Superconductivity under Pressure in $(U_{1-x}Th_x)Be_{13}$: Evidence for Two Superconducting States

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The influence of pressure P on the superconducting transition temperature T_c has been determined for the $(U_{1-x}Th_x)Be_{13}$ system. The magnitude of dT_c/dP increases by a factor of 3 for $x > 1.7\%$ where an increase of T_c is observed at ambient pressure. The phase diagram of $T_c(x)$ for $P = 10$ kbar shows two distinct regions of superconductivity.

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The compound UBe_{13} belongs to a small class of heavy-electron superconductors which are characterized by enormous normal-state electronic specific-heat coefficients γ of ≈ 1 J/mole-K^2, relatively low superconducting transition temperatures $T_c \lesssim 1$ K, and extraordinarily large values for the initial slope of the upper critical magnetic field H_{c2}.[1–6] The unusual superconducting properties of these materials include power-law dependences in T for $T << T_c$ found in measurements of the spin-lattice relaxation rate,[7] ultrasonic attenuation coefficient,[8] and thermal conductivity.[9] These results have generated a great deal of excitement since they may be indicative of an unusual superconducting state in which the superconducting energy gap vanishes at points or lines on the Fermi surface.[7–9] The substitution of Th for U in UBe_{13} produces complex and unexpected behavior such as a nonmonotonic depedence of T_c on composition[10] and the observation of two features in the specific heat for some compositions.[11] The specific-heat feature at higher temperature is associated with the development of the superconducting state, while the one at lower temperature corresponds to another phase transition that occurs without destroying superconductivity. On the basis of an analogy with superfluid ^{3}He, it has been proposed that two superconducting states with different order parameters are revealed in these specific-heat data.[11] Another interpretation involving the characteristics of the ultrasonic attenuation is that an itinerant-electron antiferromagnetic state which coexists with superconductivity develops at the second transition.[12]

We have investigated the influence of pressure P to 12 kbar on the superconducting transition temperature of various compositions in the $(U_{1-x}Th_x)Be_{13}$ system. The results presented in this paper reveal a suppression of T_c by pressure that is greater by a factor of 3 for $x > 1.7\%$ than for $x = 0$. (We use x to represent the atomic percentage of Th that is substituted for U). We have constructed $T_c(x)$ phase diagrams for pressures to 12 kbar to show how the nonmonotonic behavior observed at ambient pressure evolves when pressure is applied. Two distinct regions of superconductivity are present for $P > 9$ kbar which are separated by a range of x where no superconductivity is observed. This suggests that two different superconducting states occur in $(U_{1-x}Th_x)Be_{13}$ which are affected very differently by the application of pressure.

The arc-melted polycrystalline samples used in this study were prepared in a manner described previously.[10] Nearly hydrostatic pressures to 12 kbar determined by use of a Sn manometer were applied at room temperature in Be-Cu clamped piston and cylinder devices. Other experimental details are given elsewhere.[13]

The temperature dependence of the ac magnetic susceptibility $\chi_{ac}(T)$ was determined at various pressures and the background from the empty clamp was subtracted from the data. Sharp superconducting transitions were observed at ambient pressure in good agreement with previous measurements.[10] Application of pressure typically broadens the transitions somewhat, although for $x = 2.31\%$ and 2.60%, substantially broader transitions are observed at all pressures with χ_{ac} continuing to decrease even at the lowest temperatures. No hysteresis with either temperature (within 3 mK) or pressure (within 0.5 kbar) is observed for any value of x. We define T_c as the temperature where χ_{ac} decreases by 10% of the total change observed at each pressure.

The variation of T_c with P determined in this way is shown in Fig. 1 for seven compositions in the

$(U_{1-x}Th_x)Be_{13}$ system. Data consistent with these were obtained for $x = 1.72\%$, 2.31%, and 3.40%, but are not included in Fig. 1 for clarity. Four different behaviors can be distinguished depending on the composition x. First, for $0 \leqslant x \leqslant 1.72\%$, T_c initially decreases at a rate $dT_c/dP \approx 0.016$ K/kbar, with some curvature in $T_c(P)$ as the pressure increases. Very different behavior is observed for $1.90\% \leqslant x \leqslant 2.60\%$ where a much stronger initial decrease ≈ 0.05 K/kbar is observed. At a higher pressure which increases as x increases, an abrupt reduction in the slope dT_c/dP is observed. As x changes from 3.00% to 3.78%, the magnitude of dT_c/dP when $P = 0$ decreases with strong curvature of $T_c(P)$ at higher pressure with no abrupt variations in dT_c/dP. Finally, for $x = 6.03\%$, T_c initially decreases at a rate 0.013 K/kbar, and there is a distinct rise in T_c for $P = 3.8$ kbar. Further decreases are observed in T_c as the pressure increases, with stronger suppression at the highest pressures investigated.

