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TITLE: Impurities in the Heavy-Fermion Superconductor UBe_{13}

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Impurities in the Heavy Fermion Superconductor UBe_{13}

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Small amounts of Sc, Lu, Gd, Np, Ce, Th, La, and Ba have been substituted for uranium in UBe_{13} to observe their effects. The thorium, which was the most complete study, resulted in an extremely unusual non-monoto~~p~~nic depression of the transition temperature for a non-magnetic impurity. This comes from an interplay that exists between the lowest temperature resistivity peak and the transition temperature, as the peak is depressed. These results suggest that heavy Fermion behavior is only a necessary condition for heavy Fermion superconductivity. All of the impurities tested resulted in a transition temperature depression.

I. INTRODUCTION

Observation of the interplay between magnetism and superconductivity can now be made on any size scale. Acker et al. [1] demonstrated that a mixture of finely divided niobium and $HoRh_4B_4$ powders shows reentrant superconductivity. Disorder on lattice sites can permit the coexistence of spin glass ferromagnetism and superconductivity, for example in $Ce_{0.73}$ $Ho_{0.27}$ Rh_2.[2,3] On a fully ordered but complex lattice such as $ErRh_4B_4$, reentrant superconductivity can be observed.[4] It is now clear from work on $CeCu_2Si_2$ [5] and UBe_{13} [6] that the same f-electrons in a fully ordered compound can be responsible for Curie-Weiss behavior near room temperature and heavy electron mass superconductivity below 1 K. There is now no finer scale on which to follow this interplay. As the scale decreases from the trivial mixed powder through competing order parameters in $ErRh_4B_4$ to competition within the same electron shell,[7] the problem finally becomes one of strongly interacting Fermions in a highly correlated electron state which has acquired the appellation, heavy Fermion superconductivity. Such compounds have rather unusual properties. For example, UBe_{13} has transition temperatures, T_c's, as high as 0.95 K as reported here, a critical field slope at T_c of at least -26 T/K, an electronic heat capacity of 1.1 J/mole K^2 (Joules not milli-Joules), and an electronic mass enhancement of about 200.[6] The compound $CeCu_2Si_2$ has largely identical properties[5] although preparation of reproducible samples remains difficult.

We believe that the very slight delocalization of f-electrons by some hybridization with p- or d- electrons on neighboring atoms, which yields the enormous density of states at the Fermi level, the heavy effective masses, and the very narrow energy bands, is a separable effect from the occurence of superconductivity at a slightly lower temperature. The best (and only) previous evidence for this was that $CeAl_3$, which has an even higher density of states then $CeCu_2Si_2$ or UBe_{13}, remains normal to below 10 mK.[8] Our results here will tend to support the separation of heavy Fermion behavior from heavy Fermion superconductivity. So, although it is satisfying to be able to apply the tools of superconductivity to probe this Fermi liquid state, we will offer little insight into the interaction that causes the f-electron delocalization. Nonetheless the superconducting properties that we have observed are sufficiently tantalizing to continue to permit the possibility that heavy Fermion superconductivity involves a different pairing interaction, that is, p-state superconductivity. Alternately it is possible that the mass of the f-electrons, being intermediate between those of the s-electrons and the ion cores, could lead to superconductivity via a plasma mode as suggested for d-electrons by Fröhlich.[9] Such plasmons have been recently discussed by Sinha and Varma for f-electrons in the context of mixed-valence.[10]

We have substituted a few percent of several elements on the uranium sites of UBe_{13} and made ac susceptibility and resistivity measurements on these generally polycrystalline samples. For the case of thorium substitutions we have made a more complete study of the effect of concentration and made preliminary magnetization and heat capacity measurements.

