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Thermal Vibrations of Atoms in Ag–Cd and Ag–Zn Solid Solutions

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From X-ray measurements at room and low temperatures it was found that the characteristic temperature Θ of the system Ag–Cd decreases by about 17°K in the concentration range from 0 to 30 at.% Cd. For the system Ag–Zn no systematic change of Θ with increasing concentration of Zn was observed.

Introduction

The temperature dependence of the intensity of X-ray Bragg reflexions from solids can be described by the Debye–Waller factor $\exp(-2M)$, which contains the characteristic temperature Θ, a parameter characterizing the material.

The present paper describes measurements of the integrated intensity of reflexions from the face-centred cubic metallic solid solutions of cadmium or zinc in silver; these measurements lead to a determination of their characteristic temperature and its dependence on concentration. These alloys are interesting from the following point of view. Measurements of the lattice specific heat and the elastic moduli, C_{ij}, of α-phase alloys of the noble metals near 0°K suggest a change in characteristic temperature Θ which is, according to Collins (1967), a function only of the electron/atom ratio for solutions whose ion cores are isoelectronic with the solvent; *i.e.* for the two series of Hume-Rothery alloys for example:

	Number of valency electrons				
	1	2	3	4	5
	Cu:	Zn	Ga	Ge	As
	Ag:	Cd	In	Sn	Sb

In our case both cadmium and zinc atoms have two valency electrons and hence the valency effect is the same in both alloys. On the other hand the ion cores of cadmium atoms are identical with the ion cores of silver atoms, whereas the ion cores of zinc atoms are identical with the ion cores of copper atoms. The same valency effects in both systems enable us to determine the influence of the other factors: the different atomic masses of Cd and Zn and the opposing dilatation effects during the substitution into the silver crystal lattice.

Experimental

The measurements were carried out at room and liquid nitrogen temperatures with an URS X-ray diffractometer with the use of monochromatized Cu $K\alpha$ radiation and a Geiger counter.

The samples were cooled in a vacuum chamber* by contact with a copper reservoir filled with liquid nitrogen. The temperature of the sample was determined by means of a thermocouple; the accuracy of the temperature determination was estimated to be about ±4°K.

Solid solutions Ag–Cd and Ag–Zn were prepared and homogenized by annealing for about 24 hours in vacuum at a temperature of 650°C according to Birchenal & Cheng (1949). By filing and subsequent grinding a fine powder was obtained. The effects of the deformation of the material were removed by a further anneal for 3 hours in vacuum at a temperature of 500°C. From

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* For a description of this low temperature camera see Valvoda (1969).

standard back-reflexion photographs it was found that the crystallites were sufficiently small and no noticeable broadening of the reflexion lines was observed. The powder was pressed into small copper blocks to form a flat surface for the measurements.

The reflexion lines measured were 111, 200, 220, 311, 420 and 422. The intensities were chart-recorded, with an angular velocity 2θ of the Geiger counter. The recorded reflexion lines were planimetered assuming a straight line background. The resulting areas represent the integrated intensity in arbitrary units.

Methods of calculating Θ and $\bar{u}_s^2$

(*a*) *Room temperature measurements*

The mean-square displacement $\bar{u}_s^2$ and Θ values at room temperature were determined from the measured values of integrated intensities I_T of diffraction lines with Σh_i^2 from 3 to 24 according to the relations

$$\ln I'_T = -\frac{4\pi^2\bar{u}_s^2}{a^2}\Sigma h_i^2 + \ln c_T \qquad (1)$$

and

$$\ln I'_T = -\frac{3h^2}{mka^2}\left[\frac{T}{\Theta^2} + \frac{1}{36T}\right]\Sigma h_i^2 + \ln c_T\,, \qquad (2)$$

where I'_T is the measured intensity divided by the usual factors (Lorentz, polarization, multiplicity and the square of the atomic scattering factor), a is a lattice constant, m the atomic mass, h the Planck constant, k the Boltmann constant, T the temperature and c_T the constant on the absolute intensity scale. The second formula is valid for temperatures $T > \Theta/6$ (for evaluation see for example Valvoda, 1968). The slope of the linear plot of $\ln I'_T$ against Σh_i^2 yields the $\bar{u}_s^2$ and Θ values.

Atomic scattering factors corrected for dispersion were used to calculate the I'_T values from the measured integrated intensities I_T. The absorption factor was constant in our arrangement. In the case of solid solutions the weighted-mean values of the atomic mass and atomic scattering factor were used.

