Anomalous Magnetism and Superconductivity in Lanthanide Metals at Extreme Pressure

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Under ambient pressure the only lanthanide known to superconduct is La, the superconducting state for the remaining lanthanides being suppressed by their strong local-moment magnetism. Except for possibly Ce, this magnetism is conventional and approximately obeys de Gennes scaling. Under high pressure both Ce and Eu exhibit superconductivity that may be unconventional, whereas the magnetic states of Dy, Tb, and Nd become anomalous, the magnetic ordering temperature of Dy surpassing ambient temperature at Mbar pressures. We suggest that these anomalously high magnetic ordering temperatures are an heretofore unrecognized feature of the Kondo lattice state.

Keywords: high pressure, Kondo lattice, superconductivity.

1. Introduction

As well illustrated in the theoretical work of the Professor Renato Pucci, high pressure is a thermodynamic variable that is particularly well suited to further our understanding of complex states of matter. The static multi-Mbar pressures available today through diamond-anvil cell technology are sufficient to increase the energy per atom by 1-10 eV and thus are capable of significantly altering the ground states of matter. For example, stable magnetic systems eventually destabilize under sufficient pressure, leading to new and unexpected forms of magnetism and/or superconductivity.

In the Periodic Table of Superconductivity (see Fig 1)[1] the 30 elements known to superconduct at ambient pressure appear with a yellow background whereas light green adorns the additional 23 elements that only become superconducting under high pressure. Of particular interest is the lanthanide series of elements where the magnetic $4f$ orbitals are successively filled with electrons, yielding a localized magnetic state on each ion that suppresses superconductivity. Non-magnetic La, being devoid of $4f$ electrons, is the only lanthanide that superconducts at ambient pressure.

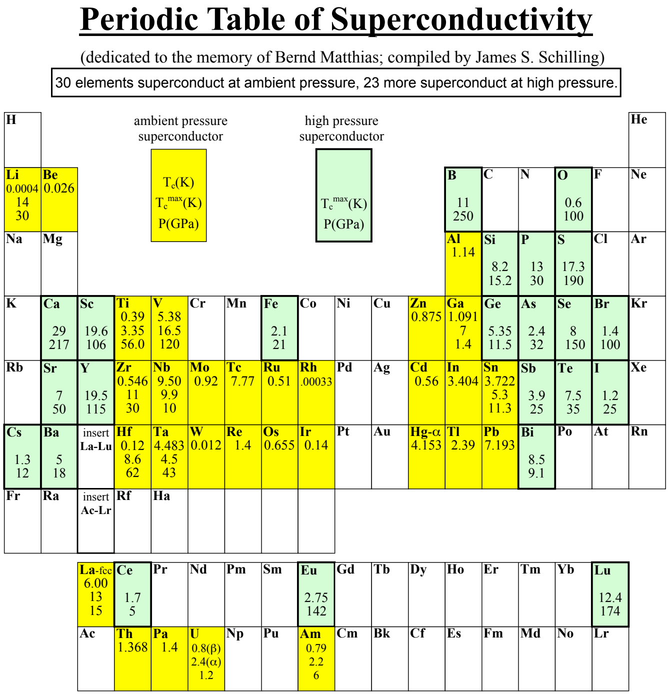


Fig. 1. Periodic Table listing elements that superconduct at ambient pressure (yellow) or only under high pressure (light green).[1] For each element the upper position gives the value of T_c(K) at ambient pressure; middle position gives maximum value $T_c^{\max}$(K) in a high-pressure experiment at the pressure P(GPa) (lower position). If T_c decreases under pressure, only the ambient pressure value of T_c is given. Sources for T_c values are given in Ref. 2.

