A simple interpolation formula for the Debye temperatures of disordered alloys.

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A simple formula is derived which expresses the Debye temperature of a disordered multicomponent alloy with small atomic radius disparity in terms of the Debye temperatures of the pure components, the mole fractions of the components, and a set of undetermined parameters, each of which can be found from the Debye temperature for one composition of each possible binary alloy made from the components. The formula is an improvement on a similar formula for the binary case due to Mitra and Chattopadhyay because the physical significance of the undetermined parameters is more readily apparent. The influence of short-range order in the binary case is considered. Application is made to the Ag–Au–Pd, Cr–Fe, and Cu–Ni systems in order to test the formula.

Recently Mitra & Chattopadhyay (1972) derived a formula which can be used to interpolate the Debye temperature of a binary alloy from the Debye temperatures of the pure metals. It contains one adjustable parameter which can be determined from a measurement of the Debye temperature at one intermediate composition. For such a formula to be useful as an interpolation formula it is necessary that the adjustable parameter be independent of composition, and that there be a physical basis for this. The purpose of the present paper is to derive a generalization of the formula to n-component alloys, and to choose a set of adjustable parameters, the physical significance and composition independence of which is somewhat more apparent than in the formula of Mitra & Chattopadhyay (1972). The influence of short-range order in the case of binary alloys is also considered. The formula is applied to the Fe–Cr, Cu–Ni, and Ag–Au–Pd systems.

The derivation of the formula begins with a result which can be deduced from a recent formal analysis of correlations in disordered binary cubic substitutional alloys [see equation (24) of Shirley (1974)]. It is that, in the classical regime, for alloys with negligible atomic radius disparity, the mean-square displacement of an atom from its lattice site is

$$\langle u^2 \rangle = \kappa T \text{ Trace } \mathbf{G}(0) = \kappa T \text{ Trace } \mathbf{g}(0)/2U'',$$

where $\mathbf{G}(0)$ is the static Green's function for the 'average' lattice evaluated at the origin. T is the absolute temperature and κ is Boltzmann's constant. The second equality holds if nearest-neighbor (n.n.) interactions only are taken into account. $\mathbf{g}$ is a dimensionless Green's function [tabulated for f.c.c. by Flinn & Maradudin (1962)] and U'' is given by

$$U'' = m_1^2 V_{11}'' + m_2^2 V_{22}'' + 2m_1 m_2 V_{12}'',$$

where m_1 and m_2 are the mole fractions of type 1 and type 2 atoms, and where V_{xy}'' is the second derivative of the interatomic potential acting between an atom of type x and one of type y, evaluated at the nearest-neighbor separation of the average lattice. If the atoms are noble or transition metals, then the most important part of the potentials at the n.n. separation is the exchange repulsion between the core electrons. The shapes of the potentials are not likely to vary greatly with composition because the core electronic configurations are generally insensitive to composition. If, in addition, the atomic radii are similar, then the second derivative is taken at about the same point on the potential curves irrespective of composition and V_{xy}'' will be largely composition independent. These considerations lead to the following generalization: For an n-component disordered cubic substitutional alloy of transition and/or noble metals of negligible atomic radius disparity,

$$\langle u^2 \rangle = C\kappa T / f \tag{1}$$

where

$$f = \sum_{i=1}^{n} \sum_{j=1}^{n} P_{ij} f_{ij}. \tag{2}$$

Here f is an average nearest-neighbor force constant, f_{ij} is a composition-independent force constant acting between n.n. atoms of type i and j, P_{ij} is the a priori probability of occurrence of an i–j atom pair as nearest neighbors (for a random alloy, $P_{ij} = m_i m_j$), and C is a numerical constant which depends on the lattice structure. For the f.c.c. lattice, $C = 2 \cdot 515$ (Flinn & Maradudin, 1962). We define the following set of $\frac{1}{2}n(n-1)$ constants:

$$\tau_{ij} = 2f_{ij}/(f_{ii} + f_{jj}) \quad (i \neq j). \tag{3}$$

τ_{ij} is the factor by which f_{ij} differs from the arithmetic mean of f_{ii} and f_{jj}. Using equation (3), equation (2) can be written

$$f = \sum_{i=1}^{n} P_{ii} f_{ii} + \frac{1}{2} \sum_{i=1}^{n} \sum_{\substack{j=1 \\ (i \neq j)}}^{n} P_{ij} \tau_{ij}(f_{ii} + f_{jj}). \tag{4}$$

Now the X-ray Debye temperature, θ, for an alloy is defined by (James, 1962)

$$\langle u^2 \rangle = \frac{9\hbar^2}{\kappa a}\left(\frac{T\varphi(\theta/T)}{\mu\theta^2} + \frac{1}{4\mu\theta} \right), \tag{5}$$

where a is the atomic mass unit, $\hbar$ is Planck's constant, φ is Debye's function, and

$$\mu = \sum_{i=1}^{n} m_i \mu_i$$

in which μ_i is the atomic weight of the ith component. Equations (1) and (5) must agree asymptotically as $T \to \infty$ so, using $\varphi(0) = 1$, one writes

$$f = (C\kappa^2 a/9\hbar^2)\mu\theta^2. \tag{6}$$

For the pure metals this becomes

$$f_{ii} = (C\kappa^2 a/9\hbar^2)\mu_i \theta_i^2, \tag{7}$$

where θ_i is the pure-metal Debye temperature. For a random alloy, substitution of (7) into (4) yields

$$\mu\theta^2 = \sum_{i=1}^{n} m_i \mu_i \theta_i^2 + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} (\tau_{ij} - 1)m_i m_j(\mu_i \theta_i^2 + \mu_j \theta_j^2) \tag{8}$$

