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Giant striction and thermal expansion anomalies in actinide systems with structural instabilities

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Abstract

A fluctuation theory is presented to discuss the phenomenon of giant striction, associated with a displacive phase transition, which takes account of both phonon and overdamped soft mode excitations – paraphonons. The expansion anomalies in uranium and plutonium below 50 K are attributed to the effects of giant striction and soft mode behaviour accompanying the transition to the incommensurate charge density wave state observed in neutron scattering experiments.

1. Introduction

Thermal expansion anomalies in magnetic materials manifesting themselves in a negative thermal expansion below the Curie temperature are now well understood in terms of the negative magnetostriction contribution to volume strain [1]. A wide range of rare-earth and actinide systems are now known to have giant spontaneous magnetostriction of the order of 10^{-2}–10^{-3} [2].

The effect of giant striction may also play an important role in non-magnetic systems with structural instabilities, for example in α-uranium and α-plutonium which according to X-ray and dilatometric measurements [3–6] possess negative low temperature expansion, the negative volume strain being comparable with the giant spontaneous magnetostriction in magnetic materials [2]. The recently detected charge density waves (CDW) in uranium [7] and the analogous prediction for plutonium [8] strongly suggest the effect of giant striction associated with the CDW phase transition being responsible for the anomalous low-temperature expansion.

Recently we presented a theory of the structural-volume effect [9–11] where the striction phenomena in structurally unstable systems were interpreted in terms of the fluctuating order parameter, similar to the spin fluctuation theory of the magnetovolume effect [12]. In this report we summarize the theory of the structural-volume effect with respect to the giant striction actinide systems, emphasizing the role of the soft mode excitations, phonons and paraphonons.

2. Structural-volume effect

To describe the structural-volume effect associated with a displacive phase transition we focus on the soft mode contribution to the free energy, which in the weak anharmonicity limit may be written in the form [10]

$$F(u,V,T)=F_0(V,T)+\frac{A}{2}u^2+\frac{B}{2}u^4 + \frac{1}{\pi}\sum_{k}^{\infty}\int_0^{\infty} d\omega\, F_{osc}(\omega)\mathrm{Im}\frac{\partial}{\partial\omega}\ln\chi(\omega,k) \quad (1)$$

Here u is the order parameter, $F_{osc}(\omega)=k_BT\ln[1-\exp(-\hbar\omega/k_BT)]$, $\chi(\omega,k)=[\omega^2(k)-\omega^2-2i\gamma\omega]^{-1}$ is the lattice susceptibility, $\omega(k)$ and γ are the frequency and damping of soft phonons and F_0, A and B depend on temperature owing to the effects of electrons and other excitation modes. In the last term of the right-hand side of eqn. (1) accounting for the soft mode fluctuations, we neglect the zero-point contribution which in weakly anharmonic crystals is independent of temperature and the order parameter.

Minimization of the free energy (1) yields the variation with temeprature of the crystal volume

$$V=V_0[1+\omega_n(T)+\omega_s(T)] \quad (2)$$

and of the order parameter in the distorted phase $(T<T_m)$ $u^2(T)=u_0^2(T)-3\delta u^2(T)$, where V_0 is the crystal volume at $T=0$ in the absence of striction, $\omega_n(T)$ is

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the conventional thermal expansion and the volume strain

$$\omega_s(T)=\frac{C_0}{K}\,[u_L^2(T)-\zeta\delta u^2(T)] \tag{3}$$

accounts for the structural-volume effect. Here T_m is the temperature of the structural transition, $u_L^2(T)=u^2(T)+\delta u^2(T)$ is the averaged squared order parameter, $u_0^2(T)=-A/B$, K is the bulk modulus in the absence of striction, $C_0=-(1/2)\partial(VA)/\partial V$ is the strictional constant,

$$\zeta=\frac{1}{\delta u^2(T)}\sum_k\left(1-\frac{C(k)}{C_0}\,\delta u^2(k,T)\right) \tag{4}$$

characterizes the spatial dispersion of the strictional parameter $C(k)=-(\rho/2)(\partial\omega^2(k)/\partial\ \ln\ V)_u$, $C(0)=C_0$, and ρ is the crystal density. We assume that the temeprature dependences of the structural-volume effect and order parameter are due mainly to the temperature variation of the thermally excited soft mode fluctuation amplitudes $\delta u(T)$, defined by

$$\delta u^2(T)=\sum_k\delta u^2(k,T)$$

$$=\frac{4\hbar}{\pi\rho}\sum_k\int_0^\infty d\omega\,N(\omega)\,\frac{\omega\gamma}{[\omega^2(k)-\omega^2]^2+(2\gamma\omega)^2} \tag{5}$$

where $N(\omega)=[\exp(\hbar\omega/k_BT)-1]^{-1}$.

