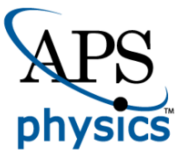

Magnetic ordering at anomalously high temperatures in Dy at extreme pressures

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Magnetic ordering at anomalously high temperatures in Dy at extreme pressures

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In an attempt to destabilize the magnetic state of the heavy lanthanide Dy, extreme pressures were applied in an electrical resistivity measurement to 157 GPa over the temperature range 1.3 - 295 K. The magnetic ordering temperature T_o and spin-disorder resistance R_{sd} of Dy, as well as the superconducting pair-breaking effect ΔT_c in Y(1 at.% Dy), are found to track each other in a highly non-monotonic fashion as a function of pressure. Above 73 GPa, the critical pressure for a 6% volume collapse in Dy, all three quantities increase sharply ($dT_o/dP \simeq 5.3$ K/GPa), T_o appearing to rise above ambient temperature for $P > 107$ GPa. In contrast, T_o and ΔT_c for Gd and Y(0.5 at.% Gd), respectively, show no such sharp increase with pressure ($dT_o/dP \simeq 0.73$ K/GPa). Taken together, these results suggest that extreme pressure transports Dy into an unconventional magnetic state with an anomalously high magnetic ordering temperature.

I. INTRODUCTION

Subjecting a solid to arbitrarily high pressures will successively break up its atomic shell structure, leading to a rise and fall in all condensed matter properties, including magnetism and superconductivity, until finally only a structureless Thomas-Fermi gas remains.[1] Although such astronomic pressures are not available in the laboratory, recent technological developments do allow measurements of the magnetic and superconducting properties of matter to multi-megabar pressures where the increase in energy (1-10 eV/atom) is sufficient to significantly alter electronic states.

Systems with magnetic instabilities exhibit some of the most fascinating properties in current condensed matter physics, including topological insulators,[2] dense Kondo behavior,[3] and exotic forms of superconductivity.[4] Some phenomena are poorly understood, an example being the extraordinarily high Curie temperature (115 K) of $CeRh_3B_2$ that lies two orders of magnitude above that anticipated from simple de Gennes factor scaling.[5] With the availability of extreme pressures, it may now be possible to transport many conventional magnetic systems into ones exhibiting new and unexpected magnetic and/or superconducting properties.

Due to the high degree of localization of their $4f$ orbitals, the heavy lanthanide metals, such as Dy, display the purest form of local moment magnetism. It can be estimated that the molar volume of the heavy lanthanides would have to be compressed approximately five-fold before the nearest-neighbor overlap of $4f$ orbitals becomes sufficient to prompt a local-to-itinerant transition.[6] Other forms of magnetic instability may require less compression. Jackson *et al.*[7] have pointed out that the heavy lanthanides Gd, Tb, Dy, Ho, Er, and Tm exhibit conventional magnetic ordering to pressures of ~ 10 GPa by virtue of an indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction;[8] this is evidenced by the fact that their respective magnetic ordering temperatures T_o decrease monotonically with pressure, obeying de Gennes factor scaling.[9] Were the $4f$ magnetic state to become unstable under extreme pressure, such scaling would *not* continue. Later work on Dy to 69 GPa finds $T_o(P)$ to be non-monotonic, but it is not clear whether de Gennes scaling is violated.[10]

Dy is a trivalent heavy lanthanide with hcp structure, a $4f^9$ electron configuration, antiferromagnetism below 178 K, and ferromagnetism below 85 K.[11] In this paper we present the results of temperature-dependent dc electrical resistivity measurements on Dy to pressures as high as 157 GPa, well above the pressure of 73 GPa where Dy suffers a 6% volume collapse at the phase transition from hexagonal hR24 to body-centered monoclinic (bcm).[12] As the applied pressure passes through 73 GPa, T_o begins to increase dramatically, appearing to rise well above ambient temperature. These and parallel resistivity studies on both Gd metal and the dilute magnetic alloys Y(1 at.% Dy) and Y(0.5 at.% Gd) suggest that, in contrast to Gd, extreme pressures transport Dy into an unconventional magnetic state with an anomalously high magnetic ordering temperature, far above that anticipated from conventional de Gennes scaling.

II. EXPERIMENTAL TECHNIQUES

Resistivity samples were cut from Dy and Gd foil (99.9% Alfa Aesar). The dilute magnetic alloys were prepared by argon arc-melting stoichiometric amounts of Y (99.9% Ames Lab[13]) with Dy or Gd dopant. Following the initial melt, the sample was turned over and remelted several times with less than 0.1% weight loss.

To generate pressures well beyond the volume collapse pressure of Dy at 73 GPa, a diamond anvil cell (DAC) made of CuBe alloy was used.[14] Three separate high-pressure experiments on Dy were carried out. In run 1 pressure was generated by two opposing diamond anvils (1/6-carat, type Ia) with 0.5 mm diameter culets. In runs 2 and 3 the anvils had 0.35 mm diameter culets beveled at 7° to 0.18 mm central flats. The Re gasket (6-7 mm diameter, 250 μm thick) was preindented to 30 μm and a 80 μm diameter hole electro-spark drilled through the center (for the 0.5 mm culet anvils the gasket

was preindented to 80 μm with a 250 μm diameter hole). The center section of the preindented gasket surface was filled with a 4:1 cBN-epoxy mixture to insulate the gasket and serve as pressure medium (see Fig. 1). The thin Dy sample (dimensions $\sim 30\times30\times5$ μm^3) was then placed on top of four thin Pt leads for a four-point dc electrical resistivity measurement. Two experimental runs were carried out on the thin Gd sample (same dimensions as for Dy) using beveled anvils as above. Further details of the non-hydrostatic high pressure resistivity technique are given in a paper by Shimizu *et al.*[15]

