Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

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An X-ray determination of the thermal expansion of α-phase Ag–Ga alloys at high temperatures.

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The lattice parameters of four Ag–Ga alloys in the solid-solution range have been determined by X-ray methods in the temperature interval of 26–522 °C using a Unicam 19 cm high-temperature powder camera. In all the cases the lattice parameters have been found to increase in a non-linear manner in the measured range of temperature and the relationship has been expressed in analytical form from the least-squares fitting of data. The linear thermal expansion coefficients have, however, been found to decrease with increasing temperature.

The study on the thermal expansion of solids which arises mostly as a result of anharmonicity in lattice vibrations is important in improving the understanding of the interatomic forces and the equation of state of solids. As the theoretical evaluations of the binding forces in terms of interatomic distances are rather complicated, considerable interest has been shown in the past in the experimental measurement of thermal expansion in metals, semiconductors, ionic crystals, *etc.* over a wide range of temperature by the conventional dilatometric, interferometric and X-ray diffraction methods. However, there have been relatively few measurements with binary alloys at high temperatures (Owen & Roberts, 1939; Quader & Dey, 1962; Rao & Rao, 1964; De, 1969; Hamalainen, Laine & Tarna, 1969). The present investigation, which forms part of our programme of study of the thermal expansion behaviour of binary alloys at high temperatures, concerns X-ray measurement of lattice expansion of four Ag–Ga alloys in the solid-solution range (α-phase) in the temperature interval of 26–522 °C.

Ag–Ga alloys containing 3·55, 9·45, 13·05 and 15·90 at.% gallium were prepared from spectroscopically pure silver and gallium (Johnson Matthey & Co., Ltd., London) in evacuated and sealed quartz capsules, the melting being done in an induction furnace. The alloys were then homogenized at 550 °C for 10 days. As there was slight loss of gallium during preparation, the actual compositions of the prepared alloys were obtained after comparing the lattice parameter values, determined from the diffractometer tracings and the analytical fit discussed later, with the experimental lattice-parameter–composition data of Hume-Rothery & Andrews (1942). X-ray photographs were taken with powder samples in thin-walled Pyrex capillaries of inner diameter 0·3 mm in the standard Unicam 19 cm high-temperature camera using Cu $K\alpha$ radiation. Powder samples were made 'strain-free' by annealing them at 522 °C for 6 h inside the chamber of the high-temperature camera. The temperatures were measured to within ±2 °C in the high-temperature range with the help of Pt–PtRh thermocouples previously calibrated against the lattice parameter of silver (Quader & Dey, 1962). Two sets of photographs were taken at each instant and the positions of the lines were measured with an optical reading device (Rich, Seifert & Co., Hamburg) having an accuracy of 0·1 mm. The lattice parameters were computed by a least-squares method with the Nelson & Riley (1945) extrapolation function, $\frac{1}{2}(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$ as the correction function for systematic errors. The accuracy in the lattice parameter measurements is ±0·0004 Å.

The mean values of the lattice parameter for the four alloys of Ag–Ga from room temperature (26 °C) to 522 °C obtained from the two sets of measurements are listed in Table 1 and the nature of variation with temperature is shown in Fig. 1. Least-squares analysis of the experimental

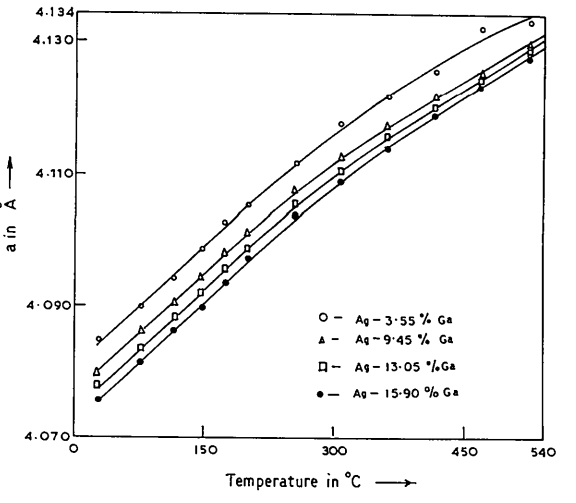

Fig. 1. Lattice-parameter–temperature plot for Ag–Ga alloys in the solid-solution range.

data on an IBM 1130 computer has led to the following analytical expressions of the form $a_T = a_0 + a_1 T + a_2 T^2$, where T refers to temperature in °C:

Table 1. *Lattice parameters and expansion coefficients at different temperatures for the* Ag–Ga *alloys* (α-*phase*)

