Evidence for strong enhancement of the magnetic ordering temperature of trivalent Nd metal under extreme pressure

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Four-point electrical resistivity measurements were carried out on Nd metal and dilute magnetic alloys containing up to 1 at.% Nd in superconducting Y for temperatures 1.5–295 K under pressures to 210 GPa. The magnetic ordering temperature \( T_o \) of Nd appears to rise steeply under pressure, increasing ninefold to 180 K at 70 GPa before falling rapidly. Y(Nd) alloys display both a resistivity minimum and superconducting pair breaking \( \Delta T_c \) as large as 38 K at 1.6 Mbar (see Fig. S1 in the Supplemental Material [8]). In the same pressure range \( P > 60 \) GPa, Dy ions in dilute concentration in superconducting Y cause giant Kondo-like pair breaking, suggesting that the anomalous increase in \( T_o \) in Dy metal may have the same origin, namely the activation of Kondo correlations as Dy nears a magnetic instability and \( J \) becomes negative [7]. Similar results are obtained for Tb [9]. In contrast, Gd fails to show either an anomalous increase in \( T_o \) or strong pair breaking in Y(Gd) under extreme pressure [9,10], presumably due to the extreme stability of Gd’s magnetic state [11].

If the anomalously high magnetic ordering temperature in Dy and Tb metals results from the increasing importance of Kondo many-body effects as the negative \( J \) increases in magnitude under extreme pressure, the Doniach phase diagram in Fig. 1 would suggest that the rapid rise in \( T_o \) with pressure should be followed by its passing through a maximum and falling rapidly to 0 K. To explore this possibility for Dy or Tb, pressures well beyond those accessible in the present resistivity experiments would be necessary. Alternately, in view of the greater spatial extent of its \( 4f \) wave function, a light lanthanide might show similar anomalous behavior in \( T_o(P) \), but at lower pressures.

Here we present temperature-dependent resistance measurements \( R(T) \) on the light lanthanide metal Nd that undergoes modulated antiferromagnetic order below \( T_n \approx 20 \) K at ambient pressure [12]. \( T_n \) is marked by a knee in \( R(T) \). Above 30 GPa, the temperature of the knee at \( T_n \) initially increases steeply with pressure, appearing to reach \( \sim 180 \) K at 60 GPa before passing through a maximum and falling towards 0 K for positive \( J \) of the same magnitude. To our knowledge, this question has yet to be addressed theoretically. An in-depth study of the evolution of the magnetic properties across the Doniach phase diagram over a wide region of parameter space should aid understanding in any particular region, including that at or near the quantum critical point.

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For lanthanide systems near a magnetic instability, the Doniach phase diagram [1] has often been invoked to illustrate the competition between the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and Kondo spin screening as a function of the negative exchange coupling \( J \) between magnetic ions and conduction electrons (see Fig. 1). In this Kondo lattice model, the magnetic ordering temperature \( T_o \) initially increases with \( |J| \), but then passes through a maximum and dives towards 0 K, the quantum critical point. In recent years, the region close to the quantum critical point has been extensively studied [2]. However, other regions in the phase diagram may also harbor interesting and unanticipated physics. The Doniach diagram has been revisited by Iglesias et al. [3] and updated by Yang et al. [4].

In general, the exchange coupling \( J \) between a magnetic ion and the conduction electrons includes both the conventional positive exchange interaction [5] and the negative covalent-mixing exchange [6]. If the magnetic state of an ion is stable, as for the majority of lanthanides at ambient pressure, the positive exchange dominates, the sign of \( J \) is positive, and \( T_o \) follows simple de Gennes scaling. However, as the ion’s magnetic state is pushed toward an instability, for example by applying sufficiently high pressure, the covalent-mixing exchange may become dominant, leading to a negative \( J \), whereby Kondo-effect phenomena strongly renormalize the RKKY interactions between ions. In this case, \( T_o \) would exhibit marked deviations from conventional de Gennes scaling. As the magnetic instability increases further, both \( |J| \) and the Kondo temperature \( T_K \) increase, eventually followed by heavy Fermion behavior, intermediate valence, and, ultimately, an increase in the valence of the magnetic ion.

Even for RKKY interactions via normal positive exchange, a reliable estimate of the magnetic transition temperature is notoriously difficult. Estimating ordering temperatures for negative \( J \) would likely be even much more difficult due to the highly correlated nature of the mediating electrons. \( T_o \) for negative \( J \) may thus lie substantially lower or higher than

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The temperature-dependent resistance $R(T)$ of Nd was measured in four separate experimental runs. Figure 2(a) shows $R(T)$ over the temperature and pressure ranges 4–295 K and 1.3–155 GPa, respectively. In run 4, temperatures to 1.5 K were reached at 51, 112, and 155 GPa. No evidence for superconductivity in Nd was found in any measurement. Referring to Fig. 2(a), the initial decrease in $R(T)$ on cooling from room temperature is moderate, followed by a sharp increase in slope $dR/dT$ marked by a kink or knee, signaling a reduction in the spin-disorder scattering $R_{sd}$ as magnetic ordering sets in. Here the magnetic ordering temperature $T_o$ is defined as the temperature where two straight red tangent lines intersect. In the present measurements, the knee in $R(T)$ is broadened by the pressure gradient across the sample arising from the nonhydrostatic pressure.

