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Relativistic effects on the thermal expansion of the actinide elements

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The room-temperature linear thermal-expansion coefficient is calculated for the light actinides thorium, protactinium, uranium, neptunium, and plutonium for the 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 of the thermal expansion and to a large extent explains the observed anomalously large thermal expansion for the neptunium and plutonium metals.

I. INTRODUCTION

Thermal expansion is one of the most basic physical properties of a solid-state system. Historically a lot of attention has been focused on this thermal effect and for almost all the elements there are experimental data available. The behavior of the linear coefficient of thermal expansion for the pure elements shows several regularities. The most obvious one is the minimum and nearly constant value in the middle of the $4d$ and $5d$ transition series as shown in Fig. 1. For the $3d$ transition elements the linear coefficient of thermal expansion shows a rather irregular behavior for the elements beyond vanadium. This can be understood from the magnetic properties of these elements since the variation of the bulk modulus, a physical property related to the thermal expansion, shows similar irregularities due to the appearance of magnetism in these metals. The light actinide metals thorium–plutonium in the $5f$ series of elements are not magnetic but still these elements show a dramatic deviation from the above-mentioned regularity in the thermal-expansion behavior for the $4d$ and $5d$ transition metals.

From Fig. 2 it can be seen that the light actinide elements and in particular uranium, neptunium, and plutonium show an *anomalously high room-temperature thermal expansion* compared to corresponding elements in the $4d$ and $5d$ transition series. This is surprising since the $5f$ electrons in the light actinides are known to be itinerant[1] and their bonding characteristics are similar to that of the d electrons for the d transition metals. This similarity is, for example, reflected in the atomic volume since the light actinides and the earlier d transition elements follow a trend with a parabolic decrease of the volume with increasing atomic number. This fact suggested, to earlier researchers, that the early actinides actually were part of a $6d$ transition series and not a $5f$ transition series.[2] In elements heavier than plutonium the $5f$ electrons can be regarded as localized and a comparison to the lanthanides is more relevant.[3,4]

There are reasons to suspect that the high and anomalous behavior of the linear coefficient of thermal expansion for the medium–heavy elements in the $5f$ transition series to a large extent originates from the relativistic spin-orbit interaction. This may explain the deviating behavior of neptunium and plutonium since for these two actinides the spin-orbit splitting of the $5f$ band will have a significant effect on the bulk properties,[5,6] while the earlier actinides will only be relatively little influenced by this relativistic effect. The present work examines to what extent the spin-orbit coupling for the $5f$ electrons increases the thermal expansion. To clearly exhibit this relativistic effect and reduce the possible influence of

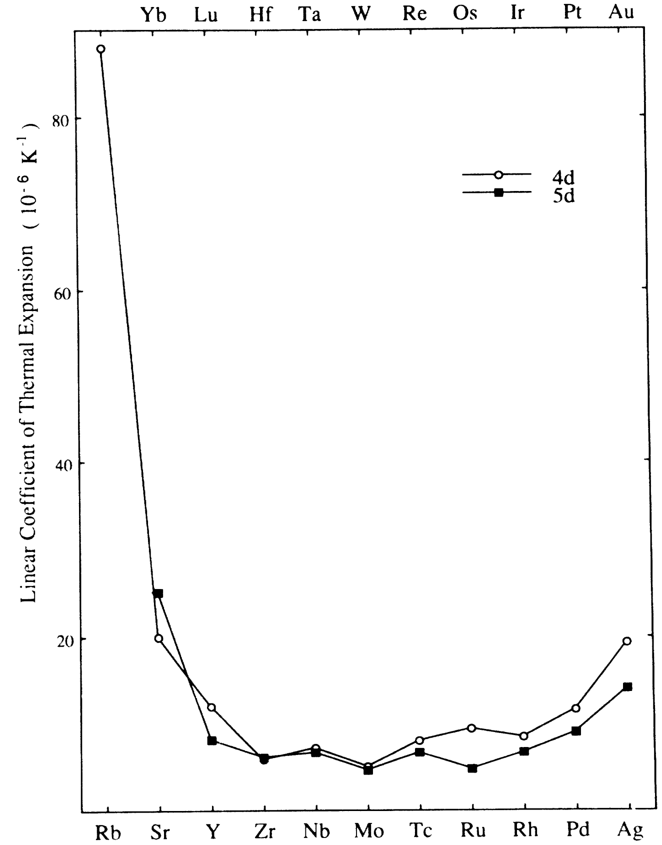

FIG. 1. The experimental linear coefficient of thermal expansion for the $4d$ and $5d$ transition metals (Ref. 17).

different crystal structures we compare calculations for the same crystal structure for all the elements. The chosen structure is the fcc structure which agrees with experimental room-temperature data only for thorium.

