Different routes to pressure-induced volume collapse transitions in gadolinium and terbium metals

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The sudden decrease in molar volume exhibited by most lanthanides under high pressure is often attributed to changes in the degree of localization of their $4f$ electrons. We give evidence, based on electrical resistivity measurements of dilute Y(Gd) and Y(Tb) alloys to 120 GPa, that the volume collapse transitions in Gd and Tb metals have different origins, despite their being neighbors in the periodic table. Remarkably, the change under pressure in the magnetic state of isolated Pr or Tb impurity ions in the nonmagnetic Y host appears to closely mirror corresponding changes in pure Pr or Tb metals. The collapse in Tb appears to be driven by an enhanced negative exchange interaction between $4f$ and conduction electrons under pressure (Kondo resonance) which, in the case of Y(Tb), dramatically alters the superconducting properties of the Y host, much like previously found for Y(Pr). In Gd, our resistivity measurements suggest that a Kondo resonance is not the main driver for its volume collapse. X-ray absorption and emission spectroscopies clearly show that $4f$ local moments remain largely intact across both volume collapse transitions ruling out $4f$ band formation (delocalization) and valence transition models as possible drivers. The results highlight the richness of behavior behind the volume collapse transition in lanthanides and demonstrate the stability of the $4f$ level against band formation to extreme pressure.

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I. INTRODUCTION

One of the central questions in the magnetism of solids is whether the electrons responsible for the magnetic phenomena are localized or itinerant in nature. This dual character emerges in actinides, where the $5f$ level is close to a localized-itinerant boundary, leading to a large diversity of physical properties and crystal structures.[1] In lanthanides, the $4f$ level is atomiclike at ambient pressure so that its contribution to the material properties only occurs through interaction with the conduction electrons. Despite the significant amount of work devoted to $4f$ and $5f$ electron systems over many years, the theoretical treatment of these levels is still very challenging. Recent advances in dynamical mean field theory have been encouraging,[2–6] but the agreement with experiment is still incomplete. In analogy to actinides, the localized character of the lanthanide $4f$ level is expected to change under sufficient pressure.[7] In particular, a sudden pressure-induced drop in the molar volume, commonly termed "volume collapse," has been observed in Ce (16% volume collapse at 0.7 GPa),[8,9] Pr (9.1% at 21 GPa),[10] Eu (3% at 12 GPa),[11,12] Gd (5% at 59 GPa),[13,14] Tb (5% at 53 GPa),[15] Dy (6% at 73 GPa),[16] Ho (3% at 103 GPa),[17] Tm (1.5% at 120 GPa),[18] and Lu (5% at 90 GPa).[19] Such volume collapses are still the subject of debate,[3,5,6,20–25] although widely thought to result from changes in the degree of $4f$ localization.

Here, we focus on the volume collapse phenomena because the sudden and often sizable change in the molar volume, and accompanying changes in electronic and magnetic properties, should facilitate the identification of its origin. In addition, except for Ce, the volume collapse is accompanied by a transition to a lower symmetry crystal structure also found in light actinides with itinerant $5f$ electrons, suggesting that a fundamental change in the character of the $4f$ electrons, perhaps from local to itinerant, may take place.

Three models often invoked to describe pressure-induced volume-collapse phenomena in the lanthanides are (1) *valence transition model*,[26] where a $4f$ electron is transferred into the *spd*-electron conduction band causing a sudden reduction in the ionic radius and enhanced metallic binding; (2) *Mott-Hubbard model*,[7] where the $4f$ states undergo a local-to-itinerant transition, the $4f$ electrons making a significant contribution to crystalline binding; and (3) *Kondo volume collapse model*,[27] where the approach of the localized $4f$ level to the Fermi energy under pressure leads to a sharp increase in the Kondo temperature T_K. In all three models, the $4f$ electrons play a critical role.

