Pressure-Induced Superconductivity in Elemental Ytterbium Metal

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Ytterbium (Yb) metal is divalent and nonmagnetic ($4f^{14}$ configuration). Under pressure its valence increases significantly leading to the expectation that magnetic instabilities and other highly correlated electron effects may appear before a stable trivalent state is reached ($4f^{13}$ configuration). We carried out electrical resistivity and ac magnetic susceptibility measurements to 179 GPa over the temperature range 1.4–295 K. No evidence for magnetic order is observed. However, Yb becomes a superconductor at 86 GPa with $T_c \simeq 1.4$ K, increasing to 4.6 K at 179 GPa. X-ray absorption spectroscopy shows that Yb remains mixed valent to at least 125 GPa, pointing to an active role of f electrons in the emergence of superconductivity in this simple, elemental solid.

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The majority of elemental solids in the periodic table are superconductors: 31 at ambient pressure and 22 more under high pressure [1,2]. The transition elements are by far the most successful. This is not surprising given the fact that d-electron character in the conduction band strongly enhances the electronic density of states at the Fermi energy $N(E_f)$, a quantity with which the critical temperature T_c increases exponentially according to the BCS theory of superconductivity. The general phenomenon in metals of s-d transfer under pressure [3,4] is also likely responsible for the unusually high values of T_c observed for the alkaline earths Ca and Sr, as well as their neighboring beginning transition elements Sc($3d$) and Y($4d$), respectively.

Of the 15 lanthanide metals, only 4 are known to superconduct: La at ambient pressure and Ce, Eu, and Lu under high pressure [1,2]. The paucity of superconductivity in the lanthanides is mainly due to their strong local-moment magnetism. This observation is consistent with the absence (presence) of superconductivity in heavy (light) actinide elements where $5f$ electrons display localized (itinerant) behavior. Yb is special in that at ambient pressure its divalent state features a nonmagnetic filled $4f^{14}$ orbital configuration, as evidenced in magnetic susceptibility measurements [5] and from the absence of magnetic ordering in resistivity studies [6].

All neutral lanthanide atoms in a vapor are divalent except Ce, Gd, and Lu which are trivalent. With the exception of Eu and Yb, all divalent lanthanides become trivalent after condensing into elemental solids whereby one $4f$ electron is transferred into the conduction band. Applying high pressure forces the atoms in a solid even closer together so that it is reasonable to anticipate that divalent atoms would eventually become trivalent or trivalent atoms tetravalent. One would, therefore, anticipate that under sufficient pressure Yb would ultimately become fully trivalent, taking on the magnetic $4f^{13}$ configuration and ordering magnetically at some temperature T_o. As discussed below, de Gennes factor considerations lead to an anticipated magnetic ordering temperature for *trivalent* Yb near 6 K.

Whether Yb reaches a fully trivalent, magnetically ordered state at sufficiently high pressure is certainly interesting in its own right. However, of far greater physical significance are the progressive changes that may occur in the electronic and magnetic properties through the application of successively higher pressure, including anomalous superconductivity, just before, during, or just after the change in valence itself. Bringing the highly localized lanthanide $4f$ state up to the Fermi energy of an s, p, d-electron conduction band would be expected to lead to a plethora of highly correlated electron phenomena with a richness much greater than is possible with s, p, d electrons alone. Examples of such phenomena include anomalous magnetism [7] or superconductivity [8], quantum phase transitions [9,10], and Kondo lattice behavior [7,11], including the anomalously high magnetic ordering temperatures reported for selected lanthanides [12–14] under extreme pressure. While examples abound of f-electron systems where magnetic order is replaced by superconductivity under pressure at quantum critical points [8,15–17], the reverse transformation is less common. It would thus seem possible that a superconducting state could emerge in Yb before a magnetically ordered state is stabilized.

