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Calculated Thermal Expansion of d and f Transition Metals

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ABSTRACT

The linear coefficient of thermal expansions for the $4d$, $5d$, and the $5f$ transition elements is considered theoretically by means of first principles electronic structure calculations. The calcluations utilize the LMTO-method within the local density approximation (LDA) for the exchange-correlation potential, and are fully relativistic. A simplified expression for the Debye temperature is combined with the Grüneisen theory to obtain the thermal expansion. The theoretical results are in relatively good agreement with experiment. The behavior of the thermal expansion for the $4d$ transition metals is very similar to that for the $5d$ transition metals, while the $5f$ metals display a different variation over the series. Especially Np and Pu show a most anomalous thermal expansion, which is suggested to originate mainly from relativistic effects.

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INTRODUCTION

Recent calculations of the thermal expansion for a number of metals with a bcc or fcc cubic structure [1] have shown to be successful. Also calculations for the actinide metals [2] have been performed with encouraging results. In the present work we review these calculations and also present new results for the $5d$ transition series of elements. In order to make the study of the $4d$ and $5d$ series complete we have also made computations for the $4d$ and $5d$ elements which possess the hcp crystal structure. Since the $5f$ elements (actinides) show an anomalous thermal expansion behavior, it is intersting to contrast this to the results for the $4d$ and $5d$ elements.

The present calculations are performed with the same approach as in the earlier works and the investigated elements are studied in their ground state crystal phases which depart from the cubic symmetry in some cases. Thus for a given temperature we determine the Helmholtz free energy as a function of the atomic volume. The free energy consists of contribution from the ground state electronic structure and the vibrating lattice for which we apply Debye theory combined with the Grünesien theory. This treatment is of a so-called quasi-harmonic type and the anharmonicity permits a study of the thermal expansion. The second section of this work considers the theory needed to determine the room temperature thermal expansion. The details of the computation of the electronic structure are briefly reviewed and a more thorough description is given in our earlier work.[2] Section three deals with the theoretical and the experimental data, the results for the $4d$ and $5d$ transition elements are presented together with early actinides Th - Pu. This part of the $5d$ transition series shows a trend in the atomic volumes from thorium to plutonium that has an obvious similarity with the atomic volumes behavior of the $4d$ and $5d$ transition series. We will show that for the $5f$ elements the behavior of the thermal expansion is in an evident contrast to what is found for the $4d$ and $5d$ elements. In order to further investigate the anomaly of the thermal expansion especially for Np and Pu we introduce various levels of approximation for the electronic structure. In the last section we discuss the obtained theoretical results and the parabolic decrease of the volume expansion coefficient for the $4d$ and $5d$ transition elements which is well understood from the bonding characteristics of the d electrons. The anomalous results for the actinides and particularly for the heavier ones Np and Pu is belived to originate essentially from relativistic effects.

THEORY

The electronic strucure is obtained self-consistently using the Linear combination of Muffin-tin Orbitals Method (LMTO) [3, 4] within the LDA for exchange and correlation potential, and the calculations where performed relativistically by solving the four-component Dirac equation for the wave functions.[5] The lattice contribution which introduces the thermal dependence of the free energy, is derived from a quasi-harmonic treatment in the framework of Debye theory [6] while, on the other hand, the electronic contribution can be restricted to a consideration of the internal energy and its volume dependence at zero temperature. The linear coefficient of thermal expansion is defined as;

$$\alpha(T) = \frac{1}{3V_0(T)}\frac{dV_0}{dT} \tag{1}$$

where the equilibrium atomic volume $V_0(T)$ is the volume that minimizes the Helmholtz free energy at a temperature T. In the treatment of the electronic structure we introduce the Wigner-Seitz radius r_0 as the radius of an atomic sphere with volume V_0 and with this parameter for the volume the definition of the linear coefficient of thermal expansion becomes:

$$\alpha(T) = \frac{1}{r_0(T)}\frac{dr_0}{dT} \tag{2}$$

Neglecting the thermal dependence of the electronic structure and electron-phonon interaction the Helmholtz free energy can be expressed as

$$F(r,T) = E_e(r) + E_{ph}(r,T) - TS_{ph}(r,T), \tag{3}$$

where E_e and E_{ph} are the electron and phonon contributions to the energy, respectively, and S_{ph} is the phonon entropy. The phonon energy contains the thermal energy, U, derived from Debye[6] theory, and the zero point energy E_0.[7] Thus the free energy is expressed in terms of the well-known Debye function, and depends on one parameter, the Debye temperature Θ.

