No role for phonon entropy in the fcc→fcc volume collapse transition in $Ce_{0.9}Th_{0.1}$ at ambient pressure

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(Received 7 October 2002; published 16 January 2003)

Phonon densities of states (DOS) were obtained from inelastic neutron scattering measurements on $Ce_{0.9}Th_{0.1}$ at temperatures from 10 to 300 K. The α phase showed a significant softening of its phonon DOS when heated from 10 to 140 K. Despite the 17% volume collapse, the phonon DOS showed little change between the γ phase at 150 K and the α phase at 140 K. This is supported by analysis of the magnetic spectra showing that most of the transition entropy can be accounted for with the crystal field and changes in the ground-state spin fluctuations. We argue that the anomalous behavior of the phonon DOS originates with the volume dependence of the ground-state spin fluctuations.

DOI: 10.1103/PhysRevB.67.014103 PACS number(s): 63.20.−e, 64.30.+t, 78.70.Nx

I. INTRODUCTION

The light rare-earth and light actinide elements undergo many structural and volume changes as a function of temperature and pressure. Quantitative aspects of the thermodynamics affecting these changes have remained elusive for over 50 years. Amongst these elements, cerium has the simplest possible change and, hence, should be understood. Cerium undergoes a pressure-driven phase transition between its two face-centered cubic (fcc) solid phases, which differ in volume by about 17% at 300 K, 0.7 GPa.[1,2] At higher temperatures and pressures, however, this volume difference is reduced, and cerium is the only element to exhibit a critical point in its pressure-temperature phase diagram at about 570 K, 2.0 GPa.[2] Many explanations of its fcc-fcc phase transition have been based on *f*-electron behavior.[3–9] However, a quantitative account of the entropy contributions is not available.

The importance of phonon (vibrational) entropy to solid-state phase transitions has become well documented over the past decade as evidenced by experimental[10–14] and theoretical[15–18] work. Recent experimental studies have shown that electronic entropy can also make a significant contribution to high temperature phase transitions in cerium and uranium.[12,14,19,20] A detailed study of γ-cerium and β-cerium revealed that the electronic entropy difference between these phases can be separated into a contribution from local and conduction band electronic states.[20] For γ-cerium and β-cerium localized $4f$ electrons contributed a crystal field entropy difference because of a change in local crystal symmetry. With α-cerium, however, the crystal-field states do not exist because of very strong hybridization of the f states with the conduction band, so all of the crystal-field entropy can be gained in the $\alpha \rightarrow \gamma$ transition. In the present work, inelastic neutron scattering is used to measure the magnetic and phonon scattering from polycrystalline cerium, alloyed with thorium to suppress an intervening hexagonal phase.[21] From these spectra the vibrational entropy and the entropies associated with spin fluctuations and crystal-field excitations are obtained.

II. EXPERIMENT

Samples of $Ce_{0.9}Th_{0.1}$ were prepared by arc melting cerium (99.99%) and thorium (99.9%) into two 60 g ingots. These ingots were cold-rolled and sheared into more than 20 strips and homogenized for 24 h at 600 °C. To remove the rolling texture each strip was twisted. The sample was mounted in a closed-cycle helium displex refrigerator on the LRMECS spectrometer at the Intense Pulsed Neutron Source of the Argonne National Laboratory. An incident neutron energy of 25 meV was used. Because of the hysteresis in the transformation temperature (133 K on cooling and 164 K on heating)[21] the α phase was measured first at 10 K, then at 100 K, then at 140 K, and the γ phase was measured first at 300 K and then at 150 K. Phase fractions were determined by performing *in situ* diffraction measurements after removing the Fermi chopper and using the full spectrum of neutrons from the moderator. The γ phase runs showed no α phase, but the α-phase runs contained $(10\pm1)\%$ γ phase, much as reported by others.[21] The α-phase data were corrected for the small γ-phase contamination by subtracting the γ-phase spectra scaled by the phase fraction and a thermal factor. All raw data were corrected for self-shielding, sample environment background, detector efficiency, and the k_i/k_f phase-space factor.