La's neighbor, Ce, is magnetic with one $4f$ electron, but becomes superconducting under pressure at 5 GPa.[3] As seen in Fig 2, at 7 kbar (0.7 GPa) Ce suffers a large 16% volume collapse within the fcc structure[4] whereby its magnetic moment appears to be quenched. Near this volume-collapse pressure a dilute (2 at.%) concentration of magnetic Ce impurities in La is seen to strongly suppress La's superconductivity over a narrow pressure region.[5] This is the hallmark of Kondo effect phenomena with giant pair breaking.[6] A Kondo resistivity minimum has also been observed in dilute La(Ce) alloys.[7] Ce's volume collapse itself can be accounted for within the Kondo volume collapse model of Allen and Martin.[8]

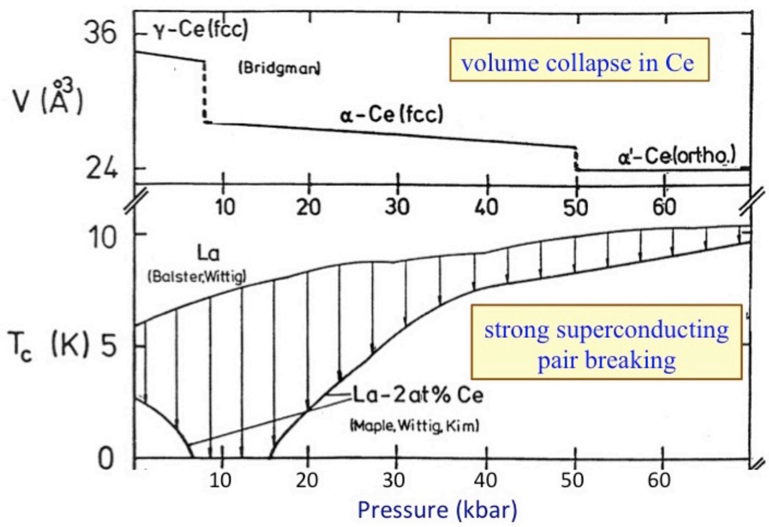


Fig. 2. (upper) Molar volume versus pressure in kbar (0.1 GPa), showing 16% volume collapse at 0.7 GPa ($\gamma-\alpha$ transition).[4] (lower) Superconducting transition temperature of the dilute magnetic alloy La(2 at.% Ce) versus pressure compared to that of pure La.[5] The very large superconducting pair breaking in the alloy leads to a "sinkhole-like" depression of T_c near 1 GPa.

The appearance of Kondo effect phenomena indicates that the magnetic state of Ce is approaching an instability. Besides suppressing superconductivity, the Kondo effect can also quench magnetic order, sometimes leading to exotic forms of superconductivity. This scenario is illustrated in Fig 3 where the magnetic ordering temperature T_o is plotted versus the magnitude of the negative covalent mixing exchange parameter $|J|$. This is the well-known Kondo-lattice model of Doniach[9] and Yang.[10] Since the magnetic ordering strength T_{RKKY} from the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction[11] initially increases as J^2, but the Kondo temperature T_K increases exponentially with $|J|$, the latter eventually overtakes the former as $|J|$ increases and the magnetic order is quenched. The author, and probably most, if not all, scientists working in the highly correlated electron research area, have tacitly assumed that the value of T_o

from the negative covalent mixing exchange must be weaker than that arising from normal positive exchange. Our present results suggest that the opposite is the case, as we will soon see.

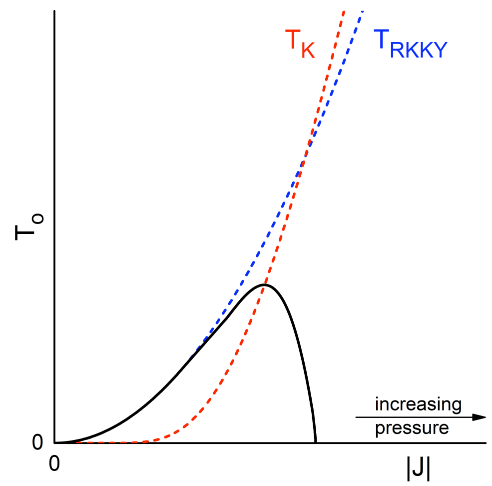


Fig. 3. Magnetic ordering temperature T_o plotted versus the absolute value of the negative exchange parameter $|J|$ according the Doniach-Yang model.[9,10] Since T_o increases only as $|J|^2$, but the Kondo temperature T_K increases exponentially with $|J|$, the latter ultimately dominates and quenches magnetic ordering.

