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Debye Characteristic Temperature as a Measure of the Ordering Parameter. I. General Theory

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The Debye characteristic temperature of a binary alloy has been expressed in terms of ordering parameter, the Debye characteristic temperature of the constituent metals and the proportions of the metals. This has been done by considering the non-central force model with electron gas participation. The first- and second-nearest-neighbour interactions only have been considered. This expression is found to predict correctly the Debye characteristic temperatures of Cu_3Au as a function of the long-range ordering parameter.

Introduction

Since order–disorder phenomena depend upon the distribution of atoms in the different lattice sites, all structure-sensitive properties (electrical, thermal, mechanical *etc.*) are expected to change with a change in order. Therefore all these properties can be used as a measure of the ordering in the material. The frequency spectrum of the solid will also depend upon the distribution of atoms and, as the Debye characteristic temperature is connected with the frequency spectrum, the Debye characteristic temperature will also change as a result of order–disorder phenomena. Up till now no theoretical work has been reported connecting the Debye characteristic temperature with the ordering. In the course of the present investigation an expression connecting the Debye characteristic temperature with the state of order has been derived.

Part II of this series of papers (Mitra & Chaudhuri, 1974) reports, with the help of this expression, the determination of the ordering parameter of α-brass which cannot be determined by usual X-ray methods; the present theoretical investigation was taken up precisely for this purpose. Comparison of existing experimental data for Cu_3Au with the derived expression is reported in Part I to establish the validity of the theoretical expression derived.

Theoretical

The Debye characteristic temperature Θ of a crystal for both b.c.c. and f.c.c. lattices including the effect of the electron gas can be written as (de Launay, 1953)

$$\Theta = C\left[\frac{c_{12}+2c_{44}}{M}\right]^{1/2}$$

where

$$C=\frac{h}{k}\left[\frac{qN}{4\pi V}\right]^{1/3} a^{3/2} f(c_{11},c_{12},c_{44}) \qquad (1)$$

and c_{12} and c_{44} are the elastic constants of the crystal, h is Planck's constant, K is Boltzmann's constant, V is atomic volume, a is the lattice constant, M is the atomic weight, and $f(c_{11},c_{12},c_{44})$ is the function of elastic constants c_{11}, c_{12}, c_{44}.

By considering the central-force model, de Launay (1953) has deduced relations connecting the elastic constants and force constants of f.c.c. and b.c.c. crystals. He has neglected the angular forces. But in ordinary metals, the angular force constants between the nearest-neighbour atoms are of the same order of magnitude as the central force constant. Also, the electron gas contributes considerably to elastic constants. Thus from considerations of a non-central force model and electron gas participation (which has been assumed to follow the ion motion exactly in acoustic waves) the relations between the force constants and the elastic constants of the metals having the f.c.c. structure are given by (see the Appendix)

$$\begin{aligned} a(c_{11}+2c_{12}) &= 4\alpha_2+8\gamma-4\beta+\delta \\ a(c_{11}-c_{12}) &= 6\alpha_1+4\alpha_2-4\gamma+2\beta \\ ac_{44} &= 2\alpha_1+2\beta \end{aligned} \qquad (2)$$

where α_1, α_2, γ and β are the different central and angular force constants due to the nearest and next-nearest-neighbour interactions and δ is the force constant arising from the electron gas. Alternatively, from (2) we get,

$$a(c_{12}+2c_{44}) = 2\alpha_1+2\beta+4\gamma+\frac{\delta}{3}\,. \qquad (3)$$

For binary alloys, as a result of the like and unlike neighbours, there are three different kinds of atomic force constants, for example, α_1^{AA}, α_1^{BB} and α_1^{AB}. Atomic force constants for the AB alloy are given by the average of atomic force constants for A–A, B–B and A–B pairs weighted by the probability of appearance of these pairs. For face-centred cubic alloys, as deduced by Shimizu & Niu (1967), the mean atomic force constants of the alloy AB (pq) composed of two metals A and B having the atomic proportions p and q respectively are given by

$$\alpha_1^{AB(pq)}=\alpha_1^{AA}p_A^0p_A^{nn}+\alpha_1^{BB}p_B^0p_B^{nn}+\alpha_1^{AB}(p_A^0p_B^{nn}+p_B^0p_A^{nn})$$
$$\alpha_2^{AB(pq)}=\alpha_2^{AA}p_A^0p_A^{nnn}+\alpha_2^{BB}p_B^0p_B^{nnn}+\alpha_2^{AB}(p_A^0p_B^{nnn}+p_B^0p_A^{nnn})$$
$$\gamma^{AB(pq)}=\gamma^{AA}p_A^0p_A^{nn}+\gamma^{BB}p_B^0p_B^{nn}+\gamma^{AB}(p_A^0p_B^{nn}+p_B^0p_A^{nn})$$
$$\beta^{AB(pq)}=\beta^{AA}p_A^0p_A^{nn}+\beta^{BB}p_B^0p_B^{nn}+\beta^{AB}(p_A^0p_B^{nn}+p_B^0p_A^{nn})$$
$$\delta^{AB(pq)}=\delta^{AA}p_A^0p_A^{nn}+\delta^{BB}p_B^0p_B^{nn}+\delta^{AB}(p_A^0p_B^{nn}+p_B^0p_{nn}^{A}) \quad (4)$$