III. RESULTS AND ANALYSIS

The neutron-weighted generalized phonon DOS of the α phase was obtained from the measured spectra by summing over all momentum transfers and subtracting the multiphonon scattering calculated in the incoherent approximation.[14,20] The procedure involved using a trial phonon DOS to calculate the multiphonon contribution to all orders summed over the detector angle range. The calculated multiphonon part was then subtracted from the data to give

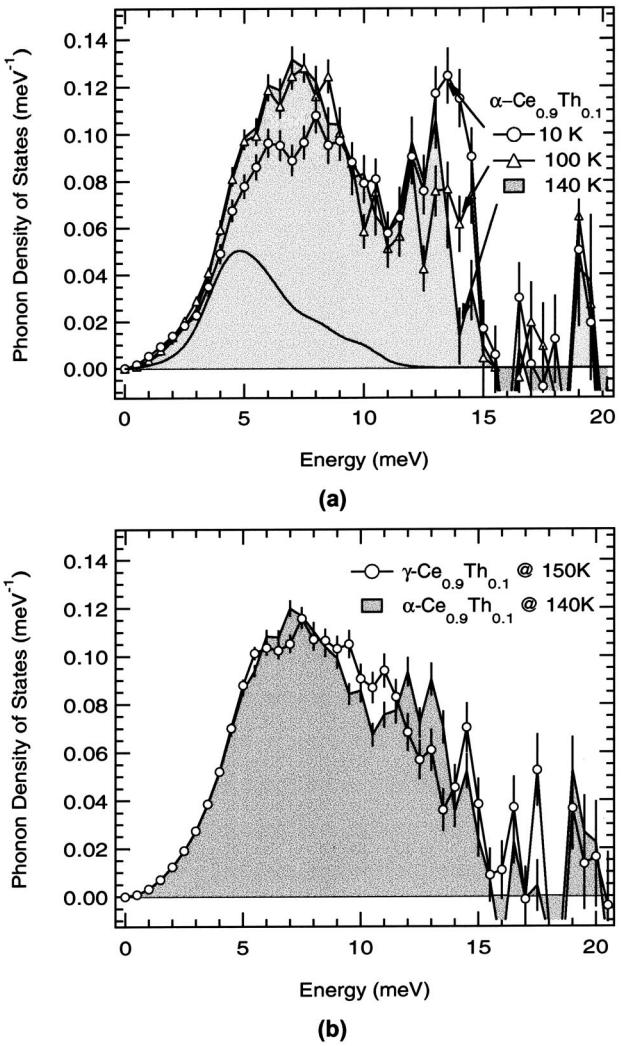

FIG. 1. Generalized phonon DOS of $Ce_{0.9}Th_{0.1}$. (a) Temperature dependence of α-phase DOS from data obtained in all detectors. Lower curve is the partial phonon DOS of Th calculated from the force constants of Stassis *et al.* (Ref. 24) using a procedure described in the text. (b) Comparison of the α phase and γ phase near the transition extracted from high-angle detector banks.

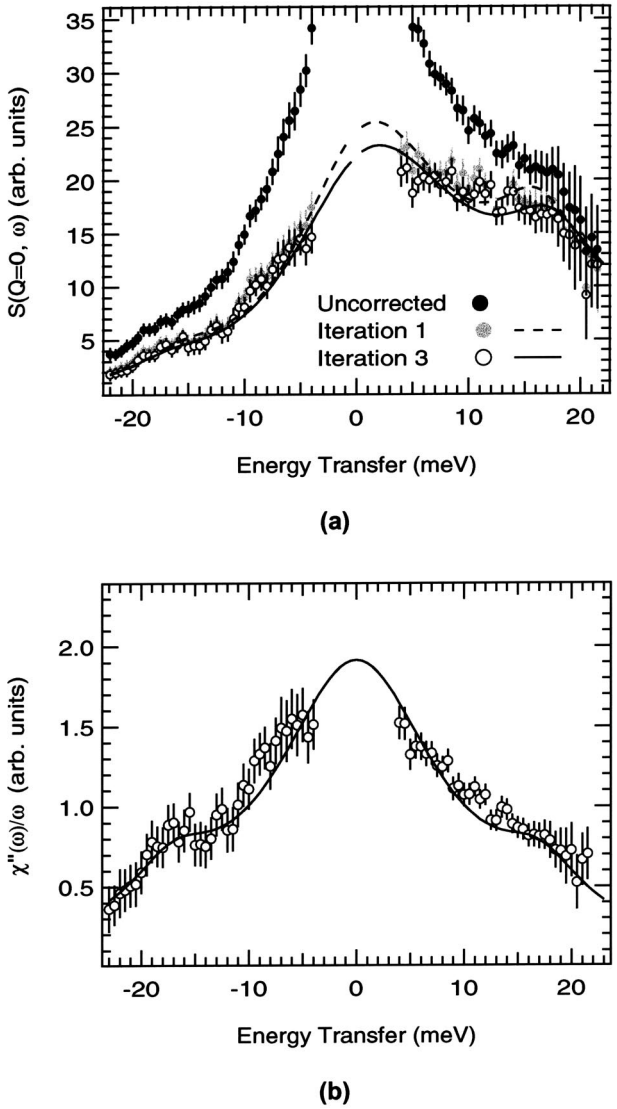

FIG. 2. Magnetic scattering from the γ phase at 150 K obtained from the low-angle data (from 1.95–51.6°). (a) Scattering function before any corrections for nuclear scattering, and after one and three phonon-correction iterations. (b) Dynamic magnetic susceptibility extracted from the data after three iterations.

