Brief Reports

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Superconductivity in amorphous actinide alloys

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Superconductivity has been studied in amorphous binary alloys of actinides containing Co, Fe, and Ni. Amorphous thorium alloys have critical temperatures of up to 3.8 K and electronic properties similar to other transition-metal amorphous alloys. By contract, amorphous uranium alloys have critical temperatures below 1.0 K and exhibit two unusual electronic properties: (1) The temperature coefficient of resistivity is quite large and negative ($\lesssim -1.3\times10^{-4}$/K) which is generally not found in other low-resistivity (<90 $\mu\Omega$ cm) amorphous alloys containing transition metals; (2) the upper critical-field gradient is the highest observed in bulk amorphous superconductors, up to 44 kOe/K. Based on the resistivity and critical-field gradient we estimate the renormalized density of states to be two to three times that of 4*d* and 5*d* amorphous superconductors. The possibility of strong spin fluctuation in these materials is discussed.

Recently, the relationship between the occurrence of magnetism and the disappearance of superconductivity in amorphous alloys has been demonstrated in zirconium-rich Fe and Co metallic glasses.[1] In these materials and in other glassy superconductors, the normal-state electronic properties resemble the trends of those observed in most amorphous *d*-band metals. The temperature coefficients of resistivity α $[=(1/\rho)(d\rho/dT)]$ follow the well-known "Mooij correlation."[2] That is, $\alpha \gtrless 0$ according to resistivity $\rho \lesssim \sim 150$ $\mu\Omega$ cm. Magnetic[1] and superconducting[3] measurements indicate that the Stoner enhancement factor is small ($S \lesssim 2$). Therefore, the influence of spin fluctuation on superconductivity is rather weak, except in the narrow concentration region where itinerant ferromagnetism emerges and superconductivity disappears.

We report a comparative study of thorium and uranium metallic glasses formed with iron, nickel, and cobalt. Thorium has no 5*f* electrons but is otherwise similar to uranium (with 5*f* electrons). The effect of 5*f* electrons is probed by superconducting- and normal-state electronic properties. Comparison is also made with 4*d* and 5*d* amorphous superconductors.

Ingots of uranium and thorium alloys were prepared by the arc-melting of high-purity starting elements in an argon atmosphere. Alloy ribbons were prepared by the technique of melt spinning. For alloy compositions reported here, x-ray (Cu $K\alpha$ radiation) analysis indicated that the samples were amorphous. Our results were different from those obtained by "splat quenching."[4] A detailed study on the formability and structure of amorphous uranium-rich alloys will be published elsewhere.[5] Four terminal measurements were performed to determine resistivity and upper critical field as a function of temperature for each sample. Measurements were taken down to ~ 0.5 K. The refrigeration techniques employed in the measurements were discussed earlier.[3] Critical current ($\gtrsim 10^7$ A/m^2) tests were also used to check the bulk nature of the transitions.

All the actinide glasses studied were found to have comparable resistivity values of less than ~ 100 $\mu\Omega$ cm. There is, however, a clear distinction between the temperature dependence of resistivity in the thorium- and uranium-rich glasses. For the former, the temperature coefficients of resistivity are positive and small ($\alpha \simeq +0.3\times10^{-4}$/K), as expected from the "Mooij correlation." On the other hand, α values are negative and large for the uranium alloys ($\alpha \simeq -1.3$ to -2.0×10^{-4}/K). Resistivities as a function of temperature for two samples are shown in the inset of Fig. 1. The rapid drop in resistivity below ~ 10 K in $Th_{75}Ni_{25}$ is due to superconducting fluctuation above $T_c \simeq 3.7$ K. The unusual behavior in $\rho(T)$ for the uranium-rich glasses will be discussed. Also illustrated in Fig. 1 are the upper critical fields H_{c2} for the $Th_{75}Ni_{25}$, $U_{78}Fe_{22}$, and $U_{85.7}Co_{14.3}$ alloys. The closed circles represent the end points of the transitions ($\rho=0$). All ρ-H traces show narrow transition widths ($\lesssim 3$ kOe), even in high fields. It can be seen that the initial critical-field gradients in the two uranium alloys are significantly higher than that in the thorium alloys. Following the procedure described in Ref. 3, we have evaluated the actual field gradients (dH_{c2}/dT) at T_c using the visual values. For large spin-