II. EXPERIMENTAL METHODS

We prepared most samples in a standard argon arc-furnace. Pieces of pure master MBe_{13} compounds (M = Sc, Lu, U, Gd, Ce, Th, and La) were melted together to form the pseudo-binaries, or because such fragments often shatter when initially melted, all three constituents were melted together simultaneously. All samples were turned and melted at least seven times. Compositions were corrected for weight losses by assuming equal losses of beryllium and MBe_{13} as indicated by x-ray powder diffraction measurements on the residue left in the arc-furnace. Because of the high vapor pressure of barium, single crystals of $Ba_{0.022}U_{0.978}Be_{13}$ were prepared in an aluminum flux by dissolving UBe_{13}, beryllium, and barium in the aluminum at 1400°C and slow cooling. Due to its radioactivity, both $NpBe_{13}$ and $Np_{0.011}U_{0.989}Be_{13}$ were similarly prepared as single crystals. Test annealing at 1000°C showed essentially no effect upon ac susceptibility or resistivity. So all data reported here are from unannealed samples. We used standard x-ray diffraction methods, standard ^3He and dilution refrigerator ac susceptibility and 4-probe ac resistivity techniques, and a S.H.E. magnetometer for our measurements. Because some of the superconducting transitions were quite broad, we report all T_c's as onsets.

III. RESULTS AND DISCUSSION

The resistivities of several samples of $Th_xU_{1-x}Be_{13}$ are shown in Fig. 1. It is of course unusual for an intermetallic compound to show an increase from room temperature, but this trend is just enhanced scattering from the narrow band that is developing. As thorium is added, more typical metallic behavior becomes clear as the band is broadened by this non-magnetic impurity. The two features in the $X=0$ curve in the figure are more interesting. Thorium additions shift the 2.5 K peak to lower temperatures and demonstrate that the flat shoulder at 10 K is another peak as it shifts to higher temperatures. The lattice is expanded by the thorium. This must be the dominant cause of the peak shifts because for all of the impurities tried, these shifts correlate with the lattice parameter changes.

¶ – Table I lists the lattice parameters of MBe_{13} for all elements M that were tried. A simple Vegard's Law, linear interpolation works to determine the lattice effects of any addition to UBe_{13}. So for all elements that expand the lattice, the lower temperature peak moves to even lower temperatures and the high temperature peak to higher temperatures. While for lattice contractions, the peaks move towards each other. This is independent of the electron per atom variations within the impurities listed.

The higher temperature peak has the look of scattering by crystal field levels. That is, the shape, the temperature, and the shifts with lattice size are typical. However, preliminary inelastic neutron scattering measurements showed no sign of any crystal field excitations at the required energies and temperature.[11] Although we have no explanation for this higher temperature feature, a similar one occurs in $CeCu_2Si_2$[12] and $CeAl_3$.[13] However, the shape, temperature, and sensitivity to impurities of the lower resistivity peak is even more uncommon for materials that do order magnetically. Fig. 2 shows the resistivities of several samples in the ^{3}He temperature range. For the X=0 sample the lower peak occurs at 2.5 K and is only a few degrees wide. Hence this scattering shows that the electrons are going into a highly correlated state. To our knowledge, only UBe_{13} and $CeCu_2Si_2$[12] show such a feature. The compound $CeAl_3$ does show a change of slope at 5.5 K[13] that may have a similar origin.

Although such anomalies below 10 K are unusual, it is even more unusual to find enormous increases in c/T vs T^2 plots (the electronic term) over the same temperature range in the same compounds, $CeAl_3$[14] $CeCu_2Si_2$,[12] and UBe_{13}.[14] We associate these phenomena with the development of a highly correlated state that occurs at the expense of the localization of f-electrons. There are no other possibilities, except of course those specifically associated with the detailed mechanism for this state formation.

