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LETTER TO THE EDITOR

Calculation of the properties of some metals and alloys

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Abstract. A simple empirical potential is employed to describe the atomic interactions in face-centred cubic (FCC) metals and alloys. Using this model, the finite-temperature properties of some FCC metals and alloys, i.e. Ag, Cu and Ag–Cu disordered alloys have been calculated via a free energy minimization approach under the quasiharmonic approximation (QA). The calculation yields excellent agreement with the experimental results.

For years the determination and calculation of thermodynamic functions for alloys have been the subject of active research [1–6]. Among the approaches developed so far, the calculation of phase diagram (CALPHAD) method [1–3] is a well established and widely applied technique. In this approach, thermodynamic functions are derived by fitting the equilibrium phase diagram, which in turn reproduce correctly the thermodynamic data for the equilibrium alloys. They are, not surprisingly, prone to large errors when applied to *metastable* alloys by extrapolation [7]. In order to apply this approach to metastable alloys, acquisition of thermodynamic data for the metastable alloys is necessary. However, it sometimes requires detailed and very complex experimental procedures. Another often-employed method is a simple approach developed by López, Alonso and Gallego [8] from Miedema's model of the heat of formation [6]. Although it has been proved successful in some binary and ternary systems, since most of the thermodynamic data produced by this scheme are unrelated to temperature, it often disagrees with experimental data. Caution is thus suggested when using this approach. In addition, neither method is capable of predicting the properties of metals and alloys, since they do not reveal the relationship between the energy and the atomic coordinates. New and physical methodologies are therefore desirable for both equilibrium and metastable alloys.

In this letter, we first introduce a simple empirical potential and demonstrate its validity in describing the atomic interactions in FCC metals and alloys. We then use this potential to calculate the properties of Ag, Cu and Ag–Cu disordered alloys, and compare the results with the experimental data.

A short-range potential similar to that proposed by Rosato *et al* [9] is adopted in the present work to describe the atomic interaction in the FCC metals and alloys, where the cohesive energy is given by:

$$E_c = \sum_i -(\rho_i)^f + \sum_{i,j} A_{ij}^2 \exp\left[-2p_{ij}\left((r_{ij}/r_0)-1\right)\right]/r_{ij}. \tag{1}$$

Here, r_{ij} is the distance between atoms i and j, r_0 is the nearest-neighbour distance, f is a factor to avoid the Cauchy discrepancy of $C_{12} = C_{44}$ and is normally taken as $\frac{1}{2}$. The

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electron gas density ρ_i is given by

$$\rho_i = \sum_j \xi_{ij}^2 \exp\left[-2q_{ij}\left((r_{ij}/r_0) - 1\right)\right].$$

The four constants A_{ij}, ξ_{ij}, p_{ij} and q_{ij} are determined by fitting the available experimental data [9]. To check its validity in describing the atomic interactions, the cohesive energies of copper with FCC and BCC structures, respectively, are calculated and are shown in figure 1. The calculation confirms that FCC is the more stable form of Cu at ambient pressures, and predicts the existence of metastable BCC Cu with a lattice constant of 2.87 Å. BCC Cu is indeed observed in experiments [10, 11]. The predicted lattice constant of 2.87 Å is also in excellent agreement with the experimental results [10, 11] and predictions by first-principles calculations [12, 13].

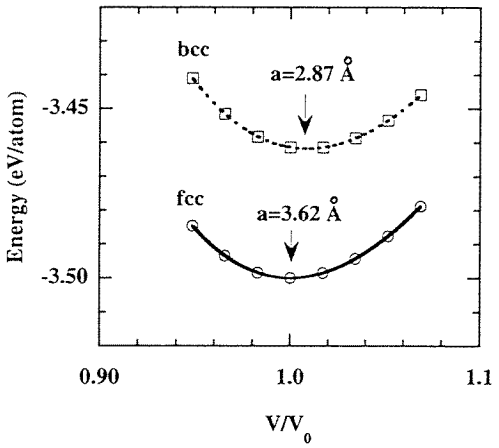

Figure 1. Cohesive energies of FCC and BCC structured Cu predicted using the empirical potential. A metastable BCC Cu form is predicted at around $a = 2.87$ Å.

In order to calculate the finite-temperature properties, the free energy of a metal/alloy is written as a function of the lattice volume and the temperature using the quasiharmonic approximation [14]:

$$F(v, T) = E_c(v) + k_B T \int_0^{\omega_{\max}} \ln\left[2\sinh\left(\hbar\omega/k_B T\right)\right]\rho(\omega)\,\mathrm{d}\omega + k_B T\,\Delta S. \quad (2)$$

In the above equation, $\hbar$ is Planck's constant, k_B is Boltzmann's constant, $E_c(v)$ is the cohesive energy and ΔS is the configurational entropy due to the partition of alien atoms in the lattice. To precisely calculate the properties, the frequency spectrum $\rho(\omega)$ is obtained by accumulating the vibration modes in the irreducible part of the first Brillouin zone. In the calculations, the equilibrium atomic coordinates are first achieved through minimizing the free energy at finite temperatures, and then the properties of interest are evaluated accordingly.