Recently Moruzzi, Janak, and Schwartz[7] calculated the thermal expansion for the fcc and bcc 4*d* transition elements and some other metals. The obtained good agreement with experimental data encouraged us to treat the thermal expansion of the actinide elements in a similar way. In order to calculate the thermal expansion we have used Helmholtz free energy which is expressed as a sum of contributions from electrons and phonons. The lattice contribution is derived from a quasiharmonic treatment using Debye and Grüneisen theory. This contribution accounts for the temperature dependence of the free energy since we neglect thermal excitations of the electrons in the calculations. To facilitate the analysis of the calculated results the Helmholtz free energy is least-square fitted to a Morse function. The equilibrium bulk properties are then easily obtained from this analytical representation of the free energy. The calculated change of the equilibrium volume as a function of temperature leads directly to the linear coefficient of thermal expansion by a numerical differentiation of the equilibrium radius with respect to the temperature. In Sec. II we present the details of our calculations of the electronic contribution to the free energy. These calculations have been performed at different levels of approximations where the most elaborate one includes the effect of the spin-orbit interaction. In Sec. III we first introduce the Debye theory for harmonic lattice vibrations to derive the expression for the free energy. The theory is then extended to include anharmonic lattice vibrations by applying the Grüneisen formulation. We allow the system to expand with temperature and recalculate the Debye temperature and Grüneisen constant. Section IV accounts for the calculated results. Bulk properties calculated within both a scalar and a fully relativistic approach are presented for all five elements. For comparison, calculations are also presented where only the *s*, *p*, and *d* partial waves are included and where all the 5*f* electrons are forced into the *spd* conduction band. This corresponds to the case that the actinide elements really would form a 6*d* transition series of elements, a view which was still rather commonly held a decade ago. Finally a discussion is given in Sec. V.

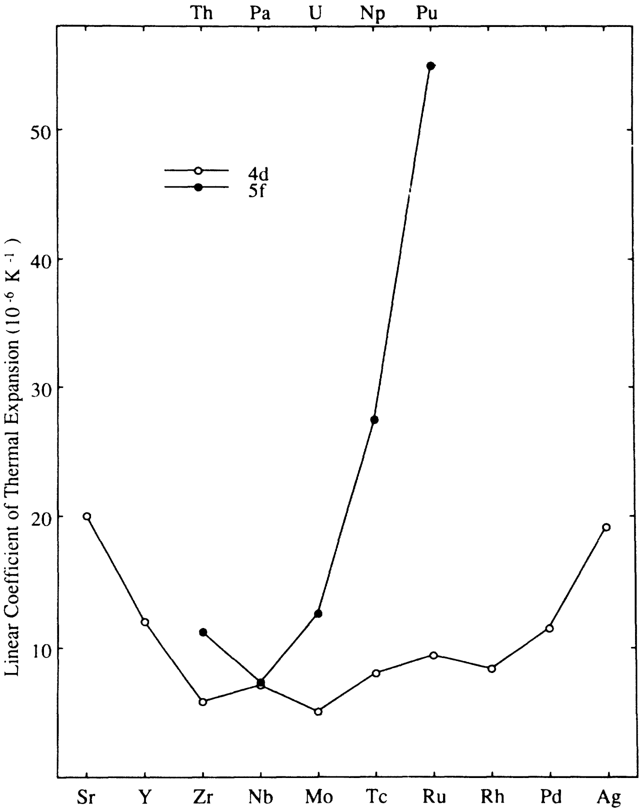

FIG. 2. A comparison between experimental values of the linear coefficient of thermal expansion for the 4*d* and 5*f* transition metals (Ref. 17). The value for Pa is an estimation.

II. DETAILS OF THE ELECTRONIC STRUCTURE CALCULATIONS

The electronic part of the Helmholtz free energy is derived from self-consistent electronic structure calculations. These are done using the local-density approximation (LDA) (Ref. 8) for the exchange-correlation potential with the von Barth–Hedin parametrization.[9] The equation of state is calculated by means of the linear muffin-tin-orbital (LMTO) method[10,11] for Wigner-Seitz radii spanning the range of approximately ±5–10% of the equilibrium radius, in intervals of 0.02 a.u. The LMTO problem is solved within the atomic-sphere approximation (ASA) where also the so-called combined correction terms[10] have been included. Scalar relativistic calculations, including relativistic shifts except for the spin-orbit term, and fully relativistic calculations, including the spin-orbit interaction,[12] are compared. All calculations are performed for a fcc crystal structure and 89 **k** points in the irreducible part of the Brillouin zone have been used. For the three heaviest elements in the present investigation (uranium, neptunium, and plutonium) the fully relativistic calculations were performed more carefully with a higher accuracy. These calculations, which used 240 **k** points, were converged to the order of 0.01 kbar in pressure for the Wigner-Seitz radius in intervals of 0.01 a.u. This more elaborate treatment was particularly important for plutonium since for this metal the calculated equation of state near the equilibrium radius was difficult to fit to an analytical function. (See the Appendix for details of the fitting function.)

In order to investigate how sensitive the obtained results are to the actual choice of crystal structure in the electronic structure calculations, we have also performed calculations for an assumed room-temperature bcc crystal structure for uranium, neptunium, and plutonium. These calculations, which include the spin-orbit interaction, were performed using 56 **k** points in the irreducible part of the Brillouin zone.

