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# IMPURITY EFFECTS IN $UBe_{13}$

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The effect of a few per cent of thorium replacing uranium in the heavy-fermion superconductor $UBe_{13}$ is dramatic. The low-temperature properties are drastically altered and a second transition of a controversial nature occurs below the onset of superconductivity. Other non-magnetic impurities are seen from various preliminary measurements to yield promise of different results. Normally such impurity studies show only gradual changes in properties, which are useful for extracting superconducting parameters, but the large effects seen in this heavy-fermion superconductor highlight its exotic nature.

## 1. Introduction

A little over 25 years ago Matthias began working on the interaction of superconductivity and magnetism [1]. With his coworkers he had been putting 3d- and 4f-electron magnetic impurities into superconductors. The results, together with the recently-found isotope effects on $T_c$, convinced him that there was a non-electron–phonon interaction causing transition metal superconductivity. Among offshoots of this work were the series of conferences on d- and f-electron superconductivity that have become this conference and also the community that studies how magnetic moments can be lost via compensation with conduction electron spins. More to the point, in the intervening years this led to the study of many alloys and pseudobinary compounds for which the materials at the end points were a superconductor and a magnet. It was hoped that such studies would offer insight into the relationship between superconductivity and magnetism, but in such phase diagrams, the interesting regions never seemed to yield new physics probably due to disorder.

In the late seventies the magnetic superconductors, such as $ErRh_4B_4$, appeared [2]. In some of these ternary compounds magnetism and superconductivity did show coexistence at last. Ultimately, little new insight resulted because the superconductivity and the magnetism involved different electrons and were simply fighting it out for the ground state using well-understood physics. However, the new physics was soon in hand with $CeCu_2Si_2$ [3], although the appreciation of it came slowly. It is not clear if Matthias understood the significance of $CeCu_2Si_2$, although he had spent enough time looking over the data with F. Steglich to believe that it was a bulk superconductor [4]. Indeed, $CeCu_2Si_2$ (and later $UBe_{13}$ and $UPt_3$) was the material Matthias was after. It took a compound, not the disordered systems, to develop the high density of electronic states at low temperatures in which, it is now clear, superconductivity and magnetism interact within the same f-electrons. These heavy-fermion superconductors and magnets [5] are fairly clearly outside of the realm of currently understood physics and are under very intense study for this reason.

The discovery of $UBe_{13}$ with its low-temperature properties so similar to those of $CeCu_2Si_2$, but otherwise a very different compound, removed the last doubts that heavy-fermion superconductors were genuine [6]. The name arose because the high electronic heat capacity indicated that the electrons (fermions) had effective masses hundreds of times larger than free electrons. The lesson from Matthias to try impurities in superconductors was heeded immediately after

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the superconductivity of $UBe_{13}$ was seen to occur [7]. The most puzzling aspect of that work was the non-monotonic depression of the onset temperature of the superconducting transitions with increasing thorium impurities. Thorium is clearly a non-magnetic impurity in $UBe_{13}$, and so the depression curve seemed unlikely and perhaps simply wrong. Ott and coworkers soon found out what was hiding under that curve [8]. There is a second transition seen in the heat capacity just below what is obviously the onset of superconductivity. The second transition is clearly associated with the interruption of the depression of the $T_c$ onsets with increased thorium additions, but its nature remains controversial as is clear from the contributions to this conference, and we leave the controversy to them.

Our purpose here is to report on more extensive measurements with other impurities in $UBe_{13}$ besides thorium, which was the only element studied as a function of concentration in ref. 7. It is quite important to know how general the existence of two transitions may be and if there are any correlations with other properties of the impurity atoms. We stress that the occurrence of a second transition of any type in a superconducting state caused by a small addition of non-magnetic impurities severely tests our present understanding of superconductivity.

## 2. Samples and measurements

We used arc-melted, polycrystalline samples for these measurements. The techniques for preparation and measurements have already been reported [7, 8], but several specific additions are needed. Uranium and beryllium react with a great deal of movement and expansion. For all of these samples, a single piece of impurity material was added to pure uranium and beryllium so that, if the very tiny impurity piece was lost, we would simply have recognizable $UBe_{13}$. The impurities were either in pure form or as beryllium compounds for convenience. A slight excess of beryllium was added to account for the very predictable weight losses during melting so that the proportion of beryllium was usually $13 \pm 0.25$, which does not obviously affect the superconducting properties. The samples were turned and melted at least six times.

