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Physical properties of Ni fcc lattice in terms of the self-consistent phonon theory

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Abstract

The results of studies of physical properties of Ni fcc lattice obtained with the help of the reduced all-neighbour approximation of the self-consistent phonon theory are presented. The interatomic interactions are described by the modified form of the generalized Morse potential, proposed lately by Akgün and Uğur, with parameters derived from the experimental data for the lattice constant, cohesive energy, bulk modulus and elastic constants. As a test of the validity of both the model of interatomic interactions and the model of lattice dynamics the temperature variations of selected physical properties of Ni are given and compared with experimental and other theoretical data.

1. Introduction

Pairwise additive central potential functions are widely applied to various problems related to the description of the solid state [1]. Usually, the pair potential functions contain two or more adjustable parameters [2, 3]. In determining the parameters of potential energy function $\varphi(r)$ use is commonly made of the following experimental data [4, 5]: the second virial coefficient, the Joule–Thomson coefficient, the coefficient of viscosity and the zero-point properties of the crystal [6, 7]—the lattice constant, sublimation energy, compressibility and Debye characteristic temperature. The accuracy of the parameters depends on the number of shells of neighbours having influence on the pair interaction [8, 9]. Interatomic interactions in metallic crystals have been represented by various model pair potentials. The traditional (12, 6) Lennard-Jones potential, introduced originally for molecular crystals but usually used on any occasion, appeared too ineffective [10], as there is no simple expression like the r^{-6} law for the rare gas solids to represent the subtle interplay of attractions and repulsions between the mobile electrons and ions in metals. One way to improve the theoretical predictions was to generalize

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the (12, 6) Lennard-Jones potential to its (n, m) form. The parameters of the generalized (n, m) Lennard-Jones pair potential were calculated by Zhen and Davies [7] for metallic fcc, bcc and hcp crystals on the basis of the zero-point experimental data but with use of the purely static method. Calculations of the dynamic and thermodynamic properties of metallic lattices with use of the above mentioned parameters were undertaken [11] with the help of the reduced second-order approximation of the self-consistent phonon theory (RSOSCPT), which is one of the best dynamical theories of the crystal state, developed by Plakida and Siklós [12] on the basis of the double-time Green's function method [13]. As in the RSOSCPT some power series of the interatomic pair potential appear so it is more convenient to use purely exponential, not power, potential, particularly since the exponential law is a better representation of repulsion than the power one [14]. The purely exponential law of interatomic interaction is known as the $(\alpha, \alpha/2)$ Morse pair potential. Its parameters were calculated from ground-state properties with use of purely static [6] and semistatic [15] methods, and the latter were used in the self-consistent calculations.

As the mentioned Lennard-Jones and Morse potential parameters come from purely static or semistatic methods, they were calculated neglecting the zero-point vibration effects. In our earlier paper [16] we introduced the self-consistent dynamical method of fitting potential parameters to the experimental data and we applied it for noble metals in association with three model pair potentials, namely the generalized four-parameter (n, m) Lennard-Jones, (α, β) Morse and (α, m) Buckingham, which is exponential and power in repulsion and attraction parts, respectively.

In the last years Akgün and Uğur proposed [17] for fcc metallic crystals a more generalized five-parameter version of the Morse pair potential. In the present paper we study the physical properties of the Ni fcc lattice using the reduced all neighbours approximation of the RSOSCPT introduced recently by us [9, 18] for description of the heavier rare gas solids [18] and quantum crystals [9], together with the five-parameter generalized Morse potential with parameters obtained by Akgün and Uğur [17] from the experimental data for the lattice constant, cohesive energy, bulk modulus and elastic constants. As a test of effectivity of the new potential we have also made analogical calculations for the classical (α, β) Morse potential.