The averaged squared order parameter defining the volume strain (3) has a non-monotonic temperature dependence. In the ordered phase ($T<T_m$) $u_L^2=u_0^2(T)-2\delta u^2(T)$ decreases with temperature via the increase in the squared amplitudes of fluctuations $\delta u^2(T)$, while in the disordered state ($T>T_m$) $u_L^2=\delta u^2(T)$ increases. This yields the anomalous temperature dependence of the volume strain

$$\omega_s(T)=\begin{cases}\dfrac{C_0}{K}\,\{u_0^2(T)-[2+\zeta(T)]\delta u^2(T)\} & T<T_m\\[2ex] \dfrac{C_0}{K}\,[1-\zeta(T)]\delta u^2(T) & T>T_m\end{cases} \tag{6}$$

In the case of positive striction ($C_0>0$) this results in a volume contraction giving rise to a negative thermal expansion coefficient in the ordered state. In the disordered state $\omega_s(T)$ increases with temperature and leads to the normal expansion behavior.

Below we neglect the effects of ω_n, assuming them to be included in the volume strain ω_s by renormalizing $\zeta=\zeta(T)$, which may result in negative values $\zeta<0$.

3. Phonons and paraphonons

It follows from eqns. (3) and (5) that the temperature dependence of the volume strain is affected by two types of soft mode excitation giving additive contributions to $\delta u^2(T)$ and $\omega_s(T)$. In addition to the conventional phonons with relatively high frequency $\omega=\omega(k)$ which soften at a wave vector $k=k_m$, characterizing the structural instability, there exist low frequency $\omega\leqslant\gamma$, $\omega_0(T)$ ($\omega_0=\omega(k_m)$) overdamped excitations – paraphonons [10].

In the low temperature limit $k_BT\ll\hbar\omega_0,\hbar\gamma$ the effects of phonons are exponentially small and $\delta u^2(T)$ and $\omega_s(T)$ are dominated by the paraphonon contribution, resulting in the negative thermal expansion coefficient in the distorted phase

$$\alpha(T)=-aT-bT^3 \tag{7}$$

with $a=4\omega_s(0)k_B(1+\zeta/2)/3T_0^2$ and $b=a[1+\pi^2(\omega_0^2-2\gamma^2)/5g\omega_0\gamma T_0^2]$, where $k_BT_0=\hbar(\omega_0^3/g\gamma)^{1/2}$, $c^2=(1/2)\delta\omega_0/\partial k_m^2$ and $g=\hbar B/2\rho^2c^3$ is the anharmonicity parameter.

In the high temperature limit $k_BT\gg\hbar\omega(k)$ $\delta u^2(T)$ and $\omega_s(T)$ exhibit approximately linear temperature dependences owing to the soft phonons, the effect of paraphonons being negligibly small. For the high temperature phase transition ($k_BT_m\gg\hbar\omega(k)$) this results in the expansion coefficients below and above T_m defined respectively by

$$\alpha_-\approx-(2+\zeta)\,\frac{\omega_{s0}(T_m)}{T_m}\qquad \alpha_+\approx(1-\zeta)\,\frac{\omega_{s0}(T_m)}{3T_m} \tag{8}$$

(where $\omega_{s0}(T)=C_0u_0^2(T)/K$), which have opposite signs reflecting the change in sign of the structural-volume effect at the transition point.

4. Giant striction and thermal expansion anomalies in α-uranium and α-plutonium

Now we apply the above results for the structural volume effect to describe the properties of α-uranium. According to X-ray measurements [4] the change in volume is almost linear with temperature in the ranges 25–45 K and 75–180 K, the corresponding thermal expansion coefficients being equal to $\alpha_-\approx-11.0\times10^{-5}$ K^{-1} and $\alpha_+\approx3.96\times10^{-5}$ K^{-1}.

Taking account of eqn. (8) we obtain $\zeta(T_m)\approx0.204$ and $\omega_{s0}(T_m)\approx7.25\times10^{-3}$ and estimate the spontaneous striction $\omega_s(0)\approx4.69\times10^{-3}$.

The low temperature ($T<7$ K) thermal expansion of α-uranium was shown to be negative obeying eqn.

(7) with $a = 1.97 \times 10^{-7}$ and $b = 2.69 \times 10^{-9}$ [3]. Interpreting this in terms of the soft paraphonons and assuming [7] $\omega_0(T=0) \approx 1$ THz, we can estimate the anharmonicity parameter $g \approx 3 \times 10^{-3}$ and the soft phonon damping $\gamma \approx 0.55$ THz.

The interpretation of the thermal expansion anomalies of α-uranium presented here agrees well with neutron scattering data for the soft mode frequency [7] 1 THz $\leqslant \omega(k) \leqslant$ 2.6 THz, which suggests the paraphonon $T < \hbar\omega_0(T=0)/k_B \approx 7.6$ K and high temperature $T > \hbar\omega(k)/k_B \approx 20$ K regimes in accordance with the thermal expansion measurements [3–5].

Similarly, for α-plutonium thermal expansion measurements [6] yield $\alpha_- \approx -4.15 \times 10^{-4}$ K^{-1} and $\alpha_+ \approx 1.46 \times 10^{-4}$ K^{-1}, which allows us to estimate $\zeta(T_m) \approx 0.228$, volume strain $\omega_{s0}(T_m) \approx 2.56 \times 10^{-2}$ and spontaneous striction $\omega_s(0) \approx 1.82 \times 10^{-2}$.

To conclude, we have interpreted quantitatively the expansion anomalies of α-uranium and α-plutonium in terms of giant striction and soft mode phonons and paraphonons accompanying the CDW phase transitions.

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