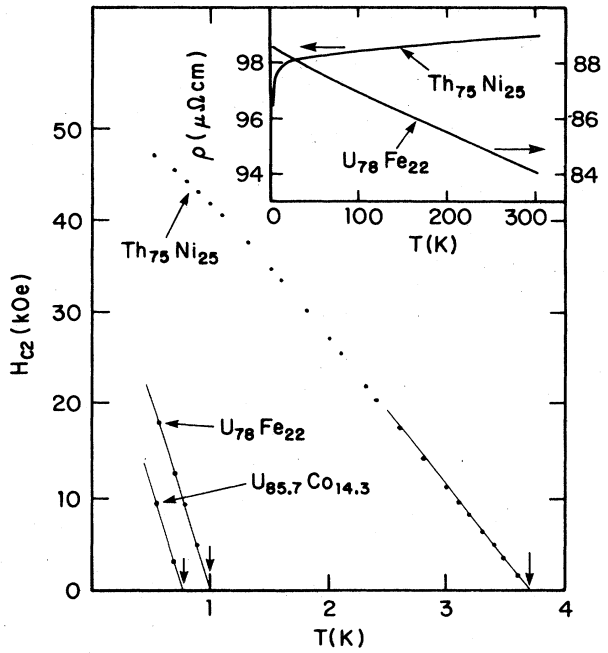

FIG. 1. Upper critical field as a function of temperature for amorphous $Th_{75}Ni_{25}$, $U_{85.7}Co_{14.3}$, and $U_{78}Fe_{22}$ alloys. Vertical arrows indicate transition temperatures. Straight lines show visual initial slopes. Inset: resistivity as a function of temperature above 4.2 K for $Th_{75}Ni_{25}$ and $U_{78}Fe_{22}$ alloys. Solid lines are traced through the data points since the latter are densely spaced.

orbit scattering, the actual gradients are about $\sim 6\%$ higher than the visual values. The critical-field gradients, together with data on T_c and ρ, are listed in Table I. The slope $-(dH_{c2}/dT)T_c = 44$ kOe/K in $U_{85.7}Co_{14.3}$ is the largest observed in bulk glassy superconductors.

In the dirty limit, one can express the renormalized density of states at the Fermi level $N^*(0)$ in the following form:[3]

$$N^*(0) = -(9.46\times10^{-7})\frac{M}{\rho d}\left[\frac{dH_{c2}}{dT}\right]_{T_c}$$

$$= -(9.46\times10^{-7})\frac{M}{mr}\left[\frac{dH_{c2}}{dT}\right]_{T_c}, \quad (1)$$

where $N^*(0)$ is given in states/eV atom when M, the molecular weight, is in grams; d, the density in g/cm^3; ρ, the normal-state resistivity, in Ω cm; and dH_{c2}/dT, the field gradient, in kOe/K. Density is taken to be the gram-atomic mass $\overline{M}$ to gram-atomic volume $\overline{V}$ ratio, where $\overline{V} = \overline{M}/d$. This procedure is demonstrated to yield values in excellent agreement (to within $\sim 1\%$) with experimental results in metal-metal glasses.[1,6] Using the density and mass per unit length (m) of the samples, resistivity ρ can be calculated from the sample cross-sectional area. The thickness of the samples is also measured by an optical microscope. Metallographically polished cross sections are being used in the measurement. Agreement to within 5% between the calculated and measured thickness is obtained. The resistance per unit length r is a well-defined quantity. Thus, the values of $N^*(0)$ for our alloys can be calculated according to expression (1). They are listed in Table I. To provide a comparison of the electronic properties between the presently studied ($6d$) ($5f$) alloys and the ($4d$) ($5d$) alloys, the maximum $N^*(0)$ values representative of the latter series are also included. Again, the values of (dH_{c2}/dT) at T_c have been corrected to obtain the actual values.[3] In order to give a systematic comparison, all $N^*(0)$ values except one ($Zr_{70}Fe_{30}$) are derived from critical-field data. It is seen that the uranium-rich alloys have $N^*(0)$ values two to three times those of the other alloys. This can be correlated with the presence of the $5f$ band in the uranium alloys. When expressed in the same unit, the $N^*(0)$ value obtained for

TABLE I. Superconducting- and normal-state properties of amorphous actinide alloys (upper portion of table) and transition-metal alloys (lower portion of table). The latter are taken from the literature. Uncertainties in ρ (see text) are about 5%.