It became clear during this work that finding reproducible $T_c$'s required that we measure fragments from the centers of the samples or, at least, with a minimum of surface, and then only from the equator. This usually reduces scatter from about 0.1 K to less than 0.05 K. Similarly, as the possibility of sample inhomogeneity became important to the question of two transitions [8], samples for X-ray powder-diffraction measurements (using film techniques) were gathered only from the many broken fragments obtained during fracture of the best pieces of the samples. The fracturing is assumed not to affect the $T_c$ onsets because complete powdering (and sieving) of pure $UBe_{13}$ yields only a slightly broadened transition with a long tail, but no change in the onset temperature. Lattice parameters were measured for over a third of all of the samples and are listed in table I. The thorium-doped samples and the yttrium- and zirconium-doped samples, which are now the best next candidates for double transitions, show no increased scatter in lattice parameter or line broadening through the composition range that is interesting at low temperatures. We can still find no evidence at room temperature for inhomogeneities that could trivialize the low temperature behavior.

It can be seen in table I that single crystals of $UBe_{13}$ (similarly true for impurity doped crystals) have a significantly larger lattice parameter than polycrystalline samples. Single crystals also have lower $T_c$'s, broader transitions, and less-sharp resistivity features. We initially thought that the lattice might be trapping aluminum atoms on beryllium sites as the crystals precipitated from their aluminum solvent. We prepared arc-melted samples containing aluminum, which are listed in table I, to simulate this situation. The $T_c$ onsets were unchanged, although the transitions were broadened. This is in strong contrast to boron, copper, and gallium substitutions on the beryllium sites, which rapidly destroy the superconductivity [9]. Annealing the samples simply sharpens the transitions, and for the lowest aluminum concentration, this yielded the sharpest transition

Table I
Lattice parameters (Å) for some samples

| | |
|---|---|
| $UBe_{13}$ (several samples) | 10.2545–10.2550 |
| $UBe_{13}$ (single crystal) | 10.2656 |
| $Th_{0.0172}U_{0.9828}Be_{13}$ | 10.2575 |
| $Th_{0.0216}$ | 10.2579 |
| $Th_{0.026}$ | 10.2591 (2) |
| $Th_{0.0308}$ | 10.2591 |
| $Th_{0.0378}$ | 10.2605 |
| $Th_{0.0598}$ | 10.2635 |
| $Th_{0.0603}$ | 10.2642 |
| $Sc_{0.0068}U_{0.9932}Be_{13}$ | 10.2539 (2) |
| $Sc_{0.0103}$ | 10.2531 |
| $Sc_{0.030}$ | 10.2523 |
| $Sc_{0.0484}$ | 10.2508 |
| $Lu_{0.0062}U_{0.9938}Be_{13}$ | 10.2540 |
| $Lu_{0.016}$ | 10.2536 |
| $LuBe_{13}$ | 10.1693 (2) |
| $Y_{0.0030}U_{0.997}Be_{13}$ | 10.2543 |
| $Y_{0.0081}$ | 10.2541 |
| $Y_{0.0124}$ | 10.2545 (2) |
| $Y_{0.0146}$ | 10.2545 (3) |
| $Y_{0.0176}$ | 10.2540 |
| $Y_{0.020}$ | 10.2544 (2) |
| $Y_{0.0332}$ | 10.2540 |
| $YBe_{13}$ | 10.2398 (2) |
| $Zr_{0.0108}U_{0.9892}Be_{13}$ | 10.2533 (2) |
| $La_{0.008}U_{0.992}Be_{13}$ | 10.2562 (2) |
| $La_{0.025}$ | 10.2586 (2) |
| $UBe_{12.99}Al_{0.01}$ | 10.2564 |
| $UBe_{12.99}Al_{0.01}$ (annealed) | 10.2556 (2) |
| $UBe_{12.97}Al_{0.03}$ | 10.2571 (2) |
| $UBe_{11.15}$ | 10.2543 |
| $UBe_{15.0}$ | 10.2545 |

that we have seen in a $UBe_{13}$ material. Presumably the aluminum scavenged impurities as it left the lattice (because the lattice contracted). We also suspected that the single crystals, which solidify about 1000°C lower than the polycrystals, could incorporate excess beryllium or uranium interstitially or by vacancies on the other sites. However, the severely-off-stoichiometry samples at the end of table I show almost no change in lattice parameter. We still have no explanation for the differences between single- and polycrystals.

