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Influence of 5f electrons on transport properties in uranium-based metallic glasses*

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Abstract

In order to study the influence of 5f electrons on the superconducting and the magnetic properties of uranium glasses, X-ray, upper critical magnetic field and susceptibility measurements were performed on three binary metallic glass systems: U–Fe, U–Co and U–Ni. For each alloy system a continuous range of uranium-rich compositions prepared by splat cooling has been examined. It is found that these samples have ferromagnetic inclusions which may be due either to ferromagnetic impurities or to the formation of clusters with high transition metal densities. The superconducting transition temperature is reduced by strong spin fluctuations. Both the superconductivity and the spin fluctuation are due to the presence of the 5f electrons.

1. Introduction

The electronic and magnetic properties of actinide metals and their compounds are largely determined by the partially filled 5f shell. The character of the 5f electrons varies from the itinerant electronic state in the early actinides (superconductivity) to the localized electronic state (magnetic structure) in the late actinides via the intermediate spin fluctuation state. Especially in uranium compounds all these electronic states are present.

Superconductivity of uranium compounds was first discovered in the U_6X alloys ($X \equiv$ Mn, Fe, Co, Ni) [1]. Later, coexistence of superconductivity and spin fluctuation phenomena was reported for U_6Fe [2] and U_6Co [3]. Today these uranium compounds are subjects of the growing class of 'heavy fermion' superconductors, which are characterized by a large coefficient of the electronic term in the specific heat γ and by a large initial slope of the temperature dependence of the upper critical field $(dB_{c2}/dT)_{T_c}$. However, the γ values of these compounds are not so extremely large as, for instance, in UBe_{13} [4] and UPt_3 [5].

In this paper we report on studies of the influence of the 5f electrons on amorphous U–(Fe, Co, Ni) alloys which can be prepared in a wide

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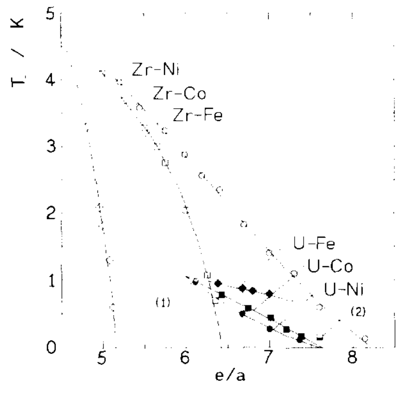
*Dedicated to Professor W. Bronger and Professor Ch. J. Raub on the occasions of their 60th birthdays.

concentration range [6]. This allows a continuous variation of the density of the 5f electron states at the Fermi surface. Susceptibility measurements of some of these alloys indicate a spin glass behaviour which corresponds to regions of relatively high local transition metal density of the samples [7]. Furthermore, in 1985 Poon *et al.* [8] showed that these uranium-based metallic glasses become superconducting below 1 K. Recently we have concluded that these glasses correspond to a strong spin fluctuation system because of the large γ values known from specific heat measurements and the low T_c values [9, 10].

In contrast with zirconium-based metallic glasses the uranium glasses show a rather unusual behaviour of T_c as a function of the valence electron concentration *e/a* (Fig. 1). For the Zr–Fe and Zr–Co glasses T_c strongly decreases at a certain *e/a* ratio. This is not observed in the uranium systems. For U–Fe T_c decreases only slightly with increasing *e/a* ratio. In the U–Co and U–Ni systems this decrease becomes larger, but is still much smaller compared with the corresponding zirconium glasses.

The strong decrease in T_c for the Zr–Fe and Zr–Co systems is understandable in terms of spin fluctuation phenomena. Spin fluctuations tend to stabilize parallel spin configurations and act as pair breakers. Their presence is reflected in the simultaneous increase in the magnetic susceptibility with decreasing T_c. In the zirconium glasses the increase of spin fluctuations corresponds to the increase of the density of the 3d electron states at the Fermi surface. However, this interpretation cannot explain the T_c dependence of the uranium glasses (Fig. 1). In order to explain this discrepancy we performed X-ray, susceptibility, resistivity and upper critical field investigations on these systems.