Whereas early x-ray absorption measurements found Yb to be trivalent (or nearly trivalent) at 34 GPa [18], a later study over the same pressure range concluded that Yb's valence saturates at approximately 2.7 [19]. Theoretical calculations indicate that the valence of Yb does indeed increase with pressure, but the estimated degree of increase depends on the approximations used [20]. The equation of state and structural phase transitions in Yb have been determined at ambient temperature to pressures as high as 202 GPa [21], extended very recently to 230 GPa [22]. These authors conclude that Yb is trivalent for pressures of 100 GPa and above.

Studying the anticipated nonmagnetic-magnetic transition in Yb would provide important information to further our understanding of highly correlated electron phenomena in, for example, Yb-based compounds [23–27] that exhibit heavy fermion, quantum critical, non-Fermi liquid, magnetic ordering, and/or unconventional superconductivity. Very recently β-$YbAlB_4$ [23] was reported to be the first superconducting Yb-based heavy-fermion system, where $T_c \simeq 80$ mK.

Previous high-pressure transport studies on Yb have focused on the metal-insulator transition below 5 GPa [28,29]; another resistivity experiment extended the pressure range to 16 GPa [30]. Neither magnetic ordering nor superconductivity were observed above 2 K. In this Letter we extend previous transport, magnetic, and x-ray absorption measurements on Yb to pressures exceeding 100 GPa (1 Mbar). Both electrical resistivity and ac magnetic susceptibility measurements confirm that Yb becomes superconducting above 80 GPa at 1.4 K with T_c increasing to ~4.6 K at 179 GPa. No sign of magnetic order is observed over this entire pressure range. In fact, x-ray absorption studies show that Yb remains mixed valent to at least 125 GPa. The emergence of bulk superconductivity in the presence of mixed valency near a magnetic instability points to an active role of f electrons. The relative simplicity of an elemental solid harboring these phenomena should facilitate theoretical studies and further understanding of other $4f$ and $5f$ electron systems with more complex binary and ternary compositions.

To generate pressures beyond 1 Mbar, a membrane-driven diamond anvil cell made of CuBe alloy was used. Four-point dc electrical resistivity measurements used a thin square-shaped Yb sample (Alfa Aesar, 99.9%) placed atop four thin Pt leads with a 4:1 cBN-epoxy mixture used to insulate the rhenium gasket and serve as pressure medium. The ac susceptibility $\chi(T)$ measurements used a MP35N gasket (neither superconducting nor magnetic) and were conducted without pressure medium. X-ray absorption measurements across the Yb L_3 edge (8.9 keV) were carried out at beam-line 4-ID-D of the Advanced Photon Source. Extensive details on the various experimental techniques are provided in the Supplemental Material [31].

The temperature dependence of the resistivity for Yb, $R(T,P)$, was determined for pressures exceeding 1 Mbar in two separate experiments. The data obtained in the first are shown in Fig 1(a) and its inset for pressures to 179 GPa. Careful examination reveals that all $R(T)$ data increase smoothly with temperature over the entire temperature range 1.4–295 K, giving no evidence for magnetic order.

