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X-ray Studies on Debye Characteristic Temperatures of Disordered Binary Substitutional Alloys

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An expression has been derived for the Debye characteristic temperatures of disordered binary substitutional alloys in terms of the Debye characteristic temperatures of the component metals, concentration of the solute atom and an unknown parameter which can be found from the Debye characteristic temperature of the alloy at any particular concentration. Debye temperatures of polycrystalline specimens of copper, nickel and copper–nickel (20, 30, 40, 50, 60, 80 and 90% nickel by weight) alloys have been determined by X-ray diffraction methods. Intensities of different reflexions have been measured with the help of a highly accurate counter-diffractometer technique and corrected for temperature diffuse scattering, diffuse scattering due to random distribution of guest atoms in host sites and difference in sizes of different atoms (in case of alloys only) and incorrect background. Debye temperatures have been plotted against concentration and the variation has been compared with theoretical predictions. Experimental results are found to agree satisfactorily with the predictions obtained during the present investigations.

Introduction

The effect of foreign atoms on lattice vibrations in crystals has attracted much recent attention. Since substitutional binary alloys form important examples of foreign atoms in the host lattice, such systems are good specimens of experimental verification of the theories. Although the knowledge of the frequency spectrum is the most useful one from which all thermodynamic properties of solids can be determined, its theoretical or experimental determination is fraught with great difficulties. The Debye temperature is another important parameter of lattice vibrations which can be more easily evaluated theoretically and subjected to experimental tests apart from its usefulness in different branches of solid state physics.

The problem of finding an expression for the Debye temperature of a disordered solid solution in terms of the Debye temperatures of the component metals has been taken up by several workers. Although some of these authors have compared the predictions of their own theories with experimental results, a complete comparative study of all these theories in the light of experimental results has not yet been undertaken. In the course of the present investigation an attempt has been made to achieve this with the help of X-ray diffraction studies of some copper–nickel alloys. It may be mentioned that although the copper–nickel system affords a very good example of binary substitutional alloys, the variation of the Debye temperature of this alloy system in the whole concentration range has not been studied by the X-ray diffraction method. Recent advances in X-ray analysis techniques have made it possible to achieve a very high degree of accuracy in the measurement of X-ray intensities and hence of Debye temperatures. It is because of these considerations that the present work has been undertaken. A new expression of the Debye temperature of a disordered binary substitutional alloy has been derived taking into account the average force constants of the alloy and also on the basis of a model of lattice vibrations subject to noncentral forces. The predictions of this theory have also been compared with the present experimental results.

Previous theoretical studies

The earliest and simplest attempt at finding an expression for the Debye temperature of an alloy is based upon the Neumann–Kopp rule (mentioned in Swalin, 1962) which assumes the validity of the additivity of the specific heats of the component metals in the alloy so that

$$C_v^{AB(pq)}=pC_v^A+qC_v^B\,,$$

where $C_v^{AB(pq)}$ is the specific heat of the alloy $AB(pq)$ composed of the metals A and B in atomic concentrations p and q respectively. C_v^A and C_v^B are the specific heats of the component metals A and B. At low temperatures, since $C_v=\frac{12\pi 4R}{3}(T/\Theta)^3$, where T is the temperature in °K, we get

$$\frac{1}{\Theta^3_{AB(pq)}}=\frac{p}{\Theta^3_A}+\frac{q}{\Theta^3_B}\,, \tag{1}$$

where $\Theta_{AB(pq)}$, Θ_A and Θ_B are the Debye temperatures of the alloy $AB(pq)$ and its component metals A and B respectively. Again at high temperatures,

$$C_v=3Nk\left[1-\frac{x^2}{20}+\frac{x^4}{560}\ldots\right]$$

where N is the total number of atoms, k is the Boltzmann constant and $x=\Theta/T$. Retaining the first two terms we get

$$\Theta^2_{AB(pq)}=p\Theta^2_A+q\Theta^2_B\,. \tag{2}$$

Simerská (1963) has given an expression for $\Theta_{AB(pq)}$ from the Neumann–Kopp rule which is