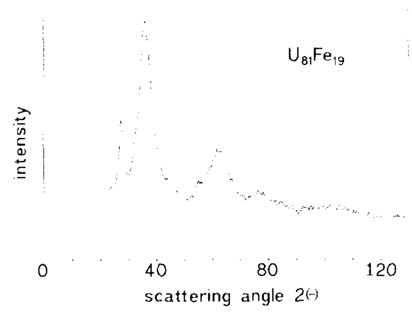


Fig. 1. Superconducting transition temperature T_c as a function of valence electron concentration for Zr–(Fe, Co, Ni) [11] and U–(Fe, Co, Ni) glasses: ◇, Zr–Fe; □, Zr–Co; ○, Zr–Ni; ◆, U–Fe; ●, U–Ni; ■, U–Co. In contrast with the uranium glasses T_c of Zr–Fe and Zr–Co decreases strongly with increasing iron or cobalt concentration. In addition, the T_c values of the pseudobinary uranium glasses $(U_{10}Zr_{90})_{67}Ni_{33}$ (◒) and $(U_{75}Th_{25})_{40}Co_{60}$ (□) are plotted.

Fig. 2. X-ray diffraction data for a glassy $U_{81}Fe_{19}$ splat using Cu Kα radiation. The prepeak at $2\Theta = 28°$ belongs to an oxide surface layer.

2. Experimental details

Alloys of U–X with X≡Fe, Co, Ni were prepared by the splat quenching technique in the concentration range between 50 and 83 at.% U (see ref. 10). The amorphous state was checked by X-ray diffraction using Cu Kα radiation. With the exception of $U_{83}Co_{17}$ which shows some crystalline peaks, the typical X-ray pattern for metallic glasses according to the mean U–U and U–X distances is visible in the scattering diagram for all samples. As an example Fig. 2 shows the X-ray diffraction data for $U_{81}Fe_{19}$. The intensity of the prepeak at $2\Theta = 28°$ which is observed in all samples can be reduced by grinding the surface, indicating that this peak is caused by an oxide surface layer.

For resistivity, susceptibility and upper critical field measurements small ribbons with a width of 2–3 mm were cut from each splat between the core and the boundary of the splat. To determine the density, the volume was measured by means of an optical microscope. The error of about 8% is mainly due to the thickness variation over the sample. Before each measurement the oxide surface layer was removed by means of mechanical grinding.

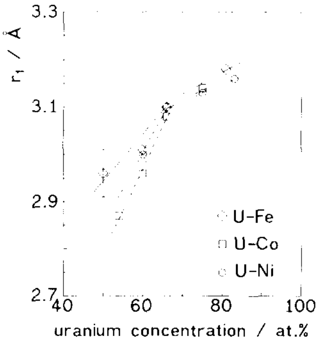
Magnetic susceptibility measurements were carried out in a conventional SQUID susceptometer adapted to a 5 T magnet. The upper critical field measurements were carried out by the standard four-terminal technique in a ^3He–^4He dilution refrigerator down to 13 mK in a magnetic field up to 11 T. The surface of the samples was oriented perpendicular to the external magnetic field. The temperature was measured with both a calibrated germanium and a calibrated carbon resistor down to 50 mK. Below 80 mK a ^{60}Co-in-^{59}Co nuclear orientation thermometer was used. The resistivity and superconducting transition measurements have been reported previously [12].

3. Results and discussion

3.1. *The atomic structure*

The systematics in the occurrence of superconductivity and magnetic order in uranium compounds is usually represented by a critical value for the distance between nearest-neighbour uranium atoms. This critical U–U atomic distance is known as the Hill limit [13] and amounts to 3.4–3.6 Å. Below this value no spontaneous magnetic order is generally found whereas beyond this value no superconductivity occurs except in UBe_{13} [4] and UPt_3 [5].

From X-ray diffraction measurements the total reduced distribution function was calculated for all actinide glasses studied in this paper. In Fig. 3 the mean atomic distances taken from the centre of gravity of the main peak of the total reduced distribution function are plotted *vs.* the uranium concentration. The three uranium systems were found to have a comparable concentration-dependent atomic structure. A similar result has already been reported for the U–Co system [14]. The mean nearest-neighbour distances