It is important to note, however, that $4f$-electron involvement is not required for a volume collapse to occur. The transition metal elements Y and Sc lack $4f$ electrons, but display volume collapses of 3% (at 99 GPa[28]) and 4% (at 140 GPa[29]), respectively; both are trivalent with conduction electrons whose *spd* character closely matches that of the trivalent lanthanides. In fact, a volume collapse is observed in many elements and compounds devoid of $4f$ electrons.[30–33] The volume collapse in Y and Sc is likely promoted by the ubiquitous $s \rightarrow d$ charge transfer under pressure whereby the number of d electrons in the conduction band n_d increases. In fact, across the entire lanthanide series, it has been shown that the variation in n_d plays the dominant role in determining the crystal structure at both ambient and high pressure.[34] For this reason, it is important to realize that simple $s \rightarrow d$ charge transfer must also be considered as a viable model for pressure-induced volume collapse in *all* lanthanides, whether they contain $4f$ electrons or not.

The isostructural $\gamma \rightarrow \alpha$ phase transition in Ce at 0.7 GPa exhibits the largest (16%), and most thoroughly studied, volume collapse of any lanthanide.[8,9] That the $4f$ electrons play an important role in this transition is clear from the large (80%) and abrupt drop in the magnetic susceptibility at 0.7 GPa,[35] thus supporting the Kondo or Mott-Hubbard models. However, recent results also point to the importance of lattice dynamics in Ce's volume collapse.[24]

For Gd and the heavier lanthanides, relatively high pressures (>50 GPa) are required to trigger the volume collapse. Due to the technical challenges associated with experiments at these higher pressures, the volume collapse in the heavier lanthanides has received less attention. Both Gd and Tb display a 5% volume collapse at, respectively, 59 and 53 GPa to a monoclinic $C2/m$ structure.[13,15] The emergence of such a low-symmetry phase typical for the light actinides is usually attributed to the onset of $4f$ binding, i.e., the Mott-Hubbard picture. However, the same phase is found in pure Y near 1 Mbar,[28] thus an $s \rightarrow d$ transfer scenario cannot be ruled out. Both theoretical[36] and x-ray spectroscopic[21,23] studies report that Gd's bare local moment remains intact through the volume collapse transition. This result is consistent with both the Kondo collapse picture or simple $s \rightarrow d$ charge transfer. A continuous increase in hybridization between $4f$ and conduction electrons under pressure was observed in resonant inelastic x-ray scattering (RIXS) measurements for Gd and interpreted as evidence for a Kondo driven volume collapse model.[21] However, no clear correlation between the degree of $4f$ delocalization and the volume collapse transition in Gd could be established. Therefore the mechanism responsible for the volume collapse in Gd, Tb, and the remaining heavy lanthanides remains unclear.

We examine the origin of the pressure-induced volume collapse in Gd and Tb by carrying out electrical resistivity measurements on dilute Y(Gd) and Y(Tb) magnetic alloys to pressures as high as 120 GPa. The suppression of superconductivity in the Y host is used to probe changes in the magnetic state of the Tb and Gd ions, e.g., as a result of Kondo screening. Since the spd character of conduction electrons in Y closely matches that of the trivalent lanthanides, experiments on these diluted Y alloys are expected to mimic the interaction between $4f$ and conduction electrons in the pure Tb and Gd metals, provided that $4f$-$4f$ overlap is minimal. X-ray absorption near edge structure (XANES) and nonresonant x-ray emission spectroscopy (XES) measurements carried out in Tb metal under pressure in this work, together with similar measurements already published for Gd,[21,23] indeed corroborate that direct $4f$-$4f$ interactions remain largely unchanged in the studied pressure range, as seen from the absence of changes in local moment. The XANES and XES measurements allow us to probe $s \rightarrow d$ charge transfer and possible changes in $4f$ valence and local moments. For Tb, our spectroscopic results exclude the valence transition and Mott-Hubbard scenarios and provide evidence that a pressure-induced $s \rightarrow d$ charge transfer takes place. However, the electrical resistivity measurements strongly suggest that the volume collapse in Tb has a significant magnetic component and is, in fact, triggered by the many-body Kondo resonance. For Gd, on the other hand, we do not observe any clear signature of a Kondo resonance in the Y(Gd) alloys in the vicinity of the volume collapse transition. Considering that such signatures are clearly observed in Y(Pr) and Y(Tb) alloys in the vicinity of their volume collapses, we conclude that a Kondo-driven collapse in Gd is unlikely. Taken together with previous x-ray spectroscopic results on Gd showing absence of $4f$ band formation or loss of local moments but significant $s \rightarrow d$ charge transfer, we suggest that the latter may be the driving force behind the volume collapse in Gd metal.