The curves in Fig. 2 show an interplay between the low temperature resistivity anomaly and T_c that supports the view that they have separate causes. For X=0, the maximum is at 2.5 K and the T_c is 0.95 K. For X=0.0089, the maximum has moved to below 1 K and the increased electron scattering has depressed T_c to 0.72 K. In the next curve the maximum is just gone, and the T_c is pushed down to 0.5 K. Then for X=0.026 the source of scattering has completely disappeared, and the T_c comes back up to 0.69 K. For further thorium additions, the T_c continues to drop in a manner consistent with the usual T_c depression in a superconductor by non-magnetic impurities. Figure 3 shows a plot of these T_c's and includes the somewhat less dramatic behavior seen by ac susceptibility. Preliminary heat capacity measurements show the same T_c for the X=0.0089 and the 0.026 samples.[15]

Several observations can be made from Fig. 2. If this resistive anomaly were a precursor of heavy Fermion superconductivity, its temperature, height, or both would decrease monotonically with the T_c depression by impurities. There would be no interplay. Another point is that pure UBe_{13} has an enormous residual resistivity (even with a T_c depression by a magnetic field) in any readily accesible temperature range. Hence experiments that require low electron scattering, such as de Haas-van Alphen effect, will be difficult. Figure 2 suggests that approximately a factor of ten can be gained by adding 1.75 % Th. Therefore more measurements may actually be possible on a system that would normally be considered "dirtier."

The final point to be made from Figs. 2 and 3 involves the effect of microscopic order. For two of the compositions the resistive T_c's are lower than the inductive ones. Usually resistive T_c's are higher (and transitions narrower) because the percolation limit wins in real materials, which contain microscopic inhomogenities. We conclude that since there is also a non-monotomic interplay between the T_c's from these two measurements, there are important microscopic effects that depend sensitively on homogeneity. (A similar situation occurs in U_6Fe that has been made amorphous by two different techniques.[16]) We have observed other sensitivities to lattice perfection for pure UBe_{13}. It is usual, when comparing T_c's from polycrystals and single crystals of the same material, to find a sharper transition for a single crystal but the same onset for for both forms. Our UBe_{13} samples do show sharper transitions for single crystals, but it is the centers of the transitions that coincide. Again it is a question of microscopic structure, but there is an implication that some sort of imperfection can raise T_c. We have not found it yet. Finally, when our samples are powdered as a check on flux exclusion, ac susceptibility shows a decrease in the "throw" of the transition by roughly a factor of five. Because heat capacity measurements rule out a large component of a non-superconducting second phase, we believe that UBe_{13} shows an extreme sensitivity to damage, particularly because the high angle x-ray lines show no broadening for this powder. All of these points suggest an unusual dependence on lattice perfection.

Within this context, a comparison to $CeCu_2Si_2$ should be made. There is a lack of reproducible properties for samples of $CeCu_2Si_2$.[12,17] Since it is ternary instead of binary, tetragonal instead of cubic, and peritectoidal[17] instead of congruent, it is clear that $CeCu_2Si_2$ must remain more difficult to study than UBe_{13} assuming that they are equally sensitive to lattice imperfection. Indeed, the discovery of the similar properties of these two compounds is one of the strongest demonstrations that the properties of $CeCu_2Si_2$ are correct.

Preliminary magnetization data for low temperatures are shown in Fig. 4. We conclude that the resistivity anomalies are not magnetic in origin, as is consistent with other data. We expect that as the thorium destroys the correlated state, the uranium atoms will tend towards a local moment state as in other uranium band systems, for example UAl_2.[18] These data are consistent with that view.

Preliminary T_c depression data for Sc, Lu, Gd, Np, Ce, La, and Ba are shown in Table I for dilute concentrations. For lattice parameters that are close to uranium and thorium the depressions are similar to those from thorium. Gadolinium presumably yields a slightly greater depression because it is a local moment impurity. Scandium, which is small, and barium, which is large, result is rather small depressions. The possibility that they did not go into the uranium lattice is ruled out by x-ray lattice parameter measurements. Lutetium is by far the most anomalous. For two compositions, no superconductivity was seen down to 0.045 K. Unlike the resistivity results there is no correlation of T_c with lattice parameter, again suggesting a decoupling of these phenomena. Since the original goal of the substitutions was to raise the T_c above that of UBe_{13}, we have not yet checked for nonmonotonic depressions as a function of impurity concentration. The magnetic susceptibility of $NpBe_{13}$ is similar to that of UBe_{13}.[19] However, ac susceptibility measurements on single crystals of $NpBe_{13}$ down to 0.09 K showed no superconductivity.