$$\Theta_{AB(pq)}=\Theta^p_A\,.\,\Theta^q_B\,. \tag{3}$$

Again on the assumption of the independence of vibrations of the component atoms in the alloy Simerská (1963) has derived an expression for the Debye temperature of the alloy appropriate to X-ray measurement given by

$$\Theta_{AB(pq)}=\Theta_A\Theta_B\left(\frac{m_Am_B}{pm_A+qm_B}\right)^{1/2} \times\left(\frac{pZ_A+qZ_B}{qZ_Bm_A\Theta^2_A+pZ_Am_B\Theta^2_B}\right) \tag{4}$$

where m_A, m_B, Z_A, Z_B are the masses and the atomic numbers of A and B atoms respectively. Simerská (1963) has compared her experimental results of silver–aluminum alloys with the predictions of the expressions (3) and (4) and has found that equation (4) gives a better but not a satisfactory agreement with the experimental results.

Rezanov & Masharov (1962) have attacked the problem from a different and more sophisticated standpoint and, using the method of variations, obtained an expression of the specific heat of a binary disordered substitutional alloy. Equating this expression to the corresponding Debye expression of specific heat at low temperature in terms of Debye temperature they obtained

$$\Theta^2_{AB(pq)}=\Theta^2_A\left(1+\frac{m_A}{\mu}p\right)\left[1-2p\left(1-\frac{\Theta^2_0}{\Theta^2_A}\right)\right] \tag{5}$$

where $\dfrac{1}{\mu}=\dfrac{1}{m_A}-\dfrac{1}{m_B}$ and Θ_0 is the Debye temperature of an artificial crystal which can be evaluated by putting $p=1$ in which case $\Theta_{AB(pq)}$ should be equal to Θ_A. At low concentration it can be seen from the equation (5) that the Debye temperature varies linearly with concentration. This conclusion was obtained earlier experimentally by Rayne (1957, 1958) in copper–germanium and copper–zinc systems.

Litzman (1963) has derived an expression for the Debye–Waller temperature factor of an alloy in terms of the reciprocal matrix. It is shown that under certain approximations one can separate the influence of the interatomic force constants from that of the masses of the alloy atoms. However, the reciprocal matrix cannot be easily obtained. Therefore, Litzman's theory is not easily amenable to numerical computations and hence not suitable for comparison with experiment.

Syneček (1962) has calculated the effective mean-square amplitude of the thermal vibrations of atoms in binary substitutional metallic solid solution in terms of the order parameter and the nearest neighbour force constants. Recently, Valvoda & Syneček (1967) have extended the previous work and by considering that the root-mean-square amplitude of vibration of an atom is dependent upon the number of like and unlike atoms in its first coordination shell derived the following expression of the Debye temperature of a binary substitutional alloy appropriate to X-ray diffraction measurement

$$\frac{1}{\Theta^2_{AB(pq)}}=\frac{pm_A+qm_B}{pZ_A+qZ_B}\left[\frac{pZ_A}{m_A\Theta^2_A}+\frac{qZ_B}{m_B\Theta^2_B} +jpq\alpha(1-\alpha_1)\left(\frac{Z_A}{m_A\Theta^2_A}+\frac{Z_B}{m_B\Theta^2_B}\right)\right] \tag{6}$$

where j is the total number of atoms in the first coordination sphere of any atom, α_1 the order parameter, α a parameter giving the change in vibrational state of the A (or B) atom if an arbitrary A atom in the first coordination sphere of A (or B) atom is replaced by a B atom, related to the vibrational states of atoms in the pure components.