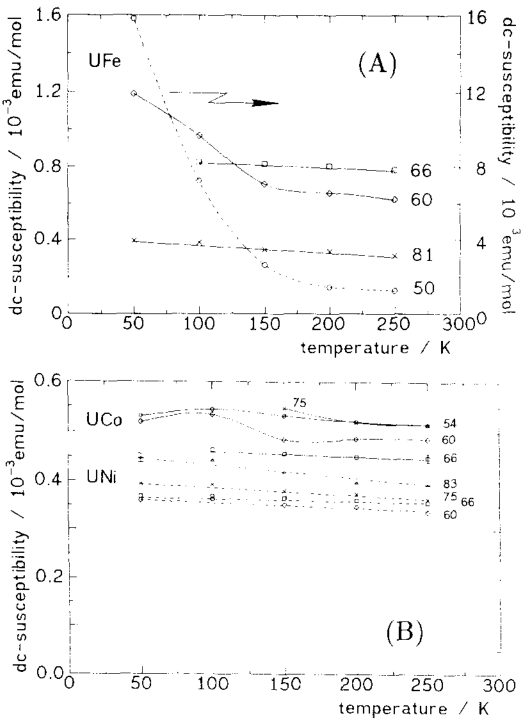


Fig. 3. Mean atomic distances r_1 taken from the centre of gravity of the main peak of the total reduced distribution function *vs.* uranium concentration: ◇, U–Fe; □, U–Co; ○, U–Ni. The data for the U–(Fe, Co, Ni) glasses can be described by two straight lines which intersect at (68 ± 2) at.% U. This may be due to two different phases.

Fig. 4. Magnetic susceptibility *vs.* temperature for (A) the U–Fe glasses and (B) the U–Co (——) and U–Ni (– – –) glasses. All samples were measured in a magnetic field of 1 T. (The numbers beside the curves give the uranium concentrations.)

($r_1 < 3.18$ Å) are well below the Hill limit which indicates a U–U atomic distance also below the Hill limit. Therefore we expect no spontaneous magnetic order in our samples. The data for the U–(Fe, Co, Ni) glasses can be described by two straight lines which intersect at (68 ± 2) at.% U. This may be due to the formation of a second phase below 68 at.% U with higher transition metal density in the environment of the uranium atoms.

3.2. *The susceptibility*

Susceptibility measurements were performed both on samples with an oxide surface layer in a magnetic field of 0.5 T [15] and on polished samples in a magnetic field of 1 T. In comparison with the χ values of the polished samples, those of the oxide samples are about 5–15% larger. This may be due to any of several UO_x phases at the surface. Additionally, higher χ values can be obtained when ferromagnetic impurities, which cause a field-dependent susceptibility, are present.

For all polished samples the temperature dependence of χ taken at $B = 1$ T is shown in Fig. 4. The susceptibility of the U–Ni glasses varies linearly with temperature, whereas some U–Co and U–Fe glasses deviate from linearity to larger χ values below 170 K. Especially for $U_{60}Fe_{40}$ and $U_{50}Fe_{50}$ the susceptibility increases dramatically, indicating a magnetic ordering.

More detailed investigations on $U_{66}Fe_{34}$ lead to the conclusion that the magnetic ordering is caused by ferromagnetic inclusions. In Fig. 5 $\chi(T)$ is plotted for two different $U_{66}Fe_{34}$ samples but both with an oxide surface layer. The sample represented by curve a shows a magnetic ordering temperature at about 150 K and a hysteresis below 110 K for field cooling (FC) and zero-field cooling (ZFC) cycles. Such behaviour has already been observed by Cornelison *et al.* in $U_{66}Fe_{34}$, $U_{66}Co_{34}$ and $U_{66}Ni_{34}$ [7] and by DeLong *et al.* in crystalline UFe_6 [16]. Cornelison *et al.* concluded that this behaviour is caused by stable transition metal moments developed in regions of relatively high local transition metal density (cluster model). In contrast, DeLong *et al.* explained the ordering temperature by ferromagnetic impurities such as UFe_2 and UH_3 which have an ordering temperature in the range between 150 and 180 K. The sample represented by curve b shows only a small hysteresis below 30 K for FC and ZFC cycles. This may be due to UO_2 with an ordering temperature of 30 K which probably covers the surface of the samples. In contrast with the curve a sample no magnetic field dependence of χ was observed in the curve b sample. This also explains that the susceptibility at room temperature of the curve a sample is somewhat higher than that of the curve b sample because of unsaturated moments.

Summarizing, the non-linear temperature dependence of the susceptibility indicates ferromagnetic inclusions in the uranium glasses. However, it is not yet clear whether these inclusions are due to ferromagnetic impurities [16] or to the formation of magnetic clusters with high transition metal densities [7].

