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Anharmonic pair potential study in face-centred-cubic structure metals

I V Pirog, T I Nedoseikina, I A Zarubin and A T Shuvaev

Institute of Physics, Rostov State University, 194 Stachki Avenue, Rostov-on-Don 344090, Russia

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Abstract

Temperature dependencies of Ni, Cu and Mo metals EXAFS spectra were studied in order to determine the anharmonic pair potential. The potential parameters for metals with cubic structure—Ni, Cu, Mo as well as for Pb (Stern E A *et al* 1991 *Phys. Rev. B* **43** 8850), Au, Ag (Newville M and Stern E A <http://krazy.phys.washington.edu/paper/ag-au.html>)—obtained earlier, were analysed to find correlations with other physical characteristics. It was found that a , b potential parameter values correlate with cohesive energy and interatomic distance for face-centred-cubic structure metals. Obtained potential parameter values were used to determine thermodynamics parameters, including the linear coefficient of thermal expansion, the Debye temperature, the bulk modulus and the Grunesien parameter.

1. Introduction

It was shown for the first time by Stern *et al* [1] for the example of the metal Pb that the anharmonic pair potential parameters can be obtained by XAFS spectroscopy. The following potential expression was used:

$$V(\Delta r) = a(\Delta r)^2/2 + b(\Delta r)^3 + c(\Delta r)^4, \quad (1)$$

where Δr is the deviation of interatomic distance from the equilibrium one R_0 and a , b , c are the potential parameters. The effect of such a potential on EXAFS was treated through cumulant expressions. In order to consider the anharmonicity effects the EXAFS function $\chi(k)$ in the single scattering theory with cumulant expansion up to the fourth-order terms is given by [3]

$$\chi(k) = \sum_j \frac{N_j S_0^2}{k R_j^2} f_j(k, \pi) \exp\left(\frac{-2R_j}{\lambda(k)}\right) \exp\left(-2\sigma_j^2 k + \left[\frac{2}{3}\sigma_j^{(4)} k^4\right]\right) \\ \times \sin\left(2kR_j + \delta_j(k) - \left[\frac{4}{3}\sigma_j^{(3)} k^3 - \frac{4\sigma_j^2 k}{R_j} \left(1 - \frac{R_j}{\lambda(k)}\right)\right]\right)$$

where N is the coordination number of the scattering atoms with interatomic distance R , S_0^2 the square of the many-body overlap term, λ the electron mean free path, k the photoelectron wavenumber and the sum is over the coordination shells of neighbours of the absorbing atom. $f(k, \pi)$ is the atomic backscattering amplitude and $\delta(k)$ is a net phase shift. The terms σ^2 , $\sigma^{(3)}$ and $\sigma^{(4)}$ are the second-, third- and fourth-order cumulants of the interatomic distance distribution. Within the classical limit cumulants can be written in terms of the anharmonic pair potential parameters and the temperature [2]:

$$\sigma^{(1)} = \Delta R \approx \frac{-3bk_B T}{a^2} \left[1 + \frac{k_B T}{a^2} \left(\frac{45b^2}{a} - 32c \right) \right] \quad (2)$$

$$\sigma^2 \approx \frac{k_B T}{a} \left[1 + \frac{k_B T}{a^2} \left(\frac{36b^2}{a} - 12c \right) \right] \quad (3)$$

$$\sigma^{(3)} \approx \frac{-6b(k_B T)^2}{a^2} \left[1 + \frac{k_B T}{a^2} \left(\frac{144b^2}{a} - 84c \right) \right] \quad (4)$$

$$\sigma^{(4)} \approx \frac{(k_B T)^3}{a^4} \left[\frac{108b^2}{a} - 24c \right]. \quad (5)$$

By using these expressions for the cumulants the anharmonic pair potential parameters can be obtained through temperature-dependent XAFS data.

In the work [2] the expressions for several macroscopic characteristics of solids (the linear expansion coefficient, the Grunesien parameter, the Debye temperature, the bulk modulus) were obtained in terms of pair potential parameters.