Alloys	T_c (K)	ρ (near T_c) ($\mu\Omega$ cm)	$-(dH_{c2}/dT)_{T_c}$ (kOe/K)	$N^*(0)$ (states/eV atom)
$U_{85.7}Co_{14.3}$	0.78	73.4	44	6.9
$U_{72}Co_{28}$	0.6	87.3	. . .	. . .
$U_{85.7}Fe_{14.3}$	1.0	85.6	40.5	5.8
$U_{78}Fe_{22}$	0.98	88.7	43	5.2
$U_{85.7}Ni_{1.43}$	0.53	73.5	. . .	. . .
$U_{72}Ni_{28}$	< 0.5	90	. . .	. . .
$Th_{75}Ni_{25}$	3.7	97	17.3	2.6
$Th_{80}Co_{20}$	3.8	91.5	17.3	2.8
$Zr_{75}Rh_{25}$[a]	4.3	160	33.8	2.5
$Zr_{75}Cu_{25}$[b]	3.18	158	34	~ 2.6
$Zr_{70}Fe_{30}$[b]	0.5	. . .	. . .	2.6[c]
$(Mo_{0.6}Ru_{0.4})_{86}B_{14}$[d]	6.88	125	~ 26.6	~ 1.7
$La_{80}Al_{20}$[e]	4.43	163	~ 26	~ 2.9

[a]Reference 3.
[b]Maximum values of $N^*(0)$ chosen from published data on amorphous Zr-rich alloys. See, for example, Ref. 1; also D. G. Onn, L. Q. Wang, and K. Fukamichi, Solid State Commun. **47**, 479 (1983).
[c]From specific-heat measurement.
[d]M. Tenhover, W. L. Johnson, and C. C. Tsuei, Solid State Commun. **38**, 53 (1981).
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TABLE II. Electron and electron-phonon parameters for amorphous actinide alloys. $N(0)$ has the same units as $N^*(0)$ in Table I.

Alloys	$P_l^2=1$, $I=0.35$ eV $N(0)$	λ_{sf}	$\lambda_{e\text{-ph}}$	S	$P_l^2=0.35$, $I=0.4$ eV $N(0)$	λ_{sf}	$\lambda_{e\text{-ph}}$	S
$U_{85.7}Co_{14.3}$	2.13	0.73	1.52	3.9	2.17	0.69	1.48	7.6
$U_{85.7}Fe_{14.3}$	2.00	0.56	1.32	3.3	2.08	0.51	1.26	6.0
$U_{78}Fe_{22}$	1.93	0.49	1.20	3.1	2.03	0.43	1.12	5.3
$Th_{75}Ni_{25}$	1.26	0.13	0.94	1.8				
$Th_{80}Co_{20}$	1.32	0.14	0.98	1.9				

the $U_{85.7}Fe_{14.3}$ ($\simeq U_6Fe$) glass is similar to that determined from specific-heat measurement for thin-film glassy U_6Fe.[7] This is $\sim 35\%$ lower than that determined for crystalline U_6Fe.[8]

Rietschel and Winter,[9] and Orlando and Beasley[10] have proposed that spin fluctuation can affect the superconducting properties in some refractory metals and their compounds. The inverse correlation [low T_c, large $N^*(0)$] observed in the uranium-rich glasses suggests that these materials are exchange-enhanced paramagnetic superconductors. The anomalous behavior in $\rho(T)$ (Fig. 1) is also consistent with this notion. In fact, the electron-paramagnon scattering mechanism can lead to negative temperature coefficients of resistivity (TCR).[11] The resistivity is then given by $\rho=\rho_0[1-(T/T_s)^2]$, where T_s is the order of the spin-fluctuation temperature T_{sf}. It is difficult to separate the magnetic contribution from the nonmagnetic one in our uranium alloys. The magnitudes of change in resistivity $\Delta\rho=\rho(4.2\text{ K})-\rho(300\text{ K})\simeq 4$ to 6 $\mu\Omega$ cm, however, are comparable to those observed in γ-U alloys of the body-centered cubic structure.[12] Other nearly magnetic actinide (e.g., Np, Pu) alloys also show decreasing ρ at increasing temperature which can be described by the paramagnon model.[13] Incidentally, γ-U alloys also are superconductors with $T_c\simeq 2$ K.[14] It should be mentioned that in amorphous simple metal alloys of Mg-Zn with low resistivity (~ 60 $\mu\Omega$ cm), negative TCR were also observed at higher temperatures followed by the occurrence of maxima in $\rho(T)$ at decreasing temperatures.[15] The existence of negative TCR over the entire temperature range ($T\gtrsim T_c$) in the uranium alloys is definitely unusual for low-resistivity metallic glasses.