To determine the Pauli susceptibility χ_p^{exp} we use the χ^{exp} values at $T = 250$ K in order to minimize the effect of the ferromagnetic inclusions.

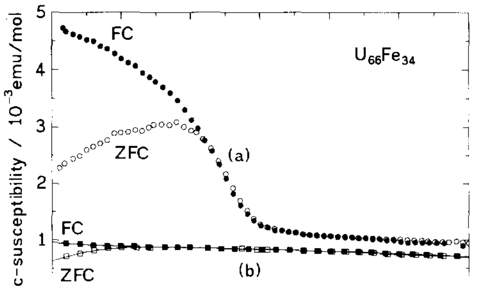


Fig. 5. Magnetic susceptibility *vs.* temperature for two selected $U_{66}Fe_{34}$ samples measured in a magnetic field of 0.5 T: curve a, a sample showing a magnetic ordering temperature at 150 K and a hysteresis below 110 K for FC and ZFC cycles; curve b, a sample showing no ordering temperature but a hysteresis below 30 K.

In Fig. 6 χ^{exp} is plotted *vs.* the uranium concentration. The U–Fe glasses show a rapid increase of χ^{exp} whereas the susceptibility of the U–Co and U–Ni systems is nearly constant over the whole concentration range (the deviation of the $U_{60}Fe_{40}$ sample may be due to a mixture of different concentrations also observed in resistivity [12] and T_c measurements). In contrast with the zirconium glasses where an increase of the susceptibility coincides with a decrease of T_c due to spin fluctuations, the change of the large magnetic susceptibility of the uranium glasses seems to have no drastic influence on T_c. In particular, the U–Fe glasses show a dramatic increase of χ without any severe change of T_c going from lower to higher iron concentrations. This relation between T_c and χ also supports the assumption that our samples have ferromagnetic inclusions.

From the Pauli susceptibility the electron density of states at the Fermi surface $N_\chi(0)$ can be calculated. The ratio of the susceptibility χ^{exp} and the bare γ value determined from specific heat measurements varies between a factor of 4 and 20 which strongly deviates from the expected value of unity. This deviation may be due either to a large Stoner enhanced Pauli susceptibility or to a large Van Vleck susceptibility χ_{vv} taking into account the partially filled d and f orbitals. Therefore it is rather difficult to separate the Pauli susceptibility $\chi_{\mathrm{p}}^{\mathrm{exp}}$ from the experimental susceptibility χ^{exp}.

For a rough estimation of $\chi_{\mathrm{p}}^{\mathrm{exp}}$ the experimental susceptibility may be written as

$$\chi^{\mathrm{exp}} = S\chi_{\mathrm{p}} + \chi_{\mathrm{vv}} + \chi_{\mathrm{dia}} \tag{1}$$

where $S\chi_{\mathrm{p}} = \chi_{\mathrm{p}}^{\mathrm{exp}}$ is the Stoner enhanced Pauli susceptibility and χ_{dia} the diamagnetic susceptibility dominated by the diamagnetic core susceptibility. The core susceptibility for all four elements is small, for the U^{+2} ion about $\chi_{\mathrm{dia}}^{\mathrm{core}} = -0.053 \times 10^{-3}$ e.m.u. mol^{-1} [17] and for iron, cobalt and nickel $\chi_{\mathrm{dia}}^{\mathrm{core}} \approx -0.03 \times 10^{-3}$ e.m.u. mol^{-1} [18]. The Van Vleck term belonging to

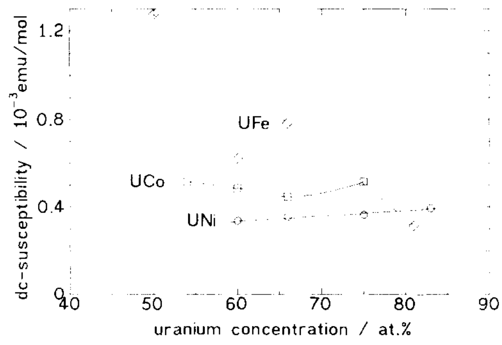


Fig. 6. Magnetic susceptibility χ^{exp} for $T = 250$ K *vs.* uranium concentration. The U–Fe glasses (◇) show a dramatic increase of χ^{exp} with decreasing uranium concentration while the susceptibility of U–Co (□) and U–Ni (○) remains nearly constant. For the $U_{60}Fe_{40}$ sample the deviation of the χ value from the linear rise may be due to a mixture of different concentrations.

