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Neutron irradiation of heavy-fermion superconductors

B. Andraka, M. W. Meisel, J. S. Kim, P. Wölfle, and G. R. Stewart
Department of Physics, University of Florida, Gainesville, Florida 32611

C. L. Snead, Jr.
Brookhaven National Laboratory, Upton, New York 11973

A. L. Giorgi and M. S. Wire
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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Upon neutron irradiation by 10^{18} neutrons/cm^2, $E > 1$ MeV, the superconducting transition temperatures of UBe_{13} and UPt_3 fall by 40% and 60%, respectively—a factor of 3 more rapid than found in any other superconductor. We argue that this extreme sensitivity of heavy-fermion superconductors (HFS's) to neutron-irradiation-induced defects does *not* serve as evidence for unconventional pairing, since the defects produced apparently act as magnetic impurities. Such ease of magnetic impurity formation in HFS's, already found in UPt_3 by chemical doping, makes any attempt to investigate unconventional pairing via introduction of nonmagnetic defects more difficult. The neutron irradiation severely affects the low-temperature spin-fluctuation specific heat of UPt_3. An explanation for the drastic suppression of T_c by doping with "nonmagnetic" Cu in UBe_{13} is proposed.

Since the discovery[1] of superconductivity at 0.6 K in the high effective mass f-electron system $CeCu_2Si_2$, the nature of the electron pairing in such a (so-called) "heavy-fermion" superconductor (HFS) has been the subject of much investigation.[2,3] It is fair to say that the question remains open as to whether standard s-wave Bardeen-Cooper-Schrieffer (BCS) pairing, or some non-$l=0$, unconventional pairing causes superconductivity in $CeCu_2Si_2$ and in the other, later discovered, HFS's UBe_{13} (Ref. 4) and UPt_3 (Ref. 5). One way to address this question is to introduce, in a controlled fashion, nonmagnetic impurities and measure their influence on the superconducting transition temperature T_c. The decrease in the T_c of an unconventional superconductor due to a concentration c of nonmagnetic impurities is[6] given by

$$|T_c - T_{c0}|/T_{c0} \simeq \alpha c (T_F/T_{c0}) \sin^2\delta ,$$

where $\alpha \sim 1$, T_F is the Fermi temperature, and δ is the scattering phase shift. Such a rapid, linear decrease of T_c with nonmagnetic impurity concentration may be taken[7] as strong evidence for nontrivial pairing, since only magnetic impurities serve as strong pair breakers in a BCS superconductor. A standard technique of introducing nonmagnetic impurities in a controlled way is to use neutron irradiation.

We have neutron irradiated bulk samples of single-phase, annealed polycrystalline UPt_3 to fluences of 10^{18} and 10^{19} neutrons/cm^2 and UBe_{13} to a fluence of 10^{18} neutrons/cm^2 ($E > 1$ MeV) at the High Flux Beam Reactor at Brookhaven. The energy of the neutron fluence was greater than 1 MeV; the samples were water cooled during irradiation to retard any annealing effects. The initial T_c and T_{c0} of the UPt_3 was 0.50 ± 0.01 K and of the UBe_{13} was 0.87 ± 0.02 K as measured by the onset of the drop in resistivity at the superconducting transition. Measurements of the irradiated T_c values were also performed resistively. Due to the broadening of the resistive transitions by irradiation, T_c's were taken as the begin-

