Record high magnetic ordering temperature in a lanthanide at extreme pressure

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Abstract. Today’s best permanent magnet materials, SmCo₅ and Nd₂Fe₁₄B, could likely be made significantly more powerful were it not necessary to dilute the strong magnetism of the rare earth ions (Sm, Nd) with the 3d transition elements (Fe, Co). Since the rare-earth metals order magnetically at relatively low temperatures $T_o \leq 292$ K, transition elements must be added to bring $T_o$ to temperatures well above ambient. Under pressure $T_o(P)$ for the neighboring lanthanides Gd, Tb, and Dy follows a notably nonmonotonic, but nearly identical, dependence to $\sim 60$ GPa. At higher pressures, however, Tb and Dy exhibit highly anomalous behavior, $T_o$ for Dy soaring to temperatures well above ambient. We suggest that this anomalously high magnetic ordering temperature is an heretofore unrecognized feature of the Kondo lattice state.

Measurements of the magnetic and superconducting properties of matter can now be carried out to multimegabar pressures where the increase in energy (1 - 10 eV/atom) is sufficient to significantly alter these properties and possibly result in novel many-body states of matter. Stable magnetic systems can destabilize under extreme pressure, leading perhaps to surprising new forms of magnetism and/or superconductivity.

Rare-earth elements play a central role in many modern technologies, including permanent magnets, computer memories, and applications requiring giant magnetostriction. The high degree of localization of their magnetic 4f electrons results in relatively weak interatomic exchange interactions and low magnetic ordering temperatures, the highest being $T_o \simeq 292$ K for Gd metal [1]. This is unfortunate since the strongest permanent magnets, SmCo₅ and Nd₂Fe₁₄B, require the addition of a substantial concentration of a magnetic transition metal, Co or Fe, in order to raise $T_o$ to a temperature well above ambient. Unfortunately, this addition dilutes the strong magnetism of the rare-earth component. A significant increase in $T_o$ for rare-earth materials devoid of transition elements could lead to many new applications.

Here we report the results of resistivity studies on the neighboring rare earths Gd, Tb, and Dy to extreme pressures [2, 3]. Above 60 GPa the magnetic ordering temperatures of Tb and Dy show a significant increase, $T_o$ for Dy soaring to $\sim 400$ K at 157 GPa. We suggest that at extreme pressures, in contrast to Gd, both Tb and Dy enter an anomalous Kondo lattice state that is responsible for the significant increase in $T_o$. This scenario receives support from the fact

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that in the pressure region above 60 GPa dilute magnetic impurities of Tb and Dy are able to drastically suppress the superconducting transition temperature of Y.

Resistivity samples are cut from 99.9% pure elements Dy and Gd (Alfa Aesar) and Tb and Y (Ames Lab [4]). The dilute magnetic alloys are prepared by argon arc-melting stoichiometric amounts of Gd, Tb, and Dy dopant with Y. To generate pressures to 1-2 Mbar, a diamond anvil cell (DAC) made of CuBe alloy [5] is fitted with two opposing diamond anvils (1/6-carat, type Ia) with 0.35 mm diameter culets beveled at 7° to 0.18 mm central flats. A Re gasket (6-7 mm diameter, 250 µm thick) is preindented to 30 µm and a 80 µm diameter hole electro-spark drilled through the center. The center section of the preindented gasket surface is filled with a 4:1 cBN-epoxy mixture to insulate the gasket and serve as pressure medium (see Fig. 1). The thin sample (dimensions ∼30×30×5 µm³) is then placed on top of four thin Pt leads to allow a four-point dc electrical resistivity measurement. Further details of the non-hydrostatic high pressure resistivity technique are given in a paper by Shimizu et al. [6].

A He-gas-driven membrane allows the pressure to be changed at any temperature above 3 K [7]. Pressure is determined using both ruby fluorescence [8] and Raman spectroscopy from the frequency shift of the diamond vibron [9]. Temperatures as low as 1.3 K can be reached in an Oxford flow cryostat. Further experimental details of the DAC and cryostat are given elsewhere [2, 5, 10, 11].

