PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 50, NUMBER 5 1 AUGUST 1994-I

Ultrahigh-pressure phase transformations in the $Ce_{0.43}Th_{0.57}$ alloy: Implications for f-electron behavior under compression

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(Received 25 February 1994)

Ultrahigh-pressure transformations in the $Ce_{0.43}Th_{0.57}$ alloy were investigated up to 253 GPa (volume compression $V/V_0=0.402$) in a diamond anvil cell utilizing synchrotron x-ray diffraction. Unlike Ce, a first-order isostructural–fcc-to-fcc transition under pressure was not observed in this alloy. At the initiation of f-electron bonding, the fcc-to-bct transition was observed at 17 GPa. This pressure is close to the corresponding transition pressure in Ce metal (12 GPa) and is considerably lower than that in Th metal (60 GPa). The present experiments suggest that there are strong nonlinearities in transition pressure as a function of alloying content for f-electron alloys.

The f-electron metals and alloys have been the focus of intense experimental and theoretical high-pressure research in the past several decades.[1,2] This is largely due to the unique behavior of f electrons under pressure and their delocalization and participation in bonding. In particular, cerium (Ce) and thorium (Th) metals show two opposite extremes in f-electron behavior. Ce has one localized electron in the f-shell, while Th has an unoccupied f band just above the Fermi energy. Ce has a very interesting phase diagram. At ambient pressure and room temperature, Ce is normally obtained in the fcc (γ) phase. A volume collapse of about 16% occurs on decreasing temperature and/or increasing pressure at the $\gamma\rightarrow\alpha$ transition. At room temperature, the volume collapse is observed at 0.7 GPa. The $\gamma\rightarrow\alpha$ phase transition in Ce has been explained by the $4f$ delocalization (Mott transition) model[1] and also by the "Kondo-collapse" model.[2] The collapsed fcc (α) phase further transforms to an intermediate body-centered monoclinic phase (α'') at 5 GPa and to a body-centered-tetragonal (bct) phase at 12 GPa (Ce data have been reviewed by Olsen *et al.*[3]). These structural transitions are related to the changes in electronic structure. The localized $4f$ electron in Ce can be affected by pressure to participate in bonding and, as a consequence, low-symmetry crystal structures are observed. Th metal occupies a unique position in the Periodic Table. It is a transition-metal element with strong s-d hybridization and is on the threshold of being a regular light actinide element with $5f$-band occupation. Th is the only element that has an unoccupied $5f$ band only 1.5 eV above the Fermi level. At ambient conditions, Th is at fcc phase. At room temperature and high pressure, the fcc phase transforms to bct phase at 60 GPa.[4,5] Theoretical calculations have now confirmed the lowering and subsequent occupation of the $5f$ band in Th with increasing pressure.[6,7]

Ce-Th alloys offer some unique opportunities to vary the f behavior continuously from one extreme (localized f, Ce) to the other extreme (band f, Th). The addition of Th to Ce is known to cause the compression of an fcc lattice by chemical substitution. The combination of the diamond anvil cell ultrahigh-pressure technique and alloying allows us to probe f behavior under combined chemical and pressure variables. The critical alloy composition of the Ce-Th system is $Ce_{0.73}Th_{0.27}$ and the critical temperature is 148 K. When the Th component is higher than the critical value, the alloy system will not show the isostructural volume collapse ($\gamma\rightarrow\alpha$) that is typical behavior of pure Ce metal. Most previous studies were concentrated on the alloys with the Th composition well below the critical composition.[8,9] In our experiments, the Th component in the alloy sample is above the critical value. The linear extrapolation of transition pressures for fcc to bct transition suggests that the fcc$\rightarrow$bct transition should occur at about 36 GPa in $Ce_{0.43}Th_{0.57}$ alloy.

The Ce-Th alloy sample was fabricated by arc melting the constituent elements and splat cooling to room temperature at the Institute of Transuranium Elements (ITU), Karlsruhe, Germany. The measured lattice parameter is 5.0894(5) Å. The alloy composition ($Ce_{0.43}Th_{0.57}$) was calculated from the lattice parameter data of Waber, Harris, and Raynor.[10] Several experiments were carried out with different pressure markers (Pt, Cu, and ruby) to verify the consistency of the results. In the pressure range 0–70 GPa, the pressure was measured by the ruby fluorescence and copper pressure stan-

dard. In the ultrahigh-pressure range above 100 GPa, the platinum pressure standard was used. The alloy samples were studied in the diamond anvil cell by the energy dispersive x-ray diffraction (EDXD) technique with the synchrotron source at the X-17C beam line, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The experiments in the pressure range (0–70 GPa) were carried out with diamond anvils of 300 and 600 μm in diameter. For ultrahigh-pressure study in the range 70–253 GPa, beveled diamond anvils with central flat size 15 μm, bevel angle 8.5°, and culet size 350 μm were employed. The transition pressures and the equation of state of this alloy measured by different pressure markers gave consistent results.