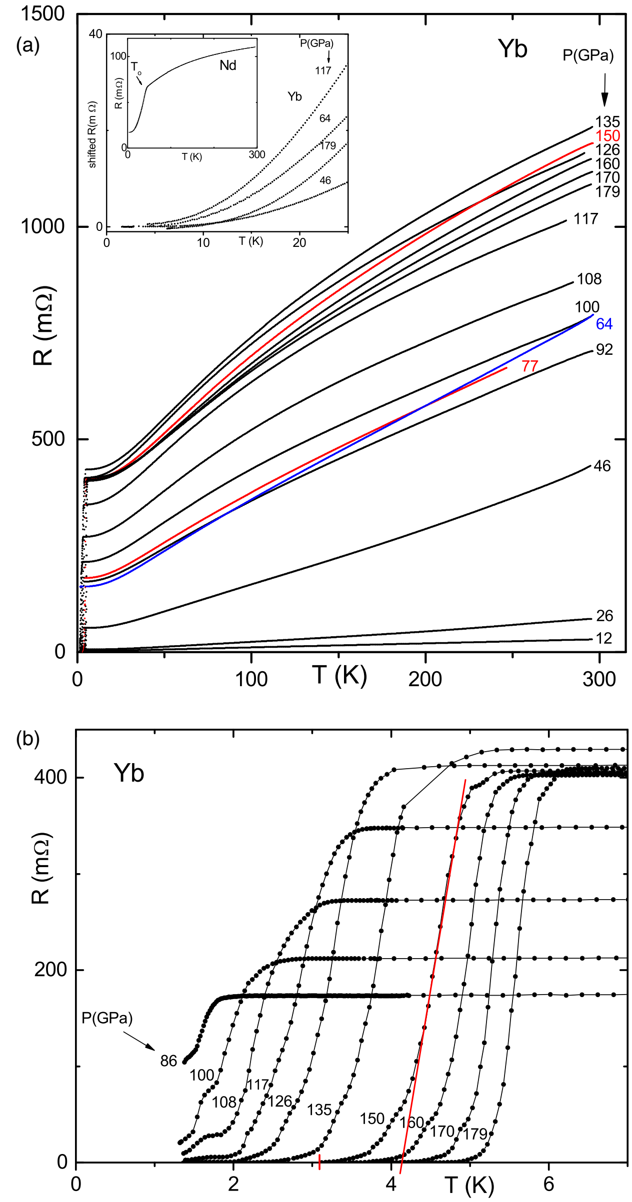

FIG. 1. (a) Resistance of Yb in run R1 versus temperature from 1.4 to 295 K for pressures to 179 GPa at low temperature. The maximum value of the residual resistance ~430 mΩ corresponds to a resistivity of approximately 10 $\mu\Omega$ cm. Inset shows smooth $R(T)$ dependence below 25 K; note that residual resistance at 4 K has been subtracted off. Inset inside inset shows sharp break in slope of $R(T)$ for Nd signaling magnetic ordering at $T_o \simeq 44$ K [12]. (b) Resistance data from (a) for temperatures 1.4 to 7 K showing superconducting transitions for pressures 86 GPa and above. Data at 86 GPa are from run R2. Here T_c is defined (see, for example, data at 150 GPa) as temperature where the straight red line through data hits the temperature axis; vertical tick marks temperature where $R(T)$ vanishes.

The inset inside the inset displays for an earlier experiment on Nd [12] the typical break in slope of $R(T)$ (resistivity knee) that signals the occurrence of magnetic ordering at the temperature $T_o \simeq 44$ K. At both ambient and low temperatures the resistance of Yb is seen to increase with pressure to 135 GPa, but then to decrease at higher pressures. Part of the large increase in the resistance is due to the plastic deformation of the sample under the nonhydrostatic pressure.

For pressures of 86 GPa and above the resistance at low temperatures is seen to fall towards zero, pointing to a transition to superconductivity. This is illustrated more clearly in Fig 1(b) where the resistance is seen to fall completely to zero at most pressures to 179 GPa. In addition, no change in the shape of the transition is observed if the current is reduced from 0.5 to 0.1 mA, thus pointing to bulk, rather than filamentary, superconductivity. These results were confirmed by a second resistivity experiment to extreme pressures.

A superior test for superconductivity is a measurement of the magnetic susceptibility. In Fig. 2(a) the real part of the temperature-dependent ac magnetic susceptibility $\chi\prime(T)$ of Yb is shown for one of three experiments. The onset of superconductivity is signaled by a large (40–60 nV) diamagnetic transition at 109, 116, 123, and 132 GPa, whereas no evidence for superconductivity is seen above 1.4 K at 92 GPa. To enhance the visibility of the superconducting transition, the temperature-dependent background signal at 72 GPa has been subtracted from the data shown. The inset to Fig. 2(a) shows the raw data for $\chi\prime(T)$ at 116 GPa. The superconducting transition is found to shift to lower temperatures under magnetic fields to 250 Oe at the rate 1.36 mK/Oe.