II. EXPERIMENTAL

Dilute magnetic alloys Y(0.5 at.% Tb), Y(0.5 at.% Gd), and Y(1 at.% Pr) were prepared by argon arc-melting stoichiometric amounts of Y and dopant (Tb, Pr, Y - 99.9% pure, Material Preparation Center of the Ames Laboratory;[37] Gd - 99.9% pure, Alfa Aesar). The melting procedure was repeated several times to promote homogeneity, the weight loss being always less than 0.1% of total mass. No significant concentration of other impurities or clustering was detected by x-ray fluorescence (XRF) and x-ray absorption fine structure (XAFS) measurements, as detailed in the next section. The high-pressure dc electrical resistivity measurements were performed in a membrane-driven diamond-anvil cell with both standard (300 μm culet diameter) and beveled (350 to 180 μm culet diameter) anvils. A rhenium gasket was insulated using a 4:1 c-BN-epoxy mixture which also served as pressure medium. The ruby fluorescence technique was used to determine pressure in all experiments.[38] Four-point resistance was measured using leads cut from a thin Pt foil. The current used was chosen to keep the power dissipated in the sample always below 0.5 μW. The pressure cell was cooled using an Oxford He flow cryostat; after the initial cooling, the temperature was always kept below 120 K. The sample's lateral dimension was $\sim 1/3$ of culet diameter; the thickness was <20 μm. The small sample was placed on top of the Pt leads and electrical contact was made by pressing the sample into the leads. Further experimental details are given elsewhere.[39]

XANES measurements were carried out on a Tb foil at the L_3 absorption edge ($2p \rightarrow 5d$ transition) at PNC/XSD (20-BM) beamline of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). A "symmetric" cell (Princeton University) was prepared with diamonds of 300 μm bevelled to 180 μm culet diameter. A partially perforated plus full anvil pair was used to reduce anvil attenuation of x-ray intensity and improve counting statistics. A rhenium gasket was preindented to 30 μm, and a sample chamber of 80-μm diameter was laser drilled in the center of the indentation. A small piece of Tb foil (Alfa Aesar, 99.9% purity) was loaded together with ruby balls, the later used for pressure calibration. Neon pressure medium was loaded using the COMPRESS/GSECARS system.[40] The experiment was performed at room temperature, and pressure applied manually using the cell screws. XANES was measured in transmission mode, both incident and transmitted intensities were detected using N_2 filled ion chambers. Kirkpatrick-Baez mirrors focused the x-ray beam to $\sim 3 \times 5$ μm^2.

Nonresonant Tb L_γ x-ray emission (XES) experiments were performed at HP-CAT (16-ID-D) beamline of the APS, ANL. A "symmetric" cell was used with full diamonds of 300 μm culet diameter. Photon energy was fixed at

11.3 keV. Data were collected using the diamond-in gasket-out geometry, thus an x-ray transparent Be gasket, preindented to 50 μm, was used. The center of the gasket was replaced with a pressed c-BN/Epoxy insert. A 100-μm hole was carefully laser drilled in the center of the insert, and used as sample chamber. The cell was loaded with Tb foil (Alfa Aesar, 99.9% purity) and ruby balls; Si oil was used as pressure media. The experiment was performed at room temperature, and pressure applied manually using the cell screws. XES data were measured using a scintillator detector coupled to a Si (444) analyzer. The data were normalized by the incident beam intensity which was detected with a N_2 filled ion chamber. Kirkpatrick-Baez mirrors focused the x-ray beam to $\sim 40 \times 60$ μm^2.

III. SAMPLE CHARACTERIZATION

XRF measurements were carried out on the three Y(RE) (RE = Pr, Gd, Tb) alloys in order to verify the dopant content and check for unwanted impurities. The measurements were performed at the 4-ID-D beamline of the APS, ANL. An incident photon energy of 7.55 keV was used and fluorescence photons were collected using a four-element silicon drift energy dispersive detector in a normal incidence geometry. Measurements were performed at room temperature. Figure 1 shows the data normalized so that the L_α peak has 1000 counts. The incident photon energy lies between the L_3 and L_2 edges for Gd and Tb, but above L_2 for Pr, thus extra fluorescence lines appear in the latter's spectrum. This result confirms the presence of dopants and absence of significant presence of other impurities.