2. Interatomic interactions in solid Ni

Interatomic interactions in the Ni fcc lattice are represented in this paper by two versions of the (α, β) Morse pair potential: classical (M), which is the four-parameter one

$$\varphi_M(r) = \frac{\alpha\beta}{\alpha - \beta} D_0 \left\{ \frac{1}{\alpha} \exp \left[\alpha \left(1 - \frac{r}{r_0} \right) \right] - \frac{1}{\beta} \exp \left[\beta \left(1 - \frac{r}{r_0} \right) \right] \right\}, \quad \alpha > \beta \quad (1)$$

and modified (AU), which is the five-parameter one

$$\varphi_{AU}(r) = \frac{\alpha\beta}{\alpha - \beta} D_0 \left(\frac{r_0}{r} \right)^\gamma \left\{ \frac{1}{\alpha} \exp \left[\alpha \left(1 - \frac{r}{r_0} \right) \right] - \frac{1}{\beta} \exp \left[\beta \left(1 - \frac{r}{r_0} \right) \right] \right\}, \quad \alpha > \beta. \quad (2)$$

The last equation is equivalent to the original of Akgün and Uğur [17] and was obtained by the following substitutions: $r_0 = r_0^{AU}$, $D_0 = D^{AU}$, $\gamma = n^{AU}$, $\beta = \alpha^{AU} r_0^{AU}$, $\alpha = m^{AU} \alpha^{AU} r_0^{AU}$.

As we see, the modified AU potential (2) is obtained from the classical M one (1) by simply multiplying by a factor $(r_0/r)^\gamma$, which, in the opinion of Akgün and Uğur, should exhibit the correct nature of the interatomic forces, particularly at short distance. The real meaning of this modifying factor is to be verified in the present study.

In equations (1) and (2) α and β are the dimensionless parameters describing the slope of the potential curve; r_0 and D_0 define the potential minimum and are, respectively, the equilibrium distance of two isolated atoms and the energy of their dissociation. The four above parameters are obtained self-consistently (dynamically) [9] by fitting to the zero-point experimental data for the nearest neighbour mean separation l_0 , the cohesive energy E_0 and the isothermal bulk modulus B_0 [19]. The parameter γ is taken from Akgün and Uğur [17] and was obtained from elastic data.

3. The basis of the self-consistent calculations

The self-consistent method of incorporating atomic vibrations consists in replacing the pairwise static potential (for instance equations (1) or (2)) with its dynamical self-consistent version according to the following renormalization scheme [12]:

$$\tilde{\varphi}(r) = \sum_{k=0}^{\infty} \frac{1}{k!} y^k r_0^{2k} \varphi^{(2k)}(r), \quad (3)$$

where y is the renormalization parameter or broadening parameter, which depends on the temperature range and the form of the self-consistent potential and its derivatives. In particular, for the anharmonic crystals in the low ($k_B T \ll \omega_{0L}$) and high ($k_B T \gg \omega_{0L}$) temperature limits we get the following equations for y [12]:

$$y \approx \lambda (\omega_L/B_1 + C_1 k_B T/\beta_1^3), \quad k_B T \ll \omega_{0L} \quad (4)$$

$$y \approx 6\lambda k_B T (A + \beta_1^2/24) \quad k_B T \gg \omega_{0L}. \quad (5)$$

The exact expressions for the symbols appearing in (4) and (5) are given in appendix. k_B and ω_{0L} are the Boltzmann constant and the maximal value of the vibrational frequency in the harmonic approximation, respectively.

According to (3), the two pair potentials considered in the present paper take the forms

$$\tilde{\varphi}_M(r) = \frac{\alpha\beta}{\alpha - \beta} D_0 \left\{ \frac{1}{\alpha} e^{\alpha(1 - \frac{r}{r_0} + \alpha y)} - \frac{1}{\beta} e^{\beta(1 - \frac{r}{r_0} + \beta y)} \right\}, \quad (6)$$

$$\tilde{\varphi}_{M^*}(r) = \frac{\alpha\beta}{\alpha - \beta} D_0 \left(\frac{r_0}{r} \right)^\gamma \sum_{k=0}^{\infty} \left[\frac{1}{k!} y^k r_0^{2k} \sum_{j=0}^{2k} \left(\frac{r_0}{r} \right)^j \left(R_{kj} e^{\frac{-\alpha r}{r_0}} - A_{kj} e^{\frac{-\beta r}{r_0}} \right) \right], \quad (7)$$