Present theoretical considerations

The Debye temperature Θ of a crystal is given by (James, 1950)

$$\Theta=C\,\frac{K^{1/2}}{M^{1/3}\varrho^{1/6}} \tag{7}$$

where $$C=\frac{h}{k}\left(\frac{9N}{4\pi}\right)^{1/3}\frac{1}{f^{1/3}(\sigma)}\ \text{for }\Theta=\Theta_D$$

and $$C=\frac{h\sqrt{3}}{k}\left(\frac{3N}{4\pi}\right)^{1/3}\frac{1}{f'^{1/2}(\sigma)}$$

for $\Theta=\Theta_M$. Θ_D and Θ_M are the Debye temperatures appropriate to specific heat and X-ray diffraction measurement respectively. K is the bulk modulus, M the atomic weight of the atom, ϱ the density of the material, k the Boltzmann constant and N Avogadro's number. $f(\sigma)$ and $f'(\sigma)$ are functions of the Poisson ratio of the material given by

$$f(\sigma)=\left\{\frac{1+\sigma}{3(1-\sigma)}\right\}^{3/2}+2\left\{\frac{2(1+\sigma)}{3(1-2\sigma)}\right\}^{3/2}$$

$$f'(\sigma)=\frac{1+\sigma}{3(1-\sigma)}+\frac{4(1+\sigma)}{3(1-2\sigma)}\,.$$

The bulk modulus K can be expressed in terms of the elastic constants as

$$K=\frac{c_{11}+2c_{12}}{3}\,. \tag{8}$$

The relation between the elastic constants and the force constants is given by De Launay (1956) by comparing the secular determinant of the Born–von Karman lattice and that of the sound waves in a continuous medium in a central force model. It is, however, not reasonable to neglect the angular forces for ordinary metals because the angular force constant between nearest neighbour atoms is of the same order of magnitude as the central force constant between next nearest neighbour atoms even for the alkali metals in which the interaction between ion cores is weak. Niu & Shimizu (1967), considering a non-central force model in which the nearest neighbour central, next nearest neighbour central, and nearest neighbour angular forces are operative (the corresponding force constants being α_1, α_2 and β respectively), have deduced by a method similar to that of De Launay (1956) the relations between the force constants and the elastic constants. For face-centred cubic lattices they are given by

$$\begin{aligned}\alpha_1+3\beta&=ac_{44}\\ \alpha_1+4\alpha_2-\beta&=a(c_{11}-c_{44})\\ 2(\alpha_1-\beta)&=a(c_{12}+c_{44})\end{aligned}\tag{9}$$

where a is the lattice constant.

In case of binary alloys there are three different kinds of atomic force constants between different atoms, for example, α_1^{AA}, α_1^{BB} and α_1^{AB} as the atomic force constants between nearest neighbour atoms. Here α_1^{AA} and α_1^{BB} are atomic force constants for pure A and B metals respectively. Atomic force constants for the AB alloy are given by the average of atomic force constants for the A–A, B–B and A–B pairs weighted by the probability of appearance for these pairs. In the case where cubic A and B metals make only cubic alloys by alloying in the whole range of atomic concentration, Niu & Shimizu (1967) have derived expressions for mean atomic force constants of the alloy $AB(pq)$ composed of two metals A and B in the atomic proportions p and q respectively which are

$$\begin{aligned}\alpha_1^{AB(pq)}&=(\alpha_1^{AA}+\alpha_1^{BB}-2\alpha_1^{AB})p^2+2(\alpha_1^{AB}-\alpha_1^{BB})p+\alpha_1^{BB}\\ \alpha_2^{AB(pq)}&=(\alpha_2^{AA}+\alpha_2^{BB}-2\alpha_2^{AB})p^2+2(\alpha_2^{AB}-\alpha_2^{BB})p+\alpha_2^{BB}\\ \beta^{AB(pq)}&=(\beta^{AA}+\beta^{BB}-2\beta^{AB})p^2+2(\beta^{AB}-\beta^{BB})p+\beta^{BB}.\end{aligned}\tag{10}$$

Combining equations (8) and (9) the bulk modulus of an alloy can be written as

$$K_{AB(pq)}=\frac{4}{3a^{AB(pq)}}\,[\alpha_1^{AB(pq)}+\alpha_2^{AB(pq)}-2\beta^{AB(pq)}].\tag{11}$$

