The state of 4f electrons in Gd and Tb at extreme pressure: localized or itinerant?

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The sudden decrease in molar volume exhibited by most lanthanides under high pressure is widely believed to result from 4f-electron interactions. We demonstrate that these “volume collapse” transitions in Gd and Tb metals have entirely different origins, despite their being neighbors in the periodic table. While the collapse in Gd is caused by s → d electron transfer without involvement of 4f electrons, that in Tb is largely driven by an enhanced negative exchange interaction between local 4f and conduction electrons under pressure (Kondo resonance). These findings are derived from element- and orbital-selective x-ray absorption and emission spectroscopic measurements on Tb and Gd metals together with electrical resistivity studies on dilute magnetic alloys to pressures as high as 120 GPa. The results highlight the richness of behavior behind the volume collapse in lanthanides and demonstrate the stability of the 4f level to extreme pressure.

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 atomic-like 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 [2,3], 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 [4]. In particular, the precise origin of the sudden pressure-induced drop in the molar volume observed in Ce, Pr, Eu, Gd, Tb, Dy, Ho, Tm, and Lu [5], commonly called “volume collapse”, is still the subject of intense debate [5,8,11], although widely thought to result from 4f interactions. Here we focus on the volume collapse phenomena because the sudden and often sizeable 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 (itinerant 5f electrons), indicating a fundamental change in the character of the 4f electrons, perhaps from local to itinerant.

Three models often invoked to describe pressure-induced volume-collapse phenomena in the lanthanides are: (1) valence transition model [12], 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 [6], 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 [13], where the approach of the localized 4f level to the Fermi energy under pressure leads to a sharp increase in the Kondo temperature TK. In all three models the 4f electrons play the dominant 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 [14]) and 4% (at 140 GPa [15]), 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 [16,17]. The volume collapse in Y and Sc is likely promoted by the ubiquitous s → d charge transfer under pressure whereby the number of d electrons in the conduction band nd increases. In fact, across the entire lanthanide series it has been shown that the variation in nd plays the dominant role in determining the crystal structure at both ambient and high pressure [20]. For this reason it is important to realize that simple s → 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 γ → α phase transition in Ce at 0.7 GPa exhibits the largest (16%), and most thoroughly studied, volume collapse of any lanthanide [21,22]. 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 [23]. Recent experimental results point to the Kondo model as the appropriate description of the volume collapse in Ce [5,24,25].

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 GPa and 53 GPa to a monoclinic C2/m structure [26, 27]. 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 also found in pure Y near 1 Mbar [14], thus suggesting an s → d transfer scenario. Both theoretical [28] and x-ray spectroscopic [8, 29] 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 → d charge transfer. In summary, the mechanism responsible for the volume collapse transition in Gd, Tb, and the remaining heavy lanthanides remains unclear.

In this Letter we examine the origin of the pressure-induced volume collapse in Gd and Tb by carrying out x-ray absorption near edge structure (XANES) and non-resonant x-ray emission spectroscopy (XES) studies, as well as electrical resistivity measurements on dilute magnetic alloys to pressures as high as 120 GPa, where the suppression of superconductivity is used to probe the magnetic state of the Tb or Gd ions. For Gd our present results together with earlier spectroscopic studies [8, 29] clearly support an s → d charge-transfer-driven volume collapse. In Tb our spectroscopic results directly exclude the valence transition and Mott-Hubbard scenarios and give evidence for pressure-induced s → d charge transfer. However, the present resistivity measurements strongly support that, as for Ce, the volume collapse in Tb at 53 GPa has a significant magnetic component and is, in fact, triggered by the many-body Kondo resonance. Taken together, the present results indicate that the 4f level in the lanthanide is considerably more stable than previously believed.