The $T_c$'s presented in this paper are the onsets of the transitions as measured by ac susceptibility (372 Hz). This was also done in ref. 7 where an implicit apology (no longer necessary) pointed out that the width of the transitions was often equal to $T_c$. Now that the compositions have been varied more widely, we see that the widths for impurity concentration above around 2% have this tendency, while below 1% they are often as sharp as for pure $UBe_{13}$. For the remainder of the paper, we note that all samples are polycrystalline, have impurities that substitute on the uranium site, and of course, are still cubic and disordered (to the best of our knowledge).

## 3. Results

In fig. 1 we give an example of how drastically even small substitutions for uranium in $UBe_{13}$ can influence both the normal and superconducting state. Although the thorium and the lutetium concentrations are virtually the same in both samples, the temperature dependence of the low-temperature specific heat is clearly different. The 3.3% Th induces a second phase transition in the superconducting state ($T_c = 0.6$ K) at about 0.4 K. The same amount of lutetium, however, suppresses superconductivity and also reduces the electronic specific heat parameter considerably to about half of the value of the thorium-doped sample at its transition temperature. The entropy gain of the lutetium-doped sample is clearly shif-

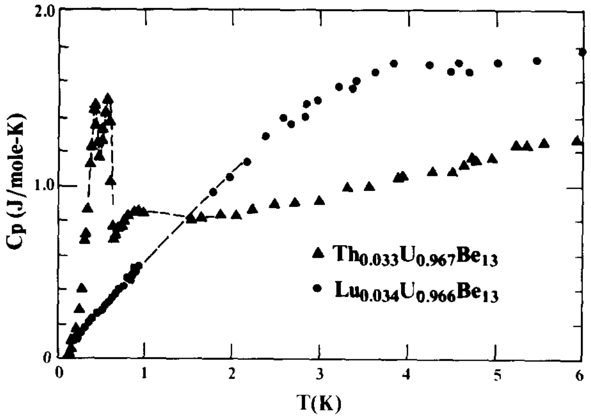

Fig. 1. Specific heat $C_p$ vs. temperature $T$ of Th- and Lu-doped $UBe_{13}$ between $T = 0.15$ and 6 K.

ted to higher temperatures indicating that these impurities also change the electronic structure of the low-temperature normal state. This may be also seen in the temperature dependence of the electrical resistivity in fig. 2 where the low-temperature resistivity maximum is far more slowly depressed for lutetium than for thorium [7]. (Impurities on the beryllium sites, on the other hand, leave the heat capacity unchanged [9], as far as is known.)

Figs. 2 and 3 show the electrical resistivities as a function of temperature for various concentrations of lutetium and scandium. The average room temperature value for all eight samples is 107 $\mu\Omega \cdot$cm, where the scatter is well within the geometric uncertainties. Although we still have no explanation for the shape of the resistivity curves, we can comment on changes with impurities. In pure $UBe_{13}$ there is a maximum at about 2.5 K and a fairly flat shoulder near 20 K. The flat shoulder shifts somewhat with impurity size. Thus in figs. 2 and 3 the shoulder seems to move to lower temperature causing an initial drop in resistivity around 40 K for less than 1% impurities. For this case lutetium and scandium decrease the lattice parameter. For thorium [7] and lanthanum, which increase the lattice parameter at the same rate, the shoulder moves to higher temperature, yielding a maximum near 35 K. Yttrium and zirconium cause less rapid depressions. This is likely because yttrium contracts the lattice rather slowly, and zirconium, although very much smaller, has a (non-controversially) higher valence and is thus a more complex case. Cerium, which must not be taken as a non-magnetic impurity, has the least effect on the resistivity. Because of this rough correlation with lattice parameter change, the shoulder could be a crystal-field effect. However, there is no other evidence for this.