For a transition with full shielding from a bulk superconductor the volume susceptibility changes by the amount $\Delta\chi = -1$. In the present experiment the accuracy of the estimate of $\Delta\chi$ is limited due to the small sample size and relatively large demagnetization factor (~0.8). Nevertheless, in the present experiment $\Delta\chi$ can be estimated from the magnitude of the transition signal ΔS in two different ways: (i) from the geometry of the primary or secondary coil system plus the shape or volume of the Yb sample, and (ii) by comparing the measured transition size for Yb $\Delta S = 40-60$ nV to that (110 nV) for the known bulk superconductor NbTi measured in the same experiment, after correcting for the differing shapes and volumes of the two samples. Both methods yield for Yb the estimate $\Delta\chi = -0.7$ to -1.2, thus confirming that the transitions in Yb under pressure in Fig 2(a) are consistent with bulk superconductivity.

The imaginary part $\chi_1\prime\prime(T)$ in the 1st harmonic was also measured at all pressures as well as the imaginary part in the 3rd harmonic $\chi_3\prime\prime$; all three are compared in Fig 2(b). Whereas the temperature-dependent background signal was subtracted for the two 1st harmonic susceptibilities, no subtraction was necessary for $\chi_3\prime\prime$. We define T_c to be the temperature of the midpoint of the transition in $\chi_1\prime(T)$, a temperature that corresponds approximately to that where the resistivity falls to zero [38]. These results were confirmed by two further ac susceptibility experiments.