III. THEORY FOR THE FREE ENERGY

It is simple to obtain a number of ground-state bulk properties of a system provided that there is an analytical representation of its free energy available. For this purpose we have performed self-consistent Morse fits to the calculated free energy at different temperatures. In agreement with the work by Moruzzi *et al.*[7] the free energy is represented as a Morse function with the Wigner-Seitz radius (r) and the temperature (T) as variables

$$F(r,T)=be^{-\lambda r}+ce^{-2\lambda r}(+\text{const}) \ . \tag{1}$$

Here b, c, and λ account for the temperature dependence and the last term is a constant of no importance for the present investigation. This yields, directly from the fitting parameters b, c, and λ, the finite-temperature equilibrium properties such as atomic volume, bulk modulus, and entropy. The thermal expansion is then obtained numerically from the calculated equilibrium volume by means of a second-order central difference formula. In order to make this article relatively self-contained we will review the formalism[7] necessary to calculate the free energy.

A. Helmholtz free energy

The total free energy for a metallic system is, at least for moderate temperatures, dominated by the separate contributions from electrons and phonons. It is physically well justified to neglect the electron-phonon coupling as well as the entropy contribution from the electrons. Neglecting also the thermal dependence of the electronic structure the finite-temperature free energy $F(r,T)$ takes the form

$$F(r,T)=E_e(r)+E_{\text{ph}}(r,T)-TS_{ph}(r,T) \ . \tag{2}$$

E_e and E_{ph} are the electron and phonon contributions to the energy, respectively, and S_{ph} is the phonon entropy. Godwal and Jeanloz[13] introduced a contribution from thermal excitations of the electrons but for temperatures up to room temperature this contribution to the equation of state was found to be negligible in the present investigation. The temperature-independent analytical ansatz for the electron energy, E_e, is of the same analytical form as above for the Helmholtz free energy, namely a Morse function

$$E_e(r)=b_0e^{-\lambda_0 r}+c_0e^{-2\lambda_0 r}+\text{const} \ . \tag{3}$$

The parameters b_0, c_0, and λ_0 are adjusted to fit the equation of state, $P_e=P_e(r)$, obtained by means of LMTO electronic structure calculations (see the Appendix). The phonon energy contains the thermal energy, U, derived from Debye theory, and the zero-point energy E_0. The phonon energy is expressed as

$$E_{\text{ph}}=U+E_0=9k_BT\left[\frac{T}{\Theta}\right]^3\int_0^{\Theta/T}\frac{x^3}{e^x-1}dx+\frac{9k_B\Theta}{8} \ , \tag{4}$$

where Θ denotes the Debye temperature and k_B is Boltzmann's constant. Inserting the corresponding expression for the phonon entropy (see the Appendix) the free energy takes the form

$$F(r,T)=E_e(r)-k_BT\left[3\left[\frac{T}{\Theta}\right]^3\int_0^{\Theta/T}\frac{x^3}{e^x-1}dx -3\ln(1-e^{-\Theta/T})-\frac{9\Theta}{8T}\right] \ , \tag{5}$$

where the integral is recognized as the Debye function. The Debye function is available in tabulated form[14] but is more conveniently represented analytically by cubic splines or other functions fitted to the tabulated data. The free energy is now determined except for one parameter, the Debye temperature.

B. Debye temperature

First we apply Debye theory in order to derive an expression for the Debye temperature, valid for the equilibrium lattice separation. As is well known, however, the Debye theory only considers harmonic vibrations of the lattice and cannot account for the thermal expansion which instead is a consequence of anharmonicity of the lattice vibrations. The anharmonic behavior of the lattice is often treated by means of Grüneisen theory. To do this we extend the expression of the Debye temperature to include a dependence on the lattice separation which will be described by the Grüneisen parameter γ. For a given temperature, however, the Grüneisen parameter is approximated by a constant and its value depends on the free energy itself, or rather the equilibrium volume which is obtained from the free energy. The determination of γ therefore requires an iterative procedure, which is found to converge rapidly. A self-consistent analytical representation of the free energy at the actual temperature is then obtained. 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 quasiharmonic type.

In the Debye theory the highest phonon frequency is the cutoff frequency, ω_D, given by

$$\omega_D=\left[\frac{6\pi^2v_m^3}{V}\right]^{1/3} \ . \tag{6}$$

Here V is the Wigner-Seitz volume and v_m is the average velocity of sound in the crystal. With r as the Wigner-Seitz radius the Debye temperature becomes

$$\Theta=\frac{h\omega_D}{2\pi k_B}=\frac{hv_m}{rk_B}\left[\frac{9}{16\pi^2}\right]^{1/3} \ . \tag{7}$$

As a good approximation for isotropic crystals[15] we use an average value for the velocity of sound expressed in the shear and longitudinal velocities, v_s and v_l:

$$v_m=\left[\frac{1}{3}\left[\frac{2}{v_s^3}+\frac{1}{v_l^3}\right]\right]^{-1/3} \ . \tag{8}$$

The mean velocity v_m is expressed as a function of the bulk modulus B, which in this case is calculated for a static lattice by means of the fitting parameters b_0, c_0, and λ_0 in Eq. (3) (see the Appendix).

