Origin of the volume collapse under pressure in elemental Dy

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Abstract. Most lanthanide metals exhibit a volume collapse at a critical pressure $P_c$; for Dy this pressure is $\sim 73$ GPa. The primary mechanism responsible for the volume collapse is a matter of debate and may involve the 4\textit{f} electrons themselves or be the result of simple pressure-induced $s \to d$ transfer in the conduction electrons. Possible mechanisms involving the 4\textit{f} electron system include: (i) valence increase, (ii) 4\textit{f} band formation, and (iii) increased 4\textit{f}-conduction electron hybridization leading to a Kondo volume collapse. The present high pressure resistivity experiments on the dilute magnetic alloy Y(Dy) to 114 GPa give evidence for the validity of the Kondo volume collapse model for elemental Dy.

1. Introduction
The lanthanide metals have many interesting properties which are closely related to their strongly localized 4\textit{f} electrons. For example, at ambient pressure dysprosium (Dy) has the largest magnetic moment of any elemental metal. Furthermore, one can expect that at sufficiently high pressure the lanthanides may undergo dramatic changes when their 4\textit{f}-electron wave functions get closer and begin to overlap.

One of the most fascinating phenomena in the lanthanide metals under pressure is their volume collapse (VC) at a critical pressure $P_c$ that is usually accompanied by a high-to-low-symmetry structural phase transition, see [1], for example. The majority of lanthanides suffer a VC. At ambient temperature Ce has a 16\% VC at 0.7 GPa, Pr 9.1\% at 21 GPa, Eu 3\% at 12 GPa, Gd 5\% at 59 GPa, Tb 5\% at 53 GPa, Dy 6\% at 73 GPa, Ho 3\% at 103 GPa, Tm 1.5\% at 120 GPa, and Lu 5\% at 90 GPa [2].

Three models involving 4\textit{f} interactions have been proposed to account for the pressure-induced VC phenomena in the lanthanides at $P_c$: first, the \textit{valence transition model} where a 4\textit{f} electron jumps into the \textit{spd}-electron conduction band, enhancing the crystalline binding; second, the \textit{Mott-Hubbard model} where the 4\textit{f} electrons no longer remain localized but become itinerant (local-to-band transition) and participate in the crystalline binding; third, the \textit{Kondo volume collapse model} where the approach of the 4\textit{f} state to the Fermi energy under pressure leads to an increase in the Kondo temperature $T_K$ and the Kondo binding energy $kT_K$. This additional binding reduces the sample volume and further enhances $T_K$ and $kT_K$, ultimately leading to the so-called Kondo volume collapse. In addition, there is a fourth model where the 4\textit{f} electrons play no role whatsoever. In the $s \to d$ \textit{charge transfer model}, the increase in the number of $d$
electrons in the conduction band with pressure causes a structural phase transition accompanied by a VC.

The VC in cerium (Ce) was discovered more than 60 years ago [3]. Ce’s VC is the largest (16%) and occurs at the lowest pressure (0.7 GPa) of any lanthanide. The sudden large drop in Ce’s magnetic susceptibility at the VC is clear evidence that the 4f electrons play an important role [4]. Recent spectroscopic measurements such as x-ray absorption near-edge structure (XANES) [5], resonant inelastic x-ray scattering (RIXS) [5], and non-resonant x-ray emission spectroscopy (XES) [6] strongly support the Kondo volume collapse model for Ce. Interestingly, in the dilute magnetic alloy La(Ce) the superconducting transition temperature $T_c$ is strongly suppressed at a pressure very near that where the VC in pure Ce occurs [7]. This would suggest that Ce’s VC is driven by the Kondo resonance [2]. However, similar studies on other lanthanides are needed to establish whether the close proximity of the pressure required for the VC in the pure metal and the strong suppression of $T_c$ in the dilute magnetic alloy is accidental or not.