High-pressure L_3 XANES and L_γ XES experiments were performed at room temperature on a Tb foil (Alfa Aesar, 25 μm thick, 99.9% purity) at the 20-BM and 16-ID-D beamlines, respectively, of the Advanced Photon Source, Argonne National Laboratory. A “symmetric” cell (Princeton University) was used. XANES spectra were collected in transmission mode; a full anvil was paired with a partially perforated anvil to improve statistics and neon was used as pressure medium. The XES data were collected using a diamond-in gasket-out geometry coupled with a Be gasket with c-BN insert and silicon oil as pressure medium.

The high-pressure resistivity measurements were carried out on the dilute magnetic alloys Y(0.5 at.% Tb), Y(0.5 at.% Gd), and Y(1 at.% Pr) prepared by argon arc-melting stoichiometric amounts of Y and dopant (Tb, Pr, Y - 99.9% pure, Ames Laboratory; 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. The high-pressure experiments were carried out using a membrane-driven diamond-anvil cell with rhenium gasket 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 [30]. The alloy characterization and further experimental details are given in the supplemental material [7].

Before considering in detail our present experimental findings on Gd and Tb, it is useful to first discuss the results of earlier experiments on Ce and Pr. When a volume collapse occurs at a critical pressure P_c, 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 “sinkhole-like” suppression over a region of pressure near P_c [31]. Maple, Wittig and Kim [32] carried out such experiments on dilute magnetic alloys of La(Ce) and found that T_c began to show a dramatic “Kondo-sinkhole” suppression at 0.7 GPa, precisely 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 [33–36] which has aided in the understanding of such complex and interesting behavior as the reentrant superconductivity observed in La(Ce)Al_2 [37].

As a second example, consider Ce’s neighboring lanthanide, Pr, which suffers a 10% volume collapse at the much higher pressure of 21 GPa [40, 41]. Many years ago Wittig showed that, as for La(Ce) [32], there is a marked suppression of T_c for the dilute magnetic alloys La(Pr) [39] and Y(Pr) [42] beginning near 21 GPa, the pressure where Pr’s volume collapse occurs. Unfortunately, Wittig’s experiments were limited to 27 GPa so the full recovery of T_c(P) could not be observed (see inset to Fig. 1(a)). In our recent T_c(P) measurements on Y(1 at.% Pr) which extend Wittig’s earlier work to much higher pressures. For pressures well above 40 GPa it is seen that the pressure dependence of T_c 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 [33, 36]. XANES studies confirmed that Pr remains trivalent to 26 GPa [43]. As found for Ce, XES studies on Pr metal find no change in the bare local magnetic moment across the volume collapse transition [44], giving strong support to the conclusion that this transition in Pr is Kondo driven.

Since the 4f^7 orbital in Gd metal is half filled, its local
magnetic state is the most stable of all lanthanides; Gd’s 4f⁷ level, in fact, is located ∼9 eV below the Fermi level [28]. XANES and XES experiments show no change in either the valence or local magnetic moment of Gd under pressure across the volume collapse at 59 GPa [8, 29]; this excludes the valence transition or 4f local-itinerant (Mott-Hubbard) transition models. A small increase in the degree of 4f⁸ hybridization was observed by resonant Laα XES [8].

Further information on the mechanism responsible for the volume collapse in Gd is given by the Tc(P) data shown in Fig. 1(b) for pure Y and Y(1 at.% Gd). Compared to La, Y is the superior superconducting host for the present studies since its ionic radius closely matches that of the heavy lanthanides and, above 20 GPa, Tc increases in a simple, monotonic manner to pressures as high as 120 GPa (see Fig. 1) [38]. In contrast to what is observed for La(Ce), La(Pr), and Y(Pr) alloys, no “Kondo-sinkhole” or marked suppression of Tc(P) is observed in Y(Gd) at a pressure anywhere near that (59 GPa) where Gd’s volume collapse occurs. This result gives clear evidence that the volume collapse in Gd is neither due to the giant Kondo resonance nor is magnetic in origin, but rather is the result of simple s → d charge transfer.

