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Calculation of Thermodynamical Properties of Silver Using a Lattice-Inverted Many-Body Potential*

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The thermodynamical properties of silver are calculated by using a recent model of many-body potential from lattice inversion method. The predictions of the phonon dispersion relation, the Grüneisen constant and the linear thermal expansion coefficient are all in coincidence with experiments. Of more importance, the present approach represents an efficient way of building potential functions capable of depicting the thermodynamics of metals for the Finnis-Sinclair model.

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The simulation of structure and energetics of metals requires reliable interatomic potentials. The Finnis-Sinclair model (FSM) is one of the widely-used models for interatomic interactions which fill both physical origin and computational efficiency.[1-3] However, the accuracy of the FSM potentials was challenged by its application to thermal expansion.[4] The thermal expansion coefficients predicted by the FSM are too small and even negative in many cases. Foiles *et al.* pointed out that the error originates from the lack of information about higher derivatives of cohesive energy in FSM.[5] The potentials in FSM are fitted from elastic constants only, which are observed at equilibrium lattice. Foiles *et al.* resolved the question by using their potentials of embedded-atom method[6] and obtained excellent agreement with experiment. The cohesive energy as a function of lattice parameter in their model was required to obey the universal equation of cohesion proposed by Rose *et al.*[7] The cohesion equation was found to be a fairly good description of anharmonic effect.

In this letter, we use a recent lattice-inverted many-body potentials for the FSM to calculate the thermodynamical properties of silver.[8] The results of the phonon dispersion, the vibrational density of state, the specific heat versus temperature and the thermal expansion coefficient are given. The agreement of the predicted thermal expansion with experiment indicates that our potential functions for the FSM are suitable for thermodynamical simulation.

The basic equation of the FSM is

$$E_{\rm coh} = \frac{1}{2}\sum_{i\neq 0}\Phi(R_i) - \sqrt{\sum_{i\neq 0}\rho(R_i)}\ , \tag{1}$$

where $\rho(r) = h^2(r)$, $h(r)$ is the effective hopping integral which includes the $s-d$ hybridization in transition metals, $\Phi(r)$ is the pair potential including the pair potential contributed by

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nearly-free s electrons and the two-body repulsion between ions. In the present model, the lattice sum of square hopping integral is an exponential function versus the nearest neighbor distance

$$\sum_{i\neq 0}\rho(R_i) = 4(E_s - E_v)^2 \exp\left[-\alpha\left(\frac{R_1}{R_{1e}} - 1\right)\right] \tag{2}$$

with

$$\alpha = \sqrt{\frac{18\Omega_e(C_{12} - C_{44})}{E_s - E_v}} ,$$

and the lattice sum of pair potential with respect to the nearest neighbor distance is

$$\begin{aligned}\frac{1}{2}\sum_{i\neq 0}\Phi(R_i) = & -E_s\left[1 + \sqrt{\frac{9B\Omega_e}{E_s}}\left(\frac{R_1}{R_{1e}} - 1\right)\right]\exp\left[-\sqrt{\frac{9B\Omega_e}{E_s}}\left(\frac{R_1}{R_{1e}} - 1\right)\right] \\ & +2(E_s - E_v)\exp\left[-\frac{\alpha}{2}\left(\frac{R_1}{R_{1e}} - 1\right)\right] ,\end{aligned} \tag{3}$$

where Ω_e is the equilibrium atomic volume, R_{1e} the equilibrium nearest neighbor distance, E_s the sublimation energy, E_v the unrelated vacancy-formation energy and C_{12}, C_{44} are the elastic constants. The individual potential functions are obtained by using the lattice inversion method for fcc-type lattice.[9,10]

In the present model, the dynamical matrix can be written by

$$D(\boldsymbol{K}) = 2\sum_{i\neq 0} A_i \sin^2\left(\frac{\boldsymbol{K}\cdot\boldsymbol{R}_i}{2}\right) + \frac{1}{32(E_s - E_v)^3}\boldsymbol{X}(\boldsymbol{K})\boldsymbol{X}(\boldsymbol{K}) , \tag{4}$$

where

$$A_i = \Phi''_{\rm eff}(R_i)\frac{\boldsymbol{R}_i\boldsymbol{R}_i}{R_i^2} + \frac{\Phi'_{\rm eff}(R_i)}{R_i}\left(i - \frac{\boldsymbol{R}_i\boldsymbol{R}_i}{R_i^2}\right) ,$$

$$\boldsymbol{X}(\boldsymbol{K}) = \sum_{i\neq 0}\rho'(R_i)\sin(\boldsymbol{K}\cdot\boldsymbol{R}_i)\frac{\boldsymbol{R}_i}{R_i} ,$$

$\Phi_{\rm eff}(r)$ is the effective pair potential, defined as

$$\Phi_{\rm eff}(r) = \Phi(r) - \frac{1}{2(E_s - E_v)}\rho(r) . \tag{5}$$

The experimental data of R_{1e}, E_s, E_v and C_{12}, C_{44} of Ag as the inputs of the present approach are taken from Ref. 6. The phonon dispersion curves are plotted in Fig. 1. The results are in perfect agreement with the experimental values of Kamitakahara and Brockhouse.[11] The phonon density of state is plotted in Fig. 2.