From the assumption of an isotropic crystal[16] one can, with Poisson's ratio ν and the atomic mass M as the only input, approximately calculate the Debye temperature from first-principles electronic structure calculations. With Eqs. (7) and (A12) the Debye temperature is expressed as

$$\Theta=\frac{h}{k_B}\left[\frac{4\pi}{3}\right]^{-1/6}\left[\frac{2}{3}\left[\frac{2}{1-2\nu}\right]^{3/2}+\frac{1}{3}\left[\frac{1}{1-\nu}\right]^{3/2}\right]^{-1/3}\left[\frac{3}{1+\nu}\right]^{1/2}\left[\frac{rB}{M}\right]^{1/2} . \tag{9a}$$

In the work by Moruzzi *et al.*[7] Poisson's ratio is approximated to be $\frac{1}{3}$ independent of the element. This is appropriate for the 4d transition metals and a number of other metals but somewhat less accurate for the light actinide elements. The early actinides have Poisson's ratio[17] of about 0.25 except for plutonium where it is only 0.15. Therefore the generalized expression above, considering the different Poisson's ratio, is needed to obtain the Debye temperature. However, in order to keep the calculations free from experimental input, 0.25 is used as a representative value for Poisson's ratio for all the present actinide elements. By explicit calculations we have found that the calculated properties are rather insensitive to the actual choice of Poisson's ratio.

Introducing a function $f(\nu)$ the expression for the Debye temperature in Eq. (9a) is rewritten in the form

$$\Theta=\frac{h}{k_B}\left[\frac{4\pi}{3}\right]^{-1/6} f(\nu)\left[\frac{rB}{M}\right]^{1/2} . \tag{9b}$$

When the radius and the atomic mass are given in atomic units and the bulk modulus in kbar the Debye temperature is given by (in K)

$$\Theta=67.48 f(\nu)\left[\frac{rB}{M}\right]^{1/2} . \tag{9c}$$

For convenience we label the Debye temperature as Θ_0 when it is evaluated at the equilibrium radius, r_0. It depends implicitly on the temperature, since r_0 is a function of T, and is given by

$$\Theta_0\equiv\Theta(r_0)=67.48 f(\nu)\left[\frac{r_0 B(r_0)}{M}\right]^{1/2} , \tag{10}$$

where the bulk modulus is calculated at the equilibrium radius.

So far we have not included the anharmonic behavior of the lattice vibrations. For this purpose we define the Grüneisen parameter[18]

$$\gamma=-\frac{\partial \ln\Theta}{\partial \ln V} . \tag{11}$$

Then the expression for the Debye temperature in Eq. (9b) is used to derive the Grüneisen parameter as a function of volume and bulk modulus and we obtain

$$\gamma=-\frac{1}{6}-\frac{1}{2}\frac{\partial \ln B}{\partial \ln V} . \tag{12}$$

From the definition of the bulk modulus in the Appendix [Eq. (A6)] we can directly derive an approximation to γ from derivatives of the static lattice pressure

$$\gamma=-\frac{2}{3}-\frac{V}{2}\frac{\partial^2 P/\partial V^2}{\partial P/\partial V} . \tag{13}$$

This form of γ is often referred to as the Slater approximation,[19] and is one of three commonly used expressions for the Grüneisen parameter.[20] In Eq. (13) the pressure is obtained from the electronic structure calculations, i.e., no zero-contribution to the pressure is included.[21] This leads to a rather complicated expression for the Grüneisen parameter as a function of volume, involving the Morse parameters b_0, c_0, and λ_0 in Eq. (3). The Grüneisen parameter, however, evaluated at the equilibrium radius, $r_0(T)$, is used to define a constant Grüneisen parameter at the given temperature, T. With a constant Grüneisen parameter for a fixed temperature we obtain from Eq. (11) the nonlinear relation $\Theta V^{\gamma}=\text{const}$, which gives the volume dependence of the Debye temperature as

$$\Theta(r,r_0)=\Theta_0\left[\frac{r_0}{r}\right]^{3\gamma} . \tag{14}$$

This expression for the Debye temperature is the same as that used by Moruzzi *et al.*[7]

We have now reached a stage at which the volume dependence of the total free energy can be calculated for a given temperature. In order to obtain the variation of the equilibrium radius as a function of temperature, $r_0(T)$, the above-described method with self-consistent Morse fits to the free energy is carried out as a function of temperature. At each temperature we apply quasiharmonic theory and the new free energy is obtained from the calculated Debye temperature and Grüneisen constant. In practice this is performed for increasing temperatures starting at zero temperature, where the free energy is dominated by the electronic part. In Eq. (3) the Morse fit to the electronic contribution serves as a good starting solution for the iterative Morse fittings to the free energy in Eq. (1) at zero temperature. The temperature is then slowly increased stepwise in order to maintain good starting solutions in the iterative procedure. In this manner rapidly convergent Morse fits to the free energy is obtained. Having obtained a self-consistent Morse fit and therefore $r_0(T)$, the linear coefficient of thermal expansion is simply calculated as

$$\alpha(T)=\frac{1}{r_0(T)}\frac{dr_0(T)}{dT} . \tag{15}$$

IV. RESULTS

Several bulk properties are easily obtained from the analytical representation of the room-temperature free energy. In the present work we are particularly interested in the thermal expansion and the atomic volume. In order to obtain the thermal expansion it is also necessary to calculate the bulk modulus and the entropy (see the Appendix) both of which are found to be in reasonable agreement with experimental data. It deserves to be mentioned that the influence of the spin-orbit coupling on the calculated bulk modulus is most significant for neptunium and plutonium. The lowering of the bulk modulus is indeed substantial for plutonium and the calculated result is in good agreement with experiment. The behavior of the calculated entropy through the series is found to resemble the experimental data quite well, even though there is a nearly constant discrepancy of the order of 10%.