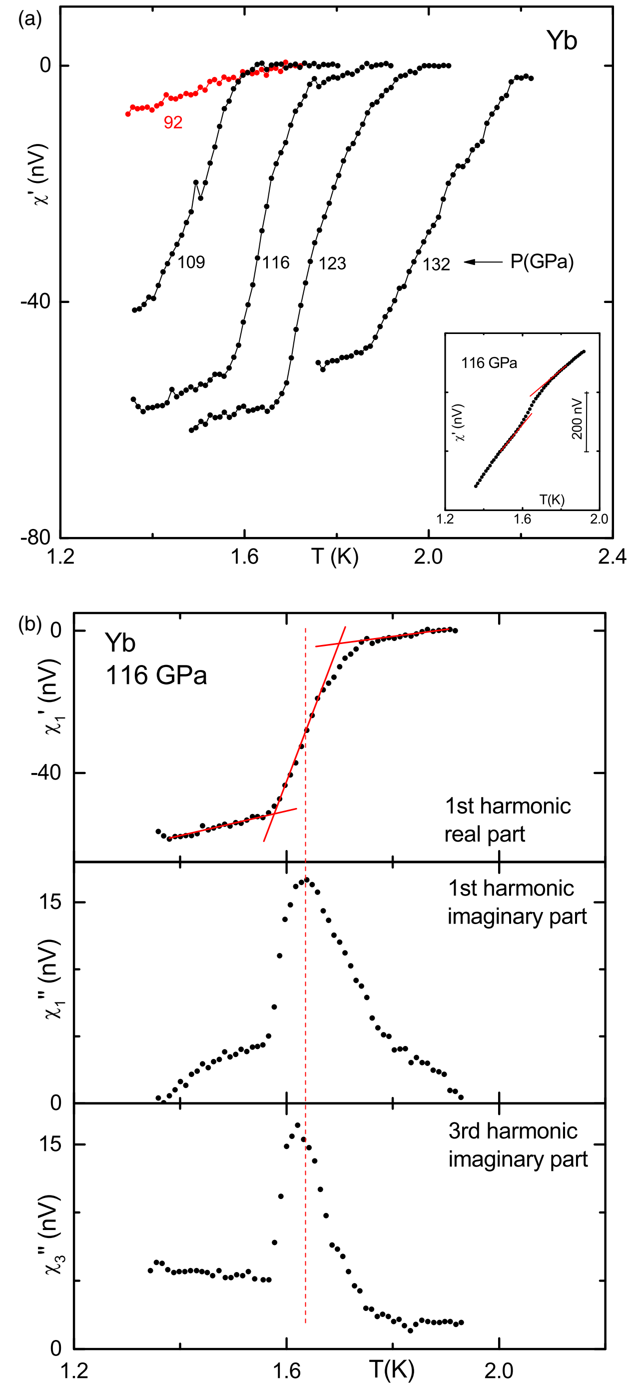

FIG. 2. (a) Real part of the 1st harmonic of ac susceptibility versus temperature for Yb in run X3 showing strong diamagnetic shielding of superconducting transition for pressures above 92 GPa at low temperature. Background signal from nonsuperconducting Yb at 72 GPa has been subtracted from data. Inset shows superconducting transition at 116 GPa in raw data. (b) For Yb at 116 GPa, temperature dependence of the 1st harmonic of real and imaginary parts of ac susceptibility with background was subtracted as in (a) and compared to the 3rd harmonic of the imaginary part of ac susceptibility where no background subtraction was necessary. All three susceptibilities clearly define the superconducting transition temperature.

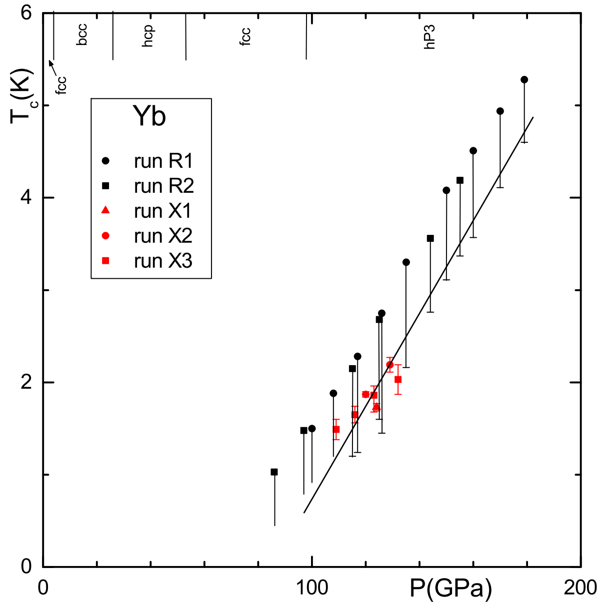

FIG. 3. Superconducting transition temperature of Yb versus pressure for all resistivity and ac susceptibility measurements. In the legend "R" and "X" are values from resistivity and ac susceptibility measurements, respectively. For resistivity T_c is defined as temperature where $R(T)$ extrapolates to zero, lower error bar where $R(T)$ actually reaches zero. In ac susceptibility T_c is defined as the temperature at the transition midpoint for the real part of the 1st harmonic, upper and lower error bars giving temperatures where the straight lines through data intersect, as in the upper panel of Fig. 2(b). The long straight line gives the best estimate of T_c versus pressure with slope 50 mK/GPa. Structures at the top of the graph for Yb follow the structure sequence at room temperature [21,22]: fcc(I) to bcc at 4 GPa, to hcp at 26 GPa, to fcc(II) at 53 GPa, to hP3 at 96 GPa.

During the entire resistivity experiment no electrical contact occurred between the sample and Pt contact strips with the metal gasket or pressure cell. To check whether the Pt contact strips themselves might become superconducting at extreme pressure, a separate experiment was carried out on a Pt sample alone. No evidence for a superconducting transition was seen in the resistivity measurements to 168 GPa pressure above 1.4 K. To check whether the MP35N gaskets used in the ac susceptibility measurements might become superconducting under pressure, a separate experiment was carried out on an empty gasket containing no Yb sample. Again, no sign of a superconducting signal was observed. The present experiments thus show that Yb metal indeed becomes superconducting for pressures of 86 GPa and above.

