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Calculation of the thermal expansion of metals using the embedded-atom method

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The linear coefficient of thermal expansion of the fcc metals Cu, Ag, Au, Ni, Pd, and Pt are computed using the semiempirical embedded-atom method to determine the energetics. The results are in good agreement with experiment. The importance of including the equation of state in the determination of the empirical functions is discussed.

The calculation of the atomic structure of complicated defects in metals requires a computationally efficient approximation for the total energy of the system. The recently proposed embedded-atom method (EAM) due to Daw and Baskes[1] is a semiempirical approach which fills this need. It has been applied to date to a variety of problems in pure metals and alloys. In particular, it has been used to study phonon dispersion,[2] liquid-metal structure,[3] surface relaxations,[1,4] and reconstructions,[5] point defects,[4] dislocation motion and fracture[6] of pure metals, and has been applied to segregation of alloys at interfaces.[7,8] A similar approach proposed by Finnis and Sinclair[9] (FS) has been used by various workers[10–13] to study defect properties in bcc metals.

The accuracy of the FS potentials has recently been challenged due to the observation by Marchese, Jacucci, and Flynn[14] that the thermal expansion of the metals predicted from these interactions is too small and in many cases negative. The thermal expansion of the pure metals provides a test of the anharmonicity of the interactions since a truly harmonic crystal has no thermal expansion.[15]

In this note the results of the calculation of the thermal expansion of the fcc metals Cu, Ag, Au, Ni, Pd, and Pt using the EAM will be presented. The results are in good agreement with experiment. First, the EAM and FS interactions will be briefly reviewed. Then the results of the thermal expansion will be presented and compared with experiment.

In the EAM the total energy of the system is given by the sum of two contributions, the interaction of each atom with the local electron density associated with the remaining atoms of the system, called the embedding energy, and a pair interaction reflecting electrostatic interactions between the atoms. In particular, the total energy is written

$$E_{\mathrm{tot}}=\sum_i F_i(\rho_i)+\tfrac{1}{2}\sum_{ij,i\neq j}\phi_{ij}(R_{ij}) \; . \tag{1}$$

In this expression, F_i is the embedding energy of atom i, ρ_i is the electron density at atom i, and $\phi_{ij}(R_{ij})$ is the pair interaction between atoms i and j separated by the distance R_{ij}. The electron density at each site is computed from the superposition of atomic electron density, i.e.,

$$\rho_i=\sum_{j\neq i}\rho_j^a(R_{ij}) \; . \tag{2}$$

Here $\rho_j^a(R)$ is the atomic electron density at a distance R from the nucleus of atom j. The embedding energies and pair interactions are then determined empirically by fitting to the sublimation energy, lattice constant, elastic constants, vacancy formation energy, and the zero-temperature equation of state of the pure metals. The resulting functions are describe in detail in Ref. 4 and are used here without further modification.

The FS interactions have a form similar to the EAM, though the physical motivation behind this approach is different. In the FS case, the energy of the d bands is modeled by the square root of the bandwidth which is assumed to be determined by the sum of the overlaps with surrounding atoms.[9] This bandwidth term is supplemented by a pair interaction. In particular, the energy is written as

$$E_{\mathrm{FS}}=-A\sum_i\left[\sum_{j\neq i}f(R_{ij})\right]^{1/2}+\tfrac{1}{2}\sum_{ij,i\neq j}V(R_{ij}) \; . \tag{3}$$

The function $f(R)$ represents the overlaps and $V(R)$ is the pair interaction. In practice, the constant A and the function f and V are determined empirically to fit the lattice constant, heat of sublimation, elastic constants, and vacancy formation energies. The EAM and FS models of the interatomic interactions are very similar in practice. In both cases, the pair interaction is supplemented by a term which is a *function* of a sum over surrounding atoms.

The thermal expansion for the EAM interactions have been computed in a quasiharmonic approximation.[16] For a given lattice constant and temperature, the free energy is computed from the sum of two terms. The first is the energy of the ideal lattice at that lattice constant computed using Eq. (1). The second term is the free energy associated with the vibrational modes of the solid. The vibrational density of states required to compute this free energy is determined at each lattice constant from the dynamical matrix of the solid as described in Ref. 2. The optimum lattice constant for a given temperature is then determined by minimizing the total free energy with respect to the lattice constant. The coefficient of thermal expansion at room temperature is then computed from the temperature derivative of these lattice constants. (The thermal expansion can also be computed from constant pressure Monte Carlo simulations.[17] However, that approach does not account for the quantum effects which are important for temperatures less than or near the Debye temperature.[15]) The results for the coefficient of thermal expansion, evaluated at room temperature, are presented in Table I along with experimental values.[18] The agreement is good indicating that the average anharmonicity of the interactions in the EAM is reasonable.

The origin of the difference between the quality of the computed thermal expansions for the EAM and for the FS interactions may be associated with the details of the empirical procedures used to determine the functions in the two techniques rather than with intrinsic differences between Eqs. (1) and (3). In the determination of the EAM functions in Ref. 4, the total energy of the fcc lattice under uniform compression and dilation was required to obey the universal equation of state proposed by Rose *et al.*[19] For the case of the FS potentials, the functions were only required to fit the elastic constants, in particular the bulk modulus. Therefore, no information about the higher derivatives of the energy is included in the fitting in the FS case. The universal equation of state, though, provides a good description of the anharmonic contributions to the total energy for uniform dilation. Thus this aspect of the anharmonicity is built into the EAM functions discussed here. For the FS potentials only the harmonic part of the energy is required to be correct. It is worth noting that the EAM functions determined in the earlier work of Daw and Baskes for Ni and Pd were also only fit to the elastic constants but not the full equation of state. Like the FS potentials, these functions yield poor values for the thermal expansion; 4.0 and 7.6×10^{-6} K^{-1} for Ni and Pd, respectively. This suggests that the difference in the ability to predict the thermal expansion is not due to the differences between the energy expressions in Eqs. (1) and (3), but rather to the amount of information about the equation of state of the solid used in the determination of the functions.

In summary, the thermal expansion predicted by the EAM using functions that reproduce the zero-temperature equation of state of the solid is in good agreement with experiment. The failure of the FS potentials to describe the thermal expansion may be due to the fact that these functions were not required to reproduce the equation of state.

TABLE I. Comparison of the linear coefficient of thermal expansion at room temperature computed using the EAM and experimental values.

Element	α(EAM) (10^{-6} K^{-1})	α(expt) (10^{-6} K^{-1})
Cu	16.4	16.7
Ag	21.1	19.2
Au	12.9	14.1
Ni	14.1	12.7
Pd	10.9	11.5
Pt	7.8	8.95

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