The anharmonicity which is necessary to obtain a thermal expansion is introduces by means of Grüneisen theory. Therebye the Debye temperature now includes a dependence on the volume. For a given temperature, the Grüneisen parameter γ is approximated by a constant. Since its value will depend on the free energy itself, or rather the equilibrium volume, its determination requires an iterative procedure. Therefore the free energy is calculated in a self-consistent manner and the iterative process is found to converge rapidly. This approximate treatment of the lattice vibrations with a mixture of Debye and Grüneisen theory and a constant γ for a fixed temperature is of a so-called quasi-harmonic type.

The main problem that remains is the determination of the Debye temperature. In agreement with Moruzzi et al.[1] and Ref. 2 we choose

$$\Theta = const\sqrt{\frac{rB}{M}} \tag{4}$$

where B is the static lattice bulk modulus and M the atomic mass. The anharmonic behavior of the lattice is now introduce by means of the Grüneisen parameter γ defined as

$$\gamma = -\frac{\partial ln\Theta}{\partial lnV} \tag{5}$$

The Debye temperature is however related to the bulk modulus in Eq. (3) and γ can therefore be expressed:

$$\gamma = -\frac{1}{6} - \frac{\partial lnB}{2\partial lnV} \tag{6}$$

From the definition of the bulk modulus

$$B = -V\frac{\partial P}{\partial V} \tag{7}$$

we obtain the so-called Slater approximation for the Grüneisen parameter

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

With a constant γ for a fixed temperature we can write Eq. (4) as $\Theta V^{\gamma} = const$, and therefore the volume dependence of the Debye temperature becomes

$$\Theta(r, r_0) = \Theta_0(\frac{r_0}{r})^{3\gamma} \tag{9}$$

where r_0 is the equilibrium atomic radius and Θ_0 is the Debye temperature obtained ar r_0 at temperature T. This is also the expression used by Moruzzi et al.[1]

For the cubic structure the volume only depends on a single lattice parameter, while for the hcp structures two parameters are needed, a and c. To minimize the numerical efforts for the hcp metals we have chosen a restricted variation in the sense that c/a is taken to be a constant and is set equal to its experimental value.

RESULTS

In Fig. 1 we compare the calculated thermal expansion with experimental data for the $5d$ transition elements. The theory gives a parabolic type of behavior through the series with a minimum around rhenium and osmium. The experimental data [8] show a similar behavior, except that the value for rhenium is larger than for the neighboring elements tungsten and osmium. A possible explanation for this deviation could be that our treatment is a

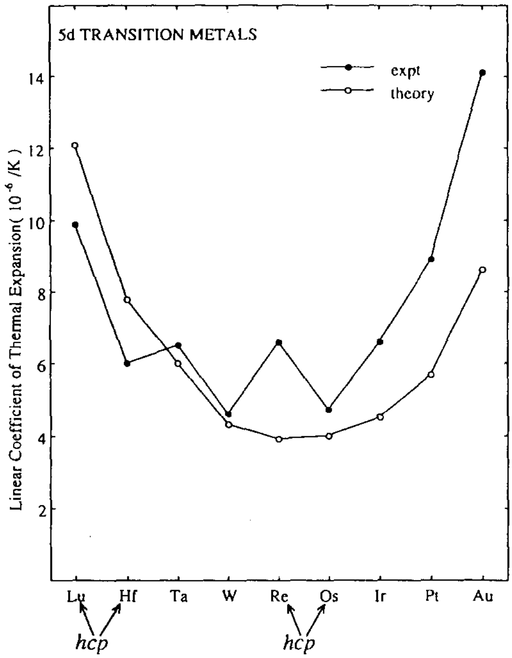

Fig. 1 The linear coefficient of thermal expansion for the $5d$ transition elements. Filled (open) circles refer to experimental[8] (theoretical) values. The experimental data for technetium is an estimation.