Despite the similar ionic radii of Y and dopants, the absence of dopant clustering has to be verified as such clustering could lead to magnetically ordered islands inside the Y host and potentially affect the value of superconducting transition temperatures, T_c, in the Y alloys. XAFS measurements were carried out to probe the local environment around dopants. Experiments were performed at APS beamline 4-ID-D at the L_3 edge of Pr (5.964 keV), Gd (7.243 keV), and Tb (7.514 keV) using the same fluorescence geometry as in the

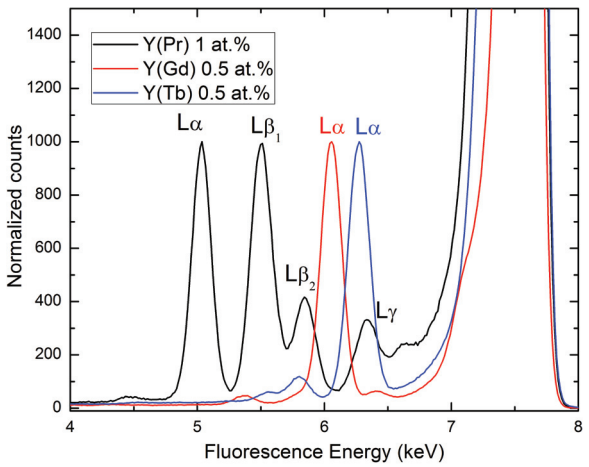

FIG. 1. (Color online) X-ray fluorescence spectra. Data were taken at an incidence energy of 7.55 keV and normalized to the L_α peak intensity.

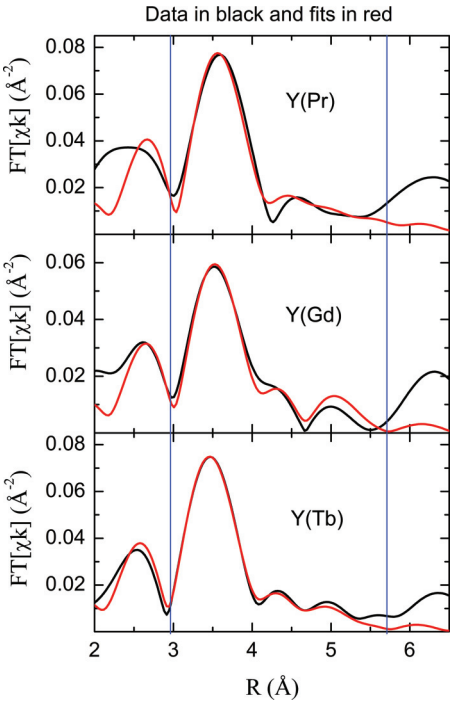

FIG. 2. (Color online) Fourier transform of the XAFS data collected at the L_3 edge of Pr, Gd, and Tb in their respective alloys.

XRF measurements. The photoelectron wave number was limited by the presence of the L_2 edge. All experiments were performed at room temperature. XAFS data were analyzed using IFEFFIT/HORAE[41,42] and FEFF6[43] software. The spectra in the k = 3–8 Å^{-1} range were truncated using a Hanning window and fits were performed in real space within r = 2.8–5.3 Å up to the third coordination shell. XAFS spectra and fits are shown in Fig. 2. Fits with mixtures of RE-Y and RE-RE first neighbor distances were attempted. For the three samples, the fraction of RE-RE neighbors was zero within experimental error ($\sim$5%), proving that no significant RE clustering is present. XAFS shows a systematic reduction in Y-RE distance in going from Pr to Tb (see Table I) as expected from the well-known lanthanide contraction. Furthermore, the Y-RE distances are in very close agreement with the RE-RE distances in the pure compounds (Table I; we note that the first neighbor distances for the pure Y and RE metals are similar[44]). The presence of a clear lanthanide contraction in the Y(RE) alloys, which results from the response of outer spd valence electrons to an increasingly attractive nuclear potential poorly screened by the additional $4f$ electrons, is additional evidence for the closely matched character of

TABLE I. Y-RE distances measured with XAFS here compared to RE-RE distances obtained by diffraction in pure RE metals.[44] Y-Y distance in pure Y metal is 3.6474(7) Å.[44]

RE	XAFS (Å)	Diffraction (Å)
Pr	3.65(2)	3.6725(7)
Gd	3.62(2)	3.6360(9)
Tb	3.59(1)	3.6010(3)

spd conduction electrons in the Y(RE) alloys and the pure RE metals. This in turn provides sensible justification for mapping results on the interaction between conduction electrons and local moments obtained from electrical resistivity measurements in the Y(RE) alloys to their pure RE metal counterparts.