The influence of pressure on the phase boundary $T_c(x)$ can be determined from these data by use of linear interpolations between data points and linear extrapolations of the lowest-temperature data. The resulting isobars for $T_c(x)$ are shown for several pressures in Fig. 2(a) where the dashed lines indicate the behavior expected at low temperatures. At ambient pressure, a distinct minimum in $T_c(x)$ is observed for $x = 1.72\%$, followed by a broad maximum and subsequent decrease of T_c. Both of these features persist and are shifted to higher x by the application of pressures to 12 kbar. For $P > 9$ kbar, no superconductivity is observed for $x \approx 3\%$, although distinct superconducting transitions are still observed for $x = 6.03\%$, even when $P = 12.6$ kbar.

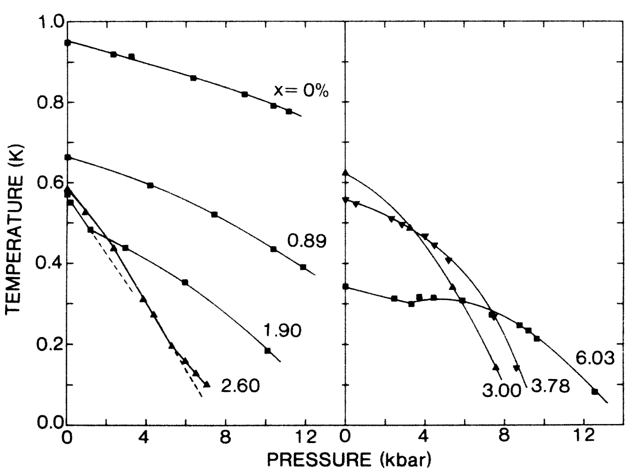

FIG. 1. The superconducting transition temperature vs pressure determined from ac magnetic susceptibility data for various compositions in the $(U_{1-x}Th_x)Be_{13}$ system. Similar results are found for $x = 1.72\%$, 2.31%, and 3.40%. Smooth curves have been drawn through the data points, and for $x = 1.90\%$ and 2.60%, the dashed line shows a linear extrapolation of data at lower pressure. The data for $x = 0$ are from Ref. 13.

The isobars of $T_c(x)$ in Fig. 2(a) reveal that two different behaviors are present for each pressure separated by the minimum in $T_c(x)$ at x_{min}. For $x < x_{min}$, a monotonic decrease of $T_c(x)$ is observed as the pressure increases, and the magnitude of the slope dT_c/dP also becomes larger with increasing x. This indicates that pressure and substitution of Th for U work together to suppress superconductivity more strongly for $x < x_{min}$. For convenience, we will refer to this behavior as type-A superconductivity. For $x > x_{min}$, an abrupt increase of T_c occurs with a maximum and subsequent decrease for higher x. The position of this maximum is pressure dependent, moving to higher concentration as P increases. We will refer to superconductivity in the region under this maximum as type B.

The variation of T_c with pressure shown for various concentrations in Fig. 1 can now be explained by consideration of the two different behaviors observed for type-A and type-B superconductivity as described above. For $0 \leqslant x \leqslant 1.72\%$, the monotonic decrease of T_c with pressure shows no anomalous behavior, consistent with the occurrence of type A for all pressures and temperatures. For $1.90\% \leqslant x \leqslant 2.60\%$, a much stronger decrease is initially observed as pressure