IV. PROGNOSIS

There is a great deal of work to be done. For superconductivity the question of alternate pairing or alternate mechanisms must be answered. The sensitivity to imperfections, the resistivity features, and the high effective mass seem to hold the possibility of some new physics. If, as we believe, the superconductivity is a bonus on heavy Fermions, then the mechanism of the delocalization of f-electrons must be described.

Are there more of these materials? The 5f-electron series is the most likely place to look because the basic f-electron localization is stretched out over several elements rather than completely taking place at cerium.[7,20,21] Obviously many very narrow band systems exists in the 5f-electron series[20] that should be considered in more detail. Hill demonstrated that cerium, uranium, neptunium, and plutonium could be divided into superconductors and magnets by considering only the spacing of the f-electron elements.[22] That is, he treated the case of delocalization by direct f-f overlap. However he had a few compounds that should have been magnetic because of a large spacing but were not. He knew that the moments disappeared because of hybridization with non-f-electrons. These exceptions now can be seen to include $CeCu_2Si_2$ and UBe_{13}. This is where we look. After all, these two materials were not believed to be bulk superconductors when first reported to go superconducting.[23,24] It is now clear that materials that seem to just miss being magnets because of hybridization should be considered.

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Table I. Superconducting Transition Temperatures of $M_xU_{1-x}Be_{13}$ samples from ac susceptibility.

element M	lattice parameter of MBe_{13} (Å)	concentration X	T_c onset (K)
Sc	10.10[a]	0.0152	0.70
Lu	10.173[a]	0.016,0.034	0.045
U	10.255-10.260[b]	pure	0.95
Gd	10.27[a]	0.0147	0.42
Np	10.276[a]	0.011	0.62
Ce	10.376[a]	0.0158	0.55
Th	10.395[a]	0.0175	0.60
La	10.44[a]	0.017	0.53
Ba	10.53[c]	0.022	0.80

[a] W. B. Pearson, A. Handbook of Lattice Spacings and Structures of Metals and Alloys, Vol. 2, Pergamon, Oxford, 1967.

[b] measured for several samples, single and polycrystalline.

[c] extrapolated from our dilute sample.

Figure Captions

Fig. 1. Resistivity of thorium doped pseudo-binary compounds between 1.4 K and 300 K. The curves are offset vertically for clarity with their zeroes indicated. The vertical scale for each sample varies somewhat, but the height of the high temperature value indicates the proper normalization.

Fig. 2. Resistivity of thorium doped samples from 0.4 K to higher temperatures. Both axes are shifted for clarity. The onset of superconductivity is seen for all samples except X=0.0675.

Fig. 3. Superconducting transition temperatures of $Th_xU_{1-x}Be_{13}$ by ac susceptibility and resistivity.

Fig. 4. Magnetic Susceptibility of $Th_xU_{1-x}Be_{13}$.