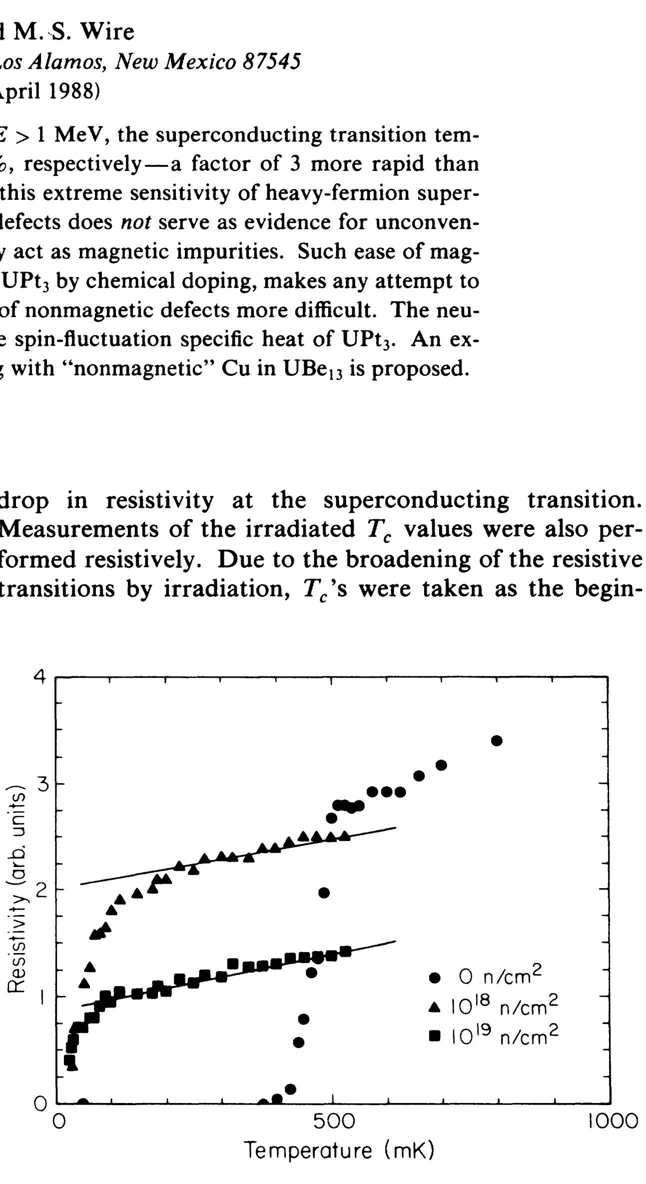

FIG. 1. Resistivity, in arbitrary units, vs temperature for unirradiated UPt_3, and UPt_3 irradiated to a total fluence of 10^{18} neutrons/cm^2 (triangles) and 10^{19} neutrons/cm^2 (squares). The breadth of the superconducting transitions in the irradiated samples makes determination of T_c somewhat uncertain. Using the criterion of a 10% fall from the extrapolation of the higher temperature data as determining T_c, rather than the more conservative "first deviation" method used in the text and for Fig. 2, would give $T_c=0.10\pm0.01$ K for UPt_3 irradiated to 10^{18} neutrons/cm^2, or an ~80% reduction in T_c. The lines are guides to the eye.

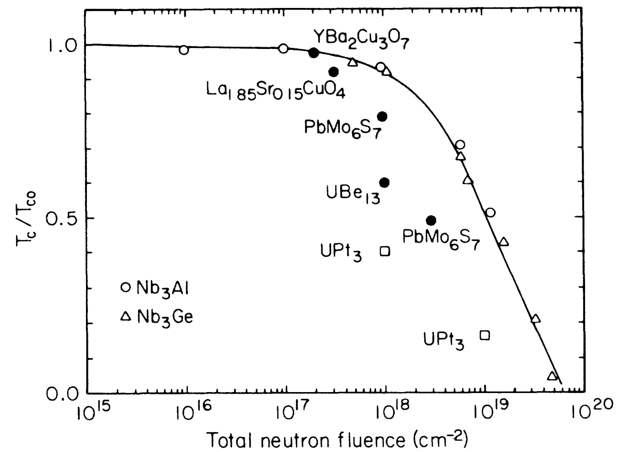

FIG. 2. T_c as a function of neutron fluence ($E > 1$ MeV) for $A15$ compound studies Nb_3Al (Ref. 9) and Nb_3Ge (Ref. 10) (the solid line is a guide to the eye for these data), the new high-T_c superconductors (Refs. 11 and 12), Chevrel phase (Ref. 8) $PbMo_6S_7$, and UBe_{13} and UPt_3.

ning of the falloff from the higher temperature trend in resistivity, rather than trying to determine the midpoint of these broad transitions. The low-temperature resistivity data for the UPt_3 samples are shown in Fig. 1. As can be seen, our method of determining the depression of T_c onset with fluence is a conservative estimate of the suppression of T_c.