(*b*) *Measurements at room and low temperatures*

The low temperature measurements were carried out at 85°K. Let $T_2 = 293$ and $T_1 = 85\,°\mathrm{K}$. From equation (2) it follows that

$$\ln\frac{I'_{T_1}}{I'_{T_2}} = \frac{3h^2}{mk}\left[\frac{1}{a_2^2}\left(\frac{T_2}{\Theta_2^2} + \frac{1}{36T_2}\right) - \frac{1}{a_1^2}\left(\frac{T_1}{\Theta_1^2} + \frac{1}{36T_1}\right)\right]\Sigma h_i^2 + \ln c \qquad (3)$$

where I'_{T_1} and I'_{T_2} are the measured intensities divided by the factors cited above at the low and room temperatures respectively (the difference between these factors at T_1 and T_2 is caused by the small change of Bragg angle if T changes from T_2 to T_1). The temperature dependence of Θ was taken into account in the following manner. It was found by Michalchenko & Kushta (1963) that the temperature dependence of Θ for such elements as for example Al, Ag, Pb, Cu and Fe was well described by the relation

$$\frac{\mathrm{d}\ln\Theta}{\mathrm{d}T} = -2\gamma\beta \qquad (4)$$

where γ is the Grüneisen parameter and β the coefficient of volume expansion. According to equation (4) we can express Θ_1 (the low temperature value of Θ) as

$$\Theta_1 \simeq \Theta_2 \exp 2\gamma\beta(T_2 - T_1) = \Theta_2 C \qquad (5)$$

where we assume C to be a constant. It is convenient to express the value of the lattice constant a_1 at the low temperature T_1 in a similar manner:

$$a_1 = a_2 \,.\, g \qquad (6)$$

where g is given by the ratio of the experimentaly determined values of a_1 and a_2.

Taking Θ_1 and a_1 according to (5) and (6) and substituting in (3) we obtain

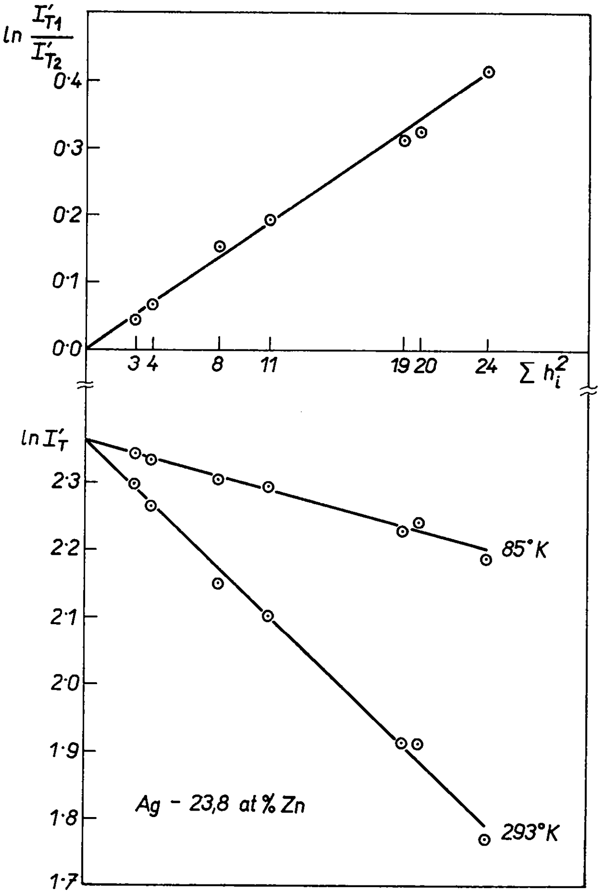

Fig. 1. The dependence of $\ln\frac{I'_{T_1}}{I'_{T_2}}$ and $\ln I'_T$ on Σh_i^2 for the alloy Ag–23·8 at.% Zn ($T_1 = 85\,°\mathrm{K}$; $T_2 = 293\,°\mathrm{K}$).

$$\ln \frac{I'_{T_1}}{I'_{T_2}} = \frac{3h^2}{mka_2^2}\left[\frac{1}{\Theta_2^2}\left(T_2 - \frac{T_1}{g^2C^2}\right) + \frac{1}{36}\left(\frac{1}{T_2} - \frac{1}{g^2T_1}\right)\right]\Sigma h_i^2 + \ln c\,. \quad (7)$$

The slope of the linear plot of $\ln \frac{I'_{T_1}}{I'_{T_2}}$ against Σh_i^2 yields Θ_2, the value of Θ corresponding to room temperature. The values of $\overline{u_s^2}$ can be obtained from the Θ values by means of the relation

$$\overline{u_s^2} = \frac{3\hbar^2}{mk}\left[\frac{T}{\Theta^2} + \frac{1}{36T}\right] \quad (8)$$

as follows from equations (1) and (2).