We now discuss the results of our electrical resistivity and synchrotron spectroscopic measurements on Tb metal. Tb is much more likely than Gd to exhibit 4f-driven instabilities under pressure, since Tb’s 4f⁸ level lies only ∼3 eV below the Fermi energy [45]. To establish whether or not 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 Tc(P) dependence is plotted in Fig. 2 for three independent runs and compared to that for pure Y. Beginning at about 53 GPa, a marked suppression of Tc is evident for the alloy with in-

**FIG. 1.** (color online) Pressure dependence of Tc for (a) Y(1 at.% Pr) and (b) Y(0.5 at.% Gd) compared to that for Y [38]. 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. 39.

**FIG. 2.** (color online) Pressure dependence of Tc 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 (■).
creasing pressure. Within experimental error, this onset pressure is identical to that (53 GPa) where the volume collapse occurs in pure 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 independent of pressure, i.e. $dT_c/dP \approx 0$. The present experiments thus suggest that the Kondo effect plays a role in the volume collapse in Tb at 53 GPa.

High-pressure L$_3$ XANES data on Tb are presented in Fig. 3(a). Were Tb to undergo a 4$f^8$ to 4$f^7$ valence transition under pressure, a peak would appear at the position of the arrow under 4+; no such transition is observed to 65 GPa. Thus a valence transition does not contribute to the volume collapse in Tb at 53 GPa. In Fig. 3(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 5$d$ states. These results indicate that $s \rightarrow d$ charge transfer does indeed occur in Tb under pressure, suggesting that this mechanism also contributes to Tb’s volume collapse. However, while $s \rightarrow d$ transfer occurs throughout the entire pressure range measured, the sharp deviation in $T_c(P)$ due to strong Kondo pair breaking begins at precisely the pressure (53 GPa) where the volume collapse occurs in Tb, i.e. the same scenario as for Ce and Pr. The Kondo resonance thus appears to play a more important role in Tb’s volume collapse than $s \rightarrow d$ charge transfer.

Changes in the character of Tb’s 4$f^8$ local magnetic moment can be studied using XES. The XES L$_\gamma$ line is shown in Fig. 3(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 4$d_{3/2}$ electron, and the energy of the resulting L$_\gamma$ x-ray emission is analyzed with an x-ray spectrometer (Fig. 3(b)). The probability of the 4$d_{3/2} \rightarrow 2p_{1/2}$ transition depends on the initial ($2p_{1/2} 4d_{3/2}$) and final ($2p_{1/2} 4d_{3/2}$) states. The final 4$d_{3/2}$ state is split by the exchange interaction with the 4$f^8$ level which leads to the splitting of the L$_\gamma$ line seen in Fig. 3(b). The ratio between the peak intensities is known to be related to the total angular momentum of the 4$f$ state [5, 8, 46]. 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$_\gamma$ splitting gives direct evidence that the local character of the 4$f^8$ 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.

In conclusion, taken together, the present resistivity and spectroscopy studies show convincingly that the volume collapse in Tb metal at 53 GPa arises predominantly from the Kondo many-body resonance, a conclusion we reached earlier for Ce and Pr, but not for Gd. Furthermore, we conclude that the volume collapse in Gd arises simply from $s \rightarrow d$ charge transfer, thus emphasizing the importance of considering this model as a viable explanation for volume collapse phenomena, whether or not the system in question contains 4$f$ or 5$f$ electrons. Further work is planned to identify the mechanism(s) behind the volume collapse in many of the remaining lanthanides.

As remarked earlier, the 5$f$ level in actinides is known to be close to a local-itinerant transition [1], which has been expected to emerge in the lanthanide 4$f$ electrons by $\sim 1$ Mbar within the Mott-Hubbard model [2]. However, the present results indicate that the lanthanide 4$f$ level is considerably more stable than usually believed. For all lanthanides, except possibly Ce, pressures well beyond 1 Mbar may be required to render the 4$f$ electrons itinerant.

![FIG. 3. (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$_\gamma$ non-resonant XES for Tb. A 4$f^8$ local-itinerant transition is not observed.](image-url)
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