In comparison to T_c suppression via neutron irradiation observed in all other superconductors, BCS as well as the new high-T_c materials, this (conservatively determined) T_c suppression observed in the HFS's UPt_3 and UBe_{13} is extraordinary. For comparison, selected data[8–12] for Chevrel, A-15 compounds, and high-T_c oxide superconductors are shown in Fig. 2, together with our results for the HFS's. Until the present work, Chevrel phase superconductors had the greatest known sensitivity of T_c to irradiation. For 10^{18} neutrons/cm^2, $E > 1$ MeV, Ref. 8 reports a 21% decrease in T_c for $PbMo_6S_7$, versus 40% for UBe_{13} and 60% for UPt_3 reported here. The only previous irradiation work known to us on HFS's was a thermal neutron study[13] of UBe_{13} (where, at the fluence studied, total suppression of T_c occurred), and a 25-MeV oxygen ion damage study[14] of thin films of $CeCu_2Si_2$. In this latter study, the unirradiated T_{c0} was only 0.35 K, versus $T_{c0}=0.65$ K characteristic[1,2] of bulk $CeCu_2Si_2$. Thus, their irradiation study begin with an already "disordered" system with $T_c/T_{c0}=0.54$. It is difficult to assign equivalence of irradiation-produced defects to sample preparation defects in this thin-film study of $CeCu_2Si_2$ in order to compare with the present work. *Qualitatively,* these $CeCu_2Si_2$ results are consistent with our work.

In order to characterize more thoroughly our irradiated UPt_3 samples, the low-temperature specific heat, the magnetic susceptibility between 1.7 and 400 K, and the low-temperature magnetization versus field to 5.5 T have all been measured. Additionally, the low-temperature magnetization to 20 T of unirradiated UBe_{13} and $UBe_{12.94}Cu_{0.06}$ are reported. These results, together with the residual resistivity ratio (RRR) are presented in Table I. The low-temperature specific-heat data for the unirradiated [UPt_3(0)] and the two irradiated samples of UPt_3 are shown in Fig. 3. The upturn in C/T caused by spin fluctuations that starts below 10 K in UPt_3(0) is clearly suppressed upon irradiation until at 10^{19} neutrons/cm^2 fluence, there is only a slight upturn below 2 K. At the same time, the enhanced γ ($\equiv C/T$) at low temperatures in UPt_3(0) is decreased 57% by 10^{19} neutrons/cm^2 fluence. This result that the spin fluctuations in UPt_3 are sensitive to defects is new—doping experiments[15] at much higher levels of "defects" suppress neither γ nor the upturn in C/T. This may be useful input to theories of the spin fluctuation ground state in UPt_3.

The low-temperature magnetic susceptibility and magnetization for the UPt_3 specimens are shown in Figs. 4 and 5. Based on previous irradiation studies[16] on $A15$ su-

TABLE I. Properties of neutron-irradiated ($E > 1$ MeV) UPt_3 and UBe_{13}. Note: M^* is the magnetization at 5.5 T extrapolated from low fields assuming no local moment saturation.

