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Calculated Thermal Expansion of the Actinide Elements[1]

P. Söderlind,[2] B. Johansson,[2] L. Yongming,[2] and L. Nordström[2]

The linear thermal expansion coefficient is calculated for the early actinides thorium, protactinium, uranium, neptunium, and plutonium for a hypothetical fcc crystal structure. The relativistic spin-orbit interaction is included in these calculations. We show that the spin-orbit splitting of the 5f band gives rise to a considerable increase in the thermal expansion and, to a large extent, explains the anomalously large thermal expansion for these elements.

KEY WORDS: actinide elements; thermal expansion.

1. INTRODUCTION

Recently the linear coefficient of thermal expansion was calculated for the fcc and bcc 4d transition elements and some other metals [1]. The good agreement with experimental data encouraged us to treat the thermal expansion of the actinide elements in a similar way. This is of particular interest since the early actinides U, Np, and Pu show a behavior which is highly anomalous when compared to other elements in the Periodic Table. In this work we identify to what extent their behavior originates from the relativistic effects, especially the spin-orbit coupling for 5f electrons.

In order to calculate the thermal expansion we have used the Helmholtz free energy, which is expressed as a sum of total energies for the electrons and the phonons. The electronic part is obtained from self-consistent electronic structure calculations within the local density approximation (LDA). The equation of state is calculated by means of

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[2] Condensed Matter Theory Group, Physics Department, Uppsala University, Box 530, Uppsala S-75121, Sweden.

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the Linear Muffin Tin Orbital (LMTO) [2–4] method. The lattice contribution is derived from a quasi-harmonic treatment using Debye and Grüneisen theory. The Helmholtz free energy is least-square fitted to a Morse function. This analytical representation is used to find the minimum of the free energy with respect to volume for a given temperature. The temperature-dependent equilibrium volume leads directly to the linear thermal expansion coefficient.

2. THEORY AND CALCULATIONS

We are especially interested in calculating the temperature-dependent Wigner–Seitz equilibrium radius, $r_0(T)$. From this quantity we directly obtain the linear coefficient of thermal expansion. In order to calculate $r_0(T)$ we minimize the Helmholtz free energy for a given temperature. The total free energy contains contributions from electrons and phonons. It is physically well justified to neglect the electron–phonon coupling [5] and the entropy contribution from the electrons. Neglecting the temperature dependence of the electronic structure, the free energy $F(r, T)$ takes the form

$$F(r, T) = E_{\mathrm{el}}(r) + E_{\mathrm{ph}}(r, T) - TS_{\mathrm{ph}}(r, T) \tag{1}$$

where r is the Wigner–Seitz radius, E_{el} and E_{ph} are the electronic and phonon energies, respectively, and S_{ph} is the phonon entropy. The electron energy, obtained by means of electronic structure calculations, is fitted by a Morse function with three parameters, b, c, and λ, i.e.,

$$E_{\mathrm{el}}(r) = be^{-\lambda r} + ce^{-2\lambda r} + \text{constant} \tag{2}$$

The phonon energy contains the thermal energy, U, derived from Debye theory [6] and the zero-point energy [7] E_0,

$$E_{\mathrm{ph}} = U + E_0 = 9k_{\mathrm{B}}T\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^3}{e^x - 1}\,dx + \frac{9k_{\mathrm{B}}\Theta}{8} \tag{3}$$

where Θ denotes the Debye temperature.

Inserting the corresponding expression for the phonon entropy [7], the free energy takes the form

$$F(r, T) = E_{\mathrm{el}}(r) - k_{\mathrm{B}}T\left\{3\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^3}{e^x - 1}\,dx - 3\ln[1 - e^{-\Theta/T}] - \frac{9\Theta}{8T}\right\} \tag{4}$$

The Debye temperature, Θ, is calculated as a function of temperature and the Grüneisen theory is applied. Following the work in Ref. 1 we calculate the Debye temperature at the equilibrium radius (r_0) from the relation

$$\Theta_0 \equiv \Theta(r_0) = 41.63 \left[\frac{r_0 B(r_0)}{M}\right]^{1/2} \tag{5}$$

where B is the bulk modulus and M the atomic mass. The anharmonic behavior of the lattice vibrations is treated by means of Grünesien theory. We define the Grüneisen parameter in the Debye model as [6]

$$\gamma = -\frac{\partial \ln \Theta}{\partial \ln V} \tag{6}$$

Considering the Grüneisen parameter as a constant, we obtain $\Theta V^{\gamma} =$ constant, which gives us the volume dependence of the Debye temperature. Equation (5) for the Debye temperature is used to derive the Grüneisen parameter,

$$\gamma = -\frac{1}{6} - \frac{1}{2}\frac{\partial \ln B}{\partial \ln V} \tag{7}$$