For the Ag–Cd and Ag–Zn solid solutions the values of γ and β for pure silver were used. Lattice constants of silver and solid solutions of given concentrations were taken from Pearson's (1958) handbook.

The second method described uses the ratio I'_{T_1}/I'_{T_2} which is much less sensitive to extinction and to the presence of static displacements of atoms, and almost independent of preferred orientation, misalignment of the specimen and the atomic scattering factor. The first method, on the other hand, yields the Θ values without any additional assumption concerning the temperature dependence of Θ. Thus the two methods complement each other.

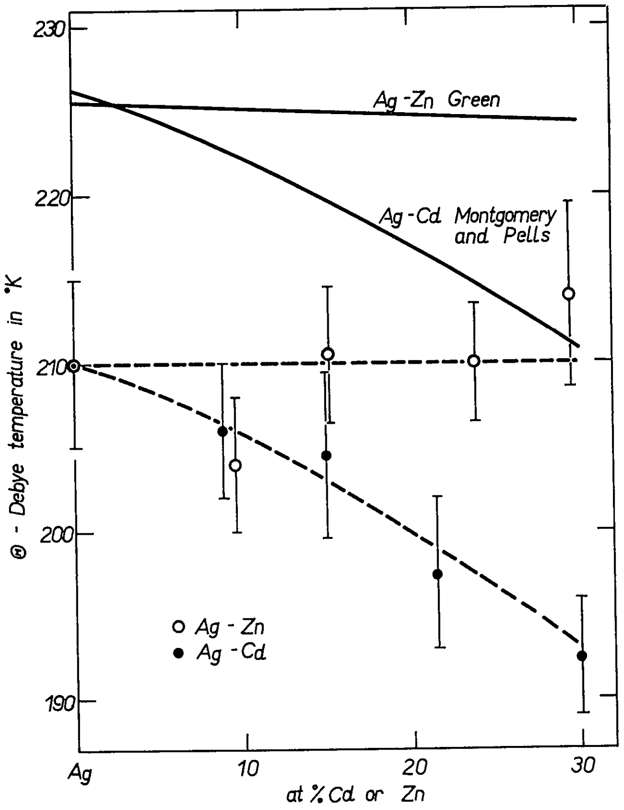

Fig. 2. The concentration dependence of Θ values for Ag–Cd and Ag–Zn solid solutions. The full lines are dependences determined by Green (1966) and Montgomery & Pells (1967) from specific heat measurements near 0 °K.

Results and discussion

The results of the calculation of Θ and $\overline{u_s^2}$ are given in Table 1 in terms of Θ_2 and $(\overline{u_s^2})_2$, the values corresponding to room temperature.

Table 1. $\overline{u_s^2}$ *and* Θ *values at room temperature*

The errors are a result of the scattering of points along a straight line.

	Method	$(\overline{u_s^2})_2 \,.\, 10^2$ (Å^2)	Θ_2 (°K)
Ag	*A*	0·87 ± 0·06	213 ± 6
	B	0·92 ± 0·05	207 ± 4
Ag– 8·8 at.% Cd	*A*	0·87 ± 0·05	212 ± 5
	B	0·98 ± 0·04	200 ± 3
Ag–14·9 at.% Cd	*A*	0·94 ± 0·03	205 ± 3
	B	0·94 ± 0·06	204 ± 7
Ag–21·4 at.% Cd	*A*	1·01 ± 0·05	198 ± 5
	B	1·00 ± 0·04	197 ± 4
Ag–30·0 at.% Cd	*A*	1·02 ± 0·02	197 ± 2
	B	1·09 ± 0·05	188 ± 5
Ag–9·5 at.% Zn	*A*	0·94 ± 0·03	209 ± 4
	B	1·03 ± 0·04	199 ± 4
Ag–15·1 at.% Zn	*A*	0·94 ± 0·04	212 ± 4
	B	0·97 ± 0·03	209 ± 4
Ag–23·8 at.% Zn	*A*	0·98 ± 0·03	211 ± 4
	B	1·00 ± 0·03	209 ± 3
Ag–29·5 at.% Zn	*A*	1·00 ± 0·02	212 ± 3
	B	0·96 ± 0·06	216 ± 8

An example of a graphical representation of the dependence of $\ln I'_T$ and $\ln \frac{I'_{T_1}}{I'_{T_2}}$ on Σh_i^2 is given in Fig. 1.

During preparation of the samples great care was taken to avoid giving rise to the extinction effect: no reduction in the intensities of low order reflexions was observed (see for example Fig. 1). The difference between the $\overline{u_s^2}$ values determined by the *A* and *B* methods lies within the limits of accuracy of our measurements. On the basis of our experiments it is thus impossible to detect the presence of static displacements of atoms should they really exist in our systems. However, because the difference in the atomic radii of the components is lower than 4% and 7% in the Ag–Cd and Ag–Zn alloys respectively we expect a negligible value of static displacements.