where p_A^0, p_B^0 and p_A^{nn}, p_B^{nn} and p_A^{nnn}, p_B^{nnn} denote the probabilities of appearance of A and B atoms at the origin, nearest-neighbour and next-nearest-neighbour lattice points respectively.

From order–disorder theory, if s is the long-range or short-range order parameter, then it can be shown (Elcock, 1956) that

$$\begin{aligned}
p_A^0p_A^{nn} &= p^2(1-s^2)\\
p_B^0p_B^{nn} &= 1+p^2-2p-p^2s^2\\
p_A^0p_A^{nnn} &= p^2(1+s)^2\\
p_B^0p_B^{nnn} &= (1-p-ps)^2\\
p_A^0p_B^{nn}+p_B^0p_A^{nn} &= 2p-2p^2+2p^2s^2\\
p_A^0p_B^{nnn}+p_B^0p_A^{nnn} &= 2p(1+s)\,[1-p(1+s)]\,. \quad (5)
\end{aligned}$$

Thus from (5) and (4) we get

$$\begin{aligned}
&\left[2\alpha_1^{AB(pq)}+2\beta^{AB(pq)}+4\gamma^{AB(pq)}+\frac{\delta^{AB(pq)}}{3}\right]\\
&\quad=(p^2-p^2s^2)\left[2\alpha_1^{AA}+2\beta^{AA}+4\gamma^{AA}+\frac{\delta^{AA}}{3}\right]\\
&\quad+(1+p^2-2p-p^2s^2)\left[2\alpha_1^{BB}+2\beta^{BB}+4\gamma^{BB}+\frac{\delta^{BB}}{3}\right]\\
&\quad+(2p-2p^2+2p^2s^2)\left[2\alpha_1^{AB}+2\beta^{AB}+4\gamma^{AB}+\frac{\delta^{AB}}{3}\right] \quad (6)
\end{aligned}$$

where α_1^{AB}, β^{AB}, γ^{AB} and δ^{AB} are the force constants of a fictitious lattice composed of atoms of atomic weight M_{AB}.

Since the value of c in equation (1) does not change very much from the original values for alloying, we will get, on rearranging from the relations (6), (3) and (1),

$$\begin{aligned}
\Theta^2_{AB(pq)}M_{AB(pq)} &= p^2[\Theta_A^2M_A+\Theta_B^2M_B-2\Theta_{AB}^2M_{AB}]\\
&\quad+2p[\Theta_{AB}^2M_{AB}-\Theta_B^2M_B]+\Theta_B^2M_B\\
&\quad-p^2s^2[\Theta_A^2M_A+\Theta_B^2M_B-2\Theta_{AB}^2M_{AB}]\,, \quad (7)
\end{aligned}$$

where $\Theta_{AB(pq)}$, Θ_A and Θ_B are the Debye characteristic temperatures of the alloy $AB(pq)$ and the component metals A and B of atomic weights $M_{AB(pq)}=pM_A+qM_B$, M_A and M_B respectively, and Θ_{AB} is the Debye characteristic temperature of the fictitious lattice AB.

For at state of complete disorder, *i.e.* $s=0$, we get the identical relation to that obtained by Mitra & Chattopadhyay (1972).

Equation (7) cannot be applied unless the value of $\Theta^2_{AB}M_{AB}$ of the fictitious lattice is known. However, this value can be calculated from the known value of $\Theta^2_{AB(pq)}M_{AB(pq)}$ of the alloy at a given state of ordering s. In the present investigation, the theory has been applied in the case of Cu_3Au alloys using Quimby's (1954) and other experimental data (Rayne, 1957; Bowen, 1954).

Discussion

The value of $\Theta^2_{AB}M_{AB}$ for the fictitious lattice has been determined from Quimby's (1954) computed data on the Debye characteristic temperature Θ of Cu_3Au for the completely disordered state $s=0$. Thus, using the value of $\Theta^2_{AB}M_{AB}$, the Debye characteristic temperatures of the alloy corresponding to different states of ordering was calculated and the variation of Θ with s for the alloy is shown in Fig. 1. It is found that the Debye characteristic temperature for the ordered state is larger than that for the disordered state. This is in qualitative agreement with the observation that the elastic constants for Cu_3Au increase on ordering. It is also found that the calculated value of Θ_{ordered} (278 °K) agrees well with the values of 285 °K from specific-heat measurement (Rayne, 1957) and of 272 °K from elastic-constant measurement (Quimby, 1954).