the 5f, 6d and 3d electrons can be estimated as [19]

$$\chi_{\mathrm{VV}}=\frac{2}{3}N_{\mathrm{A}}\mu_{\mathrm{B}}^{2}L(L+1)N_{L}\left[1-\frac{N_{L}}{2(L+1)}\right]\frac{1}{\Delta E_{L}} \tag{2}$$

Here L is the rotational quantum number, N_L the number of electrons in the L band and ΔE_L the mean energy width of the L band (N_{A} and μ_{B} have the usual meanings). The energy width of the 5f band is about 4 eV [20], while that of a d band amounts to 5 eV. Therefore the 5f electrons of uranium form the largest part of the Van Vleck susceptibility ($\chi_{\mathrm{VV}}^{\mathrm{5f}}=0.152\times10^{-3}$ e.m.u. mol^{-1}) whereas the d electron contribution is much smaller ($\chi_{\mathrm{VV}}^{\mathrm{6d}}=0.023\times10^{-3}$ e.m.u. mol^{-1} and $\chi_{\mathrm{VV}}^{\mathrm{3d}}=0.05\times10^{-3}$ e.m.u. mol^{-1} [18]). Finally, to calculate the Van Vleck term χ_{VV} we take into account the concentration of both elements.

In Table 1 the corrected susceptibilities $\chi_{\mathrm{p}}^{\mathrm{exp}}$ are listed together with the electron densities of states calculated from

$$N_{\chi}(0)=\frac{\chi_{\mathrm{p}}^{\mathrm{exp}}}{2\mu_{\mathrm{B}}^{2}N_{\mathrm{A}}} \tag{3}$$

In comparison with the electron density of states $N(0)^*$ calculated from the initial slope of the upper critical field and resistivity measurements (see next section), these values indicate a strong Stoner enhancement.

3.3. *The upper critical field*

The temperature dependence of the upper critical magnetic field was measured over the whole temperature range down to 13 mK. B_{c2} as a function

TABLE 1

The fit parameters T_c, α and λ_{so}, the resulting $(\mathrm{d}B_{c2}/\mathrm{d}T)|_{T_c}$ and $N^*(0)$, the Stoner enhanced corrected Pauli susceptibility $\chi_{\mathrm{p}}^{\mathrm{exp}}$ and the resulting electron density of states at the Fermi surface $N_{\chi}(0)$

Alloy	T_c (mK) ±1%	$\left.\frac{\mathrm{d}B_{c2}}{\mathrm{d}T}\right\|_{T_c}$ (T K^{-1}) ±3%	α ±3%	λ_{so} ±10%	$N^*(0)$ (states eV^{-1} (atom spin)$^{-1}$) ±11%	$\chi_{\mathrm{p}}^{\mathrm{exp}}$ (×10^{-3} e.m.u. mol^{-1}) ±20%	$N_{\chi}(0)$ (states eV^{-1} (atom spin)$^{-1}$) ±20%
$U_{81}Fe_{19}$	929	4.94	2.60	12	3.06	0.21	3.3
$U_{66}Fe_{34}$	870	5.19	2.74	566	2.85	0.70	10.8
$U_{60}Fe_{40}$	837	5.33	2.81	886	2.68	0.54	8.4
$U_{50}Fe_{50}$	800	5.37	2.83	777	2.29	1.20	18.6
$U_{75}Co_{25}$	578	5.34	2.82	10	2.70	0.42	6.5
$U_{66}Co_{34}$	434	5.17	2.73	55	2.51	0.36	5.6
$U_{60}Co_{40}$	280	5.59	2.79	75	2.41	0.40	6.3
$U_{54}Co_{46}$	170	5.31	2.80	75	2.22	0.44	6.8
$U_{83}Ni_{17}$	519	1.9	1	5	2.3	0.29	4.5
$U_{75}Ni_{25}$	270	5.08	2.68	6.4	3.1	0.27	4.1
$U_{66}Ni_{34}$	115	5.20	2.75	2	2.3	0.27	4.1
$U_{60}Ni_{40}$	<13					0.26	4.0