A He-gas driven membrane was utilized to change pressure at any temperature above 3 K.[16] In the measurement on the Y(1 at.% Dy) alloy, one ruby sphere was positioned at the center of, and another directly next to, the sample. The average pressure over the sample was determined *in situ* at 25 K with the standard ruby fluorescence technique using the revised pressure scale of Chijioke *et al.*[17] In the resistivity measurements on Dy and Gd, pressure was determined using both ruby fluorescence and, in the upper pressure range, Raman spectroscopy from the frequency shift of the diamond vibron.[18] The "homemade" Raman spectrometer utilizes a Nikon metallographic microscope coupled fiber-optically to a sensitive QE65000 spectrometer from Ocean Optics.[19] The values of the pressures given are averaged over the sample to an estimated accuracy of $\pm10\%$. In these experiments temperatures as low as 1.3 K were reached in an Oxford flow cryostat. All measurements in this paper were carried out with increasing pressure. Further experimental details of the DAC and cryostat are given elsewhere.[14,20,21]

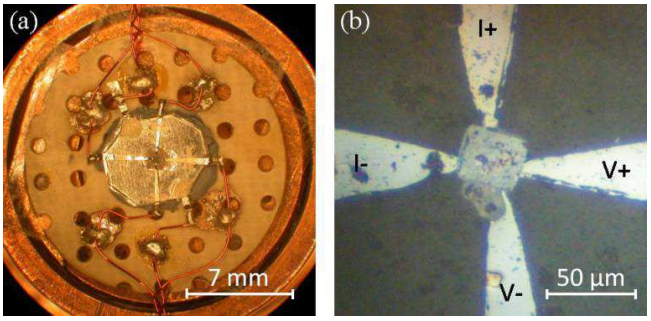

FIG. 1. (a) Image of pressure cell used with Re gasket mounted on diamond anvil for four-probe electrical resistivity measurements. (b) Image of Dy sample ($30\times30\times5$ μm^3) resting on four flat Pt leads (4 μm thick) on insulated Re gasket.

III. RESULTS OF EXPERIMENT

A. Magnetic Ordering

The present resistivity studies on Dy were carried out in three separate experiments. In Fig. 2 the electrical resistance $R(T)$ from run 3 is plotted versus temperature at 14 different pressures to 157 GPa. The residual resistance $R_d = R(5\text{ K})$ initially increases with pressure as defects are introduced into the sample through plastic deformation of pressure cell and sample by the non-hydrostatic pressure. For pressures of 56 GPa and above the pressure cell appears to stabilize, the relatively small changes (both positive and negative) in R_d at higher pressures likely arising from small displacements of the electrical contacts.

The magnetic ordering temperature T_o is identified by the kink in the $R(T)$ dependence clearly seen near 170 K at 2.1 GPa, the lowest pressure in run 3. The kink in $R(T)$ upon cooling marks the beginning of the suppression of spin-disorder scattering $R_{sd}(T)$ as magnetic ordering sets in.[22] At higher pressures this kink broadens somewhat into a "knee" due to pressure gradients across the sample, but remains clearly visible to 107 GPa. We define T_o by the intersection point of two straight lines above and below the knee, as illustrated for the data at 30 GPa in Fig. 2(a). With increasing pressure the temperature of the knee is seen to initially decrease, but then increase above 22 GPa, the rate of increase becoming very large above 76 GPa. In the pressure range 119 - 157 GPa the knee has apparently shifted above 295 K, the highest temperature of the present measurement. The temperature shift of the knee with pressure is particularly clear in the spin-disorder resistance (see Fig. 5 below).

In Fig. 3(a) T_o is plotted versus pressure to 107 GPa for all three experiments on Dy, those in run 3 extending to 157 GPa. The results are in reasonable agreement both with earlier magnetic susceptibility measurements of Jackson *et al.*[7] to 7.4 GPa and with very recent resistivity studies of Samudrala *et al.*[10] to 69 GPa. The pressure dependence $T_o(P)$ is seen to be highly non-monotonic, presumably in response to multiple structural phase transitions[12,23] (see top of the graph). Note that the phase boundaries were determined from x-ray diffraction studies at ambient temperature and may shift somewhat as the temperature is lowered.

Particularly intriguing is the dramatic increase of T_o in run 3 following the hR24 to body-centered monoclinic (bcm) transition at 73 GPa[12] where a 6% volume collapse occurs. At 119 GPa the knee in $R(T)$ is no longer visible since it has apparently shifted to temperatures above 295 K. In run 2 two additional values of T_o (169 K and 234 K) were measured at consecutively higher pressures than 73 GPa, thus confirming the rapid increase in T_o with pressure seen in run 3. These two data points from run 2 are not included in Fig. 3(a) since experimental difficulties prevented an accurate determination of the pressure.