The enthalpy and entropy of Cu at temperatures up to the melting point have been calculated by the above free energy minimization method and are listed in table 1. The experimental data [15] are also listed for comparison. The precision of the quasiharmonic (QA) in this calculation is remarkably good. The agreement between theory and experiment holds not only at low temperatures where atomic motions are quite small (and likely harmonic), but also at temperatures close to the melting point where inharmonic treatments

are necessary. In a temperature range of 298.15–1300 K, the error between the calculation and experiment is no more than 6%. Figure 2 depicts the calculated isothermal bulk modulus of Ag and Cu; available low-temperature experimental data [16] are shown for comparison (circles). The present calculation correctly predicts the bulk modulus of both metals at low temperatures, and clearly shows the decreasing trend in the bulk modulus with increasing temperature. A rough estimate of the melting point (although the present approach is not appropriate for liquids) is given by the temperature at which a dramatic increase in the lattice volume is observed. The predictions are 1200 K for Ag and 1400 K for Cu, which are comparable to the experimental results of 1234 K for Ag and 1357 K for Cu, respectively [15]. Similarly, other properties such as the thermal expansion, the specific heat, the elastic constants, etc, can be calculated.

Table 1. Calculated and experimentally measured enthalpy and entropy for Cu.

Temperature (K)	Enthalpy (kJ mol^{-1})		Error (%)	Entropy (J mol^{-1} k^{-1})		Error (%)
	Calculation	Experiment		Calculation	Experiment	
298.15	0.0000	0.0000	0.0	0.0000	0.0000	0.0
400	2.5559	2.5104	1.8	7.3307	7.2383	1.3
500	5.1159	5.0836	0.6	13.035	12.970	0.5
600	7.7952	7.7195	0.1	17.929	17.782	0.8
700	10.629	10.376	2.4	22.294	21.882	1.9
800	13.427	13.096	2.5	26.023	25.522	2.0
900	16.401	15.899	3.2	29.521	28.828	2.4
1000	19.300	18.786	2.7	32.565	31.840	2.3
1100	22.560	21.715	3.9	35.677	34.644	3.0
1200	25.386	24.665	2.9	38.144	37.238	2.4
1300	29.171	27.677	5.4	41.179	39.622	3.9

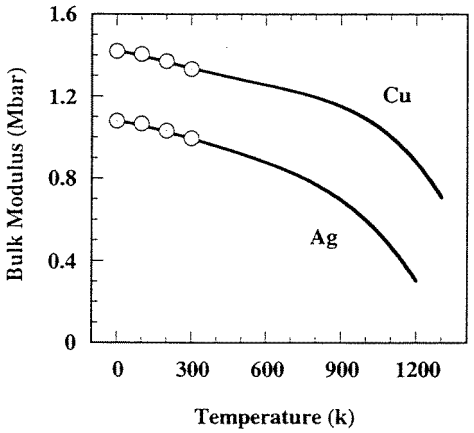

Figure 2. Calculated isothermal bulk modulus for Ag and Cu. The circles represent experimental results.

An application of this approach is to predict the properties of new or metastable alloys, which is of great significance in practice. To apply the approach to alloys, a mean-field effective potential is, for simplicity, assumed to describe the atomic interactions in the

alloys. Figure 3 depicts the room-temperature lattice constants of Ag–Cu disordered alloys predicted by this approach. The experimental data for both equilibrium [17] and metastable [18] Ag–Cu alloys are also shown for comparison. As a guide to the eye, the prediction of the phenomenological Vegard's law has been included as a dashed line. There is a positive deviation of the experimental data from Vegard's law, implying a positive heat of mixing between Ag and Cu. One sees that the present calculation accurately predicts the lattice constants for both equilibrium and metastable Ag–Cu alloys though it is based only on an empirical potential and the QA. The internal energies stored in the Ag–Cu alloys were also calculated by the above approach. They were indeed of positive sign and their values are in good agreement with the experimental results [5, 19].

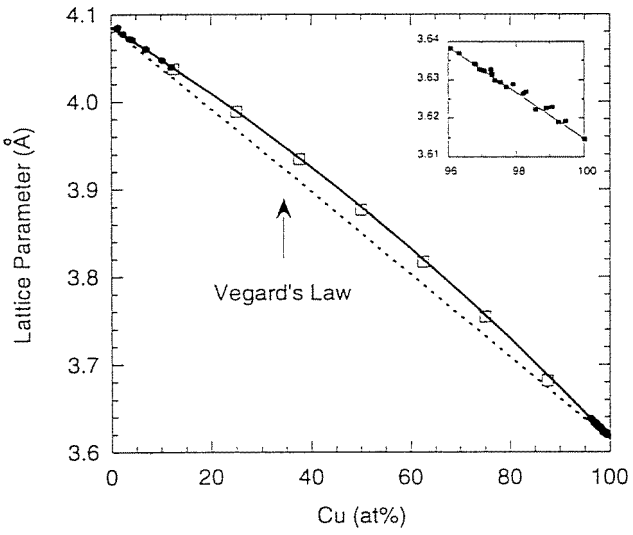

Figure 3. Room-temperature lattice parameters of the disordered Ag–Cu alloys determined by the present approach. Squares and circles represent the experimental results. The inset is an enlarged part for Cu-rich alloys.

In summary, a simple empirical potential is used to describe the atomic interactions in FCC metals and alloys. It is suitable for predicting the thermal and elastic properties of new alloys via a free energy minimization approach, which is of great significance in designing alloys.

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