where R_{kj} and A_{kj} are the matrixes defined as follows:

$$R_{00} = \frac{D_0\beta}{\alpha - \beta} e^\beta, \quad R_{i < j} = 0, \quad R_{i \neq 0, j=0} = R_{i-1, j} \left(\frac{-\alpha}{r_0} \right),$$

$$R_{i > 0, j > 0} = R_{i-1, j-1} \frac{\gamma + j - 1}{-r_0} + R_{i-1, j} \frac{-\alpha}{r_0},$$

$$A_{00} = \frac{D_0\alpha}{\alpha - \beta} e^\beta, \quad A_{i < j} = 0, \quad A_{i \neq 0, j=0} = A_{i-1, j} \left(\frac{-\beta}{r_0} \right),$$

$$A_{i > 0, j > 0} = A_{i-1, j-1} \frac{\gamma + j - 1}{-r_0} + A_{i-1, j} \frac{-\beta}{r_0}.$$

The equilibrium state of the crystal lattice at fixed temperature T and pressure p is determined by the self-consistent system of equations formed by the renormalization equation (3) and the equation of state, which in the reduced all-neighbour approximation of the self-consistent phonon theory (RANSCPT) takes the following form [9]:

$$p = -\frac{z l}{6v} \tilde{\varphi}'(l) \left[1 + \sum_{i=2}^{i_{\max}} \frac{l_i}{l} \frac{z_i}{z} \frac{\tilde{\varphi}'(l_i)}{\tilde{\varphi}'(l)} \right], \quad (8)$$

where $l \equiv l_1$, $z \equiv z_1$ and v are, respectively, the equilibrium separation of nearest neighbours, the number of nearest neighbours and the specific volume, whereas l_i and z_i are, respectively, the radius and the filling of the i th shell of neighbours. In the RSOSCPT, in which the simplifying assumption is taken that each atom interacts only with its nearest neighbours, the expression in brackets reduces to unity. It is worthwhile to point out here that, as shown by Plakida and Siklós [12], all the physical quantities connected with the crystal lattice can be expressed as functions of y , $\tilde{\varphi}$, $\tilde{\varphi}''$, $\tilde{\varphi}'''$ and l ; however, in the RANSCPT the respective equations must take into account the fact that the potential energy of the crystal consists of energies of interactions of all pairs of atoms. For example, the internal energy per atom $E(z_i)$ and enthalpy $H(z_i)$ are given by [20]

$$E(z_i) \approx E + \sum_{i=2}^{i_{\max}} \frac{1}{2} z_i \tilde{\varphi}(l_i), \quad (9)$$

$$H(z_i) \approx E(z_i) + p(z_i)v, \quad (10)$$

where E is the internal energy in the nearest neighbour approximation [21]. According to the thermodynamic relationships the molar heats at constant volume $C_V(z_i)$ and constant pressure $C_p(z_i)$ are given by [22]

$$C_V(z_i) = \left(\frac{\partial E(z_i)}{\partial T} \right)_V, \quad C_p(z_i) = \left(\frac{\partial H(z_i)}{\partial T} \right)_p,$$

then the entropy:

$$S(z_i, T)_V = \int_0^T \frac{C_V(z_i) dT}{T} + S'_0, \quad (11)$$

$$S(z_i, T)_p = \int_0^T \frac{C_p(z_i) dT}{T} + S''_0, \quad (12)$$

where $S'_0 = S(V, 0)$, $S''_0 = S(p, 0)$ and according to the third thermodynamics principle of Planck $S'_0 = S''_0 = 0$.

The above relations are used in the next section of this paper in order to show the temperature variations of the characteristic properties of Ni.