To illustrate how dramatic this increase in T_o really is, we plot in Fig. 3(b) T_o versus relative sample volume V/V_o, a parameter with a more direct physical significance than pressure P. In Fig. 3(b) the rate of increase of T_o below $V/V_o \simeq 0.51$ (above 73 GPa), is seen to be *much* steeper than the initial rate of decrease of T_o near $V/V_o = 1$ (ambient pressure). Extrapolating T_o in Fig. 3(b) linearly to $V/V_o = 0.39$ (157 GPa), yields the esti-

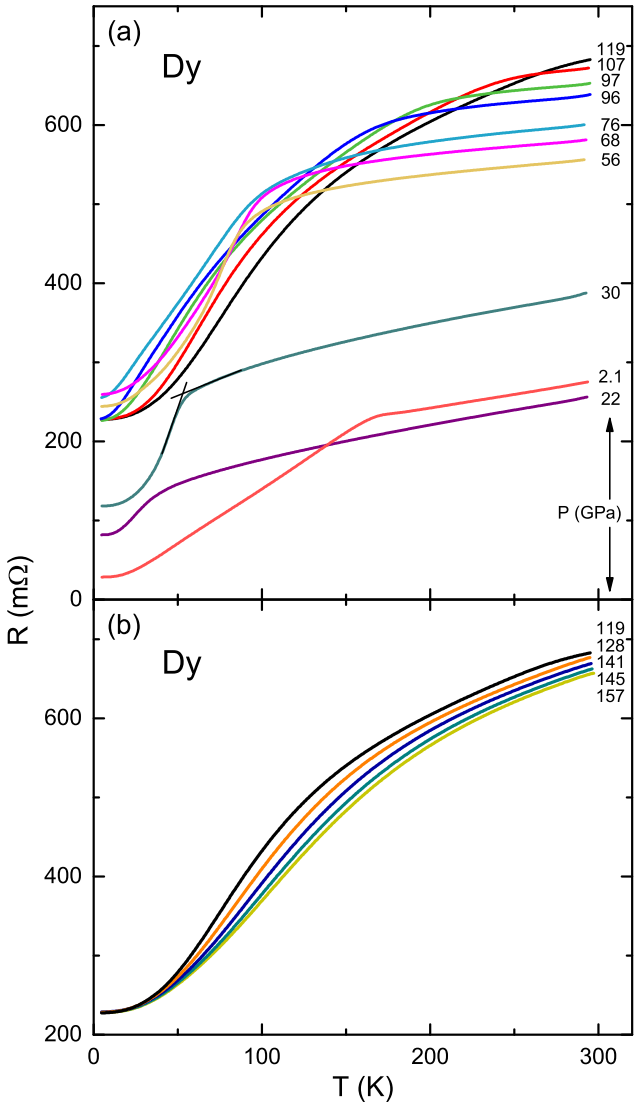

FIG. 2. (color online) Resistance of Dy from run 3 versus temperature to 295 K in pressure ranges: (a) 2.1 - 119 GPa, and (b) 119 - 157 GPa. The magnetic ordering temperature T_o is determined by the intersection point of two straight lines, as illustrated in (a) at 30 GPa.

mate $T_o \approx 430$ K.

It is interesting to compare the pressure dependence $T_o(P)$ for Dy in Fig. 3(a) to that for its lighter next-nearest-neighbor lanthanide, Gd, shown in Fig. 4. A detailed comparison of the $T_o(P)$ data for Dy and Gd reveals strikingly similar behavior to 70 GPa, but significant differences at higher pressures. Whereas $T_o(P)$ for Dy displays a sharp upturn above 73 GPa, that for Gd increases only gradually over the entire pressure range 40 - 105 GPa with no sign of a rapid upturn 59 GPa where the hR24 to bcm phase transition with a 5% volume collapse occurs.[24,25]

B. Spin Disorder Scattering

Rather than invoking a linear extrapolation, to estimate the value of T_o in Dy at 157 GPa a preferable method would be to track the shift in the spin-disorder resistance $R_{sd}(T)$ itself over the entire pressure range. For temperatures above the magnetic ordering temperature T_o, Dy is in a paramagnetic state where $R_{sd}(T)$ takes on its maximum, *temperature-independent* value. As the temperature is lowered through T_o, a knee appears in $R_{sd}(T)$ as the spin-disorder resistance begins to decrease, ultimately vanishing at the lowest temperatures. The first step in extracting $R_{sd}(T)$ from the measured resistance data $R(T)$ is to subtract off the temperature-dependent phonon resistance $R_{ph}(T)$.

According to Matthiessen's Rule, the total measured resistance is the sum of three terms, $R(T) = R_d + R_{ph}(T) + R_{sd}(T)$, where R_d is the temperature-independent defect contribution. For many lanthanides Colvin *et al.*[26] simply assumed the phonon contribution is linear in temperature to 0 K; however, such an assumption is only valid for simple *sp*-electron metals at temperatures well above the Debye temperature. In the lanthanides the conduction band has strong *d*-electron character that lends the small negative curvature to $R_{ph}(T)$ clearly seen in Fig. 2(a) for temperatures above T_o. Since $R_{sd}(T)$ is independent of temperature above T_o, the only temperature-dependent term in $R(T)$ for $T > T_o$ is the phonon resistance $R_{ph}(T)$. The temperature dependence of the phonon resistance is displayed over the widest temperature range at the pressure where T_o is lowest, i.e. for the data at 22 GPa in Fig. 2(a). We extrapolate this dependence to 0 K in the temperature region $T < T_o \simeq 40$ K to yield the temperature-dependent function $R_{ph}^{22}(T)$, the phonon resistance at 22 GPa.

Viewing the other resistance curves $R(T)$ in Fig. 2(a) at temperatures above their knee, it is evident that the temperature-dependent phonon resistance $R_{ph}(T)$ changes little with pressure. To estimate $R_{ph}(T)$ at pressures other than 22 GPa, we simply multiply the function $R_{ph}^{22}(T)$ by a "phonon factor" α chosen such that for temperatures above T_o the quantity $R(T) - \alpha R_{ph}^{22}(T)$ becomes *temperature independent*. The values of the phonon factor α are listed in Table I at all pressures to 157 GPa in run 3. For pressures of 119 GPa and above the knee in $R(T)$ apparently lies above 295 K, so that $R_{ph}(T)$ is no longer readily visible. For $P \geq 119$ GPa, there, the average value $\alpha = 0.55$ is assumed in Table I.

