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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 ΔT_c as large as 38 K/at.% Nd. The present results give evidence that for pressures above 30–40 GPa, the exchange coupling J between Nd ions and conduction electrons becomes negative, thus activating Kondo physics in this highly correlated electron system. The rise and fall of T_o and ΔT_c with pressure can be accounted for in terms of an increase in the Kondo temperature.

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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 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.

In a recent paper [7], evidence is given from electrical resistivity measurements that when subjected to pressures above 60 GPa, T_o for Dy metal begins to rapidly soar upward and pass through ambient temperature near 120 GPa (1.2 Mbar), extrapolating to ∼400 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 $T_o \simeq 20$ K at ambient pressure [12]. T_o is marked by a knee in $R(T)$. Above 30 GPa, the temperature of the knee at T_o initially increases steeply with pressure, appearing to reach ∼180 K at 60 GPa before passing through a maximum and falling towards 0 K

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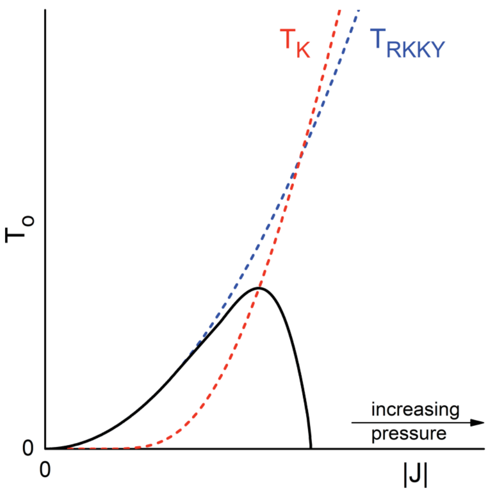

FIG. 1. Magnetic ordering temperature T_o vs absolute value of negative exchange parameter J according to the Doniach model [1]. Since T_{RKKY} increases as J^2 but is overtaken by the exponential increase of the Kondo temperature T_K, the magnetic ordering is quenched.

near 150 GPa. The superconducting pair breaking in dilute magnetic Y(Nd) alloys also begins to increase sharply above 30 GPa, reaching a maximum value near 150 GPa. These results appear consistent with a Doniach-like model where both $|J|$ and the Kondo temperature T_K increase with pressure.

Four-point dc electrical resistivity measurements with 1 mA excitation current were carried out on samples cut from Nd foil as well as dilute magnetic alloys of Y(Nd) prepared by argon arc-melting Y and Nd (99.9%, Ames Laboratory [13]) together. To generate pressures as high as 210 GPa over the temperature range 1.5–295 K, a diamond anvil cell (DAC) made of CuBe alloy was used [14]. In all measurements, pressure was generated by two opposing diamond anvils (1/6-carat, type Ia) with 0.18-mm-diameter culets beveled at 7 degrees to 0.35 mm. Four thin (5-μm-thick) Pt strips made electrical contact to the sample ($\sim 40 \times 40 \times 5\ \mu\text{m}^3$). Details of the nonhydrostatic pressure technique used were published earlier [7,15]. The pressure at room temperature was determined by Raman spectroscopy from the diamond vibron [16]. A ruby manometer [17] revealed a linear pressure increase of ~30% on cooling from 295 to 4 K. These data are used to estimate the pressure at a temperature close to that of the magnetic or superconducting transition.

High-pressure x-ray absorption near-edge spectroscopy (XANES) experiments on Nd's L_3 edge (6.208 keV) used transmission geometry at beam line 4ID-D at the Advanced Photon Source (APS), Argonne National Laboratory. Anvils with 100 μm culet diameter beveled to 300 μm and Re gaskets allowed pressures to 97 GPa. To reduce the x-ray absorption by the diamond anvils, a full anvil in combination with a fully perforated anvil and a mini anvil (~0.7 mm height) was used. A 5-μm-thick Nd foil sample from Goodfellow (99% purity) was cut to $\sim 25 \times 25\ \mu\text{m}^2$ and loaded into the sample chamber together with silicone oil as pressure medium and ruby spheres for pressure calibration [17]. The XANES measurements at ambient temperature show that Nd remains firmly trivalent to at least 97 GPa (see Fig. S4 in the Supplemental Material [8]).