4. Numerical results and conclusions

Taking the self-consistent relationships connecting the dynamic and thermodynamic quantities with any given interatomic interaction function, we have found a few sets of relatively optimal values of the modified and classical generalized Morse pair potential parameters, fitting them by the trial-and-error method to the above mentioned zero-point experimental data [19] for l_0 , E_0 and B_0 . Instead of the fourth condition we assume that either the ratio α/β or the repulsive slope parameter α obtained by Akgün and Uğur are correct and so the two series of sets of parameters have been created. The last condition seems to be especially well founded as the $\alpha = 10.53$ of Akgün and Uğur is very close to those obtained purely theoretically by Hafemeister [14] for the noble fcc metals. The fifth condition in the modified Morse potential is replaced by the assumption that the value of γ obtained by Akgün and Uğur from the room-temperature elastic data is correct. However, we have also decided to test the sensitivity of the theory with respect to the value of γ and so we have found the two additional sets of parameters α , β , r_0 , D_0 —one for γ distinctly lower than γ^{AU} and the second for γ distinctly greater than γ^{AU} .

It is worthwhile to point out here that there is a possibility of using two different values for the cohesive energy. The total energy of a system may be expressed as a sum of two- and

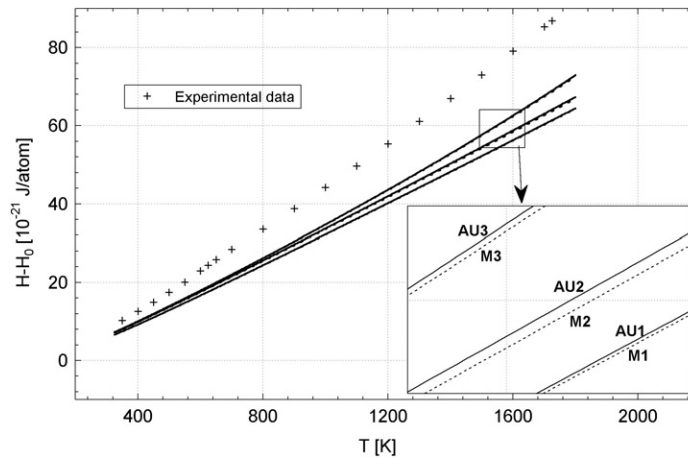


Figure 1. Temperature variations of the enthalpy of Ni in relation to its zero-point value obtained for various sets of AU and M potential parameters (see table 1). The experimental data [19] are given for comparison.

Table 1. Optimal values of the modified (AU) and classical (M) Morse pair potential parameters obtained for Ni for various input assumptions with use of the experimental data [19] for l_0 , B_0 and E_0 given below. AU1 and M1 are with the original value of α/β while the others are with the original value of α .

	AU1	M1	AU2	M2	AU3	M3	AU4	AU5
r_0 (10^{-10} m)	2.8364	2.782	2.859	2.813	2.576	2.549	2.822	3.030
D_0 (10^{-21} J)	67.22	68.83	48.90	51.07	44.47	45.6	50.24	43.25
α (—)	6.89	7.420	10.53	10.53	10.53	10.53	10.62	10.54
β (—)	3.50	3.766	1.853	2.265	4.66	5.24	2.14	0.97
γ (—)	0.44	—	0.44	—	0.44	—	0.1	1.5
α/β (—)	1.97	1.97	5.683	4.65	2.26	2.01	4.95	10.87
l_0 (10^{-10} m)		2.478			2.478		2.478	
B_0 (GPa)		182			182		182	
E_0 (10^{-21} J/atom)		-711.2			-331.2		-711.2	

many-body interactions. However, for simplicity, as in the RANSCPT, we often reject the many-body effects in explicit form, ‘hiding’ them in the pair potential parameters, and then we should use for parameter calculations the full experimental value of the cohesive energy. But if we decide to study many-body interactions separately we must take in the two-body analysis only the ionic part of E_0 , that is the cohesive energy diminished by the many-body energy. Such a diminished cohesive energy was used originally by Akgün and Uğur (we have modified the original parameters a little to improve their fitting to the experimental data), so their potential function differs distinctly from ours fitted to the total cohesive energy. For better qualitative comparisons we have also fitted to the ionic part of E_0 the classical Morse pair potential.

All our calculations were realized for various numbers of shells of neighbours and it appeared that any essential differences vanished over five shells. The final all-neighbour results for various parameters sets are presented in table 1, together with the experimental input data.