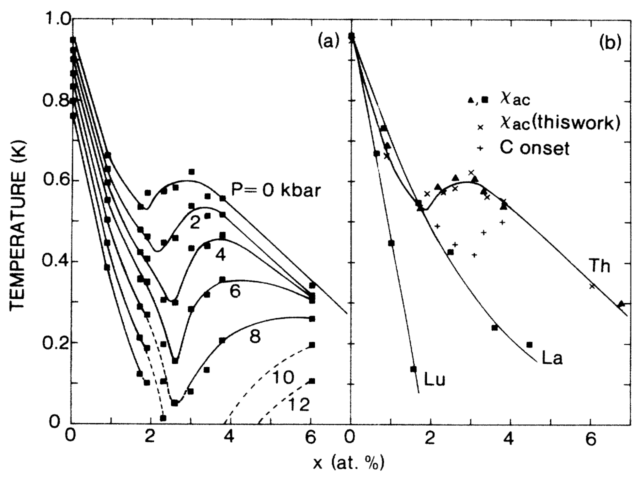

FIG. 2. Phase diagram of superconducting transition temperature T_c vs composition x for $(U_{1-x}M_x)Be_{13}$. (a) The variation of T_c vs x for $M = $ Th at various pressures determined from the data in Fig. 1. The lines are guides to the eye, and dashed lines indicate extrapolations of the data to low temperature. (b) Data (Ref. 10) for $T_c(x)$ determined from ac magnetic susceptibility for $M = $ La, Lu, and Th compared with the results of this work for $M = $ Th. The plusses show the onset temperature of a feature in the specific heat (Ref. 11) which indicates a second phase transition in the superconducting state for several values of x.

moves the maximum in $T_c(x)$ to larger x, suppressing type-B superconductivity. For sufficiently high pressure, the distinct break in slope of $T_c(P)$ and substantially smaller sensitivity of T_c to pressure indicates that type-B superconductivity has been suppressed by pressure and replaced by type A. When $x=3.00\%$, the initial decrease of T_c with P is smaller than for $x=2.60\%$, even though type-B superconductivity is expected for this x and P. This can be understood since application of pressure is moving the maximum in $T_c(x)$ to higher x, an effect that would to some extent compensate the sensitivity of type-B superconductivity to pressure observed for $1.90\% \leqslant x \leqslant 2.60\%$. Similar arguments hold for $x=3.40\%$ and 3.78%. The data for $x=6.03\%$ strongly suggest that the increase of T_c observed for $P=3.8$ kbar occurs when pressure has moved the maximum in T_c characteristic of type-B superconductivity to sufficiently high concentration to be observed for $x=6.03\%$. Further measurements are planned for $4\% \leqslant x \leqslant 6\%$ to clarify the influence of pressure on T_c for this range of compositions.

It is interesting to speculate about the behavior that might occur for higher concentrations of Th in $(U_{1-x}Th_x)Be_{13}$. Extrapolation of the present data indicates that for $x \approx 10\%$, no superconductivity would be observed at ambient pressure. However, application of pressure ≈ 10 kbar might induce type-B superconductivity at a temperature sufficiently high to be detected.

One important question concerning these results is whether pressure has substantially altered the heavy-electron superconducting state. Preliminary measurements of a sample with $x=3.78\%$ at a pressure of 8.4 kbar show that the critical magnetic field retains the enormous slope found at ambient pressure for the same composition.[14] This is a clear indication that the superconductivity found at high pressure in what we call the B phase has its origins in the heavy-electron state.

The data that we have presented can be interpreted as evidence for two different superconducting states in the $(U_{1-x}Th_x)Be_{13}$ system. It may be that more than two states occur which are not revealed in our measurements. For example, three different superconducting states have been proposed by Joynt, Rice, and Ueda[15] to explain the behavior observed in this system at ambient pressure. Our results have some implications concerning the phase diagram at ambient pressure which are illustrated in Fig. 2(b). The data for $1.90\% \leqslant x \leqslant 2.60\%$ clearly show that at sufficiently high pressure, the behavior of $T_c(P)$ is very similar to that for lower Th concentrations. This strongly implies that the lower-temperature feature observed in the heat-capacity data for this range of compositions signals a transition to the same superconducting state (type A) observed for $0 \leqslant x \leqslant 1.72\%$. No such statements can be made for higher Th concentrations since the isobars of $T_c(x)$ displayed in Fig. 2(a) show that type-A superconductivity will be suppressed by pressure more quickly than type B for $x > 3\%$, and so would not be detected by our χ_{ac} measurements. It will be interesting to measure the heat capacity under pressure for $x \approx 3\%$ to see if the second transition shows the pressure dependence expected for type-A superconductivity from the data for $x < 1.8\%$, and such an experiment is included in our future plans. In this context, it is interesting to compare the variation of $T_c(x)$ for $(U_{1-x}M_x)Be_{13}$ for $M=$La, Th, and Lu as illustrated in Fig. 2(b).[10] Also plotted in this figure is the temperature for the onset of the lower-temperature feature observed in the heat-capacity data.[11] Curvature of $T_c(x)$ is observed for $M=$La and Th, and the expansion of the lattice with x is nearly the same in these two cases.[10] The similarity of $T_c(x)$ when $x < 3\%$ for $M=$La and Th lends support to our suggestion that the lower-temperature transitions observed in the heat-capacity data are a continuation of the phase boundaries observed for $x < 1.7\%$. Other mechanisms must also be important, however, since transitions at higher temperatures are observed for $M=$Th when $x > 3\%$.