The knee in $R(T)$ at $T_o$ is seen in Fig. 2(a) to initially increase slowly with pressure, but then shoot upward for $P > 30$ GPa before passing through a maximum value $\sim 180$ K near 70 GPa, and decreasing toward 0 K near 150 GPa [see also $T_o$ in Fig. 2(b)]. A similarly rapid upward shift of the knee in $R(T)$ was also found for Dy for $P > 70$ GPa [7] (see Fig. S1 in the Supplemental Material [8]). That the knee for Dy at $T_o$ does indeed arise from magnetic ordering is supported by recent synchrotron Mössbauer spectroscopy (SMS) studies to 141 GPa [18]. Referring to Fig. 2(a), the temperature of the $R(T)$ knee for Nd agrees with the magnetic ordering temperature from magnetic studies on Nd to 1.4 GPa [19]. However, for higher pressures, particularly above $\sim 40$ GPa, the identification of the $R(T)$ knee with magnetic ordering is less clear due to the greater spatial extent of Nd’s 4f wave function compared to that of Dy. In fact, in Kondo lattice systems, a maximum (or, in some cases, a knee if the phonon scattering is sufficiently large) can appear in $R(T)$ without magnetic ordering due to the onset of coherence effects that culminate in heavy Fermion behavior at lower temperatures [20,21]. It is interesting to note that the coherence maximum or knee in $R(T)$ for the dense Kondo system CeB$_6$ shifts to higher temperatures under pressure [22], as expected if the Kondo temperature increases with pressure [21]. This contrasts to the present results for Nd above 90 GPa, where the $R(T)$ knee shifts to lower temperatures.

Support that, at least to $\sim 112$ GPa, the resistivity knee in Nd may arise from magnetic ordering is given by comparing the pressure dependence of the magnitude of the spin-disorder resistance $R_{sd}^\text{max}$ to that of $T_o$. As discussed in Ref. [7], both $T_o$ [23] and $R_{sd}^\text{max}$ [24] are proportional to $J^2N(E_F)$, where $N(E_F)$ is the density of states at the Fermi energy. Up to 112 GPa, $R(T)$ in Fig. 2(a) can be readily divided into three regions: a relatively flat region above the knee at $T_o$, a rapid decrease below $T_o$ from the temperature dependence of the spin-disorder resistance $R_{sd}(T)$, and temperature-independent defect scattering $R_d$ at the lowest temperatures. In this figure, it can be immediately seen that the magnitude of the spin-disorder resistance $R_{sd}(T)$ near $T_o$ and the value of $T_o$ itself both begin to increase strongly above 18 GPa, but then, above 95 GPa, decrease together. A crude estimate of the maximum value of $R_{sd}(T)$ is given by the expression $R_{sd}^\text{max} \sim R(T_o) - R(4\text{ K})$. The resulting dependence of $R_{sd}^\text{max}(P)$ on pressure shown in Fig. S3 of the Supplemental Material [8] closely parallels that of $T_o(P)$ in Fig. 2(b). The parallel
dependsences of $T_o(P)$ and $R_{\text{max}}(P)$ support the identification of the knee in $R(T)$ for Nd as originating from magnetic ordering. Nevertheless, to settle the matter, it is recommended that future experiments, such as SMS, x-ray magnetic circular dichroism (XMCD), or magnetic susceptibility, probe the magnetic properties of Nd directly to extreme pressures.

Another interesting feature of the data in Fig. 2(b) is that the dependence of $T_o$ on pressure for Nd between 20 and 50 GPa bears a strong resemblance to that for Dy between 60 and 110 GPa (see Fig. S1). It is as if, compared to Dy, Nd had been pressurized by approximately 50 GPa. Note that Nd takes on the double-hexagonal-close-packed (dhcp) structure at ambient pressure [25], whereas this structure does not appear in Dy until 20–40 GPa (see Fig. S1) [26]. This effect is well understood [27]. In spite of the lanthanide contraction, the structure sequence across the lanthanide series from left (light) to right (heavy) is reproduced by applying pressure to a heavy lanthanide. This apparent paradox was explained by Duthie and Pettifor [27] to be the result of $s-d$ electron transfer as the volume available to the conduction electrons outside the ion cores is diminished either by going from heavy to light lanthanides or by applying pressure. The reduction of the XANES white-line (peak) intensity under pressure in Fig. S4 is a result of this same $s-d$ charge transfer.