2. Results and Discussion

Since the normal exchange interaction and the electronic properties of the conduction electrons change relatively slowly across the lanthanide series, the values of T_o would be expected to approximately obey de Gennes scaling, whereby $T_o \propto (g-1)^2 J_t(J_t+1)$;[12] here J_t is the total angular momentum quantum number and g is the Landé-g factor. Ce is an exceptional case; T_o for Ce lies at 13.7 K in the hexagonal phase, a value 4-times higher than that (3.3 K) expected from simple de Gennes scaling compared to Gd, where T_o = 292 K.[13] Likewise, the suppression of the superconducting transition temperature ΔT_c in dilute magnetic alloys should also follow de Gennes scaling.[6] Compared to the other magnetic lanthanides in dilute (1%) alloys with superconducting La, ΔT_c for Ce is much larger than anticipated.[14] The anomalously high value of the magnetic ordering temperature T_o = 13.7 K for Ce could have been a tip off that anomalously high values of T_o might be possible within the Kondo-lattice model.

At ambient pressure Eu is a trivalent metal that orders antiferromagnetically near $T_\mathrm{o} = 90$ K.[15] Previous studies of the dependence of T_o on pressure were restricted to $P \leq 42$ GPa.[16] In recent electrical resistivity and ac magnetic susceptibility measurements to pressures as high as 142 GPa, superconductivity in Eu was found to appear for pressures above 80 GPa,[17] as seen in Fig 4. Eu thus became the latest pressure-induced superconducting element. Unfortunately the magnetic ordering temperature of Eu could not be determined in this experiment so it was not possible to investigate the possible interplay between the magnetic and superconducting states, as indicated for the Doniach-Yang model in Fig 3. Although the complete magnetic/superconducting phase diagram has yet to be mapped out, a very recent Synchrotron Mössbauer Spectroscopy (SMS) experiments to 101 GPa finds that magnetic order in Eu vanishes near the same pressure (80 GPa) where the superconducting transition appears.[19] A parallel X-ray Emission Spectroscopy (XES) experiment on Eu to 119 GPa found no evidence for a change in either Eu's local magnetic state or in its valence.[19] It would be very interesting to accurately track in a single experiment the pressure dependence of both the magnetic ordering T_o and superconducting T_c temperatures in Eu to at least 100 GPa pressure. In recent electrical resistivity measurements the pressure dependence of T_o has been determined for Dy,[20] Tb,[21] Gd,[21] and Nd[22] to pressures of ~ 150 GPa.

The magnetic ordering of the lanthanides at ambient pressure is well explained[12,23] by a conduction-band-driven indirect RKKY exchange interaction.[11] As pointed out above, the magnetic ordering temperature T_o, as well as the strength of superconducting pair breaking ΔT_c, are both expected to scale with the de Gennes factor $(g-1)^2 J_t(J_t+1)$ modulated by $JN(E_f)$,[12] where J is the exchange interaction between the $4f$ ion and the conduction electrons and $N(E_f)$ is the density of states at the Fermi energy. The heavy lanthanide Dy possesses a large local magnetic moment and orders antiferromagnetically at 178 K. The value of this ordering temperature is approximately consistent with that of Gd at 292 K since the de Gennes factor of Dy is about half that of Gd.

In Fig 5 are shown the pressure-dependent magnetic ordering temperatures of Dy and Gd from recent electrical resistivity measurements in a diamond-anvil cell to 157 GPa for Dy and 105 GPa for Gd.[20] Both lanthanides are seen to undergo similar structural phase transitions over this pressure range and exhibit a $\sim$4% volume collapse near 60-70 GPa, a much smaller value than that of Ce (16%). Up to 70 GPa the pressure depen-