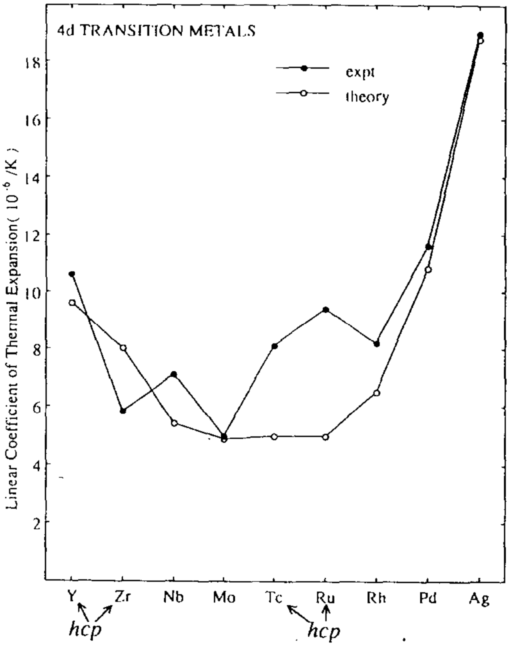

Fig. 2 The linear coefficient of thermal expansion for the $4d$ transition elements. Filled (open) dots refer to experimental[8] (theoretical) values. The theoretical values are from Moruzzi et al,[1] while the data for the hcp metals are from the present calculation.

restricted one for the hcp crystals since we let c/a have a constant value. This, however needs further investigations.

In Fig 2. we show the theoretical results by Moruzzi et al for the cubic 4*d* transition metals together with our calculated values for the hcp metals. Again the theoretical values show a minimum in the middle of the series. The experimental data also show a parabolic trend but with some exceptions for rhenium and niobium. Despite this the agreement between theory and expriment is reasonably good.

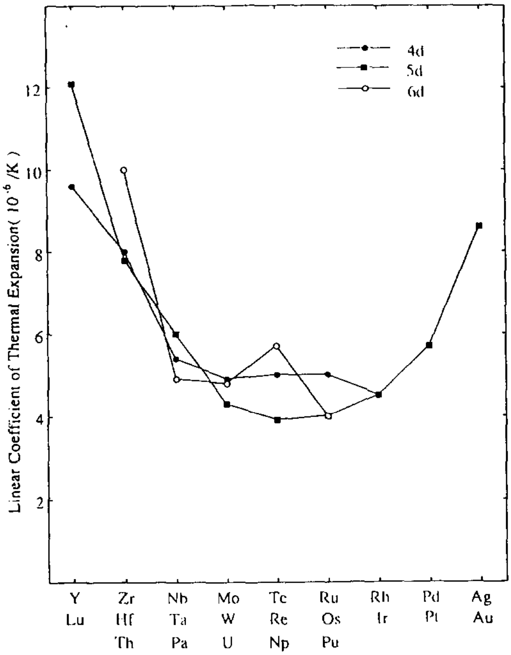

Fig. 3 The theoretical linear coefficient of thermal expansion for the 4*d* transition series. The open circles refer to calculations where the actinides are assumed to form a 6*d* transition series (see main text).

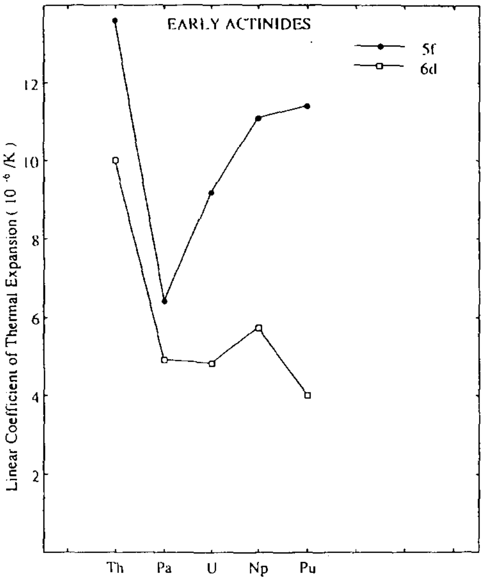

Fig. 4 Theoretical values of the actinide thermal expansion for the scalar relativistic calculations (filled circles) and calculations where the actinides are regarded as part of a 6*d* transition series (open squares).

In Fig. 3 we show the theoretical thermal expansion of the 4*d*, 5*d*, and a hypothetical 6*d* transition series. The early actinides Th - Pu are here regarded as part of a 6*d* transition series. The 5*f* electrons are for this purpose placed in the 7*s*, 7*p*, and 6*d* conduction band which are the only valence states included in the calculations. The essentially parabolic shape of the thermal expansion as we proceed in the 6*d* series from Th to Pu is obvious. The absolute values of the thermal expansion corresponding to elements with the same number of *d* valence electrons are very close except for some minor deviations for the first elements in the series. This shows that if the actinides really formed a 6*d* transition series their thermal expansion properties would be very similar to the 4*d* and 5*d* transition elements. However, experimentally this is not the case and this demonstrates that the actinides form a unique series of elements in the Periodic Table. The actinides are nowadays understood to be part of a 5*f* transition series rather than a 6*d* transition series.