Using equation (10) one can write

$$\begin{aligned}K_{AB(pq)}=\frac{4}{3a^{AB(pq)}}\,&[(\alpha_1^{AA}+\alpha_1^{BB}-2\alpha_1^{AB}+\alpha_2^{AA}+\alpha_2^{BB}\\ &-2\alpha_2^{AB}-2\beta^{AA}-2\beta^{BB}+4\beta^{AB})p^2\\ &+2(\alpha_1^{AB}-\alpha_1^{BB}+\alpha_2^{AB}-\alpha_2^{BB}-2\beta^{AB}+2\beta^{BB})p\\ &+\alpha_1^{BB}+\alpha_2^{BB}-2\beta^{BB}].\end{aligned}\tag{12}$$

Now expressing force constants in terms of elastic constants by equation (9) one gets

$$\begin{aligned}K_{AB(pq)}=\frac{1}{6a^{AB(pq)}}\,&[\{a^A(2c_{11}^A+4c_{12}^A)\\ &+a^B(2c_{11}^B+4c_{12}^B)-2a^{AB}(2c_{11}^{AB}+4c_{12}^{AB})\}p^2\\ &+2\{a^{AB}(2c_{11}^{AB}+4c_{12}^{AB})-a^B(2c_{11}^B+4c_{12}^B)\}p\\ &+a^B(2c_{11}^B+4c_{12}^B)].\end{aligned}\tag{13}$$

Here c_{11}^A, c_{11}^B *etc.* are the elastic constants of the pure A and B metals and c_{11}^{AB} *etc.* are the elastic constants of a fictitious metal whose atomic forces of interaction are α_1^{AB} *etc.* Similar notations are used for the lattice constant a. In terms of the bulk moduli of the pure metals and the fictitious metal referred above equation (13) can be written as

$$\begin{aligned}K_{AB(pq)}=\frac{1}{a^{AB(pq)}}\,&[(a^AK_A+a^BK_B-2a^{AB}K_{AB})p^2\\ &+2(a^{AB}K_{AB}-a^BK_B)p+a^BK_B].\end{aligned}\tag{14}$$

Now combining (14) and (7) and assuming $f(\sigma)$ and $f'(\sigma)$ do not change very much in the whole range of concentration

$$\begin{aligned}\Theta^2_{AB(pq)}=&\left(\frac{M_A}{M_{AB(pq)}}\,\Theta_A^2+\frac{M_B}{M_{AB(pq)}}\,\Theta_B^2\right.\\ &\left.-\frac{2M_{AB}}{M_{AB(pq)}}\,\Theta_{AB}^2\right)p^2+2\left(\frac{M_{AB}}{M_{AB(pq)}}\,\Theta_{AB}^2\right.\\ &\left.-\frac{M_B}{M_{AB(pq)}}\,\Theta_B^2\right)p+\frac{M_B}{M_{AB(pq)}}\,\Theta_B^2\end{aligned}\tag{15}$$