Praseodymium (Pr) undergoes a 9.1% VC at 21 GPa. XANES and XES studies confirm, respectively, that neither Pr’s valence [8] nor its bare 4f state [9] change for pressures exceeding that of Pr’s VC at 21 GPa. As found for Ce, in the dilute magnetic alloy La(Pr) $T_c$ is found to be strongly suppressed for a pressure very near that (21 GPa) for Pr’s VC [10]. Our recent data on Y(1 at.% Pr) (see figure 1) also show a large suppression of $T_c$ beginning at 21 GPa compared to the $T_c(P)$ dependence of the Y host [11]. Strong Kondo pair breaking is the only known mechanism able to cause such a strong suppression of $T_c$. In addition, in figure 1 it is seen that the suppression of $T_c$ is sharply reduced for pressures above 40 GPa. This is exactly what is expected from theory [12] as pressure pushes $T_K$ to values much higher than $T_c$. Similar results were found for terbium (Tb) and the dilute alloy Y(Tb) near its VC pressure of 53 GPa [2]. The close proximity of the pressure for the VC in the pure lanthanides Ce, Pr, Tb and for the very strong $T_c$ suppression in their dilute magnetic alloys with Y is clearly no accident. This close proximity implies that both phenomena have the same origin, namely, the giant Kondo resonance, thus supporting the Kondo volume collapse model for the VC in Ce, Pr, and Tb.

![Figure 1. $T_c$ versus pressure for Y(1 at.% Pr) compared to that for Y [11]. Inset shows similar graph for Y(0.5 at.% Gd). Vertical dashed lines mark pressures of VC for Pr at 21 GPa and for Gd at 59 GPa.](image-url)
It would be useful to find a counterexample. The magnetic state of trivalent gadolinium (Gd) is the most stable of all magnetic lanthanides owing to its half-filled $4f$ orbital. In fact, the $4f^7$ energy level of Gd is located far below its Fermi level [13]. XANES and XES studies on Gd show no valence or local moment transition across the VC pressure $P_c \approx 59$ GPa [1, 14]. The inset in figure 1 gives the results of our recent experiments on the dilute magnetic alloy Y(0.5 at.% Gd) to 120 GPa [2]. The fact that $T_c(P)$ for Y(Gd) shows no suppression whatsoever through the VC pressure at 59 GPa implies that the Kondo resonance plays no role in Gd’s VC; the most likely scenario is simple $s \rightarrow d$ charge transfer.

After Gd and Tb, the next heavier lanthanide metal is dysprosium (Dy) which undergoes a 6% VC at the relatively high pressure of 73 GPa. Here we present the results of electrical resistivity measurements on the dilute magnetic alloy Y(Dy) to pressures as high as 114 GPa. We conclude that the VC in Dy metal is best described by the Kondo volume collapse model.

2. Experimental Methods
The dilute magnetic alloy Y(1 at.% Dy) was prepared by argon arc-melting stoichiometric amounts of Y (99.9% pure from Ames Lab) with the dopant Dy (99.9% pure from Alfa Aesar). To promote sample homogeneity, following the initial melt the sample was turned over and remelted. Weight loss was less than 0.12%, implying the Dy content lies between 0.99 and 1.05 at.%. To generate pressures well beyond the VC pressure of Dy at 73 GPa, we used a diamond anvil cell (DAC) made of CuBe alloy [15]. Two opposing diamond anvils (1/6-carat, type Ia) with 0.18 mm culets beveled at 7° to 0.35 mm were used.

