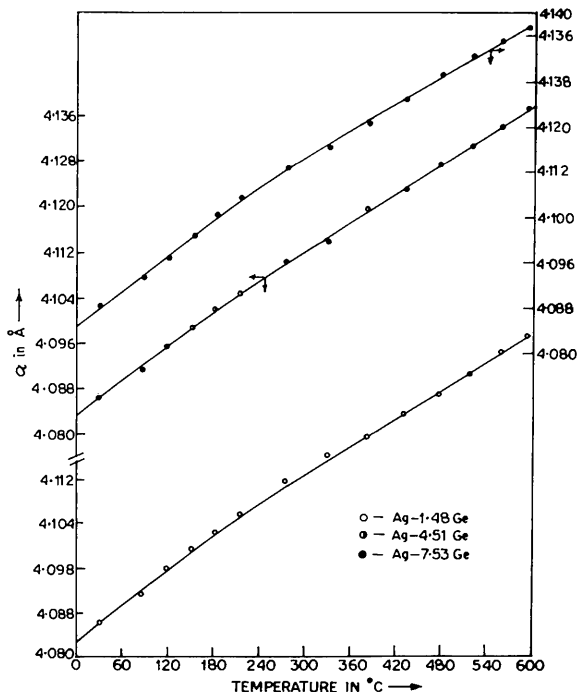


Fig. 1. Plot of lattice spacings, a , versus temperature, T , for the three Ag-Ge alloys.

(ii) Ag-4.51 at.% Ge

$$a_T(\text{\AA}) = 4.0837 + 1.0110 \times 10^{-4}T - 1.8668 \times 10^{-8}T^2.$$

(iii) Ag-7.53 at.% Ge

$$a_T(\text{\AA}) = 4.0844 + 1.0791 \times 10^{-4}T - 3.1023 \times 10^{-8}T^2.$$

(b) Cu-Ge alloys

(i) Cu-3.05 at.% Ge

$$a_T(\text{\AA}) = 3.6226 + 0.8100 \times 10^{-4}T - 1.6391 \times 10^{-8}T^2.$$

(ii) Cu-9.25 at.% Ge

$$a_T(\text{\AA}) = 3.6437 + 0.5385 \times 10^{-4}T + 5.2321 \times 10^{-8}T^2.$$

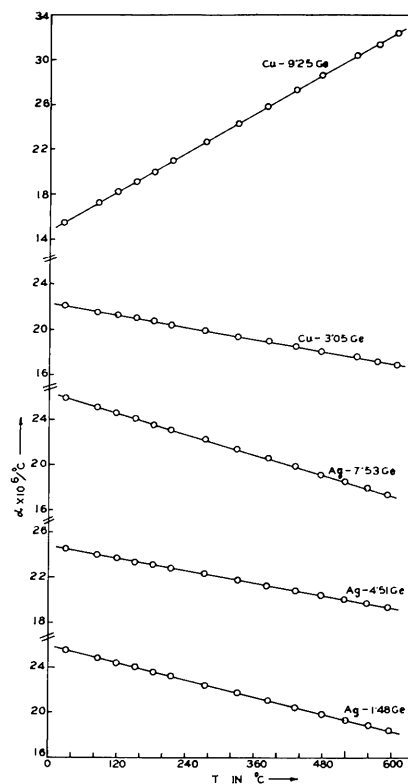


Fig. 3. Plot of thermal expansion coefficient $\alpha [= (1/a_0)(da_T/dT)_p]$ versus temperature, T , for the Ag-Ge and Cu-Ge alloys.

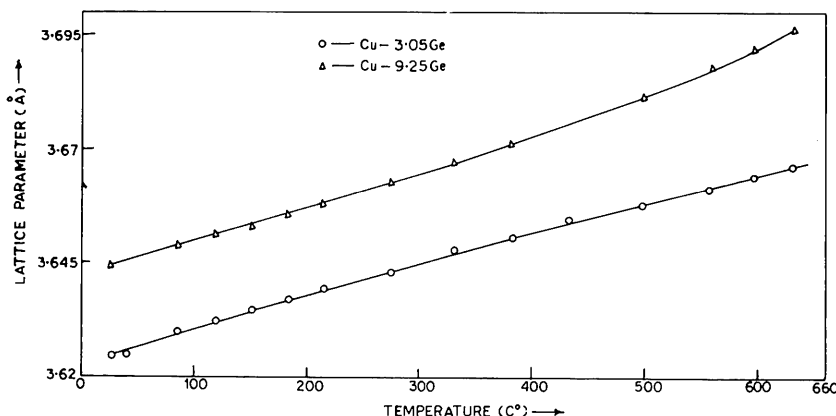


Fig. 2. Plot of lattice spacings, a , versus temperature, T , for the two Cu-Ge alloys.