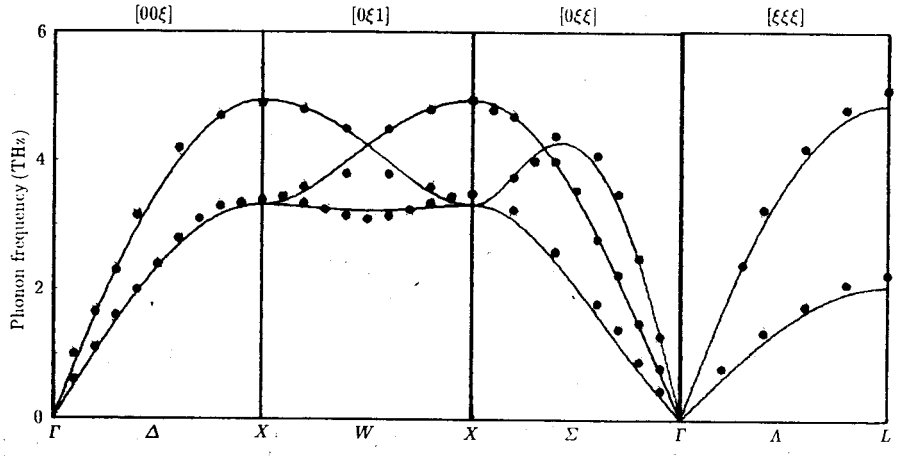

Fig. 1. Phonon dispersion for silver. The solid circles are experimental values measured at 296 K (Ref.11).

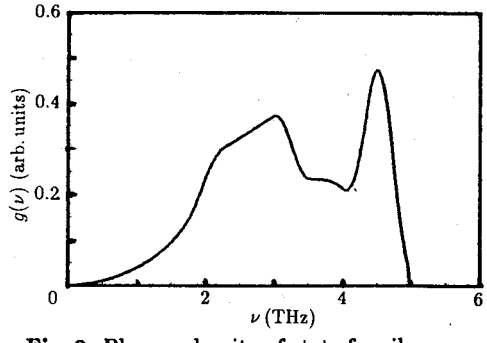

Fig. 2. Phonon density of state for silver.

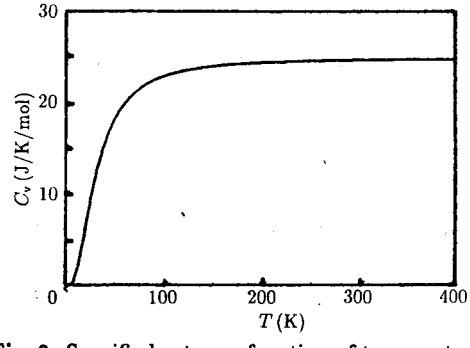

Fig. 3. Specific heat as a function of temperature for silver.

To calculate the thermal expansion, we use the Grüneisen approximation. We first calculate the specific heat at constant volume, which reads as

$$C_{\mathrm{v}}(T) = k_{\mathrm{B}} \int \frac{(\hbar\omega/k_{\mathrm{B}}T)^2 \exp(\hbar\omega/k_{\mathrm{B}}T)}{[\exp(\hbar\omega/k_{\mathrm{B}}T) - 1]^2} g(\omega) d\omega \ , \tag{6}$$

and we plot the temperature-dependence of heat capacity in Fig. 3.

The linear thermal expansion coefficient is related to the mole heat capacity as follows:

$$\alpha = \frac{\gamma C_{\mathrm{v}}}{3BN\Omega_{\mathrm{e}}} \ , \tag{7}$$

where C_{v} is the mole specific heat at room temperature, N the Avegadro constant, γ the Grüneisen constant. According to Wills *et al.*,[12] can be approximated by

$$\gamma = -\frac{1}{2}\left[1 + \Omega \frac{d^3 E_{\mathrm{coh}}/d\Omega^3}{d^2 E_{\mathrm{coh}}/d\Omega^2}\right]_{\mathrm{e}} \ . \tag{8}$$

By substituting the equation of Rose *et al.* into the above definition, the Grüneisen constant comes to be 2.47, a little greater than the experimental value 2.32. The predicted thermal expansion coefficient is $19.01 \times 10^{-6}\,K^{-1}$, very close to the theoretical result $21.1 \times 10^{-6}\,K^{-1}$ of Foiles *et al.* and the experimental value $19.2 \times 10^{-6}\,K^{-1}$.

In conclusion, we have presented a test for the lattice-inverted many-body potential. Moreover, we have also provided a modification of the FSM which makes it capable of predicting the thermal expansion of metals. While the present model is quite simple, it represents a useful way to obtain reliable interatomic potentials for thermodynamical simulation of metals.

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