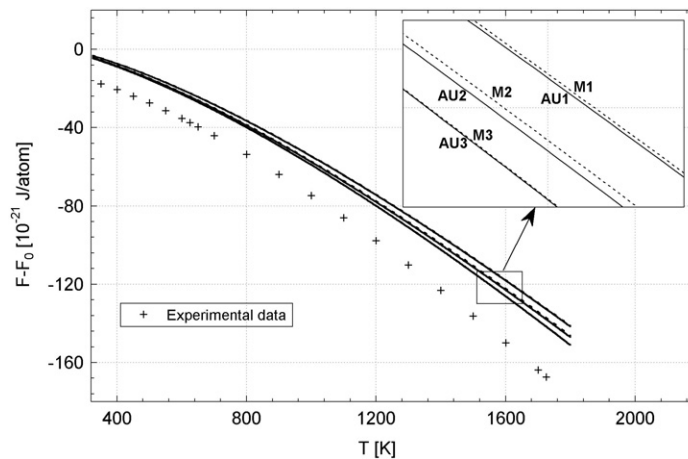


Figure 2. Temperature variations of the free energy of Ni in relation to its zero-point value obtained for various sets of AU and M potential parameters (see table 1). The experimental data [19] are given for comparison.

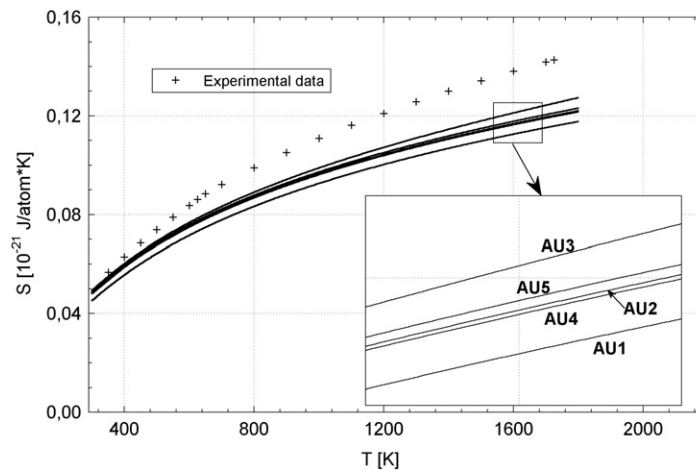


Figure 3. Temperature variations of the entropy of Ni obtained for various sets of AU potential parameters (see table 1). The experimental data [19] are given for comparison.

As we see, the classical Morse potential is always a little deeper and tighter than the modified Morse potential of Akgün and Uğur. AU3 and M3 functions which have been obtained from the ionic cohesive energy are of course distinctly shallower and tighter than the others.

Having at our disposal the potential parameters, we could carry out for Ni comparative calculations of the physical quantities for various sets of parameters. The selected results are presented, for better qualitative comparison in graphical form, together with the available experimental data (figures 1–5).

Let us notice that the curves in all the figures are assembled with respect to the additional input assumption in the method of calculating of the potential parameters ($\alpha/\beta = \text{const}$, $\alpha = \text{const}$ or $E_0 = \text{two-body cohesive energy}$). The differences are especially evident in

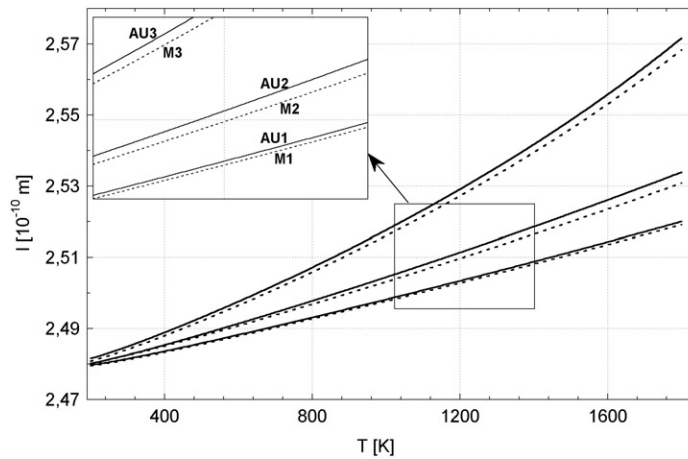


Figure 4. Temperature variations of the nearest neighbour separation in Ni obtained for various sets of AU and M potential parameters (see table 1).