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

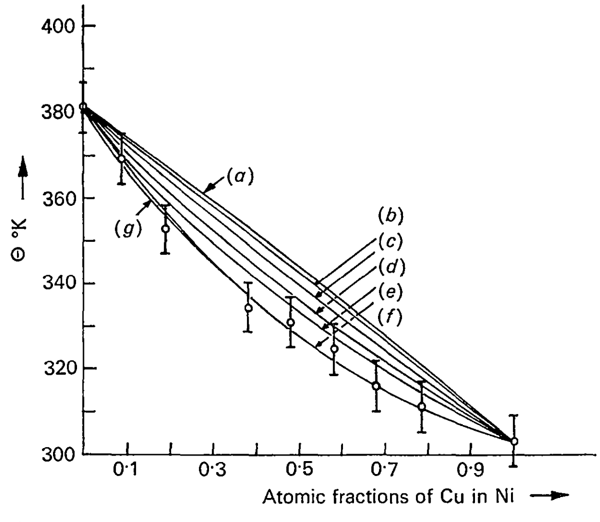

Fig. 1. Variation of the Debye characteristic temperatures of Cu-Ni alloys with concentration. (*a*) Neumann-Kopp rule, high temperature (equation 2), (*b*) Rezanov & Masharov (1962) (equation 5), (*c*) Neumann-Kopp as given by Simerská (1963) (equation 3), (*d*) Simerská (1963) (equation 4), (*e*) Neumann-Kopp rule, low temperature (equation 1), (*f*) Present model (equation 15), (*g*) Valvoda & Syneček (1967) (equation 6), ⌶ indicates experimental points.

fictitious lattice composed of atoms of atomic weight M_{AB} and with force constants α_1^{AB}, α_2^{AB} and β^{AB}.

Experimental techniques

The samples studied were spectroscopically pure copper, nickel and some of their alloys (20, 30, 40, 50, 60, 80 and 90% nickel in copper) and were supplied by Johnson Matthey & Co., Ltd. (London).

The samples were ground to fine powder by filing and were made to pass through a fine sieve. These powdered samples were then annealed at about 800°C for 12 hours in a vacuum annealing furnace to remove defects produced by cold work. Annealed powders were mixed with collodion and cakes were made on a standard sample holder of an X-ray diffractometer.

The distribution of intensity in the X-ray diffraction lines was determined by the point counting method, with the help of a Norelco diffractometer provided with EIT counter tubes. Counts were taken at angular intervals of 0·01° when a peak was scanned and 0·05° at the background. The angular settings were made manually and counts taken for 64 seconds at each setting. At the background and tail of the intensity distributions, where the counting rate was lower, the time of counting was increased so as to count at least 10000 at each setting. Thus the statistical fluctuation error was kept at less than 1% level throughout the experiment. The counting rate was corrected for dead time as well as form factor. The dead time of the Geiger counter was determined as 200 μsec, and since the supply was full-wave rectified (Klug & Alexander, 1952), the form factor was taken as 1·7.

Intergated intensities, *i.e.* the areas under the intensity distribution curves were determined with the help of a planimeter after a proper choice of the background intensities according to the method developed by Mitra & Misra (1966). The integrated intensities thus measured were corrected for temperature diffuse scattering by the method of Chipman & Paskin (1959). For alloys the intensities were further corrected for the diffuse scattering due to random distribution of guest atoms in host sites (Cochran, 1956) and due to difference in sizes of guest and host atoms (Herbstein, Borie & Averbach, 1956). The theoretical values of the atomic scattering factors were taken from Cromer & Waber (1965) who computed these from relativistic self-consistent field wave functions which include Slater's approximate exchange correction. Atomic scattering factors were corrected for anomalous dispersion. Debye temperatures were determined by the usual method described by Mitra & Chattopadhyay (1970).

Results and discussions

Fig. 1 shows the results of calculation of Debye temperatures of alloys in terms of the experimentally determined Debye temperatures of the parent metals on the basis of equation (15) (the unknown parameter being determined from the experimentally determined values of Debye temperature of 30% nickel in copper) as well as the Neuman–Kopp rule and the expressions due to Simerská (1963), Rezanov & Masharov (1962) and Valvoda & Syneček (1967). Fig. 1 also shows the experimentally determined Debye temperatures of the alloys.

It is seen from Fig. 1 that equations (1), (2), (3), (4) and (5) give nearly linear variation of the Debye temperature with concentration. Equations (6) and (15) give a marked non-linear variation of Θ with concentration and both of them fit well with experimental results. Equation (15) has the obvious drawback that it contains one unknown parameter $[M_{AB}/M_{AB(pq)}]\Theta_{AB}^2$ which has to be found from the known experimental value of the Debye temperature of the alloy at a particular concentration. Similarly equation (6) has also one unknown parameter, $\alpha(1-\alpha_1)$ which can be found in a similar way.