of T is shown for a number of samples in Fig. 7. The symbols represent the midpoints of the resistivity ρ transition curves. All the ρ–B and ρ–T traces show a narrow transition width (0.3 T or less; 35 mK or less) except those for $U_{60}Fe_{40}$ and $U_{83}Ni_{17}$. The broad transition width of these two samples is due to a mixture of different concentration ratios for $U_{60}Fe_{40}$ and due to crystalline inclusions for $U_{83}Ni_{17}$ which is indicated by the two B_{c2} curves in Fig. 7(b). Therefore the curve at lower temperatures belongs to crystalline U_6Ni and the other curve to amorphous $U_{83}Ni_{17}$ with a T_c of 400 mK and 530 mK respectively.

A linear temperature dependence over a wide range of $B_{c2}(T)$ as predicted for strongly coupled superconductors [21] is not observed for our samples. The U–Fe glasses show a deviation from the initial linearity of $B_{c2}(T)$ at $T \leqslant \frac{1}{4}T_c$ and the U–Co and U–Ni glasses at $T \leqslant \frac{1}{5}T_c$. The curvature, however, allows us to analyse the critical field data by means of the Werthamer–Helfand–Hohenberg–Maki (WHHM) theory [22, 23] which was developed for weakly coupled homogeneous superconductors in the dirty limit.

A four-parameter least-squares fit to the data was performed. The four fitting parameters were $T_c(B=0)$, $B_{c2}(0)$, the Maki paramagnetic limitation parameter α and the spin-orbit scattering parameter λ_{so}. In the case of a superconductor in the dirty limit where the coherence length is determined by the electronic mean free path, the Maki parameter α was deduced from both the electronic specific heat γ [10] and the resistivity ρ in the normal state [12] ($\alpha=(3e^2\hbar/2m\pi^2\kappa_B^2)\gamma\rho$ [22]). Together with $T_c(B=0)$ and $B_{c2}(0)$ values extrapolated from the experiment and $\gamma_{so}=5$, these four parameters were used as a guideline in beginning the least-squares fitting routine. For two samples ($U_{54}Co_{46}$ and $U_{75}Ni_{25}$) the experimental data at the lowest temperature values were not included in the fit procedure because here the measuring current already exceeded the critical current caused by experimental conditions.

The full curves in Fig. 7 illustrate the best fits to the data. The fit parameters T_c, α and λ_{so} together with the resulting initial upper critical

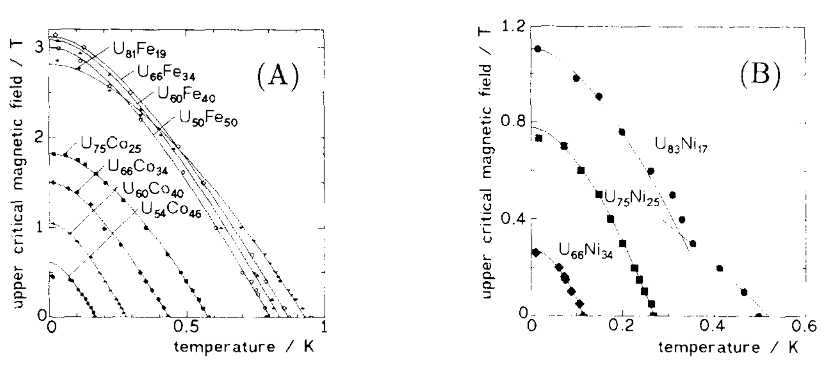


Fig. 7. The upper critical magnetic field as a function of temperature for selected (A) U–Fe and U–Co glasses and (B) U–Ni glasses. The symbols present the midpoint of the resistivity curves. The curves are fits using the WHHM theory.

field slope are listed in Table 1 (for $U_{83}Ni_{17}$ the data of the curve at higher temperatures are tabulated). Although the WHHM theory is developed for weakly coupled superconductors, the data could be fitted well for these amorphous superconductors which are in the strongly coupled limit [9, 10]. Up to now there is no suitable critical field theory for this class of superconductors.