It is natural to suppose the anharmonic pair potential parameters correlate with such microscopic characteristics of solids as cohesive energy and interatomic distance.

In fact, the greater the cohesive energy value the higher the melting temperature and the lower the atom vibration amplitudes at the moderately high temperature ($T > \theta_E$, where θ_E is the Einstein temperature) for various metals. This means the higher the cohesive energy value the larger the potential well curvature, which is determined by potential parameters for interactive atoms. In turn, cohesive energy, as a rule, is inversely proportional to interatomic distances and depends on the crystal structure type and interatomic bond type (ionic, metallic etc). Assuming a certain crystal structure type and certain interatomic bond type one can establish the relationships between anharmonic pair potential parameters and cohesive energy and bond length. Through correlation between anharmonic pair potential parameters and interatomic distances, cohesive energy could exist; however, the experimental confirmation of this supposition does not exist.

In this paper temperature-dependent EXAFS spectra for cubic structure metals Cu (face-centred-cubic, fcc), Ni (face-centred-cubic, fcc) and Mo (body-centred-cubic, bcc) were analysed to obtain cumulant dependencies on temperature and to determine anharmonic pair potential parameters. The results obtained here and earlier for fcc structure metals Pb [1], Ag and Au [2], allow analysis of anharmonic pair potential parameter dependencies on cohesive energy and interatomic distance for metals with fcc crystal structure type. Results for Mo are presented here as an exception to show the crystal structure change effects on such dependencies.

2. Experimental details and XAFS analysis

EXAFS Ni, Cu and Mo K-spectra were recorded in transmission using the EXAFS spectrometer of the Synchrotron Radiation Siberian Center with a storage ring operating at a beam energy of 2 GeV and a current of 80 mA. A Si(111) double-crystal monochromator determined the

Table 1. Anharmonic effective pair potential parameters for Cu, Ni and Mo.

Metal	a (eV Å ⁻²)	b (eV Å ⁻³)	c (eV Å ⁻⁴)
Cu	3.2 ± 0.6	-1.3 ± 0.6	1.4 ± 0.8
Ni	3.9 ± 0.5	-1.6 ± 0.5	1.7 ± 0.9
Mo	7.5 ± 0.9	-3.6 ± 0.8	0.7 ± 0.7

x-ray energy. The intensities of both incident and transmitted x-ray beams were measured with ionization chambers filled with Ar gas. The spectra for each sample were measured at six different temperatures between 293 and 633 K. Sample temperatures were maintained within 1–2 K of the nominal temperature for all measurements.

In our investigation we used Ni, Cu and Mo foils at a thickness of 5 μm.

The analysis of the EXAFS data has been performed following the routine procedure: E_0 energy was set at the first derivative inflection point for each scan; the data were normalized to the edge step, the pre-edge background was subtracted by a Victoreen-type function fit, and then $\chi(k)$ was obtained by subtracting background absorption, which was determined using a five cubic spline approximation of the data above the edge. Fourier transforms of Ni, Cu, Mo K-edge EXAFS are presented in figure 1(a), evaluated over the range of wavenumbers 3–16 Å⁻¹ for Ni, 3–13 Å⁻¹ for Cu and 4–17.5 Å⁻¹ for Mo. The first peak at about 2 Å, which corresponds to the first coordination sphere in Ni, Cu, and to the two nearest ones in Mo, was back-transformed into k -space. The fitting of $\chi(k)$ was performed to determine the parameters of the first coordination sphere in Ni, Cu and the two nearest spheres in Mo with calculated phase and amplitude functions. Under the assumption of an anharmonic Einstein model the structure parameters were determined by nonlinear fitting (figure 1(b)) using a cumulant technique up to the third- and the fourth-order terms in order to consider the anharmonicity effects [1]. The FEFF7 code [4] for calculation of backscattering phases and amplitudes was used. The metal–metal interatomic distance R , the mean-square relative displacement σ^2 and anharmonicity parameters $\sigma^{(3)}$ and $\sigma^{(4)}$ of the first coordination shell for Ni, Cu, and the same parameters of the two nearest coordination shells for Mo were obtained with an estimated uncertainty of ~3%. The fitting results are presented in figure 2.