The next step is to subtract for each pressure both this phonon resistance $\alpha R_{ph}^{22}(T)$ and the temperature-independent defect resistance R_d from the measured resistance $R(T)$, yielding the estimated spin-disorder resistance $R_{sd}(T) = R(T) - \alpha R_{ph}^{22}(T) - R_d$ displayed in Fig. 5 for data where $P \leq 107$ GPa. For increasing pressures above 76 GPa, the knee in both $R(T)$ in Fig. 2(a) and $R_{sd}(T)$ in Fig. 5 is seen to rapidly approach ambient temperature, finally disappearing above 109 GPa. This suggests that the magnetic ordering temperature of Dy

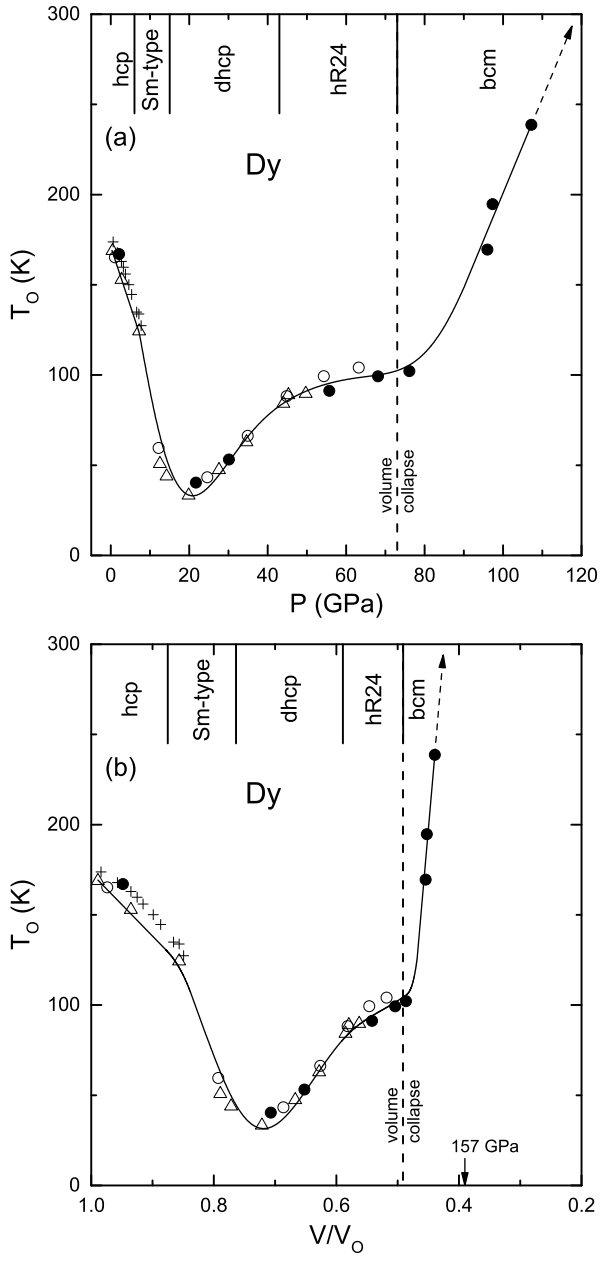

FIG. 3. Magnetic ordering temperature T_o of Dy versus (a) pressure or (b) relative volume V/V_o using equation of state from Ref. 12 (+) earlier studies to 7.4 GPa with slope $dT_c/dP = -6.7$ K/GPa;[7] (△) present resistivity measurements in run 1 with initial slope −6.5 K/GPa , (○) run 2, (●) run 3. Vertical dashed line marks pressure of volume collapse for Dy at 73 GPa. Crystal structures at top of graph are for Dy.[12] In both plots the extended solid line through data points is guide to the eye.

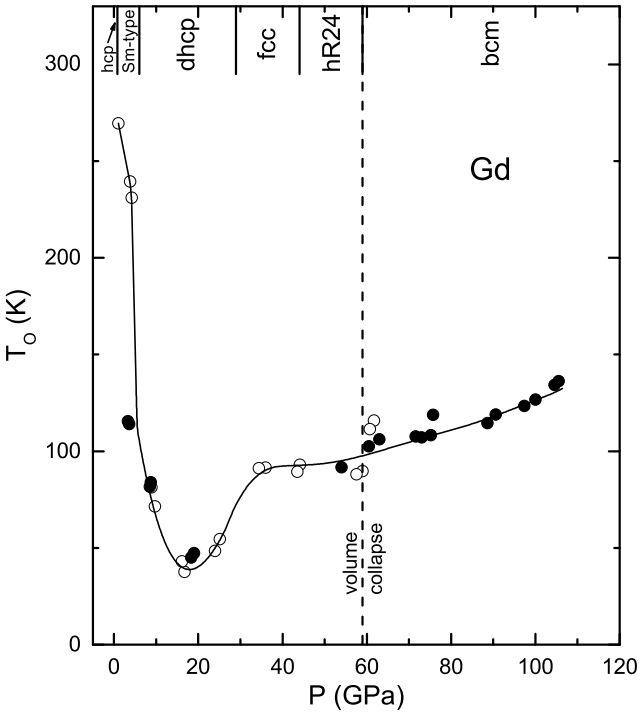

FIG. 4. Magnetic ordering temperature T_o of Gd versus pressure to 105 GPa in two experiments (○) run 1, (●) run 2. Vertical dashed line marks pressure of volume collapse for Gd at 59 GPa. Crystal structures at top of graph are for Gd.[24,25] Extended solid line through data points is guide to the eye.

lies above 295 K for pressures in the range 119 - 157 GPa.