The EDXD spectrum of the Ce-Th alloy in the diamond anvil cell showed that there is no abrupt volume collapse in the low-pressure range (0–13 GPa) and the structure of the alloy was still in the fcc (γ) phase. In the comparison of pressure-volume (PV) data, Ce metal shows a collapse of 16% at the $\gamma \rightarrow \alpha$ phase transition at 0.7 GPa, while Th metal and the Ce-Th alloy show continuous compression of the fcc (γ) phase (Fig. 1). At 13 GPa, the distortion of the fcc lattice was noticed in the EDXD patterns. This structural distortion becomes clear above 20 GPa and the diffraction pattern can be fitted by the bct structure. However, we cannot completely rule out the existence of low-symmetry crystal structures [such as the one observed in Ce (Ref. 3)] in the 10–20-GPa pressure range. The comparison of the EDXD spectrums of Ce-Th alloy at 13 and 29 GPa gives strong evidence for the fcc-to-bct phase transition (Fig. 2). The diffraction peaks (200), (220), and (310) of the fcc phase are all split into two peaks of the bct phase, while the (111) and (222) peaks of the fcc phase remain singlet. This is exactly what is expected to occur in case of fcc-to-bct structural distortion. The c/a ratio of bct phase varies as a function of pressure during the compression and decompression cycles (Fig. 3). The polynomial fits to the experiment c/a data were used to estimate the forward and the reverse transition pressures. This bct distortion from the fcc phase increases rapidly with increasing pressure. The extrapolation of the c/a data suggests the onset of bct structural transition at 17 GPa with increasing pressures. There is considerable hysteresis in the decreasing pressure cycle and the fcc phase was recovered on decreasing pressure to below 6 GPa.

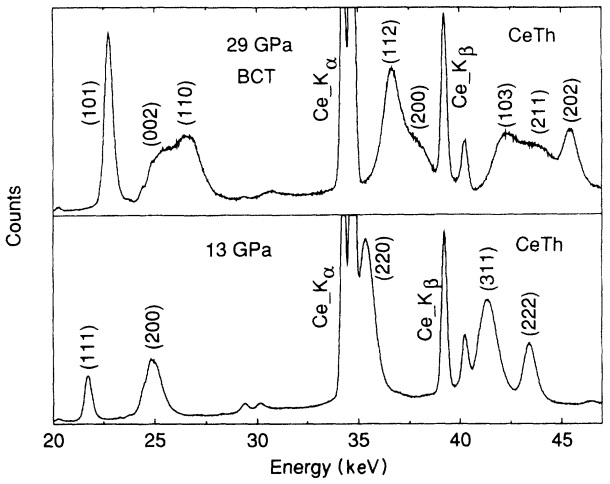

FIG. 2. Energy dispersive x-ray diffraction spectra of the Ce-Th alloy with $E_d = 58.64$ keV Å. The spectrum of the fcc phase is at 13 GPa and the bct phase is at 29 GPa. Pressures are measured by ruby fluorescence.

The bct phase of this alloy showed extensive phase stability with increasing pressure and was found to be stable at the highest pressure of 253 GPa in the present experiments. Figure 4 shows the EDXD spectrum of Ce-Th+Pt mixture at 253 GPa. Ce-Th is in bct phase at this pressure ($V/V_0 = 0.402$) and Pt is in fcc phase ($V/V_0 = 0.701$). The Pt marker pressures are based on the equation of state given by Holmes *et al.*[11]

Our measurements indicate that the compression of the Ce-Th alloy is continuous to 253 GPa and the volume changes at various transitions are below 1%. We fitted the pressure-volume data to the following universal equa-

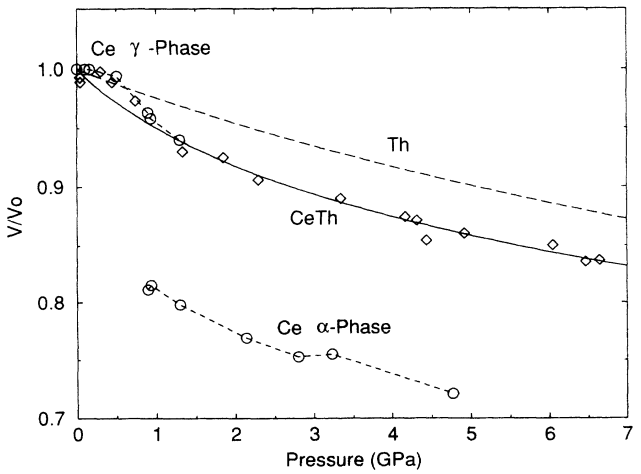

FIG. 1. Comparison of pressure-volume data for Ce-Th alloy and its constituent metals Ce and Th in the pressure range 0–7 GPa. Ce shows a collapse of 16% at the $\gamma \rightarrow \alpha$ transition. No such collapse was observed in Th metal and the Ce-Th alloy.