Sample/fluence (neutrons/cm^2)	Onset T_c (K)	RRR [$\equiv R$(300 K)/R(4.2 K)]	$\chi(T=1.7$ K) (10^{-3} emu/mol)	$\gamma(T=1$ K) (mJ/mol K^2)	$\frac{M^*-M(5.5\text{ T})}{M(5.5\text{ T})}$ at 2 K	at 7 K
UPt_3/0	0.50±0.01	5	8.0±0.1	440±5	0.082	0
UPt_3/10^{18}	0.20±0.02	2	10.0±0.1	336±5[a]	0.141	0.02
UPt_3/10^{19}	0.08±0.01	1.2	13.0±0.1	190±5[a]	0.397	0.14
UBe_{13}/0	0.87±0.02	0.65	15.0±0.1	820±10	0 (0.066 at 1.4 K and 20 T)	
UBe_{13}/10^{18}	0.52±0.01	0.74	18.3±0.1	760±10	0.077	
$UBe_{12.94}Cu_{0.06}$	<0.015		17.0±0.1		(0.148 at 1.4 K and 20 T)	

[a] This observed decrease in γ in UPt_3 (where $C/T=\gamma+\beta T^2+\delta T^2\ln T/T_{SF}$ and T_{SF} is the spin fluctuation temperature), and the accompanying weakening of the antiferromagnetic spin fluctuations coupled with the increase in the Wilson ratio ($\propto \chi/\gamma$) is yet another possible contribution to the observed decrease in T_c. Such a model is based on pairing induced by exchange of antiferromagnetic spin fluctuations.

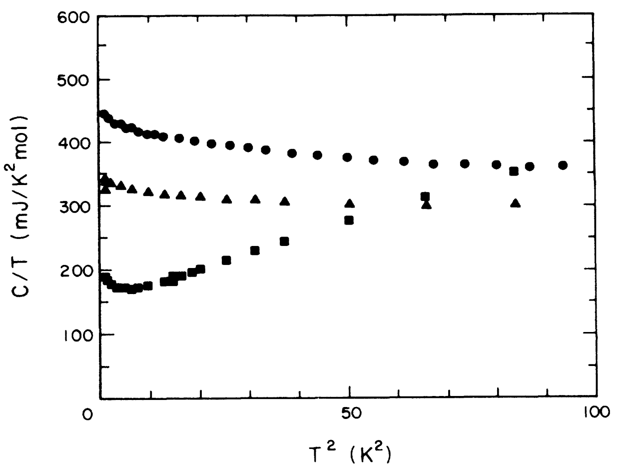

FIG. 3. Low-temperature specific heat divided by temperature vs T^2 for $UPt_3(0)$ (dots), UPt_3 (10^{18} neutrons/cm^2) (triangles), and UPt_3 (10^{19} neutrons/cm^2) (squares). These results and those for $UBe_{13}(0)$ and UBe_{13} (10^{18} neutrons/cm^2) are summarized in Table I.

perconductors, it was surprising to observe that the normal state properties of the irradiated heavy-fermion samples are so significantly altered. The possibility of whether irradiation produces *magnetic* impurities in HFS's must be thoroughly considered, since any hope of deciding the question of nontrivial pairing via irradiation depends on the clean introduction of nonmagnetic impurities. The first indication of augmented magnetic behavior of the $5f$ uranium electrons comes from the increase in the low-temperature magnetic susceptibility upon irradiation; see Table I and Fig. 4. Additional evidence for the creation of magnetic impurities by irradiation is the behavior of the magnetization M versus field H; see Table I and Fig. 5. Data at 2 K for both UPt_3 and UBe_{13} show a "bending over" of the M versus H data as the field is increased. This is usually taken as indicating a partial saturation of a local moment and is a significant effect—pure UBe_{13}, for example, has an M versus H behavior at 4.2 K to 10 T that is[17] linear to 1% or 2%; our data to 20 T in Table I show that even at this high field, M versus H deviates from linearity by less than 7%. Pure UPt_3 also shows[18] no tendency at 4.2 K to have M rise less than linearly with H up to 10 T. Assuming a local f^1 configuration for a "magnetic" uranium atom, with an effective moment of $2.54\mu_B$, the observed M versus H saturation corresponds to a fraction of "magnetic uranium impurities" created by the irradiation of approximately 2–3 % (see Table I) for the 10^{19} neutrons/cm^2 sample of UPt_3 at 2 K.