an estimate of the one-phonon scattering. The remaining intensity was used to determine a new phonon DOS that was in turn used to recalculate the multiphonon contribution. The procedure was repeated until the phonon DOS converged to within statistical errors. Covergence required two iterations. Figure 1(a) shows the final phonon DOS for the α phase. From cross-section and atomic mass considerations, the partial DOS of thorium accounts for about 23% of the generalized phonon DOS. With increasing temperature between 10 and 140 K, there is an 80% loss in intensity of the major feature at 14 meV, compensated by a gain in intensity at lower energies.

The inelastic spectra from the γ phase contained both phonon and magnetic scattering. The magnetic scattering dominates at low scattering angles, whereas the phonon scattering dominates the high angle scattering, so these two contributions could be separated.[20] The resulting generalized phonon DOS of the γ phase, shown in Fig. 1(b), was obtained by summing the phonon spectra over the high angle range 55.3°–118.5° where the phonon scattering was largest, and correcting for multiphonon scattering using the same procedure as for the α phase. To ensure a consistent comparison, the data from the α phase were also summed over the same range of 55.3°–118.5°, for the comparison of Fig. 1(b). There are small intensity differences at about 7, 10, and 13 meV, but these are all remarkably small considering the α-phase volume is 17% smaller than the γ phase. A more significant effect is the appearance of the magnetic scattering from the γ phase, similar to that seen by others in Ce (Ref. 22) and $Ce_{0.74}Th_{0.26}$ (Ref. 23).

Figure 2 shows magnetic scattering extracted from data summed over the low angle range (from 1.95°–51.6°). Several iterations were performed to ensure the removal of the

phonon scattering, Fig. 2(a). Since the magnetic scattering in cerium shows no Q dependence other than the Debye-Waller and magnetic form factors (see Fig. 1 in Ref. 22) these data are expressed as the local dynamic susceptibility, $\chi''(\omega)/\omega$, by scaling to zero momentum transfer ($Q=0$) and correcting for thermal population.[22] These data were fit to Lorentzian quasielastic scattering with a half-width of 8.5 meV and a crystal-field (CF) excitation at 16 meV with a half-width of 5 meV, Fig. 2(b). The main features are similar to those in mixed γ-phase and β-phase cerium measured at 150 K.[22] The CF excitation is better defined than in pure cerium measured at 300 K (Ref. 22) because there is less thermal broadening. Unlike with earlier measurements, however, there appears to be a small amount of extra scattering at ± 9 meV, Fig. 2. The feature does not appear to be from residual phonon scattering as its relative intensity does not decrease with Q. Thorium has no magnetic moment, so all of the magnetic scattering comes from cerium. Cubic symmetry does not allow for more than one CF splitting of the $J=5/2$ state, suggesting that the extra intensity may be due to local breaks in symmetry. Interestingly, it has been argued, based on a 16 meV cubic site CF splitting, that a hexagonal site generated by a change in closed packed plane stacking sequence should have a CF splitting at about 9 meV.[22] Stacking faults that shift the fcc stacking sequence (*ABC*) to the hexagonal sequence (*ABA*) could, therefore, account for intensity at ± 9 meV. These stacking faults are likely to occur since the material is close to the stability range of the intervening hexagonal β phase[2] which favors these rearrangements of the closed-packed planes.

IV. DISCUSSION

To resolve approximately the thorium and cerium partial phonon DOS curves, a lattice dynamics model was set up using the γ-cerium force constants determined by Stassis *et al.*,[24] treating thorium as a mass impurity. The DOS curves were calculated for a 32 atom cell with a thorium mass substitution on three random sites. Three different random thorium configurations were averaged. The partial phonon DOS of thorium was calculated by scaling by the total cross section divided by the mass. Figure 1(a) shows how the thorium partial phonon DOS resides primarily at low energies owing to its heavier mass. Evidently the temperature-dependent loss of high energy phonon modes shown in Fig. 1(a) originates mainly with the cerium partial phonon DOS. At such low temperatures (low phonon population) with almost no volume change,[21] effects of this magnitude are unlikely to originate with an asymmetry of the interatomic potential. A similar large softening of the phonon DOS of α-uranium was shown to be harmonic.[19] Although its origin has never been explained, excess softening of interatomic potentials is common in the light actinides.[25]