It is noteworthy that for pressures above 56 GPa, where the pressure cell stabilizes (see discussion above), the magnitude of the spin-disorder resistance R_{sd} tracks the magnetic ordering temperature T_o. Even in the lower pressure region where the pressure cell is not fully stable, the sign of the change in T_o and R_{sd} are the same, as seen in Fig. 5 comparing data from 2.1 to 22 GPa, where both decrease, and from 22 to 30 GPa, where both increase.

The sharpness of the knee in either $R(T)$ in Fig. 2(a) or $R_{sd}(T)$ in Fig. 5 is a measure of the width in temperature of the magnetic transition at T_o. Note that this width is broadest near those pressures where $|dT_o/dP|$ is steepest in Fig. 3. This is due to the fact that in the present non-hydrostatic pressure cell a pressure gradient exists across the sample. In the pressure region near where $dT_o/dP \approx 0$, the broadening effect due to the pressure gradient is minimal and the transition appears relatively sharp.

We now estimate the dependence of T_o on pressure for $P \geq 119$ GPa by first considering the spin-disorder resistance $R_{sd}(T)$ at lower pressures. First normalize $R_{sd}(T)$ from Fig. 5 to its value at 295 K, yielding the relative spin-disorder resistance $R_{sd}(T)/R_{sd}[(T > T_o)]$ plotted versus $\log T$ for data at 96, 97, and 107 GPa in Fig. 6. Since the magnetic ordering temperature at the higher pressures of 119, 128, 141, 145, and 157 GPa appears to lie above the temperature range of the present experiments (295 K), one cannot determine $R_{sd}(T > T_o)$ or T_o itself directly from the resistance data. However, noticing that over much of the temperature range $T < T_o$, the $R_{sd}(T)$ curves for 96, 97, and 107 GPa are approximately parallel on the $\log T$ plot in Fig. 6, we divide

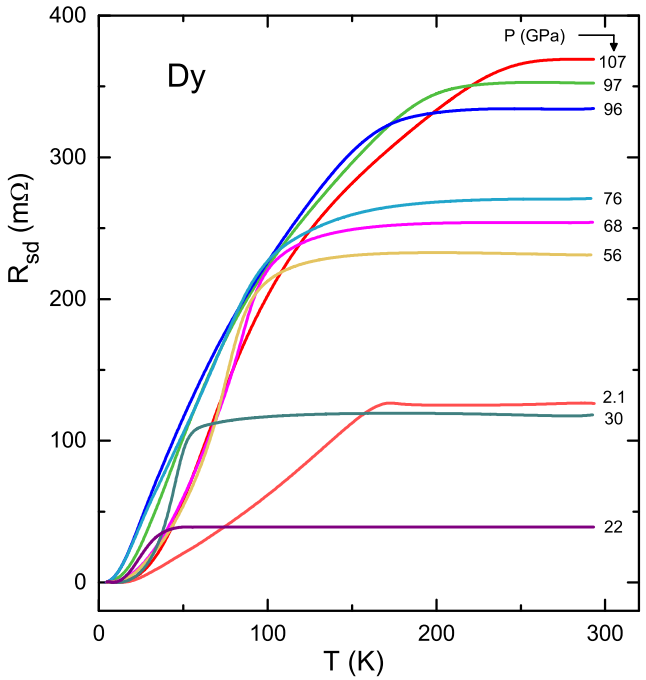

FIG. 5. (color online) Spin-disorder resistance $R_{sd}(T)$ versus temperature at pressures where T_o lies below ambient temperature (295 K). The phonon $R_{ph}(T)$ and defect R_d resistances have been subtracted off (see text).

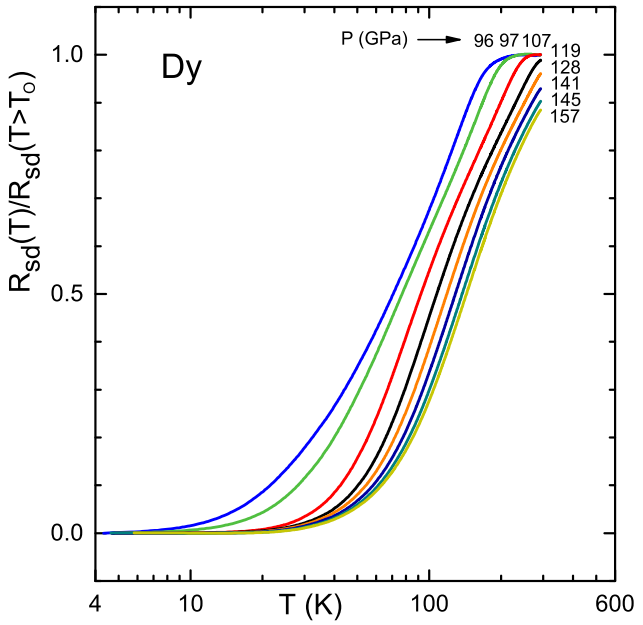

FIG. 6. (color online) Spin-disorder resistance $R_{sd}(T)$ versus $\log T$. At 119, 128, 141, 145, and 157 GPa $R_{sd}(T > T_o)$ is estimated by adjusting slopes to match those at 96, 97, and 107 GPa (see text). From relative horizontal shifts of the curves half-way down the transition, the pressure-dependence of the magnetic ordering temperature T_o is estimated (see text and Table I).

the $R_{sd}(T)$ data for $P \geq 119$ GPa by that factor which results in curves parallel to those at the lower pressures, as seen in Fig. 6. We identify this factor as the value of the temperature-independent spin-disorder resistance for $T > T_o$, as listed in Table I.