The anharmonic pair potential parameters were determined by solving a three-equation system at one temperature, using second, third and fourth cumulants (expressions (3)–(5)). The calculated values of the anharmonic pair potential parameters at different temperatures were averaged for each metal. The relative uncertainty of the potential parameters was estimated using cumulant determination uncertainty. The a , b , c parameter values for the Ni–Ni, Cu–Cu and Mo–Mo bonds are presented in table 1.

3. Results and discussion

The reliability of potential parameters found from EXAFS analysis for the metals Cu, Ni and Mo was confirmed by comparison of calculated thermodynamic values with those obtained by using thermodynamics methods. The thermodynamic values (TD) such as the isothermal bulk modulus (K), the Grunesien parameter (γ), the Debye temperature (Θ_D) and the linear expansion coefficient at 400 K (α) were calculated by employing formulae obtained in [2] with a and b potential parameters for Ni, Cu and Mo. Results obtained as well as the TD values measured by thermodynamics methods are presented in table 2. The uncertainty was estimated by calculating the sum of partial derivations over all potential parameters. As seen, the thermodynamic values obtained from XAFS agree well with those values measured by thermodynamic methods [5].

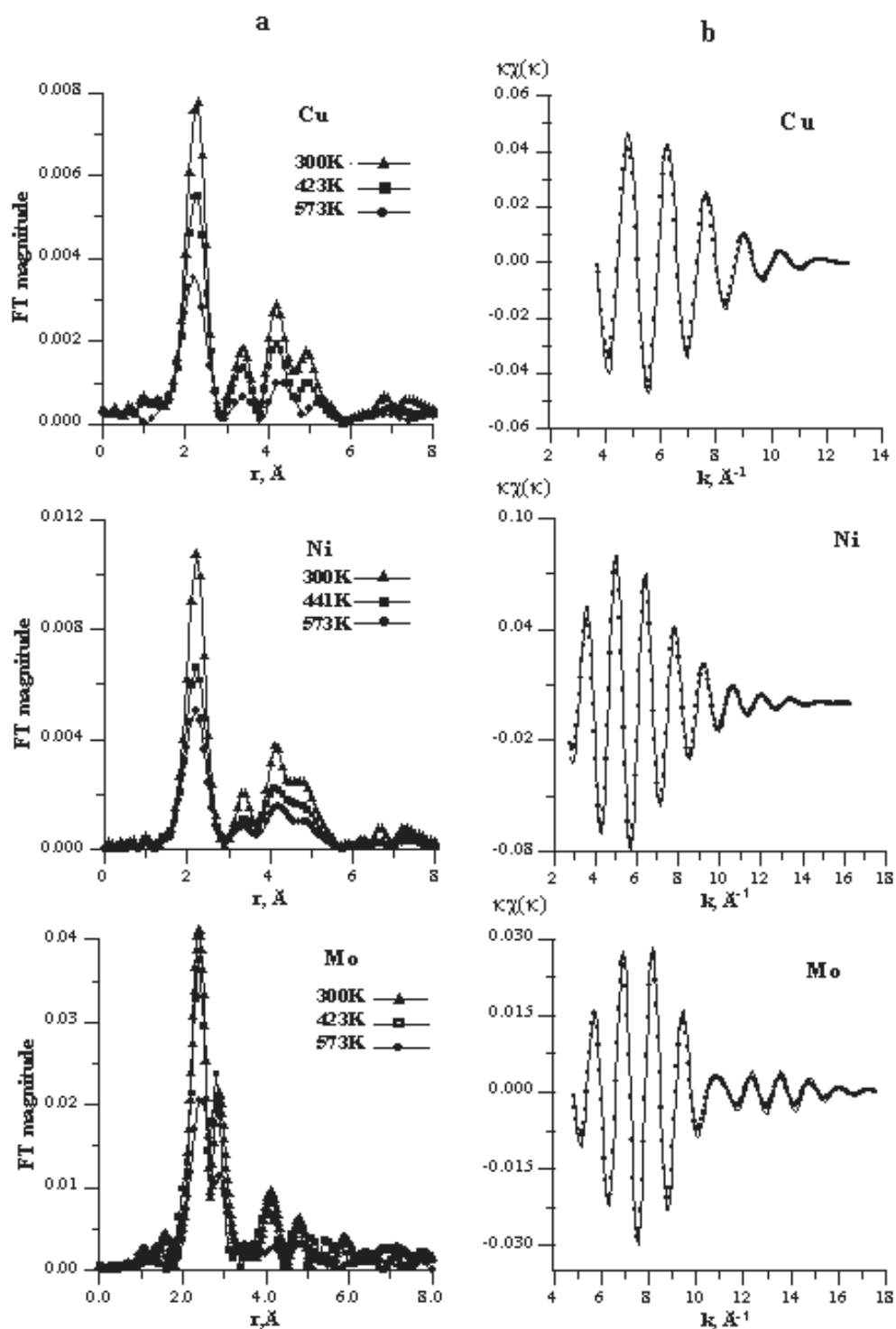


Figure 1. Fourier transforms of the Cu, Ni and Mo K-edge spectra of corresponding metals at 300, 423 and 573 K. (a) Comparison of calculated $k * \chi(k)$ (dotted curve) with experimental $k * \chi(k)$ (solid curve) for the Cu, Ni first shell and for the Mo two nearest shells at 300 K.