In Fig. 2 the electrical resistance $R(T)$ of Dy is plotted versus temperature at 8 different pressures to 157 GPa; for $P > 2.1$ GPa the data have been shifted vertically so as not to cross.
Figure 2. Resistance versus temperature for Dy at eight different pressures. Except at 2.1 GPa, the curves are shifted vertically for clarity. Red lines with small positive slope give temperature dependence of phonon resistance. See Refs. [2, 3] for details.

Figure 3. Magnetic ordering temperature $T_o$ of Dy [2], Tb [3], and Gd [2] versus pressure. (+) earlier studies to $\sim$8 GPa on Dy [13] and Tb [16]. References for crystal structures at top of graphs Dy [13], Tb [14], Gd [19]; vertical dashed line gives pressure where 5-6% volume collapse occurs. In all plots the extended solid line through data points is guide to the eye.
The magnetic ordering temperature $T_o$ is defined by the kink in the $R(T)$ dependence clearly seen near 170 K at 2.1 GPa, the lowest pressure of the experiment. 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, as illustrated for the data at 76 GPa in Fig. 2. The observed kink/knee is due to the suppression of spin-disorder scattering upon cooling as magnetic ordering begins to set in at $T_o$ [12]. For pressures above 107 GPa the knee in $R(T)$ is no longer visible, signalling that $T_o$ for Dy has shifted above 300 K. Similar resistivity data have also been obtained for Tb [3] and Gd [2].

In Fig. 3 $T_o$ is plotted to Mbar pressures for Dy, Tb, and Gd. The results are in reasonable agreement both with earlier results to $\sim$8 GPa on Dy [13] and Tb [14] as well as resistivity studies on Dy to 69 GPa [15]. The pressure dependence $T_o(P)$ is seen to be highly non-monotonic, presumably in response to changes in crystal structure (see top of graphs). It is notable that to $\sim$50 GPa the $T_o(P)$-dependences are nearly identical for all three rare earths. Above 60 GPa, however, the dependences begin to differ markedly: whereas in Gd $T_o$ increases only slowly, $T_o(P)$ in Dy displays a rapid increase that continues unabated to the highest pressure obtained 157 GPa. Above 60 GPa $T_o(P)$ for Tb first decreases but then begins to increase rapidly. One should note that above 60 GPa the compressibility of rare earths is approximately 10-times less than that at ambient pressure [13, 14]. Plotted versus relative volume, the increase in $T_o$ for Dy above 80 GPa is far more rapid than the initial decrease at ambient pressure; in fact, on such a plot $T_o(P)$ extrapolates to $\sim$400 K at 157 GPa [2].

We now address the question as to the mechanism(s) responsible for the highly non-monotonic dependence of the magnetic ordering temperature $T_o$ of Dy, Tb, and Gd on pressure. The striking similarities in $T_o(P)$ to $\sim$60 GPa for all three point to a common mechanism. The magnetic ordering of these metals at ambient pressure is well explained [16] by a conduction-band-driven indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction [17]. Within this model the magnetic ordering temperature scales with the local moment, the magnetic susceptibility of the conduction band, and the square of the exchange interaction $J$ between the 4$f$ local moment and the conduction electrons. In fact, Fleming and Liu [18] show that the initial decrease in $T_o$ with pressure for Dy, Tb, and Gd is a direct consequence of shifts in the valence band. Furthermore, Dy [13], Tb [14], and Gd [19] undergo a very similar set of structural phase transitions driven by increasing 5$d$ electron occupation with pressure [20]. Thus changes in the susceptibility of the conduction band associated with the multiple structural phase transitions are the likely cause for the highly non-monotonic dependences $T_o(P)$ shared by Dy, Tb, and Gd to $\sim$60 GPa.