IV. RESULTS AND DISCUSSION

Before considering our present experimental findings on Gd and Tb, it is useful to first discuss earlier experiments on Ce and Pr. An almost forgotten strategy to test for the presence of Kondo effect phenomena is to alloy a very dilute concentration of the magnetic component into a superconducting host and see whether the pressure dependence of T_c suffers a characteristic "sinkholelike" suppression.[45] Maple, Wittig, and Kim[46] carried out such experiments on dilute magnetic alloys of La(Ce) and found that T_c shows a dramatic "Kondo-sinkhole" suppression around 0.7 GPa, close to the pressure where the volume collapse in pure Ce occurs. The effect of the very strong pair-breaking associated with the Kondo effect in dilute magnetic alloys has received considerable theoretical support,[47–50] which has aided in the understanding of such complex and interesting behavior as the reentrant superconductivity observed in La(Ce)Al_2.[51]

As a second example consider Pr, which suffers a 10% volume collapse at 21 GPa.[10,54] As for La(Ce),[46] a marked suppression of T_c is observed in the dilute magnetic alloys La(Pr)[53] and Y(Pr)[55] beginning near 21 GPa, the pressure where Pr's volume collapse occurs. These experiments were limited to 27 GPa so the full recovery of T_c(P) was not observed [see inset to Fig. 3(a)]. Figure 3(a) displays our recent measurements on Y(1 at.% Pr), which extend the previous work to much higher pressures. For pressures well above 40 GPa, T_c(P) again approaches that for pure Y. Exactly this behavior is expected as the Kondo temperature T_K is rapidly pushed under pressure to values far above T_c where pair-breaking significantly weakens and the spin-compensated magnetic impurity appears nonmagnetic to the Y host.[47–50] XANES studies confirmed that Pr remains trivalent to 26 GPa.[56] XES studies on Pr metal also find no change in the bare local magnetic moment across the volume collapse transition,[22] and evidence for $4f$-conduction electron hybridization,[57] giving strong support to the conclusion that this transition in Pr is Kondo-driven.

We now turn to Gd. Since the $4f^7$ orbital in Gd metal is half-filled, its local magnetic state is the most stable of all lanthanides; Gd's $4f^7$ level, in fact, is located ~9 eV below the Fermi level.[36] XES experiments show no change in the local magnetic moment of Gd across the volume collapse transition,[21,23] which excludes the $4f$ local-itinerant (Mott-Hubbard) transition model. A small increase in the degree of $4f^8$ character observed in resonant L_α XES experiments[21] was interpreted as possible evidence for Kondo-like behavior in Gd. However, no correlation was found between the extent of $4f$-conduction electron hybridization under pressure and the occurrence of the volume collapse transition. Such increase in hybridization at high pressure may be interpreted as a small valence increase; however, no valence changes were observed with XANES,[23] indicating that Gd remains close to 3+ across the volume collapse, and excluding the valence transition model.