From the definition of the bulk modulus this can be expressed as

$$\gamma = -\frac{2}{3} - \frac{V}{2}\frac{\partial^2 P/\partial V^2}{\partial P/\partial V} \tag{8}$$

The equation of state is obtained from the Morse function, which is fitted to the Helmholtz energy. This leads to a rather complicated expression of the Grüneisen parameter as a function of volume. At the equilibrium radius $r_0(T)$, the Grüneisen parameter will be simplified to a linear function of r_0. We label γ in the same way as the Debye temperature,

$$\gamma_0 \equiv \gamma(r_0) = \frac{\lambda r_0}{2} \tag{9}$$

Here the Morse parameter λ is used to define a constant Grüneisen parameter for a given temperature. This approximation of the lattice behavior with a mixture of Debye and Grüneisen theory and a constant γ for a given temperature is of a so-called quasi-harmonic type. The volume- and temperature-dependent Debye temperature can, after this derivation, be calculated from the expression

$$\Theta(r, r_0) = \Theta_0 \left(\frac{r_0}{r}\right)^{3\gamma} \tag{10}$$

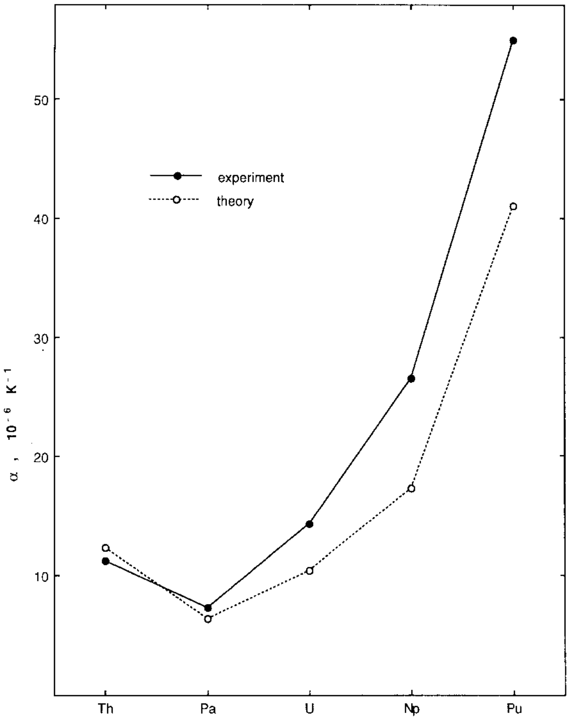

Fig. 1. Comparison between experimental and theoretical values for the linear coefficient of thermal expansion.

The total free energy as well as the equilibrium radius can now easily be calculated. Having obtained $r_0(T)$ the linear coefficient of thermal expansion is simply computed as

$$\alpha(T) = \frac{1}{r_0(T)} \frac{dr_0(T)}{dT} \tag{11}$$

3. RESULTS

The thermal expansion, calculated with the spin-orbit coupling included, is in satisfactory agreement with experimental data [8] for the three first actinides. (The experimental value for protactinium is, however, an estimation.) The agreement is not so good for neptunium as regards the absolute value but the calculations account quite well for the experimentally observed anomalous rise between uranium and neptunium. The calculated thermal expansion for plutonium is found to be very high but still considerably smaller than the experimental. A comparison between experiment and theory is shown in Fig. 1.

4. CONCLUSIONS

Analysis of the calculations shows that it is the splitting of the 5f band due to the spin-orbit coupling which gives rise to the anomalous increase in the thermal expansion for the heavier elements [9]. The remaining discrepancy with the experimental for neptunium and, especially, plutonium is most likely due to our simplified treatment of the crystal structure. We have assumed a fcc crystal structure for all the elements in the electronic structure calculations. This is appropriate for thorium but the other elements have far more complicated structures. This means, in particular, that their thermal expansion is anisotropic. The experimental data are average values, while the calculations, for cubic symmetry, give only a single coefficient of thermal expansion. At room temperature, plutonium has a monoclinic structure [10] with 16 atoms in each unit cell and this highly asymmetric configuration is most likely the origin of the remaining discrepancy between theory and experiment for plutonium.

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