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 ~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 pressure [19]. However, for higher pressures, particularly above ~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 ~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}^{max} to that of T_o. As discussed in Ref. [7], both T_o [23] and R_{sd}^{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 $R_{sd}^{max} \simeq R(T_o) - R(4\text{ K})$. The resulting dependence of $R_{sd}^{max}(P)$ on pressure shown in Fig. S3 of the Supplemental Material [8] closely parallels that of $T_o(P)$ in Fig. 2(b). The parallel

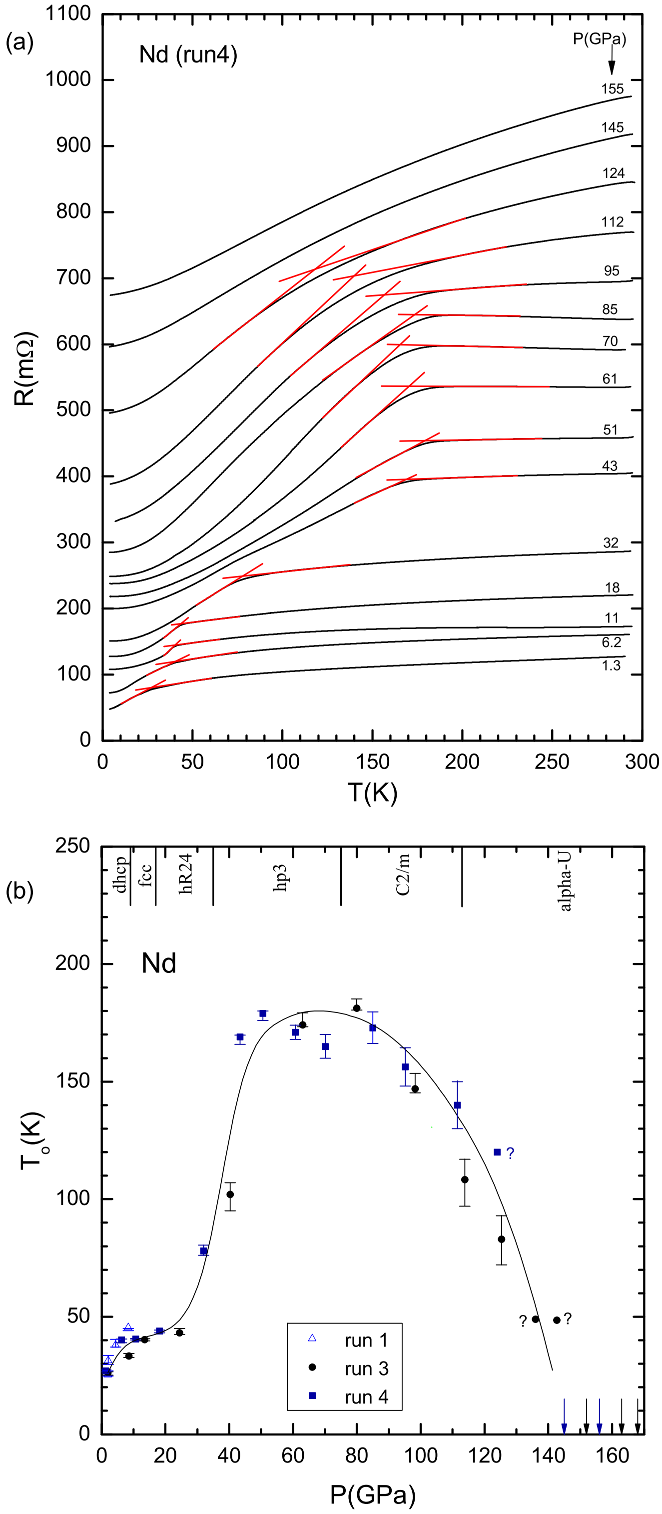

FIG. 2. (a) Four-point resistance of Nd vs temperature in run 4 at various pressures. Resistance values apply for measurement at 1.3 GPa; all other data are shifted vertically for clarity. Figure S2 in the Supplemental Material [8] gives the actual resistance values at 290 and 4 K. (b) Magnetic ordering temperature of Nd vs pressure. The extended solid line through the data points is a guide to eye. Vertical arrows give pressures in runs 3 and 4 where no magnetic transition was seen. Question marks (?) accompany data points where evidence for magnetic ordering is very weak. Structures for Nd (top of graph) were determined to 155 GPa [25].