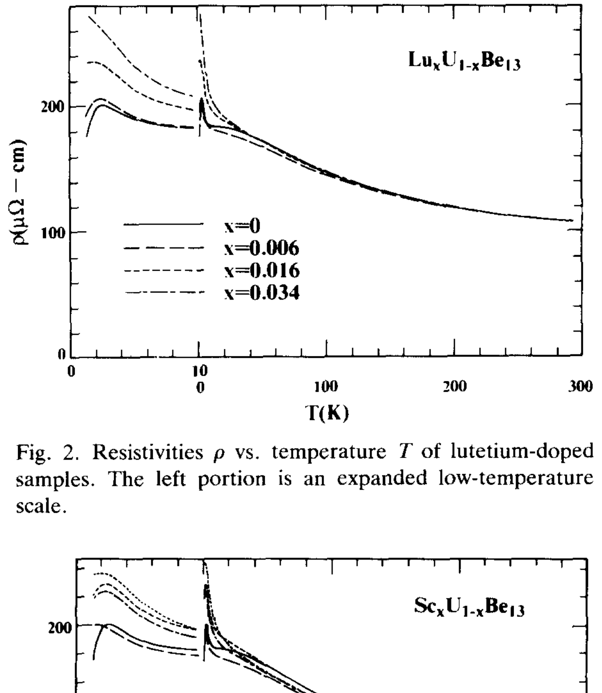

Fig. 2. Resistivities ρ vs. temperature $T$ of lutetium-doped samples. The left portion is an expanded low-temperature scale.

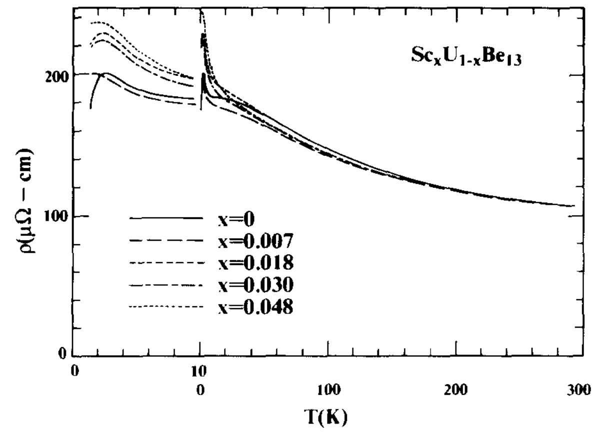

Fig. 3. Resistivities ρ vs. temperature $T$ of scandium-doped samples.

At lower temperatures, the maximum at 2.5 K tends to move to lower temperatures and wash out with increasing impurities. As far as we have checked, only scandium (fig. 3) shows the maximum moving back to higher temperatures with increasing impurities, and it is still there at 4.8%. It is thought this maximum is formed by the onset of electron correlations (or a coherent state) out of the state with severe electron scattering. Then, in fact, impurities could interfere with this and be said to move the maximum to lower temperature. As seen in fig. 2 (and more so in related systems measured by Fisk, Batlogg and Ott, unpublished) the resistivity sometimes begins to climb at low temperature with impurities in a manner that resembles a loss of carriers, as in localization. In general, a detailed understanding of the effects of impurities on resistivity in heavy-fermion materials is at present elusive.

Fig. 4 shows the temperatures of the onset of superconductivity as deduced by ac susceptibility and heat capacity [8] for thorium impurities. It is seen that the agreement is quite good and thus, that the use of ac susceptibility onset temperatures is reasonable for broad transitions. The purpose of the $T_c$ depression studies here was to look for anomalies, as with thorium, and to identify materials for further measurements. However, information can be gleaned from the general shapes of the curves. Maple has reviewed this subject [10]. Fig. 5 shows the depressions for scandium, cerium, and lutetium. They all appear linear, although the slopes vary significantly. The arrows simply indicate the lowest temperature at which we failed to find a transition. For a few magnetic rare-earth impurities that we have checked (gadolinium and heavier), the $T_c$'s seem to lie close to the lutetium line. So although we have made no systematic study, we believe that there is no particular effect on superconductivity from 4f-electron, local moments.