In Fig 3 the values for the superconducting transition temperature T_c from both resistivity and ac susceptibility measurements are plotted versus pressure. The larger pressure range for the resistivity is due to differences in pressure techniques. Within experimental error the resistivity and ac susceptibility measurements agree and find that under pressure T_c for Yb increases at the rate of approximately +50 mK/GPa. The fact that the superconductivity appears at a pressure rather close to the fcc-hP3 phase boundary suggests a possible correlation.

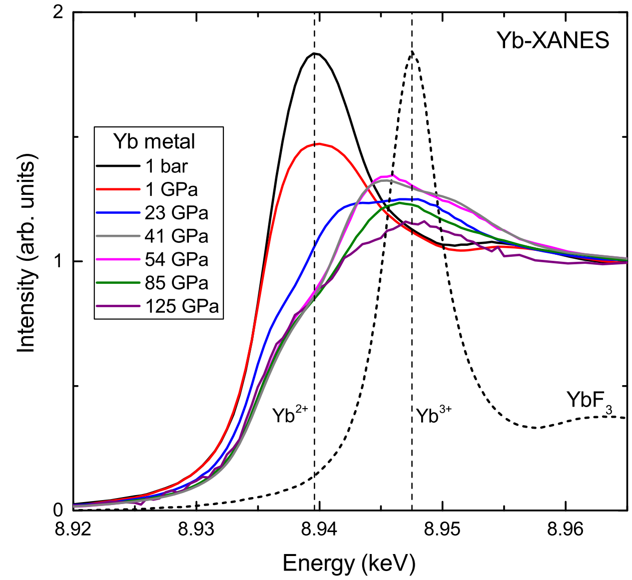

FIG. 4. Pressure dependence of L_3 x-ray absorption data at ambient temperature showing that Yb metal remains mixed valent under pressure to at least 125 GPa. Yb in YbF_3 is fully trivalent [41].

The overriding effect of high pressure on matter is to turn insulators into metals, quench magnetism, and promote superconductivity. The magnetism of the lanthanides with their highly localized $4f$ orbitals is particularly resistant to pressure quenching. For most lanthanides Mbar pressures only suffice to generate the *approach* to a reduction in the number of electrons in the $4f$ orbital [1,12]. In the case of the highly compressible divalent nonmagnetic lanthanide Yb, a full reduction might seem more likely, leaving a magnetic $4f^{13}$ state. However, Yb's divalent state is stabilized by the Coulomb correlation advantage of a full $4f$ shell. Should Yb become fully trivalent under pressure, magnetic order would be expected.

If one applies simple de Gennes scaling [39] to estimate the magnetic ordering temperature of trivalent Yb, one finds that it should be approximately 49 times lower than that of Gd or $T_o = (292\ \mathrm{K})/(49) = 6$ K. Using the ratio of the magnetic ordering temperatures of $GdRh_6B_4$ and $YbRh_6B_4$ [40], instead of the de Gennes factor, one arrives at the estimate $T_o = 4$ K. In any case the present studies find no evidence for magnetic order in Yb above 1.4 K to pressures as high as 179 GPa. This, plus the fact that Yb becomes superconducting, speaks strongly against a fully trivalent state in Yb to this pressure. To check this conclusion, an x-ray absorption measurement was carried out (see Fig. 4) that shows that Yb remains mixed valent to at least 125 GPa. In contrast, Yb in YbF_3 is fully trivalent at ambient pressure [41].