Finally, for $P=10$ kbar, the linear variation of $T_c(x)$ for $M=$Th is similar to that for $M=$Lu at zero pressure. This suggested to us that for a given impurity concentration x, T_c might be determined by the change in lattice parameter associated with both chemical substitution and pressure. The rate $dT_c/da(P)$ at which T_c changes with lattice parameter a because of the application of pressure can be estimated using the bulk modulus $B=-V\,dP/dV$ which can be calculated from the formula $B=(C_{11}+2C_{12})/3$ and values for the elastic constants C_{11} and C_{12} determined at 10 K from neutron-scattering experiments by Robinson *et al.*[16] The value $B=1.03\times10^{11}$ N/m^2 obtained is very close to the value $(1.00\times10^{11}$ N/m$^2)$ for pure Be. The rate at which $T_c(x)$ varies with lattice parameter because of the different radii r_M of the $M=$La, Lu, or Th impurity atoms, $dT_c/da(r_M)$, can be determined from x-ray diffraction data.[10] For $(U_{1-x}M_x)Be_{13}$ samples with $x \leqslant 1.9\%$, we find for a given value of x that $dT_c/da(P)$ for $M=$Th is about a factor of 10 smaller than $dT_c/da(r_M)$ for $M=$La and Lu. We plan to measure dT_c/dP for La and Lu impurities in UBe_{13} to investigate these ideas further.

Another possibility that should be considered is that the minimum in the $T_c(x)$ curve which occurs at $x \approx 1.7\%$ at zero pressure reflects the onset of a profound change in the electronic structure as tetravalent Th is substituted for U in UBe_{13}, rather than a boundary between two distinct types of superconductivity. The modified electronic structure for $x \geqslant 1.7\%$ would then be responsible for the transitions that occur within the superconducting state which may be due to a second type of superconductivity or antiferromagnetic order. Apparently, no such electronic transition takes place when trivalent La or Lu impurities are substituted into UBe_{13}. Pressure would have the effect of shifting the onset of the electronic transition to higher values of Th concentration. Marked changes in superconducting and magnetic behavior, induced through variations in chemical composition and the application of pressure, have been observed in a variety of systems. The substitution of Th for U[17,18] or Pd for Pt[18,19] in UPt_3 leads to the rapid quenching of superconductivity, followed by the development of a new charge or spin-ordered state that has not yet been fully characterized. Abrupt changes in superconducting and magnetic transition temperatures as well as different types of magnetic order are found in the $Ho(Rh_{1-x}Ir_x)_4B_4$ system.[20] Considerable variations in T_c, including the destruction and reappearance of superconductivity, in dilute $La_{1-x}Ce_x$ alloys accompany the application of pressure or the substitution of Th for La because of variations in the relative values of the superconducting and Kondo temperatures.[21] Thus, the straightforward explanation of the data we have presented here may require modification as new experiments on $(U_{1-x}Th_x)Be_{13}$ are reported.

We have investigated the influence of pressure on the superconducting transition temperature of the $(U_{1-x}Th_x)Be_{13}$ system. Considerable variations in dT_c/dP are observed which correlate with the nonmonotonic dependence of T_c on x at ambient pressure. Isobars of $T_c(x)$ for pressures to 12 kbar constructed from our data show that many characteristics of the $(U_{1-x}Th_x)be_{13}$ system can be explained by assuming that two distinct superconducting states occur.

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