Temperature (°C)	Lattice parameter a (Å)	Calculated lattice parameter from least-squares analysis (Å)	Deviation from experimental value (Å)	Coefficient of thermal expansion $\alpha \times 10^6$/° C
Ag–3·55 % Ga				
26	4·0850	4·0838	−0·0012	33·90
78	4·0902	4·0908	0·0006	32·05
116	4·0947	4·0957	0·0010	30·70
148	4·0990	4·0996	0·0006	29·56
174	4·1028	4·1027	−0·0001	28·63
200	4·1055	4·1057	0·0002	27·71
254	4·1118	4·1116	−0·0002	25·78
307	4·1178	4·1169	−0·0009	23·90
361	4·1222	4·1220	−0·0002	21·97
415	4·1260	4·1266	0·0006	20·05
469	4·1321	4·1308	−0·0013	18·13
522	4·1335	4·1345	0·0010	16·24
26	4·0850			
Ag–9·45 % Ga				
26	4·0802	4·0795	−0·0007	33·57
78	4·0864	4·0864	0·0000	31·73
116	4·0906	4·0913	0·0007	30·38
148	4·0942	4·0951	0·0009	29·24
174	4·0982	4·0982	0·0000	28·32
200	4·1013	4·1011	−0·0002	27·40
254	4·1076	4·1070	−0·0006	25·48
307	4·1127	4·1123	−0·0004	23·60
361	4·1175	4·1173	−0·0002	21·69
415	4·1217	4·1218	0·0001	19·77
469	4·1255	4·1259	0·0004	17·86
522	4·1297	4·1296	−0·0001	15·97
26	4·0801			
Ag–13·05 % Ga				
26	4·0781	4·0773	−0·0008	32·58
78	4·0835	4·0839	0·0004	31·12
116	4·0881	4·0887	0·0006	30·12
148	4·0920	4·0926	0·0006	29·24
174	4·0957	4·0956	−0·0001	28·53
200	4·0986	4·0986	0·0000	27·81
254	4·1052	4·1046	−0·0006	26·32
307	4·1105	4·1101	−0·0004	24·86
361	4·1156	4·1154	−0·0002	23·37
415	4·1203	4·1204	0·0001	21·88
469	4·1247	4·1250	0·0003	20·39
522	4·1294	4·1293	−0·0001	18·93
27	4·0785			
Ag–15·90 % Ga				
26	4·0758	4·0751	−0·0007	34·26
78	4·0817	4·0820	0·0003	32·62
116	4·0864	4·0870	0·0006	31·40
148	4·0898	4·0910	0·0012	30·37
174	4·0942	4·0942	0·0000	29·53
200	4·0978	4·0973	−0·0005	28·70
254	4·1042	4·1034	−0·0008	26·97
307	4·1092	4·1090	−0·0002	25·26
361	4·1142	4·1144	0·0002	23·53
415	4·1194	4·1194	0·0000	21·79
469	4·1240	4·1240	0·0000	20·06
522	4·1280	4·1281	0·0001	18·36
27	4·0759			

(i) Ag–3·55 Ga:
a_T (Å) $= 4{\cdot}0801 + 1{\cdot}4211 \times 10^{-4} T - 7{\cdot}2655 \times 10^{-8} T^2$

(ii) Ag–9·45 Ga:
a_T (Å) $= 4{\cdot}0759 + 1{\cdot}4060 \times 10^{-4} T - 7{\cdot}2302 \times 10^{-8} T^2$

(iii) Ag–13·05 Ga:
a_T (Å) $= 4{\cdot}0737 + 1{\cdot}3575 \times 10^{-4} T - 5{\cdot}6159 \times 10^{-8} T^2$

(iv) Ag–15·90 Ga:
a_T (Å) $= 4{\cdot}0712 + 1{\cdot}4300 \times 10^{-4} T - 6{\cdot}5378 \times 10^{-8} T^2$.

It has been observed in the above analysis that the best fit is obtained with a polynomial of second degree while the inclusion of higher-order terms gives an overall displacement of all the calculated points in one direction. The calculated lattice parameters from the above expressions and their deviations from the experimental ones are also shown in Table 1 for the sake of comparison. The coefficients of linear thermal expansion $\alpha = 1/a_0 \, (da_T/dT)_p$ have also been obtained from the above analytical expressions and the values are shown in Table 1, which also includes the lattice parameter values for the initial and final room-temperature measurements of each alloy specimen, indicating that there is no significant loss of solute gallium during the repeated heat treatments.

It may be seen from Fig. 1 that the lattice parameters increase in a non-linear manner over the whole range of temperature concerned which is also implied from the above analytical expressions. Similar behaviour has been observed in all the four compositions under investigation. The non-linearity with the increase of temperature which has earlier been observed in many cases is the manifestation of the anharmonic contribution and the vacancy concentration. It is, however, interesting to note here the linear decrease in expansion coefficient (Table 1) with increasing temperature; this follows from the equations above and the lattice-parameter–temperature plots (Fig. 1). This suggests that although there is unit-cell expansion with the increase in temperature, the rate of change of this expansion with the rate of change of temperature is not influenced accordingly. This results in a net decrease in the value of the expansion coefficient. This behaviour can only be predicted from the nature of the binding forces between the constituent atoms and the temperature variation of the Gruneisen parameter γ which is a weighted average of the Gruneisen parameters of various lattice vibrational modes γ_i defined by $-(\partial \log \omega_i / \partial \log v)T$.

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References

De, M. (1969). *Indian J. Phys.* **43**, 367–376.
Hamalainen, M., Laine, E. & Tarna, T. (1969). *J. Appl. Cryst.* **2**, 95–101.
Hume-Rothery, W. & Andrews, K. W. (1942). *J. Inst. Metals*, **68**, 133.
Nelson, J. B. & Riley, D. P. (1945). *Proc. Phys. Soc.* **57**, 160–177.
Owen, E. A. & Roberts, E. W. (1939). *Phil. Mag.* **27**, 294–327.
Quader, M. A. & Dey, B. N. (1962). *Ind. J. Phys.* **36**, 43–54.
Rao, C. N. & Rao, K. K. (1964). *Canad. J. Phys.* **42**, 1336–1342.