In deriving equation (15) it has been assumed that the functions $f(\sigma)$ and $f'(\sigma)$ do not change very much with concentration. This is a valid assumption because most metals and alloys have a Poisson ratio nearly equal to 0·30. At least this is so in the cases of copper, nickel and their alloys. The use of equation (15) should be restricted to such systems. Herbstein (1961) has pointed out that one can improve the situation by making the substitution,

$$K=\frac{E}{3(1-2\sigma)}\,,$$

where E is Young's modulus, before averaging over the longitudinal and transverse values of Θ. One obtains

$$\Theta_M=\frac{h\sqrt{3}}{k}\left(\frac{3N}{4\pi}\right)^{1/3}\frac{E^{1/2}}{M^{1/3}\varrho^{1/6}}f_1(\sigma)$$

where

$$f_1(\sigma)=\left[\frac{3-5\sigma}{(15-26\sigma)(1+\sigma)}\right]^{1/2} \qquad (16)$$

and

$$\Theta_D=\frac{h}{k}\left(\frac{9N}{4\pi}\right)^{1/3}\frac{E^{1/2}}{M^{1/3}\varrho^{1/6}}f_2(\sigma)$$

where

$$f_2(\sigma)=\left(\frac{3-5\sigma}{1+\sigma}\right)^{1/2}\{2^{5/2}(5-3\sigma)+3^{3/2}(1-2\sigma)\}\,. \qquad (17)$$

$f_1(\sigma)$ and $f_2(\sigma)$ are very much insensitive functions of σ. One can start with equations (16) and (17) instead of equation (7). But in that case one may not get a simplified relationship like equation (13).

It is surprising that, in spite of the crude assumptions, equation (1) is quite close to experimental results, whereas the variation obtained from the more sophisticated theory of Rezanov & Masharov (1962) is the second-worst fit with the experimental results. Equation (2) should have agreed better with experimental results than equation (1) since the former is valid at high temperature (room temperature) at which the experiment was performed, whereas actually it is the worst fit. The present formula [equation (15)] and that of Valvoda & Syneček [equation (6)] give equally good agreement with the experimental results and hence both of them are satisfactory additivity relations for the Debye temperature of a disordered binary substitutional alloy in terms of those of the component metals.

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Precise Measurement of Lattice Parameters of Pseudocubic Lattices*

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For accurate measurements of lattice parameters of materials where symmetry differs only slightly from cubic, difficulties arise in the determination of single lines belonging to the lattice of lower symmetry because of the overlapping profiles of the pseudocubic lines. In this contribution the profiles of single lines of lower symmetry are approximated by the Cauchy curve and the profiles of the pseudocubic lines are considered as superpositioning of these curves. The resolution of the profiles and the determination of the lattice parameters are performed by means of a computer fitting least-squares program. The conditions for solving the problem are discussed and the method is then applied to a pseudocubic perovskite.

I. Introduction

The true crystal lattice of pseudocubic structures differs only slightly from the cubic one and the particular diffraction lines are grouped together around the 'pseudocubic' positions. The line splitting is, therefore, often very small; and in the precise determination of lattice parameters, one encounters the problem of resolving the positions of the single lines. For example, in perovskite-like solid solutions of $PbTi_yZr_{1-y}O_3$ for $0{\cdot}10<y<0{\cdot}40$, the true lattice is rhombohedral ($a_r=4{\cdot}13$ Å), but the deviation of the rhombohedral angle α from 90° is only about 16′.

In this paper, a method for resolving the overlapping pseudocubic profiles is presented; and the method is applied to precise lattice parameter determinations of $PbTi_yZr_{1-y}O_3$ for $y=0{\cdot}10$, 0·20, 0·30 and 0·38.

II. Method of resolution of profiles

The procedure for resolving overlapping lines is based on the premise that a single diffraction line can be approximated by a particular analytic function and that the profile of overlapping lines can be expressed by the superposition of these single functions.

Various analytic curves for the approximation of the profile of a single line can be used according to the prob-

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