All samples show an unusually large initial slope $(\mathrm{d}B_{c2}/\mathrm{d}T)_{Tc}$, never observed in other bulk amorphous materials before. In general, in the uranium glasses the Maki parameter α, which reflects the number of broken Cooper pairs due to paramagnetic properties, increases with decreasing uranium concentration. Compared with the zirconium glasses α is larger by a factor of 1.5 [24]. These large α values correlate qualitatively with the high paramagnetic susceptibility listed in Table 1. In the U–Fe glasses the reduction of B_{c2} caused by paramagnetic properties seems to be balanced by the high spin-orbit scattering so that these samples are in the Ginsburg–Landau–Abrikosov–Gorkov (GLAG) limit ($\lambda_{so} = \infty$). For U–Co the spin-orbit scattering parameter λ_{so} is lower by a factor of about 10 and for U–Ni by a factor of about 100 compared with that of U–Fe. Therefore B_{c2} at low temperatures is more reduced for these systems as illustrated in Fig. 8 where the reduced field h^* $(h^* = B_{c2}/(\mathrm{d}B_{c2}/\mathrm{d}t)_{t=1})$ is plotted *vs.* the reduced temperature t $(t = T/T_c)$ for three selected samples.

In the dirty limit the renormalized density of states at the Fermi level $N^*(0)$ can be determined from the initial slope of the upper critical magnetic field and the resistivity in the normal state:

$$N^*(0) = 4.735 \frac{M}{\delta\rho} \frac{\mathrm{d}B_{c2}}{\mathrm{d}T}\bigg|_{T_c} \tag{4}$$

where $N^*(0)$ is given in states per electron volt per atom spin when the molecular weight M is given in grams, the density δ in grams per cubic centimetre, the resistivity ρ in micro-ohm centimetres and the initial field

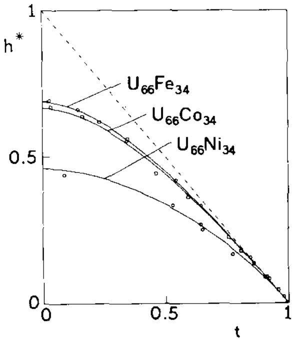


Fig. 8. Reduced field h^* $(h^* = B_{c2}/(\mathrm{d}B_{c2}/\mathrm{d}t)_{t=1})$ as a function of the reduced temperature t $(t = T/T_c)$ for three $U_{66}X_{34}$ glasses: ◇, X≡Fe; □, X≡Co; ○, X≡Ni. Normalization of B_{c2} is carried out by using the calculated initial field slope taken from Table 1.

slope is given in Torrs per kelvin. The resulting values for $N^*(0)$ are listed in Table 1. For the U–Fe and U–Co systems $N^*(0)$ decreases with decreasing uranium concentration. In the U–Ni system no general tendency can be recognized because of the large scattering of the values. Finally, $N^*(0)$ is in good agreement with the values of the electron density of states at the Fermi surface $N_\gamma(0)$ deduced from specific heat measurements [10].

3.4. Influence of the 5f electrons

Ultraviolet photoelectron spectroscopy (UPS) measurements are helpful for the interpretation of the various relations between T_c and the valence electron concentration e/a for the uranium and zirconium-glasses (Fig. 1). In Fig. 9 UPS valence band spectra ($h\nu = 21.2$ eV) of selected zirconium- [25] and uranium-based metallic glasses [26] are plotted. All spectra show two pronounced peaks. For Zr–(Fe, Co, Ni, Cu) glasses the peak next to the Fermi energy E_F is due to the 4d electron band, and for the U–(Fe, Co, Ni) glasses the narrow peak at E_F arises from the 5f electron band. The second peak in both systems, which can be attributed to the 3d electron band, shifts to higher binding energies when moving from iron to nickel and copper.

The 3d band shift to higher binding energies also involves a decrease in the electron density of states at the Fermi surface which is in good agreement with the $N^*(0)$ and $N_\gamma(0)$ measurements in both systems [10, 11]. From the Bardeen–Cooper–Schrieffer (BCS) theory it is known that a reduction of the electron density of states correlates with a reduction of T_c.