dependences of $T_o(P)$ and $R_{sd}^{max}(P)$ 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 prepressurized 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, ΔT_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 $P \geqslant 30$ 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 ΔT_c does indeed ultimately diminish for Y(Nd) can be most easily

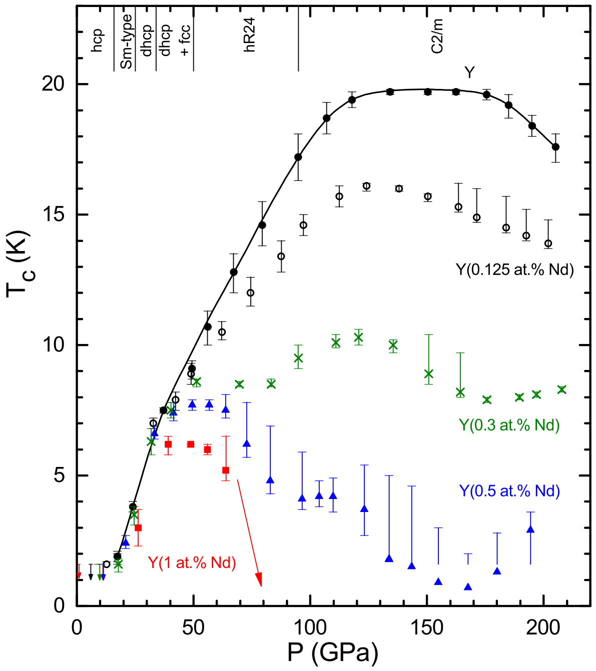

FIG. 3. Dependence of superconducting transition temperature on pressure for Y metal and Y(Nd) alloys from present resistivity studies. Above 30 GPa, strong superconducting pair breaking $\Delta T_c \equiv T_c(\mathrm{Y}) - T_c[\mathrm{Y(Nd)}]$ occurs. At the top of the figure are crystal structures of superconducting host Y determined to 177 GPa [31].

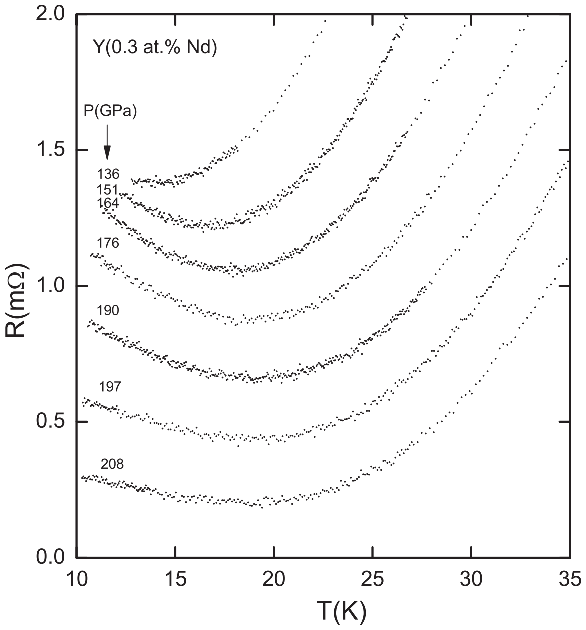

FIG. 4. Resistance of Y (0.3 at.% Nd) vs temperature at several pressures showing Kondo minima.

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 ΔT_c here is extremely large, growing to a maximum value of $\Delta T_c \simeq 38$ K/(at.% magnetic impurity). If each magnetic ion 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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