For the high-pressure resistivity measurement (see figure 2), a piece of printed circuit board was attached to the DAC piston. Four-point resistivity was measured using four flat Pt leads; two extra leads were connected to the gasket in order to check for possible electrical shorting to the sample. Six copper wires (140 µm dia.) were then soldered to the Pt leads. The Re gasket (6-7 mm dia., 250 µm thick) was preindented to 30 µm and an 80 µm dia. hole electro-spark drilled through the center of the culet preindentation. The gasket surface was covered with one-sided tape and placed on the board with clay. A small part of the tape was removed to give access to the center section of the preindented gasket surface which was then filled with a 4:1 cBN-epoxy mixture to insulate the gasket and serve as pressure medium. The 4 Pt leads (see figure 3) were arranged to allow a four-point resistivity measurement. Further details of the pressure cell used for resistivity measurements are given in a paper by Shimizu et al. [16].
The Y(1 at.% Dy) sample (dimensions 40×40×5 µm³) was then placed on top of the 4 Pt leads as shown in figure 3. One ruby sphere was positioned at the center of the sample, another directly next to the sample. As in our previous measurements on Y [11], Y(Pr), and Y(Gd) [2], sample pressure here was determined in situ at ~25 K from the shift of the $R_1$ ruby fluorescence line from the ruby sphere on the sample to ± 5% using the revised pressure scale of Chijioke et al. [17]. A He-gas-driven membrane was utilized to change pressure at any temperature above 4 K. In this experiment temperatures as low as 2 K were reached using an Oxford flow cryostat. Further experimental details on the DAC and cryostat used are given elsewhere [15].

### 3. Results and Discussion

Four-point resistivity measurements on the Y(1 at.% Dy) sample to extreme pressures were carried out to track the pressure-dependent $T_c$, as seen in figure 4. As expected for a four-point measurement, the resistance falls completely to zero below the superconducting transition for all pressures except 27 GPa where the measurement was restricted to the temperature range above 2 K. The superconducting transition temperature $T_c$ is seen to increase with pressure to 74 GPa, but then stagnate and decrease at 114 GPa, implying that $T_c(P)$ passes through a maximum at approximately 90 GPa. The width of the superconducting transition reflects the pressure gradient across the sample due to the non-hydrostaticity of the pressure medium. Note that for pressures above 63 GPa the superconducting transition sharpens noticeably as a result of $T_c$ becoming nearly pressure-independent in this pressure range. For all data the value of $T_c$ is determined from the midpoint of the superconducting transition.

In the normal state the resistance gradually increases with pressure, but exhibits a large jump between 74 GPa and 86 GPa. It is not clear whether this jump is an intrinsic property of the sample or perhaps due to the relative movement of the sample or leads in the pressure cell. A structural phase transition in the host metal Y near 80 GPa could cause such a jump; however, no phase transition in Y was observed in the pressure range 50 - 95 GPa [18]. Moreover, in the R(T) data obtained for dilute magnetic alloys of Y with Gd and Tb in Ref. [2], no significant jump was observed in the same pressure range.

![Figure 4](image-url) **Figure 4.** Resistance versus temperature for Y(1 at.% Dy) showing that its superconducting transition temperature initially increases with pressure.
In figure 5 the pressure dependence of $T_c$ for the dilute magnetic alloy Y(1 at.% Dy) is compared with that for elemental Y metal. Initially, the pressure dependence $T_c(P)$ for Y(Dy) tracks that for pure Y, pulling away slowly. However, beginning at the pressure of the VC for Y at 73 GPa, the difference in $T_c(P)$ increases rapidly, reaching nearly 9 K at the highest pressure. Such a drastic suppression of the superconductivity of the Y host can only be caused by giant Kondo pair breaking originating from the Dy magnetic impurity. This gives strong evidence that the Kondo volume collapse model is the correct description for the pressure-induced VC in Dy at 73 GPa. As pointed out in the Introduction, the same conclusion was reached for the VC occurring in Ce, Pr, and Tb. Similar studies are planned for remaining members of the lanthanide series, including the determination of the pressure dependence of the magnetic ordering temperature through the VC pressure.

Figure 5. Pressure dependence of superconducting transition temperature $T_c$ for Y(1 at.% Dy) compared to that for Y [11]. Vertical dashed line marks pressure of VC for Dy at 73 GPa.

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