One can perform a semiquantitative analysis to obtain the relevant superconducting parameters for the actinide alloys. By including the effect of spin fluctuations in the strong coupling theory, the following equations are obtained:[10,16,17]

$$T_c=\frac{\Theta_D}{1.45}\exp\left[-\frac{1+\lambda_{e\text{-ph}}+\lambda_{sf}}{\lambda_{e\text{-ph}}-\lambda_{sf}-\mu^*}\right], \tag{2}$$

$$\lambda_{sf}=\tfrac{9}{2}\bar{I}\ln\left[1+\frac{P_l^2}{12}\frac{\bar{I}}{(1-\bar{I})}\right], \tag{3}$$

$$N^*(0)=N(0)(1+\lambda_{e\text{-ph}}+\lambda_{sf}), \tag{4}$$

$$\bar{I}=N(0)I, \tag{5}$$

where Θ_D is the Debye temperature, $\lambda_{e\text{-ph}}$ and λ_{sf} are the electron-phonon and electron-electron (spin fluctuation) parameters, respectively, P_l is a momentum cutoff parameter, $N(0)$ is the bare density of states, I is the electron-electron correlation parameter, and μ^* is taken to be 0.13. Values of Θ_D for amorphous transition-metal alloys of composition $A_{100-x}B_x$ ($x<25$) are usually 30–40% lower than those found in crystalline metals A.[18,19] These empirical results will be used to estimate Θ_D for the actinide alloys. For amorphous $U_{85.7}Fe_{14.3}$, $\Theta_D(=140$ K) was determined from specific-heat measurement.[7] For alloys taken from the literature (Table I), the Θ_D values are known. Without susceptibility data, values of the two parameters I and P_l^2 are extrapolated from the transition-metal series. In practice, P_l^2 is always a fitting parameter. The choices of P_l^2 and I for transition metals have been discussed in Ref. 3. In summary, $I(\simeq 0.35$ eV) is essentially constant for transition metals according to Janak's calculation,[20] the cutoff parameters $(P_l^2)_{3d}\simeq 1.2$ and $(P_l^2)_{4d}\simeq 2$. A rough estimate of electron and electron-phonon parameters will be made by taking $(P_l^2)_{6d}\simeq 1$ and $I\simeq 0.35$ eV. Since the electron band in U is narrow,[21] $(P_l^2)_{6d5f}$ is expected to be even smaller. In fact, one can use the results of Ref. 8 (susceptibility data) to obtain a reasonable estimate of the values of the pair $\{P_l^2,I\}$. It is then noted that even for $P_l^2\simeq 0.5$, $\bar{I}$ is already close to unity, and $N(0)\simeq 1.1$ states/eV atom which is too low for U.[21] Decreasing P_l^2 to 0.35 (arbitrary value) yields $\bar{I}\simeq 0.85$ ($I\simeq 0.4$ eV) and $N(0)\simeq 2.1$ states/eV atom. It will be seen that the latter is similar to those found in amorphous U alloys. In Table II, a comparison of parameters for two values of P_l^2 for U alloys is given. One should bear in mind that the values listed are only rough estimates since these results depend on the validity of Eqs. (2) and (3). It is seen that the Stoner enhancement factors $S=1/(1-\bar{I})$ are comparable to that found in crystalline U_6Fe.[8] For the Th alloys, the values are comparable to those found in the 4d and 5d alloys (Table I). Thus, the uranium-rich glasses are simultaneously exchange-enhanced paramagnets and superconductors. These materials provide ideal systems for studying the interaction of strong spin fluctuation and superconductivity in amorphous systems independent of particular crystalline structures.

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