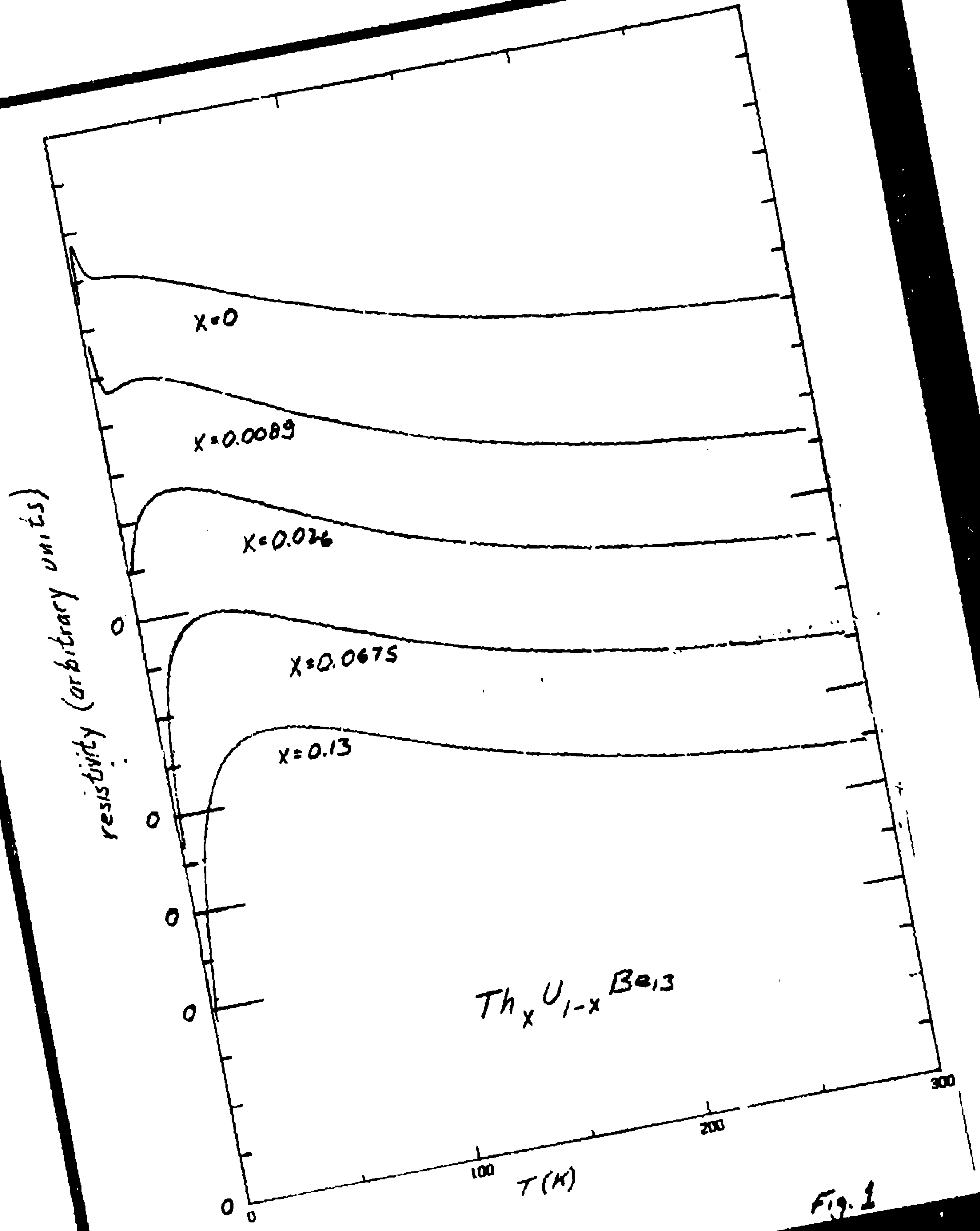
resistivity (arbitrary units)
x=0
x=0.0089
x=0.026
x=0.0675
x=0.13
0
0
0
0
0
0
100
200
300
T (K)
$Th_xU_{1-x}Be_{13}$