We now estimate the change in the value of the magnetic ordering temperature T_o from the shift of the $R_{sd}(T)/[R_{sd}(T > T_o)]$ curves along the $\log T$ axis. The resulting values of $T_o(P)$ are given in Table I for all pressures. For this estimate the reasonable assumption is made that the relative spin-disorder resistance is primarily a function of the ratio T/T_o for $P > 96$ GPa. From this analysis we infer that from 119 to 157 GPa the mean magnetic ordering temperature T_o has increased from 280 K to 370 K. In future experiments on Dy the synchrotron Mössbauer effect will be measured to extreme pressures to search for magnetic order at temperatures near and above ambient.

TABLE I. Values for Dy of the magnetic ordering temperature T_o, spin-disorder resistance R_{sd} for $T > T_o$, and phonon factor α as a function of pressure to 157 GPa.

P(GPa)	T_o(K)	R_{sd}(mΩ)	α
2.1	167	126	0.89
22	40	39	1.0
30	53	118	1.1
56	91	231	0.6
68	99	254	0.5
76	102	271	0.55
96	170	334	0.55
97	195	352	0.55
107	239	369	0.55
119	280	384	0.55
128	300	388	0.55
141	330	392	0.55
145	350	396	0.55
157	370	398	0.55

C. Suppression of Superconductivity

A long-standing strategy[27,28] to probe the magnetic state of a given ion is to alloy this ion in dilute concentration with a host superconductor and determine ΔT_c, the degree of suppression of the superconducting transition temperature. Yttrium (Y) is the ideal host superconductor for Dy since the character of its *spd*-electron conduction band closely matches that of the heavy lanthanides, Y even exhibiting nearly the same sequence of structural transitions under pressure.[29] The efficacy of this strategy is supported by the fact that T_o for Dy metal and ΔT_c for Y(Dy) alloy experience a dramatic enhancement beginning at nearly the same pressure ~ 75 GPa.

In Fig. 7 the pressure dependence of the superconducting transition temperature T_c of the dilute magnetic alloy Y(1 at.% Dy) is compared to published $T_c(P)$ data for elemental Y metal.[30] To approximately 70 GPa, T_c for Y(1 at.% Dy) is seen to increase with pressure at a somewhat slower rate than that for Y. However, just above the pressure of Dy's volume collapse at 73 GPa, the $T_c(P)$ dependence for Y(1 at.% Dy) begins to rapidly pull away from that of Y, reaching a suppression ΔT_c of nearly 9 K at the highest pressure. This dramatic suppression of Y's superconductivity by dilute Dy ions for pressures above 73 GPa points to giant Kondo pair breaking, as previously observed in high pressure studies on the dilute magnetic alloys La(Ce),[31] La(Pr),[32] and Y(Pr).[33,34] A resistivity minimum from the Kondo effect has been observed for La(Ce), but not as yet for La(Pr), Y(Pr), or Y(Dy) alloys. This may be due to the fact that the superconducting transition would obscure any resistivity minimum near T_c. The pressure and concentration ranges must, therefore, be carefully chosen so that the resistivity minimum lies somewhat above T_c.

In contrast, as seen in the published data[34] in the inset to Fig. 7, $T_c(P)$ for Y(0.5 at.% Gd) does *not* begin to deviate markedly from that of Y metal at $\sim$ 59 GPa where Gd's volume collapse occurs, but rather faithfully tracks Y's value of T_c to the maximum pressure of 127 GPa. Unlike for Dy, the magnetic state for Gd ions in Y thus appears to remain stable to this pressure, so that no Kondo effect phenomena are expected.

IV. DISCUSSION

We now seek to identify the mechanism(s) responsible for the highly non-monotonic dependence of the magnetic ordering temperature T_o of Dy on pressure, particularly its dramatic increase just above 73 GPa. Since to 70 GPa the $T_o(P)$ phase diagrams of Gd and Dy are so similar, to this pressure a common mechanism seems likely. The fact that above 73 GPa $T_o(P)$ increases dramatically for Dy, but not for Gd, suggests that in this upper pressure range Dy has entered an unconventional magnetic state, the possible nature of which we now explore.

In the previous section we noted that in Dy T_o and R_{sd} track each other as the pressure is increased. As seen in Fig. 8 this also holds for ΔT_c and R_{sd} where both quantities exhibit a sharp upturn with pressure above 73 GPa. This parallel behavior of these three pressure dependences for Dy is not completely unexpected. For a conventional lanthanide metal, the magnetic ordering temperature T_o ,[9] the spin-disorder resistance R_{sd},[35] and the suppression of the superconducting transition temperature ΔT_c in a dilute magnetic alloy[36–38] are all expected to scale with the de Gennes factor $(g-1)^2 J_t(J_t+1)$,[9] modulated by a prefactor $J^2 N(E_F)$, where J is the exchange interaction between the $4f$ ion and the conduction electrons, $N(E_F)$ the density of states at the Fermi energy, g the Landé-g factor, and J_t the total angular momentum quantum number.