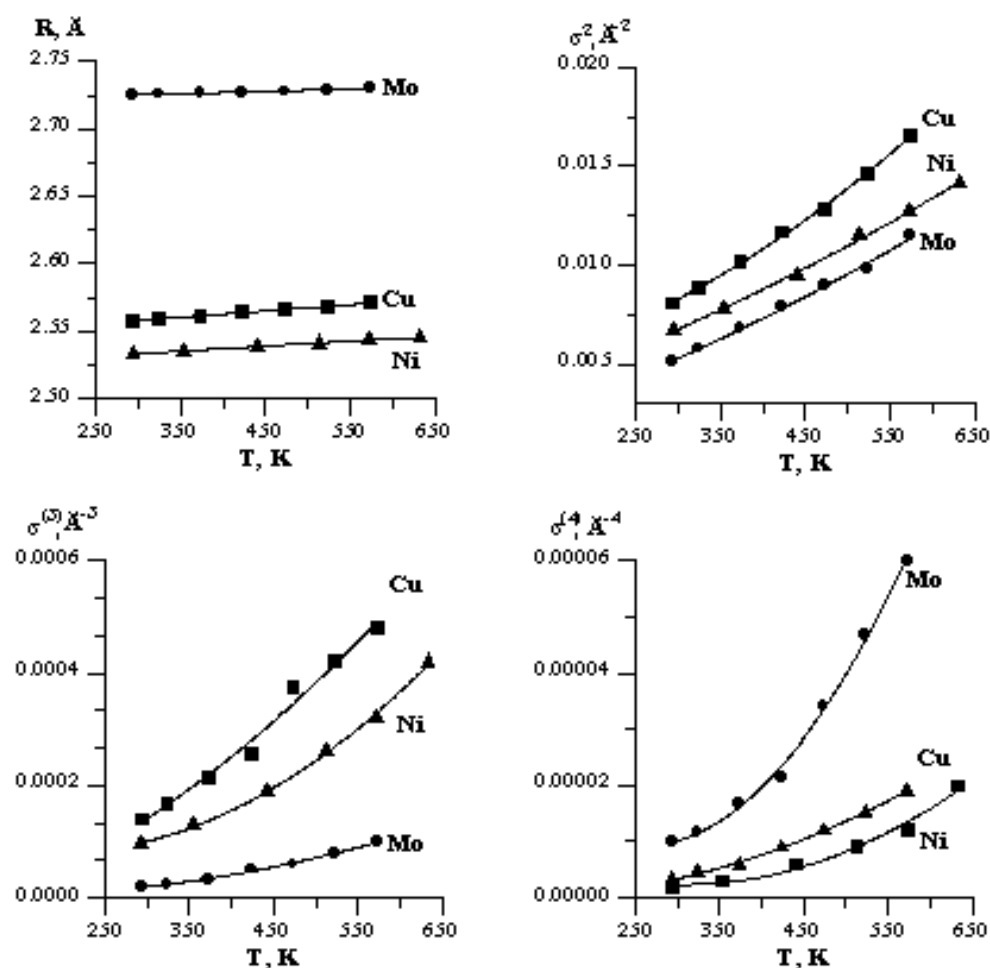


Figure 2. Fitting obtained temperature dependencies of interatomic distances and σ^2 , σ^3 , σ^4 cumulants for Ni (triangles), Cu (squares), Mo (circles).

Table 2. Thermodynamic values calculated from pair potential parameters and obtained by using the thermodynamic methods shown in brackets [6].

Metal	Ni	Cu	Mo
$\alpha * 10^{-5} \text{ K}^{-1}$ (α , TD)	$14 \pm 0.8(13.7)$	$17 \pm 0.7(17.3)$	$6.4 \pm 1.5(5.45)$
γ (γ , TD)	$2.9 \pm 0.90(2.0)$	$2.8 \pm 0.80(2.1)$	$2.53 \pm 1.08(1.58)$
$K, *10^9 \text{ P}$ (K, TD)	$250 \pm 70(180.3)$	$185 \pm 53(151)$	$327 \pm 85(253.1)$
Θ_D K (Θ_D)	$348 \pm 30(375)$	$301 \pm 22(318)$	$376.9 \pm 17(377)$

The a , b parameter dependencies on cohesive energy (E_C) and interatomic distance (R) for the cubic structure metals Cu, Ni and Mo as well as for metals Pb [1], Au and Ag [2] are shown in figures 3 and 4 respectively. As seen from figure 3(a) the a parameter increases with the cohesive energy E_C almost linearly. It is interesting to note the a parameter and E_C values for all metals are numerically close to each other in the units used. This means the a parameter could be easily estimated by taking into account the cohesive energy value.