where the restriction $i \neq j$ has been removed by taking $\tau_{ii} \equiv 1$, and where we have used

$$\sum_{i=1}^{n} m_i = 1 .$$

Equation (8) is the n-component interpolation formula. If the pure-metal Debye temperatures are known, then each of the constants τ_{ij} may be determined by measurement of the Debye temperature of one i–j binary alloy. Of course this procedure applies only to alloy systems forming a single solid-solution phase for all compositions. The formula will hold in any composition domain which encompasses a single solid-solution phase, but the determination of all of the $\mu_i \theta_i^2$ and τ_{ij} may not be as simple. In general, measurements of Debye temperatures at $\frac{1}{2}n(n+1)$ compositions will determine all of the $\mu_i \theta_i^2$ and τ_{ij}, but the compositions must be chosen so that the 'inverse' of equation (8) exists.

It should be noted that although the derivation of (8) was for X-ray Debye temperatures, it also applied to specific-heat Debye temperatures since the two differ by a factor depending on Poisson's ratio (James, 1962), which does not vary greatly from metal to metal.

For a non-random binary alloy, the *a priori* probabilities are given by

$$P_{11} = m_1^2 + m_1 m_2 \alpha , \quad P_{22} = m_2^2 + m_1 m_2 \alpha , \quad P_{12} = m_1 m_2 (1 - \alpha)$$

where α is the n.n. Cowley–Warren short-range-order parameter (Cowley, 1950). When these are used in (4) one finds

$$\mu \theta^2 = m_1 \mu_1 \theta_1^2 + m_2 \mu_2 \theta_2^2 \\ + (\tau_{12} - 1)(1 - \alpha) m_1 m_2 (\mu_1 \theta_1^2 + \mu_2 \theta_2^2) . \quad (9)$$

Short-range order is a strong function of composition and thermal history, so equation (9) shows how it can cause some scatter in τ_{12} determined at different intermediate compositions or from different specimens. The effect is limited, however, by the fact that $|\alpha|$ cannot exceed about 0·2 in the disordered phase (Moss & Clapp, 1968).

To test the validity of the ideas presented above, values of τ were computed from (9) with $\alpha = 0$ for several transition/noble metal binary alloys with small atomic radius disparity, and the results are given in Table 1. When one examines the data and the calculations which the numbers in Table 1 summarize, it is apparent that (except for the Ag–Au alloy, which has $m_{Ag} = 0·5$) the data is well spread across the composition range, and that variation in the values of τ represented as the errors in Table 1 is largely uncorrelated with the composition and is therefore probably attributable to experimental error. This indicates that τ is indeed composition independent as anticipated above. Although this is a necessary condition for the formula's usefulness, it is not especially interesting, since a parabola specified by a constant could probably fit the data as well. What is interesting, however, is to compare the values of τ in Table 1 with those computed *via* (3) using the nearest-neighbor central force constants derived by Niu & Shimizu (1967) from elastic constants data for the Ag–Au and Cu–Ni alloys. The results of Niu & Shimizu (1967) lead to $\tau(\text{Ag–Au}) = 0·95$ and $\tau(\text{Cu–Ni}) = 1·01$. These values agree with the corresponding results in Table 1, except for those derived from the data of Mitra & Chattopadhyay (1972). Since all sets of data, including those analyzed by Niu & Shimizu (1967), are independent, this indicates a possible systematic error in the data of Mitra & Chattopadhyay (1972). On

balance, then, τ does seem to reflect the strength of the unlike-atom force constant relative to the average of the like-atom force constants.

Table 1. *Values of τ for several binary alloy systems*

Alloy system	Number of intermediate compositions	τ	Reference
Ag–Au	1	0·90	1
Ag–Pd	3	1·16 ± 0·06	1
Au–Pd	3	1·29 ± 0·05	1
Cr–Fe	5	0·72 ± 0·05	2
Cu–Ni	8	1·06 ± 0·06	3
Cu–Ni	13	1·09 ± 0·12	4
Cu–Ni	7	0·80 ± 0·05	5

References: (1) Naidu & Houska (1971). (2) Shirley, Lally, Thomas & Fisher (1975). (3) Brandstetter, Ebel & Lihl (1968). (4) Faninger (1971). (5) Mitra & Chattopadhyay (1972).

The formula (8) is especially useful for multicomponent alloy systems because it is only necessary to measure θ for each pure component and for one composition of each possible binary alloy to define θ for all compositions of the alloy system. To illustrate this for a ternary system, average values of τ in Table 1 for Ag–Au, Ag–Pd, and Au–Pd were used in (8) with the pure-metal Debye temperatures to predict the Debye temperatures for the ternary alloys for which Naidu & Houska (1971) measured θ. The predicted and measured values of the Debye temperature are given in Table 2. The agreement is good except for the 75 % Pd alloy. However, when θ for the alloys $\text{Pd}(1-2x)\text{Ag}(x)\text{Au}(x)$ are plotted against x (including $x = 0$ and $x = \frac{1}{2}$), θ for $x = \frac{1}{8}$ seems anomalously low. Thus, there is a good chance of some kind of error in the measurement for $x = \frac{1}{8}$.

Table 2. *Comparison of the Debye temperature for Ag–Au–Pd ternary alloys as measured by Naidu & Houska (1971) and as predicted by equation (8)*

Alloy	Measured	Predicted
Pd(0·75)Ag(0·125)Au(0·125)	250	274
Pd(0·50)Ag(0·250)Au(0·250)	250	253
Pd(0·25)Ag(0·375)Au(0·375)	230	227

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