Since the de Gennes factor would not be expected to change under pressure, unless a valence transition occurs, the strong similarity between the highly non-monotonic pressure dependences of T_o for Dy and Gd to 70 GPa (Figs. 3 and 4) likely originates from the pressure dependence of $J^2 N(E_F)$, facilitated by a series of nearly identical structural phase transitions in both Dy[12] and Gd[24] (those for Gd occurring at somewhat reduced pressures) driven by increasing $5d$-electron occupation with pressure.[39] Indeed, electronic structure calculations for Dy suggest that its large negative initial pressure derivative dT_o/dP results from a strong decrease in $J^2 N(E_F)$.[7,40]

What causes the sharp upturn in $T_o(P)$ for Dy and the strong enhancement in $\Delta T_c(P)$ for Y(1 at.% Dy), both immediately above $\sim$ 75 GPa? The total net exchange interaction $J = J_+ + J_-$ between a magnetic ion and the conduction electrons includes a normal positive exchange component J_+ and a negative covalent-mixing component J_-.[41] For a lanthanide, J_- depends on the mixing matrix element V_{sf} and the $4f$-electron stabilization energy E_{ex} according to $J_- \propto -|V_{sf}|^2/E_{ex}$, where E_{ex} is assumed small compared to the Coulomb repulsion U between electrons on the same orbital.[42] As the magnetic ion approaches the mixed-valence regime through doping or high pressure, E_{ex} approaches zero and/or V_{sf} increases. The magnetic ordering temperature $T_o \propto J^2$

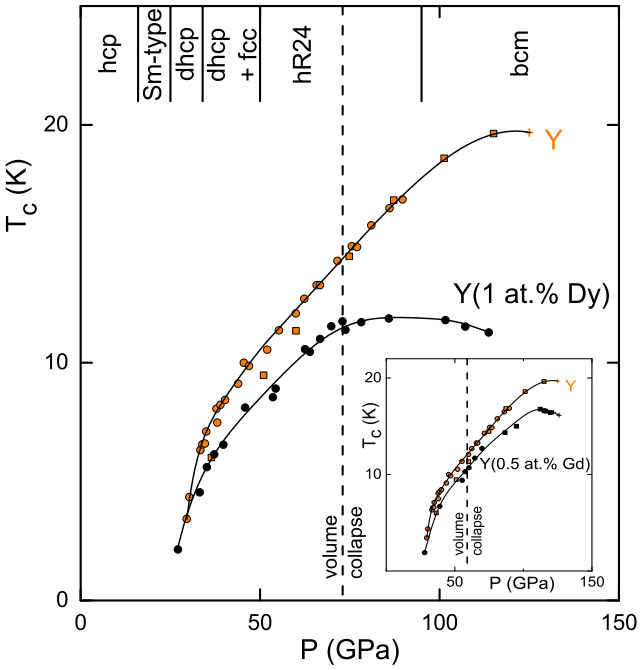

FIG. 7. (color online) T_c versus pressure for Y(1 at.% Dy) compared to that for Y.[30] Inset shows similar graph for Y(0.5 at.% Gd).[34] Vertical dashed line marks pressure of volume collapse for Dy at 73 GPa[12] and in inset for Gd at 59 GPa.[24,25] At top of graph are crystal structures taken on by superconducting host Y.[29]

would be expected to *increase* until $|J_-|$ becomes so large that the magnetic moment begins to be compensated through the exponentially increasing Kondo spin screening, as anticipated in the simple Doniach model.[43,44] We suggest that this could lead to an *anomalously high value* of T_o, such as observed for Dy at extreme pressure, a value perhaps surpassing that possible for normal positive exchange interactions. We speculate that the anomalously high magnetic ordering temperature T_o of Dy at extreme pressure may be an as yet unrecognized feature of dense Kondo physics or some related unstable magnetic state.

Anomalously high magnetic ordering temperatures are not unknown in other lanthanide systems. More than thirty years ago a remarkable ferromagnetic compound $CeRh_3B_2$ was discovered with a Curie temperature $T_o \simeq 115$ K,[5] two orders of magnitude higher than anticipated from simple de Gennes factor scaling relative to $GdRh_3B_2$ where T_o is "only" 90 K.[45] The extraordinarily high Curie temperature of $CeRh_3B_2$ has yet to be satisfactorily explained, although several attempts have been made.[46,47] That $CeRh_3B_2$ may be a dense Kondo system, or closely related to one, is indicated by the fact that the substitution of less than 0.3% of La with Ce in $La_{1-x}Ce_xRh_3B_2$ is sufficient to destroy the superconductivity of $LaRh_3B_2$, the initial rate of decrease -5.6 K/at.% Ce being among the largest ever observed for Ce impurities in a superconducting host.[48] The Kondo physics scenario for $CeRh_3B_2$ receives some support from the fact that under pressure T_o initially increases only very slightly[49] before beginning to decrease above 2.5 GPa, finally disappearing rapidly by 6.5 GPa.[47]

We emphasize that in the Kondo scenario spin screening competes with magnetic ordering, even when T_o takes on anomalously high values. In view of the exponential dependence of the Kondo temperature on $N(E_F)J$, at higher pressures than in the present studies it would be expected that Kondo spin screening would gain in importance, leading to a suppression of magnetic ordering. At still higher pressures intermediate valence behavior, a valence increase, and/or a local-itinerant magnetic transition might follow.