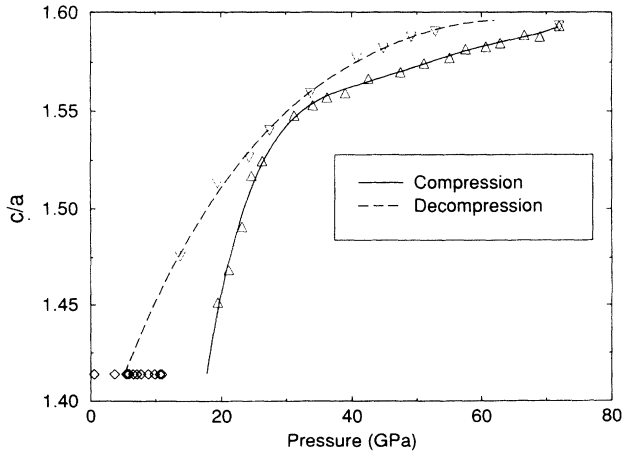

FIG. 3. The c/a ratio of the bct phase as a function of pressure. The fcc phase data are shown with a constant $c/a = 1.414$. The transition shows hysteresis on decompression of the sample.

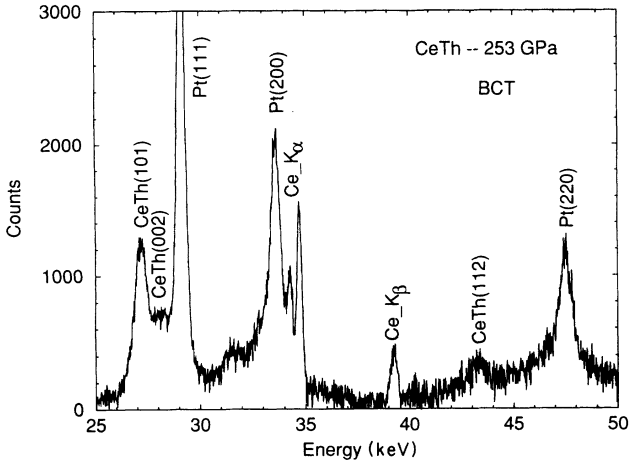

FIG. 4. EDXD spectrum of Ce-Th+Pt mixture at 253 GPa with $E_d=58.61$ keV Å. Ce-Th is at bct phase and Pt is at fcc phase. The pressure was measured by the Pt standard which is compressed to $V/V_0=0.701$. The Ce-Th sample volume compression is $V/V_0=0.401$.

tion of state:[12]

$$\ln H=\ln B_0+\eta(1-x)\ ,$$

$$H=Px^2/3(1-x)\ ,$$

where $x^3=V/V_0$ is the volume compression and $\eta=\frac{3}{2}(B_0'-1)$. V_0, B_0, and B_0' are the ambient pressure values of atomic volume, the bulk modulus, and its pressure derivative. Our data up to 253 GPa can be well represented by the above equation of state with $B_0=23.63$ GPa and $B_0'=6.09$.

Recent theoretical calculations[13] on Ce have demonstrated that both *f-spd* hybridization (Kondo terms) and *f-f* hopping (delocalization terms) are important for correct description of crystal structures in the collapsed phases. In particular, fcc→bct transition is driven by a delicate balance between 5*d*, 4*f*, and Madelung contributions to the free energy. Our experiments indicate that the fcc→bct transition pressure is a strongly nonlinear function of Th concentration x in $Ce_{1-x}Th_x$ alloys. Detailed band-structure calculation on *f*-electron alloys is needed to confirm the observed experimental trends. We provide the following conclusions.

(1) Isostructural volume collapse associated with the $\gamma\rightarrow\alpha$ transition was not observed with increasing pressure in the $Ce_{0.43}Th_{0.57}$ alloy.

(2) Phase transition from fcc to bct was observed at 17 GPa in the Ce-Th alloy. This transition pressure is close to that of Ce metal (12 GPa) and much lower than that of Th-metal (60 GPa).

(3) The bct phase of the Ce-Th alloy is stable at least up to 253 GPa where the compression $V/V_0=0.402$. In accord with recent measurements on Th metal up to 300 GPa, this indicates that the bct phase is the stable structure for an *f*-electron system at high compression.

We acknowledge the support of the Metallurgy Program, National Science Foundation (NSF), under Grant No. DMR-9296212. We also acknowledge the use of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, and thank Dr. J. Hu of beam line X-17C for her help.

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