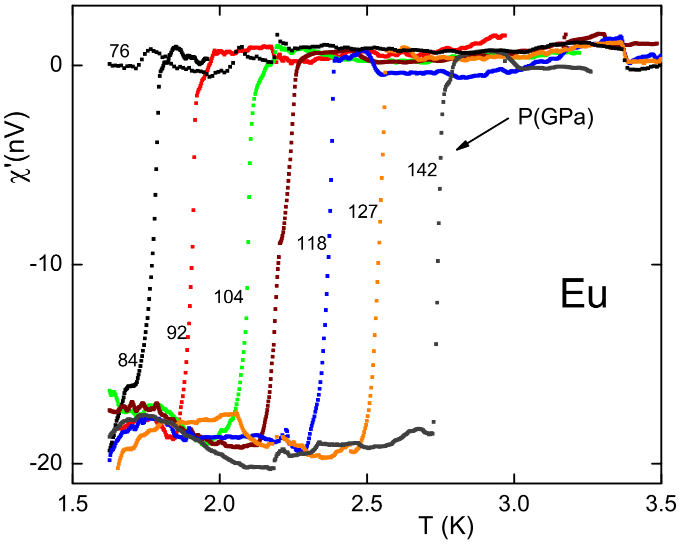
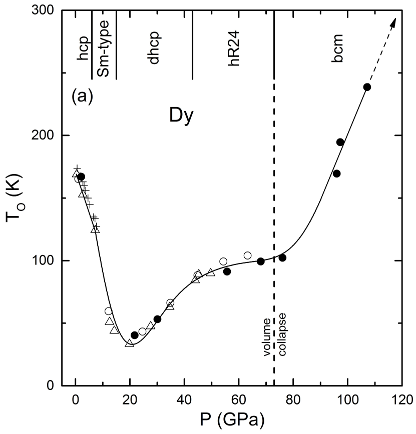


Fig. 4. Real part of the ac susceptibility versus temperature for Eu metal as pressure is increased from 76 to 142 GPa.[17] The superconducting transition appears at 84 GPa and shifts slowly under pressure to higher temperatures.

dences $T_o(P)$ for Dy and Gd are seen to be very similar. The same applies for Tb.[21] Since the de Gennes factor would not be expected to change under pressure, unless a valence transition occurs, the very similar pressure dependences $T_o(P)$ of Gd and Dy to 70 GPa point to a common mechanism and likely originate from the pressure dependence of $JN(E_f)$, facilitated by a series of nearly identical phase transitions in Dy,[24] Tb,[25] and Gd[26] driven by increasing 5d-electron concentration with pressure.[27] In fact, Fleming and Liu[28] show that the initial decrease in T_o with pressure for Dy, Tb, and Gd is a direct consequence of energy shifts in the valence band structure.

Above 70 GPa, however, the $T_o(P)$ dependences for Dy and Gd are seen in Fig 5 to differ markedly, $T_o(P)$ for Dy showing an extremely rapid increase with pressure, extrapolating to 400 K at the highest pressure of the experiment (157 GPa).[20] How rapid this increase really is most clearly demonstrated if T_o is plotted versus relative sample volume V/V_o; in such a plot it can be seen that the increase in T_o above 70 GPa is *far* more rapid



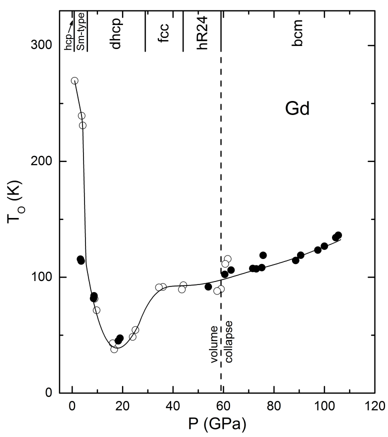


Fig. 5. Magnetic ordering temperature $T_{\rm o}$ of Dy and Gd versus pressure[20]. (+) earlier studies to ∼8 GPa on Dy.[24] References for crystal structures at top of graphs Dy,[24] Gd;[26] vertical dashed line gives pressure where 5-6% volume collapse occurs. In both plots the extended solid line through data points is guide to the eye.

than the initial decrease with pressure.[20] For lanthanides the compressibility near 70 GPa is approximately 10-times less than that at 1 bar.[24,25]