It should be noted that the values of Θ_1 determined from the low temperature measurements only suffer from a relatively large error arising from the small value of the slope of the $\ln I'_{T_1}$ *versus* Σh_i^2 lines. These values are therefore worthless for our purposes.

In Fig. 2 the values of Θ averaged over the values obtained by the *A* and *B* methods are plotted. The vertical bars represent the values of the standard deviations. Apart from uncertainties in individual Θ values it is evident that in the system Ag–Cd Θ decreases by about 17°K in the concentration range from 0 to 30 at.% Cd. For the system Ag–Zn no systematic change of Θ with concentration of Zn was observed. The same behaviour for Θ of these systems was found by Montgomery & Pells (1967) and Green (1966) from measurements of specific heat near 0°K (full lines in Fig.2). The difference between X-ray and specific heat Θ values on the absolute scale is caused by the different averaging of the frequency vibration spectrum in the two methods, together with the temperature dependence of Θ. It is also interesting to note that the application of the well known Lindemann formula for both systems gives results which agree with our measurements if we take the solidus lines as melting temperatures.

The electron concentration, as a number of valency electrons per atom, increases with increasing concentration of solutes at the same rate in both systems. We can check the change of Θ with concentration according to the proportionality

$$\Theta \sim \sqrt{\frac{a}{m}}\, f(c_{ij}) \tag{9}$$

which follows from the De Launay (1956) formula for Θ of cubic metals near 0°K, a is a lattice parameter, m is the atomic mass and $f(c_{ij})$ is a unique function of the elastic constants c_{ij}, tabulated by De Launay. In the case of solid solutions we take $m=c_A m_A + c_B m_B$, where c_A and c_B are the atomic concentrations and m_A and m_B the atomic masses of components A and B. We suppose that the main reason for the different behaviour of $\Theta_{\text{Ag-Cd}}$ and $\Theta_{\text{Ag-Zn}}$ is the decrease in the mean atomic mass in Ag–Zn solid solutions with increasing Zn concentration. The atomic weight of Cd (112, 41) is comparable to the atomic weight of Ag (107, 88), whereas the atomic weight of Zn (65, 38) is much smaller. The change of lattice constants in the two systems is in the opposite sense but in the range of concentrations studied it is smaller than 2%. If we compare $\Theta_{\text{Ag-Zn}}$ and $\Theta_{\text{Ag-Cd}}$ for any given concentration of Zn or Cd we have, according to (9)

$$\frac{\Theta_{\text{Ag-Zn}}}{\Theta_{\text{Ag-Cd}}} = \sqrt{\frac{a_{\text{Ag-Zn}}}{a_{\text{Ag-Cd}}}\,\frac{m_{\text{Ag-Cd}}}{m_{\text{Ag-Zn}}}}\;\frac{[f(c_{ij})]_{\text{Ag-Zn}}}{[f(c_{ij})]_{\text{Ag-Cd}}}\,. \tag{10}$$

For 30 at.% Zn or Cd

$$\frac{\Theta_{\text{Ag-Zn}}}{\Theta_{\text{Ag-Cd}}} = 1{\cdot}058\,.\,\frac{[f(c_{ij})]_{\text{Ag-Zn}}}{[f(c_{ij})]_{\text{Ag-Cd}}} \tag{11}$$

because $a_{\text{Ag-Zn}}=4{\cdot}018$ kX, $a_{\text{Ag-Cd}}=4{\cdot}144$ kX, $m_{\text{Ag-Cd}}=109{\cdot}26$ and $m_{\text{Ag-Zn}}=94{\cdot}5$. The ratio of the specific-heat values of $\Theta_{\text{Ag-Zn}}$ and $\Theta_{\text{Ag-Cd}}$ (measured near 0°K) for 30 at.% Cd or Zn gives 1·064 and we see that we can neglect the difference in the change of the f functions. It is thus possible to ascribe the difference in the behaviour of Θ of both systems mainly to the different rate of change of the mean atomic mass with concentration. The same valency effect in the two systems is then expressed by an approximately equal change in the f functions which depend, through the elastic constants, on the number of valency electrons.

Conclusions

From our X-ray measurements we have found that with increasing concentration of solute atoms in the systems Ag–Cd and Ag–Zn the characteristic temperature Θ decreases by about 17°K in the former system and is practically constant in the latter system in the range of concentrations from 0 to 30 at.% of solute. This different behaviour of Θ in the Ag–Cd and Ag–Zn solid solutions is ascribed mainly to the different atomic weights of Cd and Zn atoms because the valency effect is the same in both systems.

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