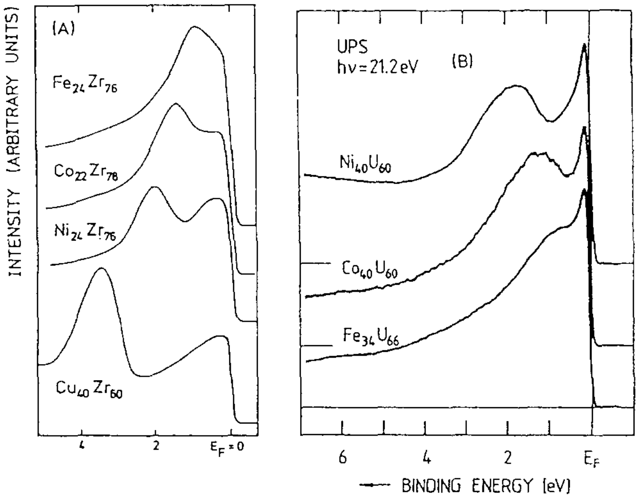


Fig. 9. UPS valence band spectra of (A) zirconium- [25] and (B) uranium-based [26] metallic glasses ($h\nu = 21.2$ eV). For Zr–(Fe, Co, Ni, Cu) glasses the band next to the Fermi energy E_F is due to the 4d electrons. For the U–(Fe, Co, Ni) glasses the narrow band at E_F is due to the 5f electrons. For both systems the band of the 3d electrons is shifted to higher binding energies when moving from iron to nickel and copper.

This behaviour is observed in the uranium samples, but not in the zirconium glasses which show the opposite behaviour [11].

In the Zr–(Fe, Co, Ni, Cu) glasses the 4d electrons at E_F are responsible for superconductivity. The increasing influence of the 3d electrons at the Fermi surface emphasizes spin fluctuations and hence T_c drops rapidly for the Zr–Fe and Zr–Co systems while the magnetic susceptibility increases [11, 17].

In the U–(Fe, Co, Ni) glasses the 5f electrons are responsible for superconductivity as well as for spin fluctuations. The density of states at E_F mainly arises from the 5f electrons of uranium (Fig. 9). The resulting high density of states at the Fermi surface (Table 1) should lead to higher T_c values. T_c is, however, reduced by spin fluctuations also due to 5f electrons. In contrast with the zirconium-based metallic glasses the increase of the 3d electron density of states at the Fermi surface has no drastic influence on the susceptibility or on the T_c dependence of the uranium concentration. Therefore only low transition temperatures and a smooth decrease of T_c with decreasing uranium concentration are expected (Fig. 1). Additionally, a further reduction of T_c by variation of the uranium concentration is caused by the decrease of the f electron density of states at the Fermi surface.

The interpretation above is supported by measurements on the pseudobinary amorphous samples $(U_{10}Zr_{90})_{67}Ni_{33}$ and $(U_{75}Th_{25})_{40}Co_{60}$. Substituting for zirconium in $Zr_{67}Ni_{33}$ by 10 at.% U, T_c is reduced from 2.9 to 0.98 K. This can be explained by strong spin fluctuations due to the presence of 5f electrons. However, $U_{40}Co_{60}$ becomes superconducting when 25 at.% U is replaced by thorium which has no f electrons. With decreasing 5f electron contribution the electron–electron interaction is also reduced, and therefore $(U_{75}Th_{25})_{40}Co_{60}$ becomes superconducting ($T_c = 160$ mK). Further increase in the thorium concentration again supresses superconductivity according to the loss of f electrons which are responsible for the high density of electron states at the Fermi surface. $(U_{75}Th_{25})_{40}Co_{60}$ also shows a pronounced 5f peak in the UPS spectrum [27] in contrast with $(U_{50}Th_{50})_{38}Co_{62}$ and $(U_{25}Th_{75})_{38}Co_{62}$ which are not superconducting. These results support the view that the Cooper pairs in the uranium glasses are formed by the 5f electrons.

4. Conclusions

We have studied the influence of the 5f electrons on the superconducting and magnetic properties in binary uranium glasses. X-ray measurements indicate no spontaneous magnetic order due to localized 5f electrons whereas susceptibility measurements as a function of temperature show that some samples exhibit ferromagnetic order. Therefore we conclude that our samples have ferromagnetic inclusions. However, it is not yet clear whether the ferromagnetic properties are due to impurities or to the formation of magnetic clusters with high transition metal densities.

From the initial slope of the upper critical magnetic field and the resistivity in the normal state we deduced the free electron density of states at the Fermi surface. Unlike in the zirconium-based metallic glasses a direct correlation between the electron density of states and T_c was found in the uranium glasses. Additionally, from UPS measurements it can be seen that the main part of the density of states is due to the 5f electrons. Therefore we conclude that the Cooper pairs are formed by the 5f electrons which are also responsible for the spin fluctuations.

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