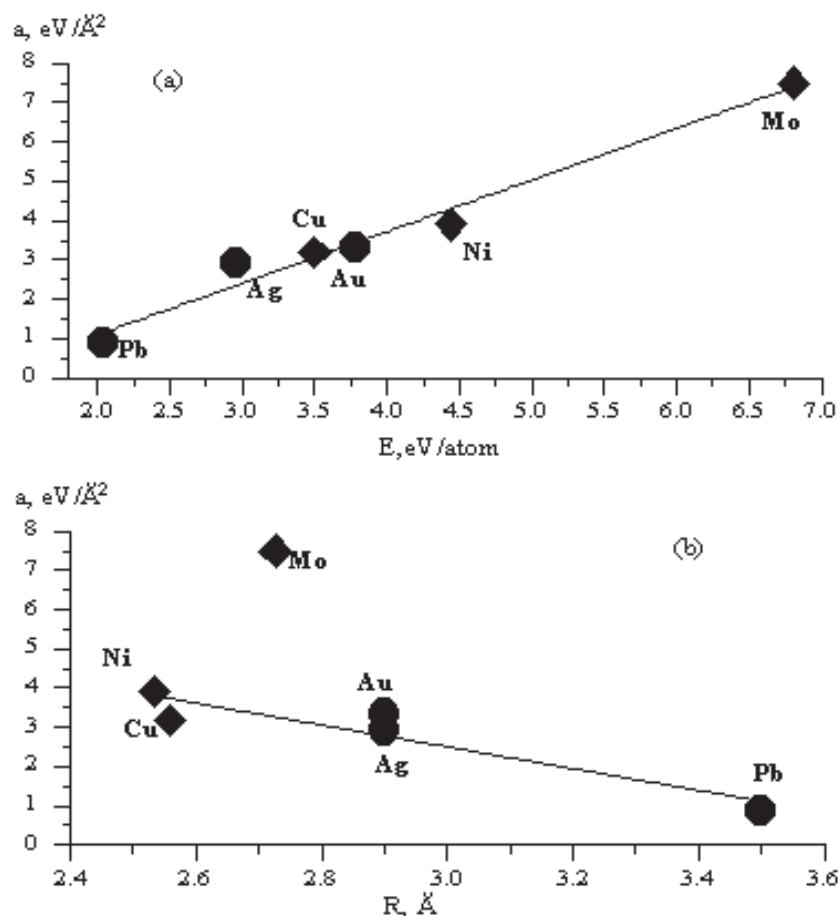


Figure 3. The a potential parameter dependence on cohesive energy E_c (a). The linear approximation was performed for Ni, Cu and Mo (squares), as well as Pb [1], Ag [2], Au [2] (circles). The a parameter dependence on interatomic distance R (b). The linear approximation was performed over fcc structure metals only: Ni, Cu (squares), Pb [1], Ag [2], Au [2] (circles).

The a parameter decreases when the interatomic distance R increases for all fcc structure metals (figure 3(b)) and this dependence is also nearly linear. As seen from figure 3 Mo has a large a parameter value. The large a parameter value and, consequently, large E_c value is caused by its bcc structure where each Mo atom has 8 + 6 atoms in its nearest environment, therefore, more valence electrons take part in bonding. It could be suggested the same effects for other bcc structure metals (for example, Nb, W) will take place.

The potential parameter b dependencies on E_c and R (figure 4) for fcc structure metals are close to linear too. Like the a parameter value the absolute value of the b parameter for Mo is large.

In all probability, the anharmonic pair potential parameter dependencies on interatomic distance and cohesive energy for the bcc structure metals will differ from those for fcc structure metals. Thus, from bcc structure Mo investigation it is clear that such an approach is applicable to certain crystal structure type.

We did not consider the same dependencies for the c anharmonic pair potential parameter, it is caused by a large uncertainty in the determination of this value (table 1).