It may be seen from the above analytical expressions and also from Figs. 1 and 2 that with increasing temperature the lattice spacing increases in a non-linear manner, the non-linearity being slightly enhanced for the Cu-9.25 at.% Ge alloy (Fig. 2). From Fig. 3 as well as from the analytical expression it is apparent that for Ag-Ge alloys there is a gradual linear decrease in the thermal expansion coefficient $\alpha = (1/a_0)(da_T/dT)_p$, with increase in temperature (from ~ 25 to $\sim 17 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$). For Cu-Ge alloys (Fig. 3), the expansion coefficient α for the initial composition (Cu-3.05 at.% Ge) is also found to decrease linearly from $\sim 22 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ to $\sim 17 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, but for the higher 9.25 at.% Ge sample the tendency is reversed and α increases rather rapidly from $\sim 15 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ to $\sim 32 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. This is, however, depicted from the nature of the slopes in the a - T plot (Fig. 2) and also from the coefficients in the analytical expressions for the Cu-Ge samples (i) and (ii).

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Comments on X-ray linear absorption coefficient of silicon for Cu $K\alpha$ and Mo $K\alpha$ radiations by J. L. Lawrence. By P. SUORTTI, *Department of Physics, University of Helsinki, Siltavuorenpenger 20 D, SF-00170 Helsinki 17, Finland*

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The reported large discrepancies between the measured and the tabulated absorption coefficients of silicon [Lawrence, *Acta Cryst.* (1977), **A33**, 343] are shown to arise from the neglect of the scattering contribution and probably from contamination of the incident beam by harmonic wavelengths.

The measured values of the absorption coefficient for single-crystal silicon are 12.9 and 6.8% lower than those quoted in *International Tables for X-ray Crystallography* (1974) (*ITXC*) for Cu $K\alpha$ and Mo $K\alpha$ radiations, respectively. However, the measured value does not include the contribution of the Bragg scattering to the attenuation, while it is accounted for in the tabulated values. According to DeMarco & Suortti (1971) this amounts in Si to 1.0% for Cu $K\alpha$ and 3.1% for Mo $K\alpha$. Moreover, the tabulated values are for the weighted means of α_1 and α_2 , whereas the experimental set-up of a perfect crystal monochromator and very small apertures suggests that only one component was selected from the X-ray beam, and presumably this was the more intense α_1 component. This would affect the attenuation coefficients by 0.2% for Cu $K\alpha$ and 0.6% for Mo $K\alpha$. Thus the difference for Mo $K\alpha$ is reduced to 3.1%, while the value for Cu $K\alpha$ is still 11.7%, low in comparison with the tabulated value. Recent measurements, as quoted by Inkinen, Pesonen & Paakkari (1970), for the neighboring element, Al, suggest that the value in *ITXC* (1974) for Cu $K\alpha$ may be too high by 1 to 2%.

The reported low value for Cu $K\alpha$ radiation probably arises from beam hardening. The attenuation of Cu $K\alpha$ in the 0.5 mm thick slab of Si crystal varies from 10^3 to 10^6 with $\varphi = 0$ to $\varphi = 60^\circ$, while the crystal is almost transparent for $\lambda/2$ and higher harmonics. Even a minute harmonic contamination of the order of 10^{-5} in the incident beam reduces the attenuation coefficient by several percent. This amount of $\lambda/2$ is almost unavoidable in the beam reflected from a perfect Si(111) monochromator, if the X-ray tube is run above the excitation voltage of about 16 kV. The actual amount depends on the operation conditions of the X-ray tube and on the width of the reflected $\lambda/2$ wavelength

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band, which is in turn determined by the beam divergences. The power in the $\lambda/2$ band is typically of the order of 1% of the characteristic radiation [see, for example, *ITXC* (1962) p. 151]. For a perfect Si crystal, the reflecting power of 222 is about 1% of that of 111 (Aldred & Hart, 1973), and a PHA (pulse-height analyzer) may reduce the $\lambda/2$ contamination by an additional factor of 10. The author implies that no curvature due to beam hardening was found in the graph of $\log I$ against $1/\cos \varphi$, but it may have been concealed by other difficulties in measuring very small count rates (a few counts per second) when approaching $\varphi = 60^\circ$.

It may be useful to note in this context that $\lambda/3$ and higher harmonics also cause subtle difficulties in absorption measurements. Although not counted in the PHA window set for the characteristic radiation they increase drastically the dead time of the counting sequence, as demonstrated by Suortti & Jennings (1977).

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