A. The atomic volume

In Fig. 3 and Table I the calculated room-temperature equilibrium volumes for the earlier actinide metals are shown for different levels of approximation. As can be seen the difference between the atomic volumes at room temperature obtained from scalar relativistic and fully relativistic calculations is small for all the actinides except for neptunium and plutonium. This agrees well with the zero-temperature results obtained by Brooks.[5] Especially for plutonium the fully relativistic calculations give a rather pronounced increase of the atomic volume, considerably improving the agreement with the experimental value. The calculated atomic volumes are slightly larger than the experimental ones[22,23] for thorium, protactinium, and uranium, while they are slightly smaller for neptunium and plutonium. Since the absolute value of the atomic volume influences the thermal expansion, calculations with a correction to the equation of state, obtained from electronic structure calculations, have been performed. This has been done in the simplest possible way, namely by adding a constant pressure term to the electronic pressure in order to obtain a room-temperature equilibrium volume in agreement with the experimental data (see Sec. V).

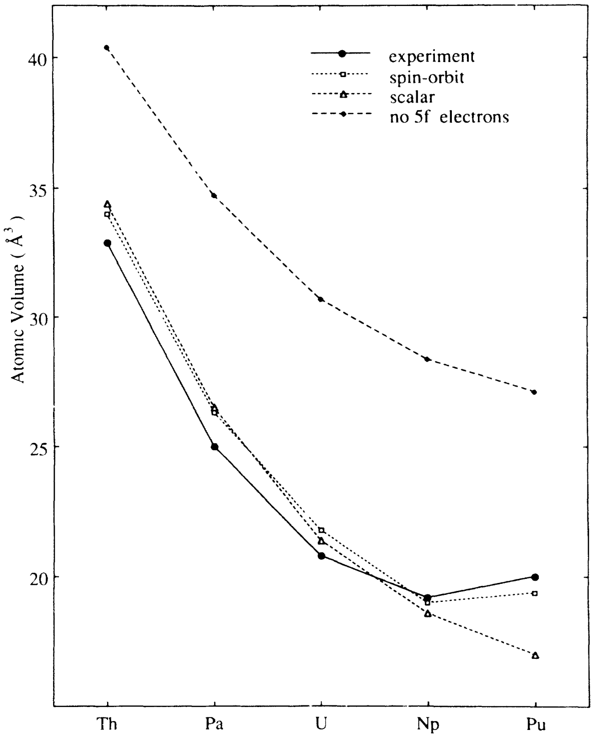

FIG. 3. The calculated atomic volumes at various levels of approximation for the earlier actinide metals together with the experimentally observed atomic volumes (Ref. 22).

TABLE I. Calculated and experimental values for the atomic volume. The experimental values are from Donohue (Ref. 22). The calculations of the equation of state are performed at various levels of approximation: (i) spin-orbit coupling (spin-orbit), (ii) scalar relativistic without spin-orbit coupling (scalar), (iii) no $5f$ orbitals and no $5f$ electrons (no $5f$). The spin-orbit calculations have also been assigned a pressure correction (see main text) in order to obtain the experimental atomic volume. The results are denoted by "ΔP."

(Å^3)	Th	Pa	U	Np	Pu
V_{expt}	32.9	25.0	20.8	19.2	20.0
$V_{\Delta P}$	32.9	25.0	20.8	19.2	20.0
$V_{\mathrm{spin\text{-}orbit}}$	34.0	26.3	21.8	19.0	19.4
V_{scalar}	34.4	26.5	21.4	18.6	17.0
$V_{\mathrm{no}\ 5f}$	40.4	34.7	30.7	28.4	27.1

The results from calculations including only s, p, and d valence electrons are also shown in Fig. 3 and will be commented on later. For uranium, neptunium, and plutonium the equilibrium atomic volumes obtained from calculations for an assumed bcc phase are found to be 5–10% smaller than the atomic volumes obtained from calculations referring to the fcc phase.

B. The linear coefficient of thermal expansion

Figure 4 shows the calculated linear coefficient of thermal expansion in two different approximations for the earlier actinide metals. The first approximation, where the elements are regarded as part of a $6d$ transition series, is denoted by "no $5f$ electrons" in the figure. The second approximation to the thermal expansion is obtained from the scalar relativistic calculations where the $5f$ electrons are included in the treatment. These calculations are denoted by "scalar" in Fig. 4. The spin-orbit interaction is still neglected at this level of approximation. Also shown in the figure are the experimental values collected by Gschneidner,[17] except for uranium where the value is taken from Barett *et al.*[24] (see Table II).