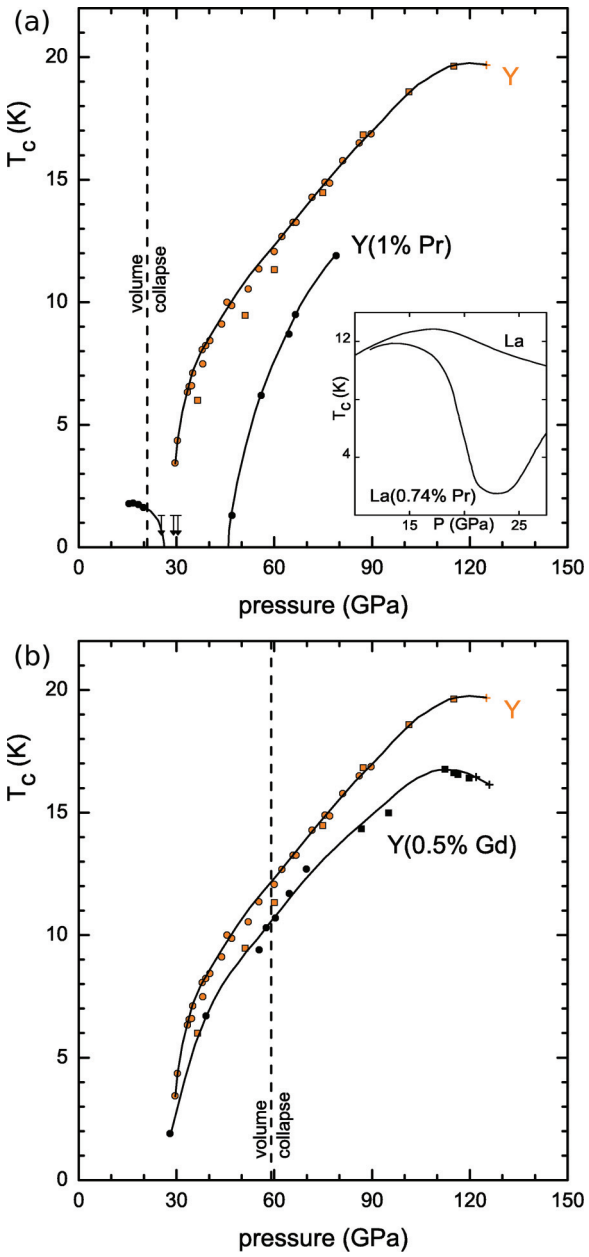

FIG. 3. (Color online) Pressure dependence of T_c for (a) Y(1 at.% Pr) and (b) Y(0.5 at.% Gd) compared to that for Y.[52] Vertical dashed lines show the critical pressure for the volume collapse in Pr and Gd. Inset in (a) shows data for La and La(0.74 at.% Pr) adapted from Fig. 2 of Ref. 53.

Further insight into the mechanism behind the volume collapse transition in Gd is given by the T_c(P) data shown in Fig. 3(b) for pure Y and Y(0.5 at.% Gd). Compared to La, Y is a superior superconducting host for the present studies since its ionic radius closely matches that of the heavy lanthanides and, above 20 GPa, T_c increases in a simple, monotonic manner to pressures as high as 120 GPa (see Fig. 3).[52] In contrast to what is observed for La(Ce), La(Pr), and Y(Pr) alloys, no "Kondo-sinkhole" or marked suppression of T_c(P) is observed

in Y(Gd) at a pressure anywhere near that (59 GPa) where Gd's volume collapse occurs. This result suggests that the volume collapse in Gd is neither due to the giant Kondo resonance nor is magnetic in origin. We note that this is not inconsistent with RIXS results,[21] which show a continuous increase in hybridization between $4f$ and conduction electrons under pressure but do not establish a correlation between this increase and the volume collapse transition in Gd. Since robust local moments remain present at the collapse transition in Gd, ruling out a Mott-Hubbard model,[21] $s \rightarrow d$ charge transfer appears to be the dominant driving force for the volume collapse in Gd. This charge transfer causes a strong reduction in the area of the main absorption peak in Gd L_3 XANES data with pressure.[23]

Tb is much more likely than Gd to exhibit $4f$-driven instabilities under pressure, since Tb's $4f^8$ level lies only ~3 eV below the Fermi energy.[58] To establish if the Kondo resonance plays a role in Tb's volume collapse, we carried out high-pressure resistivity studies on Y(0.5 at.% Tb). The T_c(P) is plotted in Fig. 4 for three independent runs and compared to that for pure Y. Beginning at about 53 GPa, a marked suppression of T_c is evident for the alloy with increasing pressure. Within experimental error, this onset pressure closely matches that (53 GPa) where the volume collapse occurs in Tb. The width of the resistive transition at 30.9 GPa (see inset to Fig. 2) arises from the pressure gradient across the sample. That this width becomes very narrow at 81.4 GPa is consistent with the fact that for pressures above 50 GPa T_c is constant. The present experiments thus suggest that the Kondo effect plays a role in the volume collapse transition of Tb metal.