Fig. 1

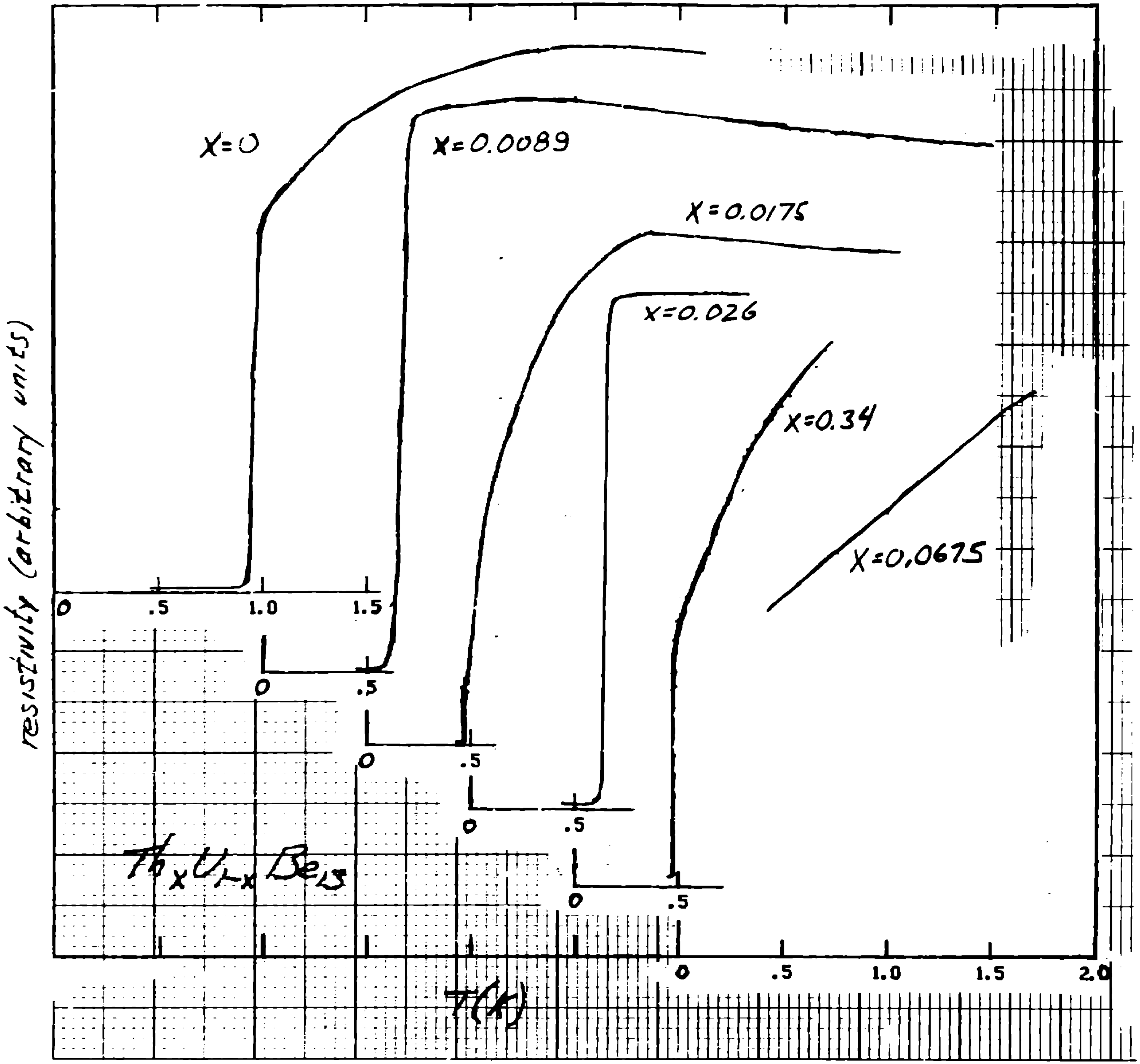
X=0
X=0.0089
X=0.0175
X=0.026
X=0.34
X=0,0675
resistivity (arbitrary units)
$Th_xU_{1-x}Be_{13}$
T(K)
0
.5
1.0
1.5
2.0