The fact that in Yb a nonmagnetic-to-magnetic transition is approached under pressure makes an exotic form of superconductivity seem possible where magnetic fluctuations play an important role [42]. This scenario has been proposed for the recently discovered heavy fermion superconductor β-$YbAlB_4$ that happens to be positioned very near to a quantum critical point [23]. In these studies a high purity single crystal of β-$YbAlB_4$ was chosen with a residual resistivity ratio (RRR) of ∼300. However, high RRR values are not a prerequisite for the appearance of heavy fermion superconductivity as evidenced by experiments on UCoGe [43], UNi_2Al_3 [44], UBe_{13} [45], and $CePt_3Si$ [46] with RRR values of 2, 33, 0.7, and 13, respectively.

In typical Kondo-lattice systems the Kondo temperature and the magnitude of the negative covalent mixing exchange J increase with pressure, passing through a Doniach-like phase diagram until magnetism is quenched at a quantum critical point [1,12], near where superconductivity may appear. In contrast, in Yb one would expect everything to go in reverse where the Kondo temperature decreases with pressure as the magnetic state stabilizes. Thus one might conjecture that the superconducting transition temperature will pass through a maximum and decrease before magnetic order sets in as Yb passes through the quantum critical point in reverse. To access these phenomena with Yb, the application of multi-megabar pressures would likely be necessary.

In summary, in the present resistivity and magnetic susceptibility experiments superconductivity has been discovered in Yb for pressures above 86 GPa with no sign of magnetic order between 1.4 and 295 K to 179 GPa. To at least 125 GPa Yb remains mixed valent. This suggests that magnetic instabilities may play a role in the appearance of superconductivity.

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Supplemental Material for *Pressure-induced superconductivity in elemental ytterbium metal*

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Details of Experiment

To generate pressures surpassing 1 Mbar, a membrane-driven [1] diamond anvil cell (DAC) made of CuBe alloy was used [2] where pressure was generated between two opposed diamond anvils (1/6-carat, type Ia) with 0.35 mm diameter culets beveled at 7° to 0.18 mm central flats. In the resistivity experiment a Re gasket (6 - 7 mm diameter, 250 μm thick) was pre-indented to 30 μm and a 90 μm diameter hole electro-spark drilled through the center. The center section of the pre-indented gasket surface was filled with a 4:1 cBN-epoxy mixture to insulate the gasket and serve as pressure medium. The thin square-shaped Yb sample (Alfa Aesar, 99.9%) with dimensions $\sim$40×40×5 μm^3 was then placed on top of four thin (4 μm) Pt leads for a four-point dc electrical resistivity measurement with 0.5 mA excitation current. After application of pressure the sample was held for 2 hours at ambient temperature before cooling down. See paper of Shimizu *et al* [3] for further details of the non-hydrostatic pressure technique.

Since a Re gasket superconducts under pressure at $\sim$4 K, a gasket made of MP35N (neither superconducting nor magnetic) was used in the ac susceptibility $\chi(T)$ measurements. The MP35N gasket was heat treated at 565°C for 4 hours resulting in an increase in HRC hardness from 48 to 52. The 90 μm hole in the pre-indented gasket was filled with Yb sample without pressure medium. The real and imaginary parts of $\chi(T)$ were determined in the first harmonic, and at some pressures in the third harmonic, using a Stanford Research SR830 digital lock-in amplifier with a SR554 transformer preamplifier and a Keithley 6221 constant ac current source.

High-pressure x-ray absorption experiments on Yb's L_3 edge (8.9 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 125 GPa.

In all experiments the pressure at room temperature was determined by Raman spectroscopy from the diamond vibron [4]. In selected experiments on Yb a ruby manometer [5] was also used, revealing an approximately linear increase in pressure of about 20% on cooling from 295 to 4 K. Since the important phenomena either occur, or are expected to occur, at temperatures near 4 K, all values of pressure in this paper are enhanced by 20% over those measured at ambient temperature using the diamond vibron. Further experimental details of the DAC, cryostat, and ac susceptibility techniques are given elsewhere [2, 6, 7].

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