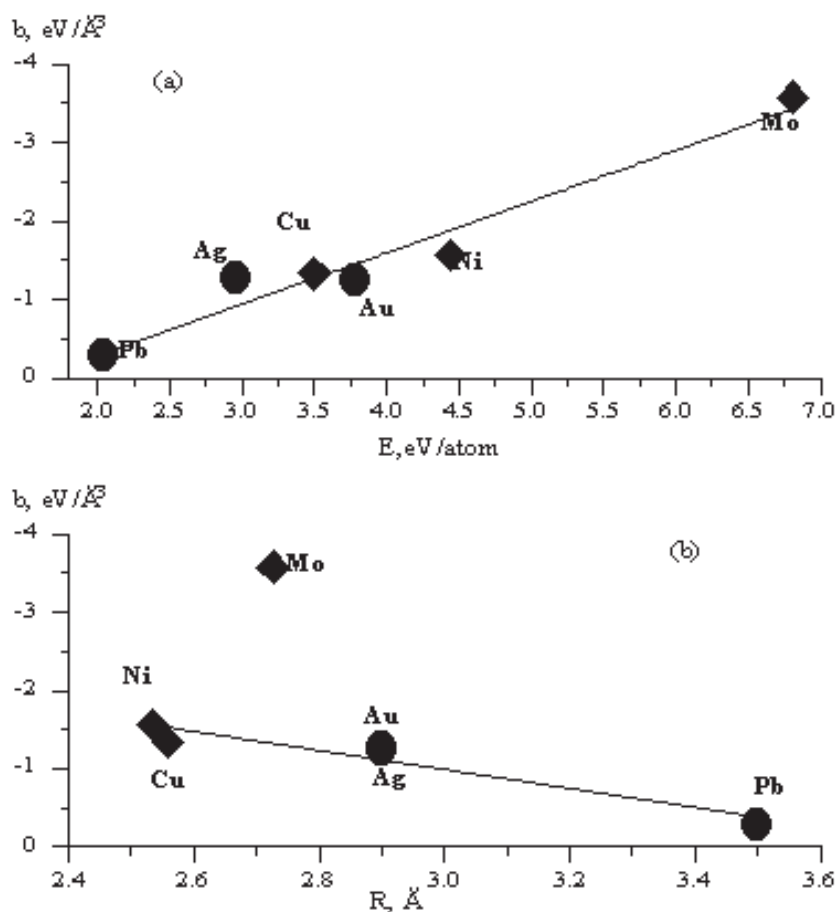


Figure 4. The potential parameter b dependence on cohesive energy E_c . (a) The linear approximation was performed over Ni, Cu and Mo (squares), as well as Pb [1], Ag [2], Au [2] (circles). The b potential parameter dependence on interatomic distance R . (b) The linear approximation was performed over fcc structure metals only: Ni, Cu (squares), Pb [1], Ag [2], Au [2] (circles).

Obtained anharmonic pair potential parameter dependencies on cohesive energy lead us to the idea of determining its value by EXAFS spectroscopy. However, the potential model used here is not suitable for this goal. In turn, a slightly different method suggested by Hung and Rehr [6], allows one to determine the dissociation energy value.

In this approach the Morse atomic pair potential

$$V_E(\Delta r) = D(\exp(-2\beta\Delta r) - 2\exp(-\beta\Delta r))$$

was applied to nearest-neighbour bond vibrations, and the following expression for the effective Einstein potential (1) was obtained:

$$V_E(\Delta r) = (5/2)D\beta^2\Delta r^2 - (5/4)D\beta^3\Delta r^3 + \dots, \quad (6)$$

where D is the dissociation energy and $1/\beta$ is the width of the potential. Using such a potential model the EXAFS cumulants were expressed through D and β parameters for fcc crystal structure type. In the high-temperature limit they are given by

$$\begin{aligned}\sigma^{(1)} &= \frac{3k_B T}{20D\beta} \\ \sigma^2 &= \frac{k_B T}{5D\beta^2} \\ \sigma^{(3)} &= \frac{3(k_B T)^2}{50D^2\beta^3}.\end{aligned}$$