For theoretical interest we performed calculations where the $5f$ electrons and $5f$ orbitals were omitted in the treatment. The $5f$ electrons were for this purpose placed in the $7s$, $7p$, and $6d$ conduction band. This treatment of the valence electrons yields much too large equilibrium volumes (Fig. 3) and much too small values for

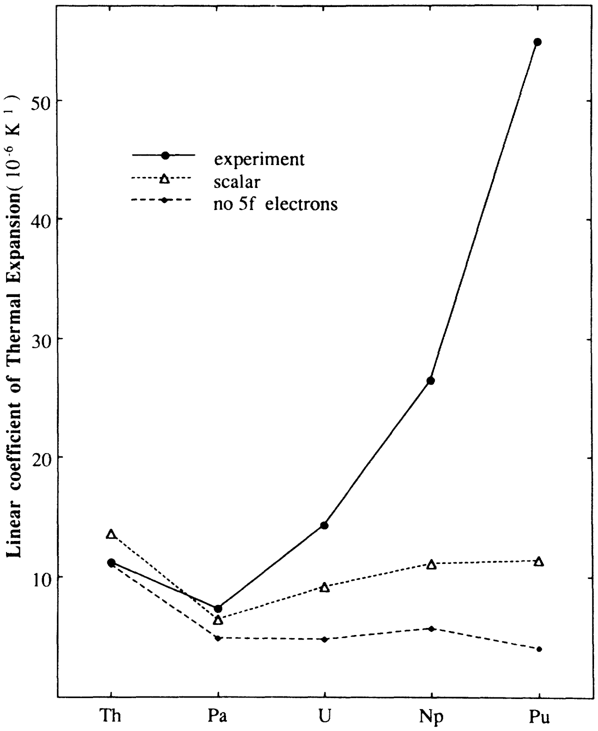

FIG. 4. The calculated linear coefficient of thermal expansion for the earlier actinide metals together with the experimentally observed values (Ref. 17, except for U, Ref. 24). The theoretical values are obtained from scalar relativistic calculations (i.e., without spin-orbit coupling) as well as from calculations where no 5*f* electrons or 5*f* orbitals are included. They are denoted by "scalar" and "no 5*f* electrons," respectively.

the linear coefficient of thermal expansion (Fig. 4). The general behavior of the atomic volume is, however, similar to that of the 4*d* and 5*d* elements. It is most interesting to notice that in this treatment the thermal expansion becomes almost identical to the thermal expansion of the 4*d* and 5*d* transition elements. In view of the experimentally observed anomalous thermal expansions of the actinides this indirectly proves that these elements form a new type of transition series, clearly distinct from the *d* transition series of elements. The scalar relativistic calculations do not show any dramatic rise of the thermal expansion for the elements beyond uranium but still they show a considerably higher thermal expansion than the calculations where the actinides were considered as a 6*d* transition series. Already within the scalar relativistic treatment of the 5*f* electrons the calculated thermal expansion of the medium–heavy actinides is a factor of 2 larger than expected for a *d* transition series of elements. This demonstrates that at least for certain bulk properties itinerant 5*f* electrons give rise to a different general behavior than what is characteristic for *d* transition systems.

In Fig. 5 the results from the fully relativistic calculations are displayed and it can be immediately seen that the results for the thermal expansion are now greatly improved. In contrast to the scalar relativistic calculations above these calculations include the effect of the spin-orbit coupling. The thermal expansion obtained from these calculations are denoted by "spin-orbit" in the figure. In order to reproduce the experimental atomic volume we have also made calculations where the electronic pressure is corrected by adding a constant pressure

TABLE II. Calculated and experimental values of the linear coefficient of thermal expansion for Th, Pa, U, Np, and Pu. The experimental values are from Gschneidner (Ref. 17). For uranium we have also listed an additional experimental value from Barret *et al.* (Ref. 24). For the notation compare table heading of Table I.

(10^{-6} K^{-1})	Th	Pa	U	Np	Pu
α_{expt}	11.2	(7.3)[a]	14.3;[b] 12.6	26.5	55.0
$\alpha_{\Delta P}$	12.3	6.4	10.4	17.3	41.0
$\alpha_{\text{spin-orbit}}$	14.2	7.7	12.8	16.0	33.2
α_{scalar}	13.6	6.4	9.2	11.1	11.4
$\alpha_{\text{no }5f}$	10.0	4.9	4.8	6.6	4.0

[a] Estimated value (Ref. 17).

[b] From Barett *et al.* (Ref. 24).