Figure 1(b) shows that in spite of the 17% difference in volume between α- and γ-phase cerium, there is little difference in phonon DOS and consequently in vibrational entropy. The entropy of the phase transition can be accounted for by other degrees of freedom. The entropy originating from crystal-field transitions and spin fluctuations in the γ phase can be calculated from Fig. 2 using a procedure described in detail elsewhere.[20] Briefly, the crystal-field entropy is calculated assuming a doublet (Γ_7) to quartet (Γ_8) 16 meV crystal-field excitation.[22] The ground-state spin-fluctuation (SF) entropy accounts for the broadening of the ground-state doublet (seen as quasielastic scattering in Fig. 2, except extrapolated to $T=0$ K where the ''Kondo'' temperature or ground-state spin fluctuation width is estimated to be $T_K \approx 40$ K). These assumptions imply that the broadening seen in the CF level results from exciting from a broadened ground state to sharp CF levels. Although this may be an oversimplification of the underlying physics, for calculating integral quantities like specific heat and entropy it is quite accurate.[20] Likewise, the small extra intensity in Fig. 2, presumably due to the presence stacking faults, is unlikely to have much of an impact on the entropy calculation. As shown in Fig. 3, the CF and SF contributions make up most of the entropy of the α-γ transition. Allen and Liu[6] have described this transition as a Kondo volume collapse transition with the Kondo spin fluctuation entropy driving the transition. This approach is equivalent to interpreting the spectra in Fig. 2 as a single broad quasielastic peak with all six states spread smoothly over the energy range.

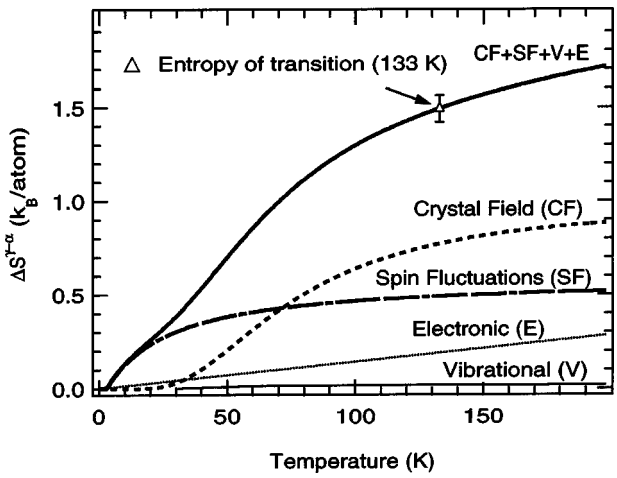

FIG. 3. Contributions to the entropy difference between the γ phase and α phase. The thick curve shows the sum of the four components. The electronic component, not obtained from experiment, was adjusted so that the sum equaled the entropy measured by Gschneidner *et al.* (Ref. 2).

The anomalous behavior of the phonon DOS could originate with the volume dependence of the spin fluctuations. Following Allen and Liu,[6] the spin fluctuation contribution to the free energy F_{SF} can be written in terms of the spin-fluctuation specific heat $C_{\mathrm{SF}}(V,T)$,

$$F_{\mathrm{SF}}(V,T)=\int_0^T C_{\mathrm{SF}}(V,T')dT'-T\int_0^T \frac{C_{\mathrm{SF}}(V,T')}{T'}dT'. \tag{1}$$