High-pressure L_3 XANES data on Tb are presented in Fig. 5(a). Were Tb to undergo a $4f^8$ to $4f^7$ valence transition under pressure, a peak would appear at the position of the arrow under 4+; no such transition is observed to 65 GPa.

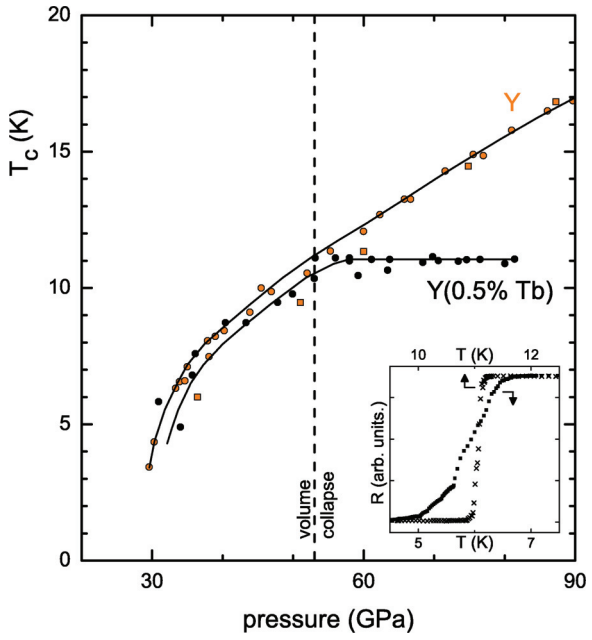

FIG. 4. (Color online) Pressure dependence of T_c for Y(0.5 at.% Tb) alloy. Vertical dashed line marks pressure (53 GPa) of volume collapse in Tb. Inset shows resistive superconducting transition at 81.4 GPa (×) is much narrower than that at 30.9 GPa (■).

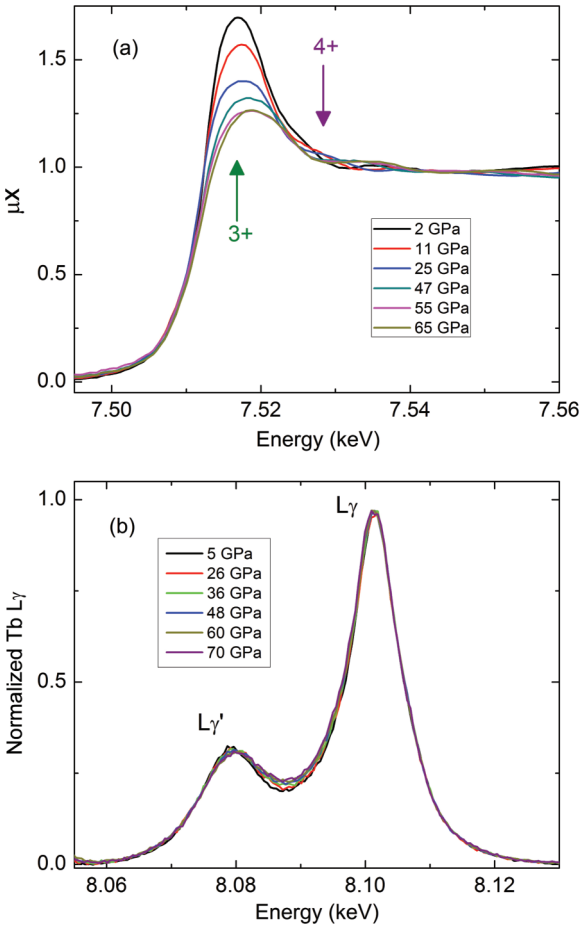

FIG. 5. (Color online) (a) Pressure dependence of L_3 XANES for Tb. No 4+ or mixed valence state is observed. Pressure-induced reduction of peak height is direct measure of $s \rightarrow d$ transfer. (b) Pressure dependence of L_γ nonresonant XES for Tb. A $4f^8$ local-itinerant transition is not observed.