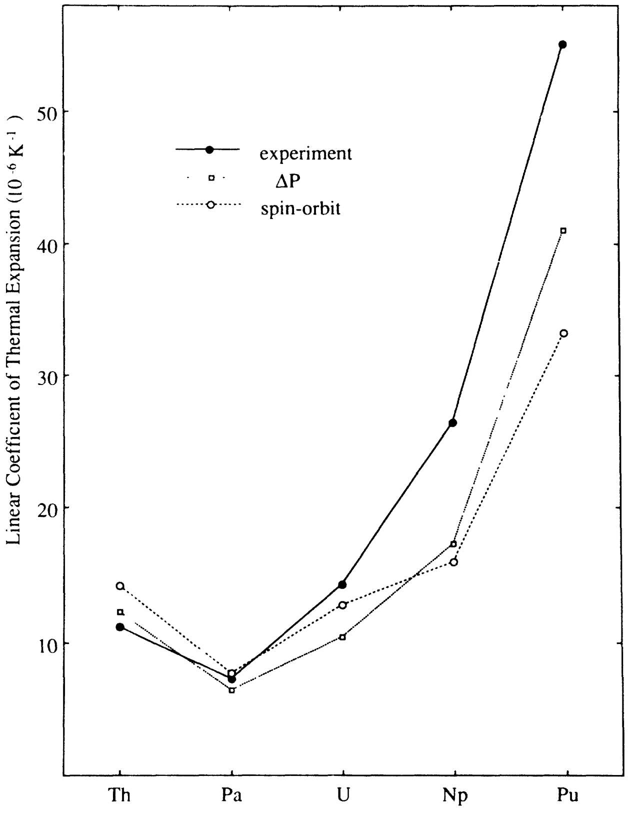

FIG. 5. The calculated linear coefficient of thermal expansion for the light actinide metals together with the experimentally observed values (Ref. 17, except for U, Ref. 24). The results from fully relativistic calculations are denoted by "spin-orbit" and from pressure corrected calculations by "Δ*P*."

term to the equation of state. These corrected calculations, which constitute the final level of approximation, are denoted by "ΔP" in Fig. 5.

As can be seen from Figs. 4 and 5, when scalar relativistic (scalar) and fully relativistic (spin-orbit) calculations are compared, the increase of the thermal expansion due to the spin-orbit interaction is small for thorium but increases when we proceed to heavier actinides. The increase for plutonium is large and with the inclusion of the above-mentioned correction for the pressure it is indeed most substantial. The thermal expansion, calculated with the spin-orbit coupling included, is in satisfactory agreement with experimental data for the first three actinides. (The experimental value for protactinium is, however, only an estimation.) As regards the absolute value the agreement is not so good for neptunium, but the calculations reproduce the experimental data in the sense that we calculate a considerably higher value than for uranium. The calculated thermal expansion for plutonium is also found to be smaller than experimental but much higher than for neptunium, when the spin-orbit coupling is included. In this respect the fully relativistic calculations account quite well for the experimentally observed anomalous rise between neptunium and plutonium. Thus we have demonstrated that the anomalous thermal expansion of the actinides to a large extent can be accounted for when the spin-orbit interaction is included in the calculations.

As mentioned above we have also performed calculations for the bcc crystal structure. The thermal expansions obtained from these calculations were found to be relatively close to the thermal expansions obtained for the fcc phase.

V. CONCLUSIONS

Analysis of the calculations shows that the $5f$ electrons of the medium–heavy actinides greatly affects their thermal expansion. The influence from the $5f$ electrons can be divided into two steps depending on the level of approximation. Firstly, the scalar relativistic results, in comparison to the results from calculations where the $5f$ states are totally neglected, demonstrate that for all the light actinides the $5f$ electrons give a positive contribution to the thermal expansion. Thus the thermal expansion becomes about twice as high as when the actinides are considered as a $6d$ transition series. Secondly, it is only when the spin-orbit interaction of the $5f$ electrons is included in the calculations that the anomalous rise of the thermal expansion for the elements beyond uranium becomes apparent. In the present work we have shown that for plutonium the thermal expansion thereby increases by about a factor of 4 relative to the scalar relativistic result.

When the actinides are treated as a $6d$ transition series the calculated thermal expansion remains practically constant as one proceeds along the series. In contrast, when the $5f$ electrons are included within the scalar relativistic calculations the thermal expansion increases with increasing atomic number beyond Pa. This is explained by the increasing occupancy of the $5f$ orbitals with increasing nuclear charge. In this respect the thermal expansion confirms the picture of the early actinides as part of a $5f$ transition series and not a $6d$ transition series since the thermal expansion is considerably affected by the occupancy of the $5f$ band. The treatment of the valence electrons as $7s7p6d$ electrons in a $6d$ transition metal has also a pronounced effect on the calculated atomic volume, which is found to increase considerably. It is most interesting to notice that in this treatment the calculated absolute values of the thermal expansion and general behavior of the atomic volume actually compare very well with the behavior of the $4d$ and $5d$ elements. Indirectly the very different values of the thermal expansion observed experimentally for the actinides relative to the d transition elements give strong evidence for a direct involvement of the $5f$ electrons in the bonding of the actinide metals.

The splitting of the $5f$ band due to the spin-orbit coupling gives rise to a most anomalous increase of the thermal expansion with atomic number. This behavior becomes more evident as we proceed through the actinide series and it reflects the fact that the spin-orbit splitting of the $5f$ band is increasing with increasing nuclear charge and hence its effect on the bulk properties becomes more pronounced. For plutonium the effect is especially large and gives a linear coefficient of thermal expansion that is about a factor of 10 larger than would have been expected for a d transition element with eight valence electrons.

The small pressure correction which was added to the equation of state for plutonium (21 kbar) and for neptunium (15 kbar) gives a higher value of thermal expansion since the correction causes the equilibrium volume to be displaced to a more volume-dependent regime of the equation of state. For the other elements in the present treatment the situation is the opposite. Here the pressure correction leads to a displacement of the equilibrium volume to a somewhat less volume-dependent regime of the equation of state and the result is a decrease of the thermal expansion.