It is also interesting to note that the size of the change in Θ on ordering from our expression ($\Delta\Theta=30$ °K) agrees well with the data obtained by Bowen (1954) from the low-temperature resistance measurement ($\Delta\Theta=22$ °K) and that from elastic-constant data ($\Delta\Theta=24$ °K). Thus, at least in these cases, equation (7) is found to predict correctly the variation of Debye characteristic temperature Θ with the state of ordering s.

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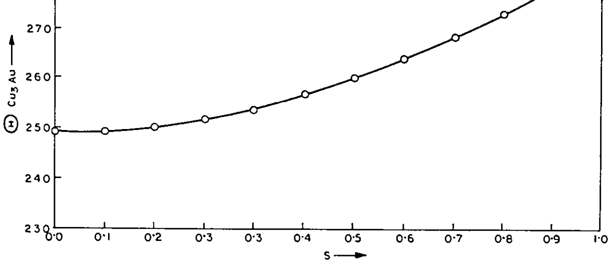

Fig. 1. Variation of Debye characteristic temperature for Cu_3Au with state of ordering.

APPENDIX

The equation of motion in the x-direction connecting the elastic constants and force constants considering nearest and next-nearest-neighbour interactions in a non-central force model for an f.c.c. crystal is given by

$$\varrho \frac{\partial^2 u}{\partial t^2} = \frac{4(\alpha_1+\alpha_2)}{a} \frac{\partial^2 u}{\partial x^2} + \frac{2\alpha_1+2\beta}{a} \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right) + \frac{4\gamma}{a} \left(\frac{\partial^2 v}{\partial x \partial y} + \frac{\partial^2 w}{\partial x \partial z}\right) \tag{8}$$

$$= c_{11} \frac{\partial^2 u}{\partial x^2} + c_{44} \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right) + (c_{12}+c_{44}) \left(\frac{\partial^2 v}{\partial x \partial y} + \frac{\partial^2 w}{\partial x \partial z}\right) \tag{9}$$

where u is the displacement in the x-direction and other symbols have the same significance as in the paper.

Using the transformations of Mitra & Gokhale (1957),

$$e = e_{11} + e_{22} + e_{33}$$
$$f = e_{11} - e_{22}$$
$$g = \tfrac{1}{2}e_{11} + \tfrac{1}{2}e_{22} - e_{33} ,$$

where e_{11}, e_{22}, e_{33} are all strains in the x, y and z directions respectively, equations (8) and (9) can be written as,

$$\varrho \frac{\partial^2 u}{\partial t^2} = \frac{c_{11}+2c_{12}}{3} \frac{\partial e}{\partial x} + \frac{c_{11}-c_{12}}{2} \frac{\partial f}{\partial x} + \frac{c_{11}-c_{12}}{3} \frac{\partial g}{\partial x} + c_{44} \left(\frac{\partial e_{12}}{\partial y} + \frac{\partial e_{13}}{\partial z}\right) \tag{10}$$

$$= \frac{4\alpha_2+8\gamma-4\beta}{3a} \frac{\partial e}{\partial x} + \frac{6\alpha_1+4\alpha_2-4\gamma+2\beta}{2a} \frac{\partial f}{\partial x} + \frac{6\alpha_1+4\alpha_2-4\gamma+2\beta}{3a} \frac{\partial g}{\partial x} + \frac{2\alpha_1+2\beta}{a} \left(\frac{\partial e_{12}}{\partial y} + \frac{\partial e_{13}}{\partial z}\right). \tag{11}$$

The above treatment presupposes the non-participation of free electrons. In the case of free electrons taking part in the propagation of elastic waves, they may be supposed to behave like a gas, propagating only longitudinal waves. The free-electron gas will then give rise to an additional force constant and in equation (11) a term $\delta/3a$ has to be added to the coefficient of $\partial e/\partial x$ as has been discussed by Mitra & Gokhale (1957). Then with the electron-gas participation, the relations between the force constants and elastic constants are given from (10) and (11) by

$$a(c_{11}+2c_{12}) = 4\alpha_2 + 8\gamma - 4\beta + \delta$$
$$a(c_{11}-c_{12}) = 6\alpha_1 + 4\alpha_2 - 4\gamma + 2\beta$$
$$ac_{44} = 2\alpha_1 + 2\beta .$$

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