In Fig 4. theoretical values of the thermal expansion is showed for two different approaches. The "5f" calculation refers ta a scalar relativistic treatment of the Hamiltonian where the important spin-orbit interaction is neglected but the other relativistic effects are included. It is only between Th and Pu that one can see a decrease of the thermal expansion in this "5f" calculation whereas it increases continously from Pa to Pu. For the heavier elements neptunium and plutonium the absolute values of the thermal expansion are strongly influenced by the different treatment of the valence electrons. The picture where the actinides are part of a 5*f* transition series gives almost a factor of four larger thermal expansion for the heaviest element Pu. The fact that the experimentally observed thermal expansion is much larger (a factor of ten) than what is observed when the actinides are hypothetically

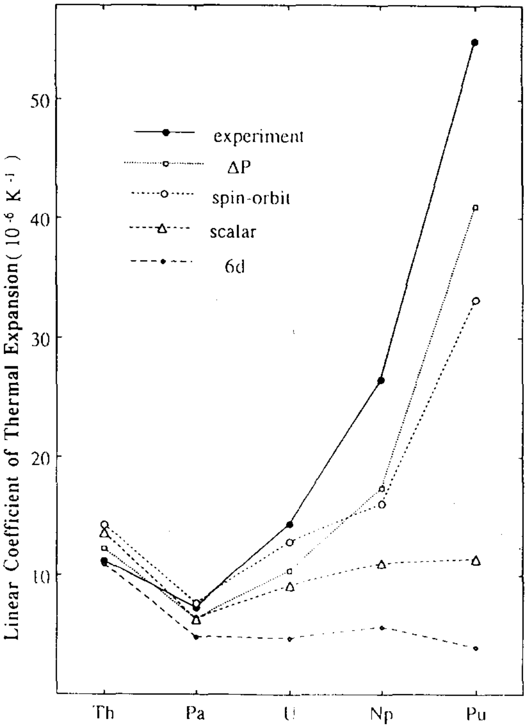

Fig. 5 The linear coefficient of thermal expansion for the early actinides at various levels of sophistication. "ΔP"refers to calculations with a correction to the pressure (see main text).

treated as 6*d* transition elements is a strong argument that these heavy elements certainly not form another *d* transition series. The thermal expansion of the early actinides in Fig. 5 is calculated at various levels of approximation. The scalar relativistic ("scalar") calculations do not show the dramatic increase of the thermal expansion as is observed experimentally for the elements from uranium to plutonium, but still the increase in comparison to the calculation denoted "6d" is most obvious. Thus it is clear that by including the 5*f* band electrons in the treatment, a quite different range of values for the thermal expansion is obtained than for the *d* transition elements. Thus the character of the dominating valence electrons (*d* or *f*) gives rise to different "canonical" behavior for the thermal expansion. Fully relativistic treatment ("spin-orbit") of the electronic structure where the spin-orbit interaction is included increases the thermal expansion substantially for Np and Pu. In the "spin-orbit" calculation the theoretically determined room temperature atomic volume for the elements differs a few percentage form that observed experimentally. For that reason we perform the calculation denoted "ΔP" which refers to values of the thermal expansion obtained at the experimental rather than the theoretical atomic volume. Thereby the steep rise between Np and Pu becomes quite well described.

CONCLUSION

Theory gives a parabolic decrease of the linear coefficient of thermal expansion with a minimum in the vicinity of the element in the middle of the 4*d* and 5*d* transition series, respectively. This trend is expected since the atomic volume decreases in a similar fashion and the minimum occurs for the most stable configuration where the *d* shell is half filled and nearly half filled. For this reason the compressibility is minimal for these elements and the corresponding thermal expansion is therefore small. The experimental values of the thermal expansion shows generally the same behavior but there are exceptions. The measured thermal expansion refers to polycrystalline bulk materials and the values of the non-cubic elements are averaged over the crystallographic directions. The value for technetium is however an estimation. The theoretical trends can be understood from the bonding characteristics of the *d* electrons and the absolute values agree satisfactorily with the experimentally observed ones.

For the actinides the inclusion of the 5*f* electrons is crucial in order to obtain agreement with experimental data. Furthermore, the anomalous behavior for Np and Pu can to a large extent be explained by the spin-orbit splitting of the 5*f* band. In reality these elements have a much more complicated structure than the fcc assumed in the calculation. Therefore the thermal expansion is strongly anisotropic for these elements while the data we are comparing with refer to average volume expansion. Thus we may expect that also the crystal structure is of importance for the volume expansion, an effect which was neglected in our theoretical treatment.

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