The spin fluctuation contribution to the isothermal bulk modulus is then

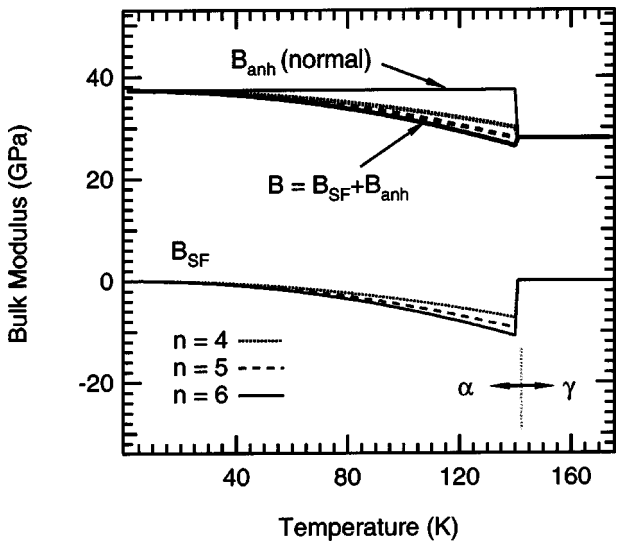

FIG. 4. Calculated isothermal bulk modulus separated into a normal anharmonic contribution, B_{anh}, and a contribution from volume dependent ground-state spin fluctuations, B_{SF}. As described in the text, the volume dependence of the spin fluctuations originates with hybridization of the f state with band electrons, where the values $n=4$, 5, and 6 correspond to *f-s*, *f-p*, and *f-d* hybridization, respectively. The normal anharmonic contribution is calculated from a standard expression: $B_{\mathrm{anh}}\cong B_0(V_\gamma/V_\alpha)^\gamma$, where the Grüneisen parameter γ is taken to be 2 and B_0 is approximated to be 28 GPa in the γ phase by taking an average of Pr and La (Ref. 6). The transition from the α phase to the γ phase has been fixed at 140 K.

$$B_{\mathrm{SF}}(V,T)=V\frac{\partial^2 F_{\mathrm{SF}}}{\partial V^2}=V\int_0^T\frac{\partial^2 C_{\mathrm{SF}}(V,T')}{\partial V^2}(1-T/T')dT'. \tag{2}$$

Rajan calculated an exact expression for the spin-fluctuation specific heat using the Coqblin-Schrieffer model[26]

$$C_{\mathrm{SF}}(V,T)=(N-1)k_B\int_{-\infty}^{\infty}\frac{g_{\mathrm{SF}}(V,\varepsilon)(\varepsilon/2k_BT)^2}{\cosh^2(\varepsilon/2k_BT)}d\varepsilon, \tag{3}$$

where $g_{\mathrm{SF}}(V,\varepsilon)$ is the spin fluctuation density of states and $N=6$ is the degeneracy in the α phase[27] ($N=2$ in the γ phase owing to the crystal-field splitting[21]). Assuming $g_{\mathrm{SF}}(V,\varepsilon)$ is a Lorentzian function in ε of half-width Γ, in the α phase with $k_BT\ll\Gamma$, it can be shown that

$$B_{\mathrm{SF}}(T\to 0)\cong-(1.65/\pi)(N-1)k_B^2V\frac{\partial^2}{\partial V^2}[1/\Gamma(V)]T^2. \tag{4}$$

The half-width Γ is known to decrease with increasing volume from 170 meV in the α phase[26] to 4 meV in the γ phase.[21] Since this decrease in width originates with hybridization of the f state with band electrons, for a functional form we assume $\Gamma(l)=170[1+\beta(l-l_0)/l_0]^{-n}$ meV, where $l^3=V$, β is adjusted so that $\Gamma=4$ meV at the γ-phase volume, and $n=4$, 5, or 6 for *f-s*, *f-p*, or *f-d* hybridization, respectively.[28] Figure 4 shows that the results for all values of n are similar and give a negative contribution, causing a softening of the bulk modulus with increasing temperature. Assuming similar trends for the interatomic force constants, this contribution is sufficient to explain the thermal softening of the phonon DOS of the α phase, Fig. 1(a). In the γ phase where the hybridization is relatively weak and $k_BT\gg\Gamma$ it can be shown that $B_{\mathrm{SF}}(T\to\infty)\to 0$, which is consistent with the relatively temperature independent phonon energies of the γ phase.[12] As shown in Fig. 4, near the transition (140 K) the change in B_{SF} is sufficient to cancel the anharmonic stiffening expected for the volume collapse of the $\gamma\to\alpha$ transition. Apparently, the volume dependence of the spin fluctuations results in the phonon DOS remaining nearly constant across the transition, Fig. 1(b), and hence nullifies the phonon contribution to the transition entropy.

V. CONCLUSION

The crystal field and spin fluctuations make a major contribution to the phase stability of α- and γ-phase $Ce_{0.9}Th_{0.1}$. The spin fluctuations not only provide a significant portion of the entropy to drive the transition but also appear to suppress the expected anharmonic vibrational entropy difference indirectly through their volume dependence. The net result is that the $\alpha\to\gamma$ transition in $Ce_{0.9}Th_{0.1}$ is a massive isostructural transition driven purely by electronic degrees of freedom.

ACKNOWLEDGMENTS

We thank A. C. Lawson and C. M. Varma for helpful discussions. This work was supported by the U.S. Department of Energy under Contracts No. DE-FG03-96ER45572 and No. W-31-109-ENG-38.

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