In spite of the fact that the present calculations clearly exhibit the anomalous thermal expansion behavior of the actinides there is a remaining discrepancy between theory and experiment for neptunium and plutonium. This discrepancy is most likely due to our simplified treatment of the crystal structure. The self-consistent electronic structure calculations are performed for an assumed cubic symmetric structure and the approximate calculation of the Debye temperature is based on the same simplification.

The comparison between the linear coefficient of thermal expansion obtained from calculations corresponding to fcc and bcc crystal structures have shown an insensitivity to the choice of cubic crystal structure. The calculations have only been performed for cubic symmetry and the computed thermal expansion is therefore necessarily isotropic. The imposed cubic crystal structure only applies for thorium, which has a fcc structure. The other elements have unsymmetric crystal structures that are far more complex. This means in particular that their thermal expansion is anisotropic and the experiment by Lawson *et al.*[23] has shown that the lattice parameters for uranium have different temperature dependence. One of them is actually decreasing with temperature and the corresponding coefficient of thermal expansion is therefore negative. Similar behavior is also known experimentally for neptunium and plutonium. The experimental data we have used refer to average values, and the calculations, due to the cubic symmetry, only give a single coefficient for the thermal expansion.

At room temperature uranium has an orthorhombic structure with four atoms per unit cell. The crystal structure of plutonium is even much more complicated. It has a monoclinic structure[22] with 16 atoms per each unit cell and this highly unsymmetric configuration is most likely the origin of the remaining discrepancy between the present calculations and experiment for the thermal expansion of plutonium. Similarly neptunium has a complex orthorhombic structure[22] with eight atoms per unit cell at room temperature. Thus also this structure is considerably more complex than the assumed fcc phase in the calculations and again we conjecture that this is the main reason for the remaining difference between our computed results and the experimental data.

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APPENDIX

At a given temperature the Helmholtz free energy is fitted to a Morse function, given by

$$F(r)=be^{-\lambda r}+ce^{-2\lambda r}+\text{const} . \tag{A1}$$

The constant is of no importance since it will not influence the calculated bulk properties. The equation of state which is defined as

$$P(V)=-\frac{\partial F(V)}{\partial V} , \tag{A2}$$

takes the form

$$P(r)=\frac{\lambda e^{-\lambda r}}{4\pi r^2}(b+2ce^{-\lambda r}) , \tag{A3}$$

where r is Wigner-Seitz radius which is related to the atomic volume V by

$$V=\frac{4\pi r^3}{3} . \tag{A4}$$

Since equilibrium corresponds to a minimum of the free energy or equivalently, zero pressure, the equilibrium radius can be formulated in terms of fitting parameters as

$$r_0=\frac{1}{\lambda}\ln\left[\frac{-2c}{b}\right] . \tag{A5}$$

The bulk modulus defined as

$$B(V)=-V\frac{\partial P(V)}{\partial V} \tag{A6}$$

simplifies at equilibrium to

$$B(r_0)=\frac{\lambda^2 e^{-\lambda r_0}}{12\pi r_0}(b+4ce^{-\lambda r_0}) . \tag{A7}$$

Within the Debye approximation the contribution to the entropy from the phonons can be calculated from the following expression:

$$S_{\text{ph}}=3k_B\left[4\left[\frac{T}{\Theta}\right]^3\int_0^{\Theta/T}\frac{y^3}{e^y-1}dy-\ln(1-e^{-\Theta/T})\right] , \tag{A8}$$

where the integral is available in tabulated form. However, one can also easily use the free energy to directly obtain the entropy as

$$S(r,T)=-\frac{\partial F(r,T)}{\partial T} . \tag{A9}$$

These two expressions have been used as an internal control of the numerical treatment. The entropy obtained this way is slightly smaller than experimentally observed entropy.[25] The discrepancy is almost constant for the elements and it is of the order of 10%.

Within the approximation of a perfect elastic and isotropic crystal[26] the longitudinal and shear velocities v_l and v_s in Eq. (8) can be obtained from the relations involving the elastic constants G and E, which are the shear and Young's modulus, respectively:

$$v_l=\left[\frac{G}{\rho}\left[\frac{4G-E}{3G-E}\right]\right]^{1/2} , \quad v_s=\left[\frac{G}{\rho}\right]^{1/2} , \tag{A10}$$

where ρ is the mass density. From Eq. (A10) and the following relations[26] for the shear and bulk modulus, where ν is Poisson's ratio:

$$G=\frac{E}{2(1+\nu)} , \quad B=\frac{E}{3(1-2\nu)} , \tag{A11}$$

we derive the mean velocity in Eq. (8) as

$$v_m=r\left[\frac{4\pi}{3}\right]^{1/2}\left[\frac{2}{3}\left[\frac{2}{1-2\nu}\right]^{3/2}+\frac{1}{3}\left[\frac{1}{1-\nu}\right]^{3/2}\right]^{-1/3}\left[\frac{3}{1+\nu}\right]^{1/2}\left[\frac{rB}{M}\right]^{1/2} . \tag{A12}$$

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