fig. 2

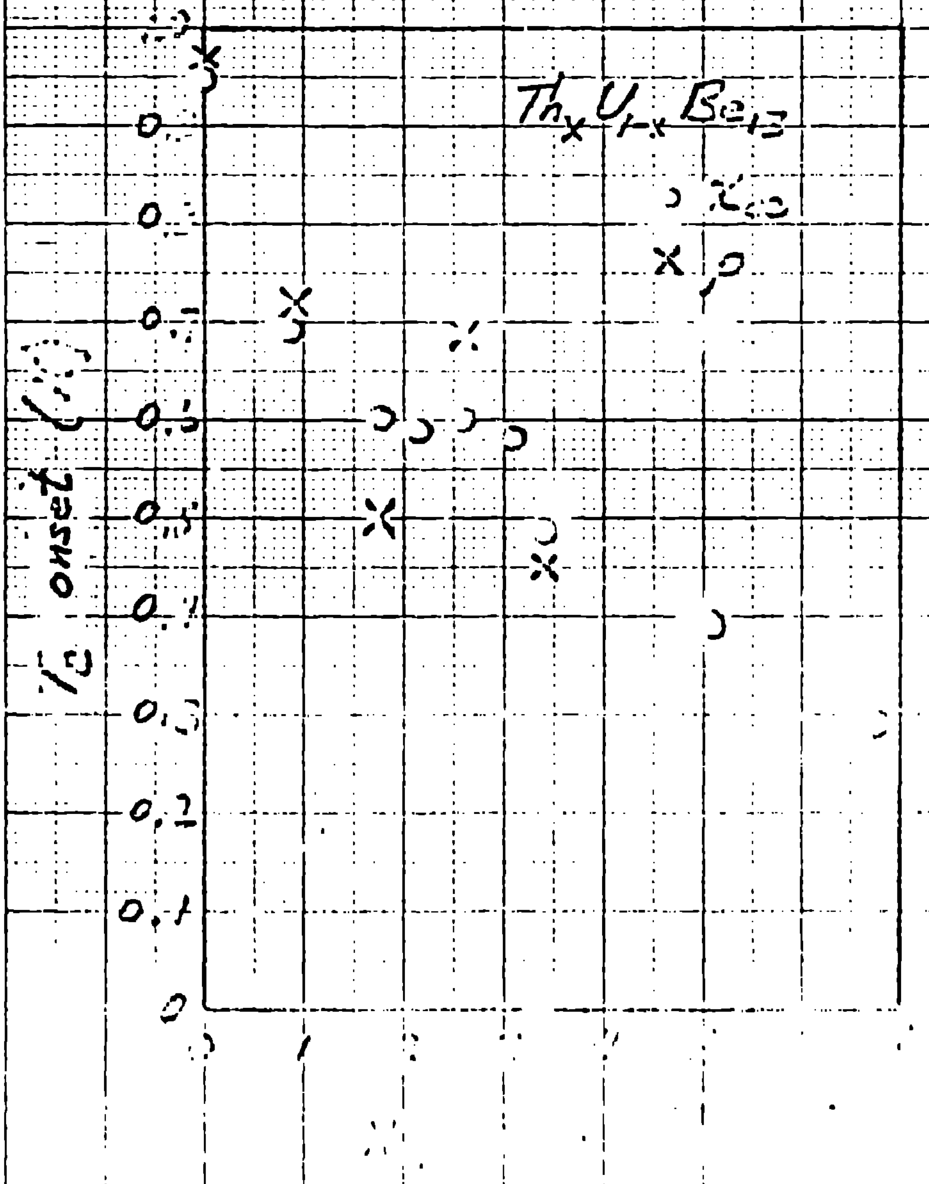

Fig. 5

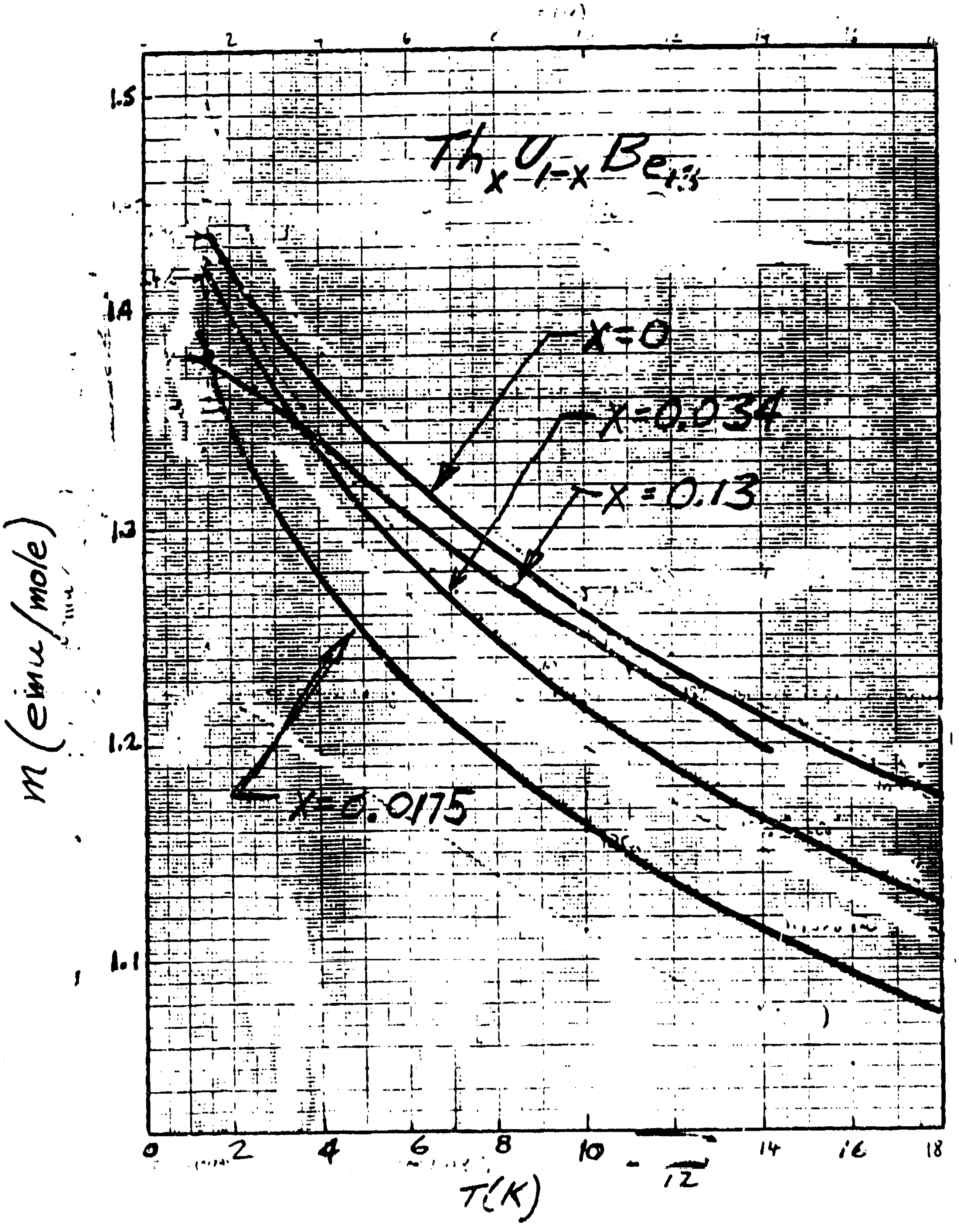
$Th_xU_{1-x}Be_{13}$
x=0
x=0.034
x=0.13
x=0.0175
1.5
1.4
1.3
1.2
1.1
m (emu/mole)
0
2
4
6
8
10
12
14
16
18
T(K)

fig. 4