Note that the $T_{\rm o}(P)$ dependence for Gd shows only a slow increase with pressure, in contrast to the results for Dy. Since the conduction electron properties of Dy and Gd are so similar, the extremely rapid increase of $T_{\rm o}$ above 70 GPa would suggest that Dy's magnetic state has changed in a significant way. This would be the case if the magnetic state of Dy at these extreme pressure is becoming unstable leading to an increase in the magnitude of the negative covalent mixing exchange parameter $|J|$ and consequently in the Kondo temperature $T_{\rm K}$. The question thus arises whether the rapid increase in $T_{\rm o}$ under pressure for Dy might be mirroring the left part of the Doniach-Yang phase diagram in Fig 3 where $T_{\rm o}$ is seen to increase rapidly with $|J|$. If this is the case, then, on the basis of Fig 3, it would be expected that at pressures well above 157 GPa, $T_{\rm o}$ for Dy would begin to fall rapidly toward 0 K. Unfortunately, pressures appreciably above 157 GPa are extremely difficult to obtain in a true four-point resistivity experiment.

That the temperature-dependent resistivity gives a reliable value for the magnetic ordering temperature $T_{\rm o}$ has been very recently confirmed through SMS measurements by Bi *et al.*[29] on Dy to pressures as high as 141 GPa.

Parallel experiments on the lanthanide Tb[21] yield results similar to those for Dy. Above 80 GPa T_o for Tb begins to rise with pressure extremely rapidly to the highest pressure of the experiment at 141 GPa.

Why does the $T_o(P)$ dependence for Gd above 70 GPa differ so markedly from that of Dy and Tb? The absence of magnetic instabilities in Gd, even at extreme pressures, is not surprising since the magnetic state of Gd with its half-filled $4f^7$ shell is by far the most stable of all elements, its $4f^7$ level lying $\sim$ 9 eV below the Fermi level.[30] A pressure of "only" 100 GPa (1 Mbar) is not nearly enough to destabilize Gd. This is reflected in the slow monotonic increase of T_o with pressure for Gd in the bcm phase seen in Fig 4.

It is well known that the electronic properties across the lanthanide series are closely related. From La to Lu the number of d-electrons per atom decreases monotonically, nicely accounting for the observed changes in crystal structure.[27] Under pressure the d-electron count per atom increases and leads to the same progression of crystal structures under pressure as from right to left across the lanthanide series.[27] The conduction electron environment of the magnetic $4f$ orbitals changes only slowly across the series. A long-standing strategy[6,14] to probe the magnetic state of a given ion in a concentrated magnetic material is to alloy the magnetic ion in dilute concentration with a superconductor and determine to what extent the superconducting transition temperature is suppressed ΔT_c. If the magnetic state of Dy becomes unstable under pressures above 70 GPa, one would expect that a dilute concentration of Dy in superconducting La or Y would show an anomalously strong suppression of superconductivity near this pressure.

That this actually occurs is seen in Fig 6 where the pressure dependence of T_c for pure Y is compared to that of the dilute magnetic alloy Y(1 at.% Dy). $T_c(P)$ for the alloy begins to markedly pull away from that of Y above 70 GPa, i.e. ΔT_c increases sharply! The pair-breaking near 120 GPa is seen to be very strong, approaching $\Delta T_c \approx 9$ K. A similar result is obtained for dilute alloys of Y with Tb.[21]

On the other hand, alloying the ultrastable Gd ion into Y gives a very different result. $T_c(P)$ for both Y and Y(0.5 at.% Gd) track each other over the entire range of pressure.[31] This result supports the scenario that the very rapid increase in T_o with pressure above 70 GPa for Dy and Tb has its origin in the increasing instability of their magnetic states. Very recent X-ray Absorption Near Edge Structure (XANES) studies confirm that no change in valence occurs in Dy to 115 GPa,[18] as was found earlier for Tb to 65 GPa.[31] As the magnetic $4f$ level approaches the Fermi