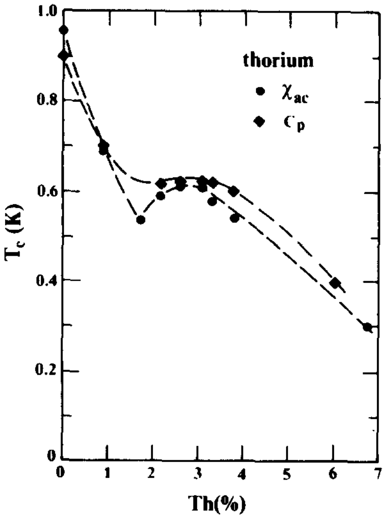

Fig. 4. Superconducting transition temperature $T_c$ vs. Th concentration, as measured by specific heat ($C_p$) and ac magnetic susceptibility measurements ($\chi_{ac}$).

In fig. 6 we see that yttrium and zirconium show features that require further study. If they have any similarities to the thorium case, the interesting region occurs over a much narrower range of compositions. The yttrium samples tended to show a lot of scatter in $T_c$'s as did the thorium and scandium samples. Such a sensitivity could be an indication of competing phenomena. The zirconium samples were quite reproducible, although they did show the broadest transitions of all of the impurities studied. This might simply be an effect of the extreme size mismatch between uranium and zirconium. Finally, lanthanum (fig. 6) has a very ordinary depression curve for a non-magnetic impurity in a superconductor. It is noteworthy mostly for looking routine in a situation where nothing else is.

The compelling variety of behavior that is seen now to exist in this extreme Fermi liquid state seems almost bewildering. Ultimately heavy-fermion materials can be viewed, nonetheless, as

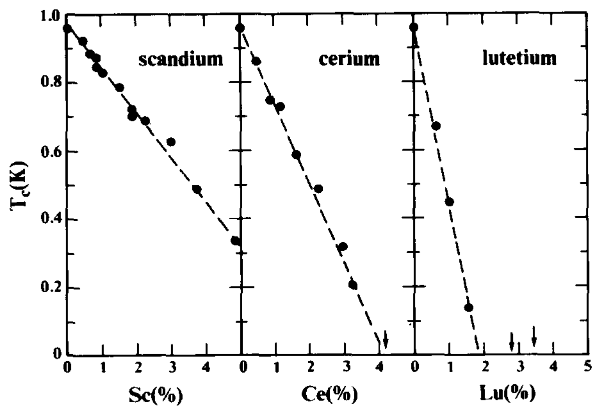

Fig. 5. Superconducting transition temperature $T_c$ vs. impurity concentration in UBe$_{13}$ containing Sc, Ce and Lu impurities.

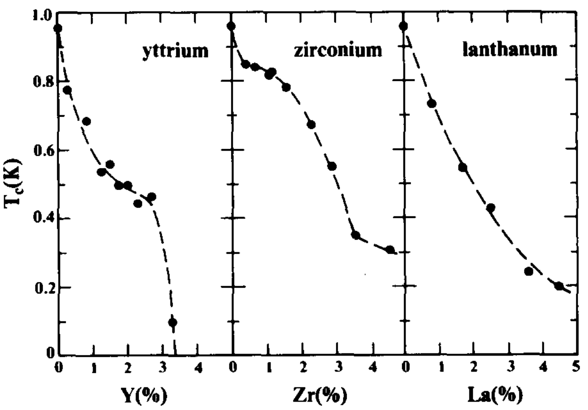

Fig. 6. Superconducting transition temperature $T_c$ vs. impurity concentration in UBe$_{13}$ containing Y, Zr and La impurities.

the limiting case of narrow-electron-energy-band metals, whatever the mechanism may be that causes this. Then there could be a simplicity to them that rivals the free electron gas, but that is additionally more important to understanding all of the physics in transition metals [11].

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## Note added in proof

Rather small, applied magnetic fields have significant effects on the low temperature resistivity features in thorium-doped samples [12].

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