It would be interesting to test whether in Nd the anomalous rise and fall of $T_o$ with pressure might signal an approaching instability in the magnetic state of each Nd ion. A longstanding strategy [28,29] to probe the magnetic state of a given ion is to alloy it in dilute concentration with a superconductor having closely similar conduction electron properties and then determine to what extent the superconducting transition temperature is suppressed, $\Delta T_c$. Yttrium (Y), a superconductor under pressure [30], is the ideal host for Nd since the character of Y’s $spd$-electron conduction band closely matches that of Nd. Comparing Figs. 2(b) and 3, it is seen that for $P \geq 30$ GPa, Y’s structural sequence matches that of Nd reasonably well. The pressure dependence of superconductivity was studied in a series of dilute magnetic Y(Nd) alloys. All results for $T_c(P)$ are shown in Fig. 3 (the superconducting transitions themselves for Y(0.3 at.% Nd) are shown in Fig. S5 in the Supplemental Material [8]). In the lower-pressure region below 30 GPa, $T_c(P)$ for the Y(Nd) alloys is seen to closely track that for pure Y. However, a marked deviation appears at higher pressures. Above 70 GPa, the superconductivity is suppressed below 1.5 K for the alloy with 1 at.% Nd concentration, with lesser suppression for 0.5, 0.3, and 0.125 at.% Nd. Such giant pair breaking is clear evidence that Kondo physics has taken hold for pressures above 30 GPa.

Even as the rise in the magnetic ordering temperature $T_o$ under pressure should be followed according to the Doniach model by its passing through a maximum and falling towards 0 K, the giant pair breaking for Y(Nd) alloys seen in Fig. 3 should diminish at even higher pressures. Theoretical work [32] has shown that the rise and fall of giant Kondo pair breaking is related to the passing of the Kondo temperature through the temperature region near $T_c$. This rise and fall has been clearly demonstrated in experimental results on La(Ce) [33], La(Pr) [34], and Y(Pr) [35] alloys, among others. That the degree of pair breaking $\Delta T_c$ does indeed ultimately diminish for Y(Nd) can be most easily
FIG. 3. Dependence of superconducting transition temperature on pressure for Y metal and Y(Nd) alloys from present resistivity studies. Above 30 GPa, strong superconducting pair breaking $\Delta T_c \equiv T_c(Y) - T_c[Y(Nd)]$ occurs. At the top of the figure are crystal structures of superconducting host Y determined to 177 GPa [31].

seen in Fig. 3 for Y(0.5 at.% Nd) at pressures above 180 GPa where $T_c$ increases, whereas $T_c$ for pure Y decreases. See also Fig. S6 in the Supplemental Material [8]. Note that the maximum pair breaking occurs at a pressure (170 GPa) roughly 20 GPa above that where $T_o(P)$ for Nd appears to approach 0 K. The degree of pair breaking across the entire lanthanide series is alloyed at 1 at.% concentration into superconducting La, the largest pair breaking occurs for Gd where $\Delta T_c \approx 5$ K/at.%Gd [29].

A clear sign that Kondo physics with a negative $J$ is playing an important role in the present experiments is the appearance of a resistivity minimum in $R(T)$ if $P > 130$ GPa for all Nd concentrations except 0.125 at.% [see data for Y(0.3 at.% Nd) in Fig. 4]. For temperatures above the superconducting transition of the Y(Nd) alloy, the present experiments on pure Y show that $R(T)$ is dominated by the large phonon contribution from the Y host. In fact, as seen in Fig. 4, the rapid decrease in this phonon contribution for pressures above 136 GPa actually allows the Kondo contribution to become visible. A quantitative estimate of the Kondo temperature is not possible due to the dominance of Y’s phonon contribution [36].

The anomalous increase of $T_o$ in Nd and the onset of strong superconducting pair breaking in Y(Nd) alloys both begin at approximately the same pressure of 30–40 GPa. This points to a common mechanism: that at this pressure, the exchange parameter $J$ has become negative, thus setting off strong Kondo correlations that seriously modify the exchange interactions between Nd ions. We suggest that as $|J|$ increases with pressure, $T_o$ begins to ramp up the left side of the Doniach phase diagram in Fig. 1. Note that whereas $T_o(P)$ in Fig. 2(b) reaches a maximum near 60–80 GPa, the maximum pair breaking occurs near 130–170 GPa, which is the same pressure range where magnetic order in Nd appears to be suppressed. In this picture, the same negative exchange parameter $J$ is responsible for both strongly enhanced magnetic ordering and the quenching of magnetic order if $|J|$ becomes sufficiently large. Future direct measurements of Nd’s magnetic properties should probe whether magnetic ordering occurs at $T_o$ over the entire present pressure range.

In summary, the magnetic ordering temperature $T_o$ of Nd appears to increase near 70 GPa to nine times its ambient pressure value before falling towards 0 K. Evidence for the involvement of Kondo physics is given both by the appearance of a resistivity minimum and extraordinarily strong superconducting pair breaking in dilute Y(Nd) alloys at extreme pressures. The authors hope this work will lead to increased theoretical activity in this area.

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