In [6] these formulae were applied to numerical calculations of EXAFS cumulants. We solved the inverse task and expressed the D and β Morse potential parameters through second- and third-order cumulants:

$$\begin{aligned}D &= \frac{k_B T}{5\sigma^2\beta^2} \\ \beta &= \frac{50\sigma^{(3)}}{75\sigma^2}.\end{aligned}$$

The dissociation energy value D and β Morse potential parameter for Ni and Cu were calculated employing the formulae presented above. They are $D = 0.41$ eV, $\beta = 1.39$ Å (0.42 eV and 1.42 Å [7]) for Ni and $D = 0.33$ eV, $\beta = 1.38$ Å (0.34 eV and 1.36 Å [7]) for Cu. In brackets we represented the D and β parameters for these metals, obtained using experimental values of sublimation, the compressibility and the lattice constant [7]. As seen, the calculated values are in a good agreement with those values taken from [7]. Thus, the dissociation energy value and β Morse potential parameter can be obtained through temperature-dependent XAFS spectra.

4. Summary

The a , b , c anharmonic pair potential parameters for Ni, Cu and Mo were obtained using the XAFS spectroscopy technique. These parameters were used to determine thermodynamic characteristics such as the isothermal bulk modulus K , the Grunesien parameter γ , the Debye temperature Θ_D and the linear expansion coefficient at 400 K, α . It has been found the a and b pair potential parameters for fcc structure metals correlate with the interatomic distance and cohesive energy. The dissociation energy value and β Morse potential parameter were determined by XAFS spectroscopy.

Acknowledgments

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