For pressures above $\sim$60 GPa, however, the pressure dependences of $T_o(P)$ for Dy, Tb, and Gd are seen to differ significantly, as pointed out above. Since their structural phase diagrams are so similar, these significant differences in $T_o(P)$ almost certainly do not originate from shifts in the energy bands but likely signal differing changes in the magnetic state of these rare earths. A long-standing strategy [21, 22] to probe the magnetic state of a given ion is to alloy the magnetic ion in dilute concentration with a superconductor and determine to what extent the superconducting transition temperature is suppressed $\Delta T_c$. As seen in the inset in Fig. 4, the pressure dependence $T_c(P)$ for Y(0.5 at.% Gd) is seen to faithfully track that for Y to the maximum pressure 126 GPa [23]. This gives evidence that over this pressure range Gd remains a conventional magnetically stable lanthanide. The absence of magnetic instabilities in Gd, even at extreme pressures, is not surprising since the magnetic state of Gd with its half-filled 4$f^7$ shell is the most stable of all elements, its 4$f^7$ level lying $\sim$ 9 eV below the Fermi level [24].

These findings for Y(0.5 at.% Gd) are in sharp contrast to those for Y(1 at.% Dy) shown in Fig. 4. As for $T_o$, the pressure dependence of $\Delta T_c$ is seen to show a sharp increase above 73 GPa, reaching the value $\Delta T_c \approx 9$ K at the highest pressure. Such a dramatic suppression of superconductivity strongly suggests that Kondo pair breaking is involved. This can occur
when the magnetic state of a rare earth nears a magnetic instability, a precursor to a change in valence where an electron jumps out of the $4f$ orbital into the conduction band. Very recent x-ray absorption near edge structure (XANES) studies confirm that no change in valence occurs in Dy to 115 GPa [25]. As the magnetic $4f$ level approaches the Fermi level, the exchange interaction with the conduction electrons takes on a negative sign, signalling the onset of strong Kondo resonance phenomena. This enhancement of the magnitude of $|J|$ with pressure causes the magnetic ordering temperature $T_o \propto |J|^2$ to increase until $|J|$ becomes so large that the local magnetic moment begins to be compensated through the exponentially increasing Kondo spin screening, as anticipated in the simple Kondo-lattice or Doniach model [26, 27] illustrated in Fig. 5. This could then lead to an anomalously high value of $T_o$, such as observed for Dy and Tb at extreme pressure, a value surpassing that possible for normal positive exchange interactions.

Figure 4. Superconducting transition temperature $T_c$ versus pressure for Y(1 at.% Dy) compared to that for Y [2]. Inset shows similar graph for Y(0.5 at.% Gd) [23]. Vertical dashed line marks pressure of volume collapse for Dy at 73 GPa [13] and in inset for Gd at 59 GPa [19]. At top of graph are crystal structures taken on by Y [15]. Extended solid line through data points is guide to the eye.

Figure 5. Magnetic ordering temperature $T_o$ plotted versus the absolute value of the negative exchange parameter $|J|$ according the Doniach model [26, 27]. Since $T_o$ increases only as $|J|^2$, but the Kondo temperature $T_K$ increases exponentially with $|J|$, the latter ultimately dominates and quenches magnetic ordering.

At pressures significantly higher than those in the present experiment, the simple Doniach model in Fig. 5 would lead one to anticipate that $T_o$ for Dy and Tb would pass through a maximum and fall rapidly to 0 K at a quantum critical point [26, 27]. Future experiments will search for this behavior either by a significant expansion of the present pressure range or by identifying a rare earth where the instabilities in the magnetic state occur at lower pressures.

In summary, measurements of the electrical resistivity of Dy, Tb, and Gd to extreme pressures show that the magnetic ordering temperature $T_o$ exhibits a highly non-monotonic pressure dependence, rising dramatically for $P > 80$ GPa to unprecedentedly high values approaching $\sim 400$ K for Dy with a similarly rapid increase for Tb. It is suggested that these anomalously high values of $T_o$ in Dy and Tb signal that these rare earths have entered an anomalous magnetic...
state, one likely related to a Kondo lattice. If so, the anomalously high magnetic ordering temperatures observed here for Dy and Tb would be an heretofore overlooked feature of the Kondo lattice state itself. A search for further lanthanide and actinide systems with anomalously high magnetic ordering temperatures would be of considerable interest and is underway.