Thus a valence transition does not contribute to the volume collapse in Tb at 53 GPa. In Fig. 5(a), it is clearly seen that the 3+ absorption peak is reduced in area with pressure. The L_3 absorption edge is dominated by the dipolar $2p_{3/2} \rightarrow 5d$ electronic excitation; thus the area of the absorption peak is directly related to the number of empty $5d$ states. These results indicate that $s \rightarrow d$ charge transfer does indeed occur in Tb under pressure, suggesting that this mechanism may also contribute to Tb's volume collapse. However, while $s \rightarrow d$ transfer occurs throughout the entire pressure range measured, as also observed in Gd,[23] the sharp deviation in T_c(P) due to strong Kondo pair breaking begins at the pressure (53 GPa) where the volume collapse occurs in Tb, much like what is found for Ce and Pr. The Kondo resonance thus appears to be the main driver in Tb's volume collapse.

Changes in the character of Tb's $4f^8$ local magnetic moment can be studied using XES. The XES L_γ line is shown in Fig. 5(b) at various pressures up to 70 GPa. In this experiment, a $2p_{1/2}$ electron is excited using high-energy x-ray photons. The hole is then filled by a $4d_{3/2}$ electron, and the energy of the resulting L_γ x-ray emission is analyzed with an x-ray spectrometer [see Fig. 5(b)]. The probability of the

$4d_{3/2} \rightarrow 2p_{1/2}$ transition depends on the initial $(2p^1_{1/2}\ 4d^4_{3/2})$ and final $(2p^2_{1/2}\ 4d^3_{3/2})$ states. The final $4d^3_{3/2}$ state is split by the exchange interaction with the $4f^8$ level which leads to the splitting of the L_γ line seen in Fig. 5(b). The ratio between the peak intensities is known to be related to the total angular momentum of the $4f$ state.[5,21,59] No significant change in the spectrum is observed throughout the pressure range measured, and, in particular, no discontinuous change in the data is observed when the collapsed phase is reached. The near constancy of the L_γ splitting gives direct evidence that the local character of the $4f^8$ orbital is preserved up to 75 GPa, thus excluding the possibility that the Mott-Hubbard ($4f$ local-itinerant) mechanism contributes to the volume collapse in Tb.

V. SUMMARY

In conclusion, taken together, the present resistivity and x-ray spectroscopy studies give evidence that the volume collapse in Tb metal at 53 GPa arises predominantly from the Kondo many-body resonance, a conclusion we reached earlier for Pr. Furthermore, we infer that the volume collapse in Gd is unlikely to be Kondo-driven, a conclusion based on the absence of any measurable effect on the T_c of Y(Gd) alloys anywhere near the volume collapse transition. We postulate that simple $s \rightarrow d$ charge transfer is the main driver for the volume collapse in Gd, thus emphasizing the importance of considering this model as a viable explanation for volume collapse phenomena in $4f$ and $5f$ electron systems.

It may seem remarkable that the changes in the magnetic properties under pressure of very dilute Pr or Tb impurity ions in a nonmagnetic, superconducting host (Y) so closely parallel the corresponding changes in pure Pr or Tb metal, as evidenced by the volume collapse. That this is no accident is corroborated by very recent experiments on Y(Dy) and Dy.[60] As remarked earlier, the closely matched character of spd conduction electrons in the Y(RE) alloys and the pure RE metals provides a natural explanation for this behavior. It appears that the similarity in the interaction between these conduction electrons and local $4f$ moments in the Y(RE) alloys and the pure RE metal counterparts, together with the absence of significant $4f$ bonding, allow for mapping the observations from electrical resistivity measurements in Y(RE) alloys to their RE metal counterparts. The lanthanide contraction observed by XAFS in the Y(RE) alloys, which mimics the contraction observed in the pure RE metals, provides further validation for the correspondence in the electronic structure of outer valence electrons in the dilute RE alloys and RE metals.

The $5f$ level in actinides is known to be close to a local-itinerant transition,[1] which has been expected to emerge in the lanthanide $4f$ electrons by $\sim$1 Mbar within the Mott-Hubbard model.[7] However, the present results together with previous x-ray spectroscopy work at high pressures indicate that the lanthanide $4f$ level is considerably more stable than what is oftentimes assumed. For all lanthanides, except possibly Ce, pressures well beyond 1 Mbar appear to be required to render the $4f$ electrons itinerant. This is consistent with suggestions of Yin and Pickett for Gd[36] and also with considerations based on the degree of nearest-neighbor $4f$ orbital overlap for all lanthanides.[61]

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