In the Kondo scenario the volume collapse in Dy at 73 GPa could well have its origin in the Kondo volume collapse model of Allen and Martin,[50] as recently proposed by Fabbris *et al.*[34] to account for the volume collapse in Tb at 53 GPa. In that study x-ray absorption near-edge spectroscopy (XANES) and x-ray emission spectroscopy (XES) experiments on Tb to extreme pressure revealed that neither a change in valence nor a magnetic local-itinerant transition occur at the volume collapse, thus giving support to the Kondo volume collapse model.[34] Since Tb has, with its $4f^8$ state, only one electron in excess of half filling, due to the particular stability of the half-filled $4f^7$ state, one would expect it to lie closer to a valence transition than Dy with its $4f^9$ state. It thus seems reasonable to assume that over the pressure range of the present experiments Dy remains trivalent with a

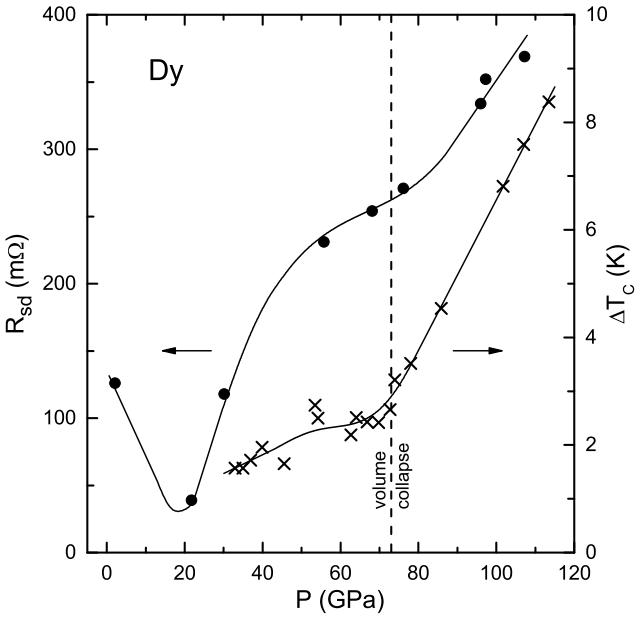

FIG. 8. Pressure dependence of both (•) the estimated spin-disorder resistance R_{sd} at 295 K and (×) ΔT_c, the reduction in the value of the superconducting transition temperature of Y(1 at.% Dy) compared to that of pure Y. Extended solid lines through data points are guides to the eye.

highly localized $4f^9$ magnetic state and that the volume collapse in Dy has its origin in the Kondo volume collapse scenario. In this sense the volume collapse in Dy at 73 GPa can be seen as an signal that Dy is entering a region of anomalous magnetism, perhaps exhibiting dense Kondo behavior, where the magnetic ordering temperature is strongly enhanced.

The absence of anomalies in $T_o(P)$, ΔT_c, and R_{sd} for Gd over the entire pressure range studied gives evidence that to 127 GPa Gd remains a conventional magnetic lanthanide. The absence of magnetic instabilities in Gd, even at extreme pressures, is not surprising since the local magnetic state of Gd with its half-filled $4f^7$ shell is the most stable of all elements, its $4f^7$ level lying ~ 9 eV below the Fermi level.[51]

An alternative explanation for the anomalously high magnetic ordering temperatures T_o in Dy might be the effect of crystalline electric fields. It has been shown that such fields are likely responsible for the significant enhancement of T_o over de Gennes scaling in a series of RRh_4B_4 compounds, where R is a lanthanide.[52,53] If strong single-ion magnetic anisotropies are present, this crystal field enhancement can be as large as the factor $3J/(J+1) = 2.6$ for trivalent Dy where $L = 6$, $S = 1$, and $J = 6$.[52,53] No crystal field effects are possible for Gd since it carries no orbital moment ($L = 0$). The lack of a sharp upturn in T_o, ΔT_c, and R_{sd} for Gd in the pressure region 60 - 127 GPa would be consistent with the absence of crystal field effects. The fact that the pressure dependence of T_o is very similar for both Gd and Dy to 73 GPa

indicates that crystal field effects, if present, would only become significant in Dy for pressures above 73 GPa, leading to the sharp upturn in T_o and R_{sd} observed.

In this crystal field scenario, however, it is difficult to understand the sharp upturn in the suppression of superconductivity ΔT_c in the dilute magnetic alloy Y(1 at.% Dy) for pressures above 73 GPa. This strong suppression of superconductivity points rather to a Kondo physics scenario with strong Kondo pair breaking.

Further experimentation is necessary to unequivocally establish the origin of the anomalous behavior of T_o, ΔT_c, and R_{sd} in Dy for the pressure region above 73 GPa. Such experiments could include the search for a resistivity minimum in the dilute magnetic alloy Y(Dy) at various concentrations, as well as an extension of the pressure range to 2 Mbar to search for the characteristic "sinkhole behavior" of $T_c(P)$ observed for Y(Pr),[33,34] La(Ce),[31] and La(Pr)[32] where the T_c-suppression ΔT_c reaches a maximum as the Kondo temperature T_K passes through the experimental temperature range, but falls off again at higher pressures where T_K far exceeds T_c. Inelastic neutron and x-ray scattering studies to extreme pressures would help establish whether crystal-field splittings play any role in the anomalously high values of T_o for Dy.

In summary, measurements of the electrical resistivity of Dy metal to extreme pressures reveal that the magnetic ordering temperature T_o exhibits a highly non-monotonic pressure dependence, appearing to rise for $P > 73$ GPa to unprecedentedly high values in the range 370 - 430 K at 157 GPa. If confirmed, this transition temperature would be the highest known transition temperature among the lanthanides, where the current highest value is 292 K for Gd at ambient pressure.[26] Parallel experiments on Gd and dilute magnetic alloys of Gd and Dy with Y suggest that under extreme pressures Dy is transformed from a magnetically conventional lanthanide into one with an unconventional magnetic state, perhaps a dense Kondo system, with anomalously high values of T_o. In contrst, Gd remains a magnetically conventional lanthanide to pressures of at least 127 GPa. A search at ambient or high pressure for further lanthanide and actinide systems with anomalously high magnetic ordering temperatures would also be of considerable interest.

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