If the mechanism(s) responsible for these anomalously high values of $T_o$ under extreme pressure can be clearly identified, one can hope to reproduce these conditions in a suitable compound at ambient pressure. This hope receives some support from the fact that the Curie temperature of the ternary compound CeRh$_3$B$_2$ is 115 K [28], a value exceeding even that of GdRh$_3$B$_2$ and 100-times higher than that anticipated from simple de Gennes scaling, surpassing even that of GdRh$_3$B$_2$. Perhaps Dy under extreme pressure and CeRh$_3$B$_2$ at ambient pressure share a common mechanism for their anomalous magnetic properties.

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References
[1] Colvin R V, Legvold S and Spedding F H 1960 *Phys. Rev.* **120** 741
[2] Lim J, Fabbris G, Haskel D and Schilling J S 2015 *Phys. Rev. B* **91** 045116
[3] Lim J, Fabbris G, Haskel D and Schilling J S 2015 *Phys. Rev. B* **91** 174428
[4] Material Preparation Center, Ames Lab, US DOE, Ames, Iowa http:www.mpc.ameslab.gov.
[5] Schilling J S 1984 *Mat. Res. Soc. Symp. Proc.* **22** 79
[6] Shimizu K, Amaya K and Suzuki N 2005 *J. Phys. Soc. Jpn.* **74** 1345
[7] Daniels W B and Ryschkewitsch W 1983 *Rev. Sci. Instr.* **54** 115
[8] Chijioke A D, Nellis W J, Soldatov A and Silvera I F 2005 *J. Appl. Phys.* **98** 114905
[9] Akahama Y and Kawamura H 2006 *J. Appl. Phys.* **100** 043516
[10] Klotz S, Schilling J S and Müller P 1991 *Frontiers of High Pressure Research*, ed H D Hochheimer and R D Etters (New York: Plenum) p 473
[11] Debessai M, Hamlin J J and Schilling J S 2008 *Phys. Rev. B* **78** 064519
[12] Coles B R 1958 *Adv. Phys.* **7** 40
[13] Patterson R, Saw C K and Akella J 2004 *J. Appl. Phys.* **95** 5443
[14] Cunningham N C, Qiu W, Hope K M, Liermann H-P and Vohra Y K 2007 *Phys. Rev. B* **76** 212101
[15] Samudala G K, Tsui G M, Weir S T and Vohra Y K 2014 *High Press. Res.* **34** 266
[16] Jackson D D, Malba V, Weir S T, Baker P A and Vohra Y K 2005 *Phys. Rev. B* **71** 184416
[17] Ruderman M A and Kittel C 1954 *Phys. Rev.* **96** 99
[18] Fleming G S and Liu S H 1970 *Phys. Rev. B* **2** 164; Liu S H 1962 *Phys. Rev.* **127** 1889
[19] Hua H, Vohra V K, Akella J, Weir S T, Ahuja R and Johansson B 1998 *Rev. High Pressure Sci. Technol.* **7** 233
[20] Duthie J and Pettifor D 1977 *Phys. Rev. Lett.* **38** 564
[21] Matthias B T, Suhl H and Corenzwit E 1958 *Phys. Rev. Lett.* **1** 92
[22] Maple M B 1976 *Appl. Phys.* **9** 179
[23] Fabbris G, Matsukoya T, Lim J, Mardegan J R L, Shimizu K, Haskel D and Schilling J S 2013 *Phys. Rev. B* **88** 245103
[24] Yin Z P and Pickett W E 2006 *Phys. Rev. B* **74** 205106
[25] Bi W, Song J, Soni V, Haskel D and Schilling J S (unpublished).
[26] Doniach S 1977 *Valence Instabilities and Related Narrow-Band Phenomena*, ed R D Parks (New York: Plenum) p 169
[27] Yang Y-f, Fisk Z, Lee H-O, Thompson J D and Pines D 2008 *Nature* **454** 611
[28] Dhar S K, Malik S K and Vijayaraghavan R 1981 *J. Phys. C* **14** L321