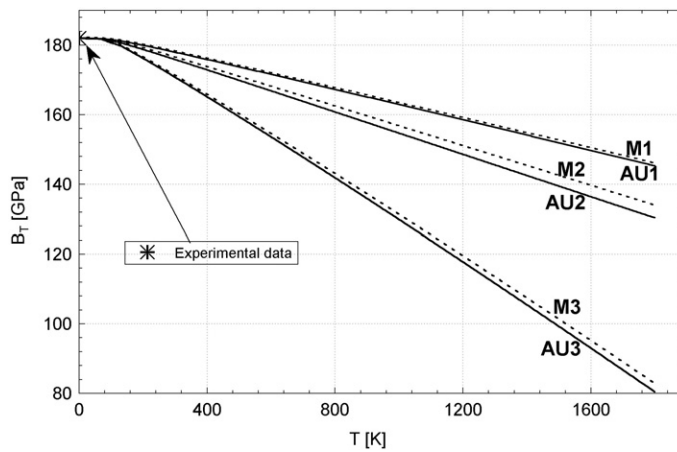


Figure 5. Temperature variations of the isothermal bulk modulus of Ni obtained for various sets of AU and M potential parameters (see table 1).

the cases of the nearest neighbour separation and bulk modulus and to a lesser degree for the thermodynamic potentials. Concerning a comparison of the AU and M pair potentials and, within AU, a comparison of the versions with various values of the parameter γ , we see that the scale of correction is rather low. On the other hand, the results for the cases with $\alpha/\beta \approx 2$ are distinctly worse than those for $\alpha/\beta \approx 10.53$ when $\alpha/\beta \gg 2$ and the latter are worse than those for parameters obtained with neglect of many-body interactions in the cohesive energy. Unfortunately, we are not sure if these last results are reliable enough as the RANSCPT does not take into account many-body interactions explicitly and so these effects should be rather hidden in the pair potential parameters. Nevertheless, we would like to note that the results for thermal expansion and bulk modulus are especially sensitive with respect to the choice of the method of treating many-body effects in calculating potential parameters.

Taking all this into consideration, we would like to state that the modification of Morse pair potential proposed by Akgün and Uğur does not play an essential role concerning the

dynamic and thermodynamic results for Ni and so should be rather applied at the final stage of fitting the theory to the experiment, in particular since the classical Morse function is more convenient in analytical derivations. On the other hand, we see that the results for parameters connected with many-body treatment are in better agreement with the experiment, which as we mentioned may be incidental but also means that we should turn to any anharmonic many-body theory of lattice dynamics. This next indicates the necessity of revision of the SCPT so it could take into account not only two-body interactions. Considering the discrepancy between the theory and the experiment in the high temperature region we should also try to increase over four (as in the RANSCPT) the number of ‘important’ terms in the lattice potential energy decomposition.

Appendix

The exact expressions for the symbols used in equations (4) and (5) are as follows:

$$\lambda = \frac{1}{zf(r, T)l_0^2}, \quad f(r, T) = \frac{\partial^2 \tilde{\varphi}}{\partial r^2} = \tilde{\varphi}'', \quad \omega_L^2 = \frac{8\hbar^2 f(r, T)}{m},$$

$$B_1 = 0.49 [1 - 7.446 \times 10^{-3} \gamma(T)], \quad \gamma(T) = \frac{\omega_L \beta(T)}{k_B T}, \quad \beta(T) = k_B T \frac{g^2(r, T)}{f^3(r, T)},$$

$$g(r, T) = \tilde{\varphi}'''(r), \quad C_1 = 1.0366\pi^4 [1 + 0.102\gamma(T)], \quad \beta_1 = \frac{\omega_L}{k_B T},$$

$$A = [1 - 0.11\beta(T)].$$

z , \hbar and m are the number of nearest neighbours, the Planck constant divided by 2π and the mass of the atom, respectively.

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