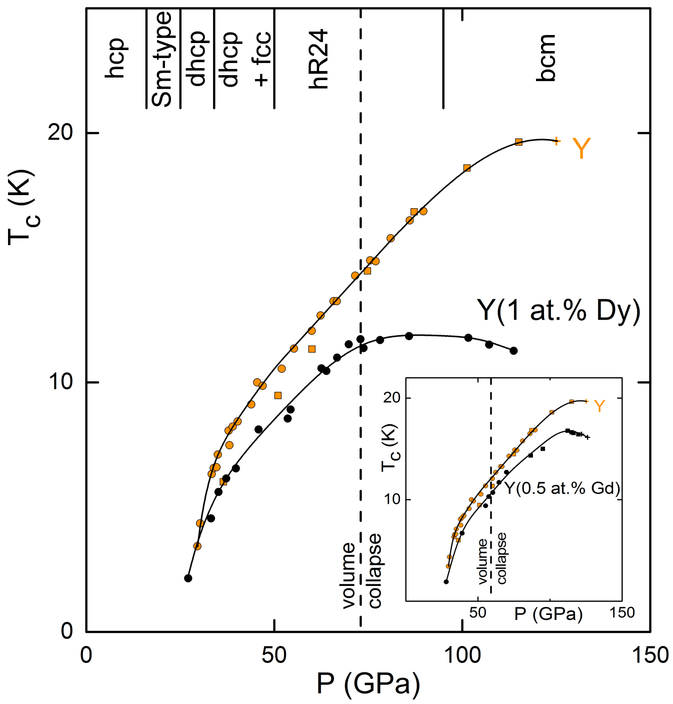


Fig. 6. Superconducting transition temperature T_c versus pressure for Y(1 at.% Dy) compared to that for Y.[20] Inset shows similar graph for Y(0.5 at.% Gd).[31] Vertical dashed line marks pressure of volume collapse for Dy at 73 GPa[24] and in inset for Gd at 59 GPa.[26] At top of graph are crystal structures taken on by superconducting host Y.[32] Extended solid line through data points is guide to the eye.

level with increasing pressure, 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 Doniach-Yang Kondo-lattice model[9,10] (see Fig 3). This then leads 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.

To establish whether or not a Doniach-Yang-like model is appropriate to interpret the present results for Dy and Tb, much higher pressures would be necessary to search for the sharp downswing in $T_o(P)$ seen in Fig 3. Since this is not currently feasible experimentally, another option is to search for a lanthanide where the anomalous dependence in $T_o(P)$ begins to occur at a much lower pressure. In very recent resistivity measurements on Nd, Song *et al.*[22] have found a Doniach-Yang-like $T_o(P)$ dependence where T_o first rises slowly, then rapidly, but then passes through a maximum and falls toward 0 K under pressure. For dilute Nd magnetic impurities in Y the suppression of superconductivity is found to be even more dramatic than for Dy or Tb impurities. In addition, for pressures near 100 GPa a Kondo resistivity minimum is found for Y(Nd) alloys. These results are the subject of a future publication.[22]

In summary, in contrast to the magnetically ultrastable lanthanide Gd, the magnetic ordering temperature T_o increases dramatically for pressures above 70 GPa for Dy and Tb and 20 GPa for Nd. In the same pressure region dilute magnetic impurities of Dy, Tb, and Nd in superconducting Y show giant pair breaking effects. These results are consistent with the scenario that under extreme pressures these three lanthanide metals approach a magnetic instability and turn into Kondo lattices.

Lanthanide elements play a central role in many modern technologies, including permanent magnets, computer memories, and applications requiring giant magnetostriction. Unfortunately, their sub-ambient magnetic ordering temperatures T_o force the addition of transition elements to substantially raise T_o, such as Fe or Co in $SmCo_5$ and $Nd_2Fe_{14}B$, the two most powerful permanent magnetic materials. If the mechanism(s) responsible for these anomalously high values of T_o under extreme pressure can be clearly identified, one can try to reproduce these conditions in a suitable compound at ambient pressure and possibly synthesize a superior permanent magnet material. This strategy receives some support from the fact that the Curie temperature of the ternary compound $CeRh_3B_2$ lies at 115 K,[33] a value even exceeding that of $GdRh_3B_2$ and 100-times higher than that anticipated from simple de Gennes scaling. We suggest that Dy under extreme pressure and $CeRh_3B_2$ at ambient pressure may share a common mechanism for their anomalous magnetic properties.

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