This is roughly consistent with the number of defects expected[19] from such a fluence, i.e., 1% defects for a fluence of 10^{19} neutrons/cm^2 ($E > 1$ MeV). In $A15$ compound studies, some consensus[20] exists that the defects produced are antisite disorder. Since the uranium used in the present study was 99.8% ^{238}U, neutron capture followed by fission and cascade defects should be a negligible added source of additional defects. Regardless of their nature, these apparently magnetic defects prevent any statement on unconventional pairing in these interesting superconductors. This is unfortunate since, with a phase shift δ of near $\pi/2$, the expected concentration c of defects ($\sim 1\%$) in the samples irradiated to 10^{19} neutrons/cm^2 is consistent with the size of the T_c suppression observed here in UPt_3 and UBe_{13}.

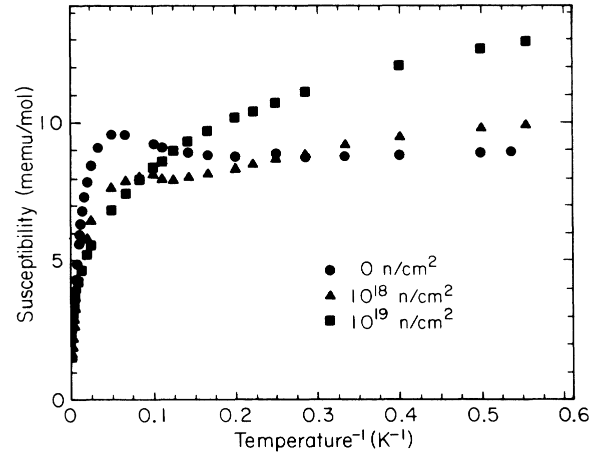

FIG. 4. Magnetic susceptibility vs inverse temperature for UPt_3. With irradiation, the low-temperature susceptibility increases substantially (see also Table I). However, around 10 K there is a crossover, such that at higher temperatures, the less the irradiation, the higher is the susceptibility. For UBe_{13}, there is no crossover—the irradiated susceptibility is higher at all temperatures by approximately 20%. The crossover in UPt_3 may be connected with the peak in susceptibility for the unirradiated sample near 20 K that is suppressed by irradiation.

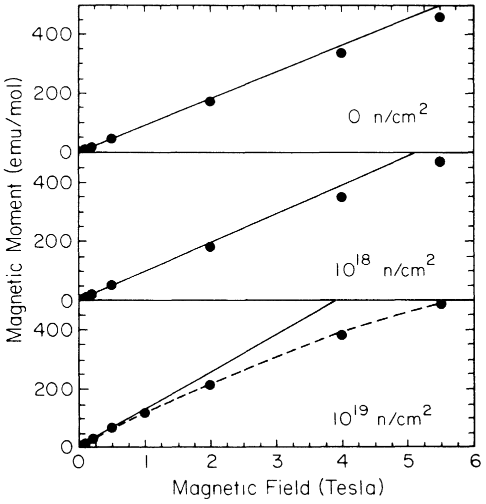

FIG. 5. Magnetization vs field at 2 K for unirradiated and the two irradiated UPt_3 samples. Note the strong deviation of the irradiated samples from the linear behavior of the unirradiated sample. The straight lines are extrapolations from the linear low-field data for each sample.

However, despite this negative result, the results presented here coupled with a simple "Kondo-lattice" model give a new possible explanation for the destruction of T_c in HFS's when supposedly "nonmagnetic" impurities are doped onto the non-f-atom sublattice. The best example of this is $UBe_{12.94}Cu_{0.06}$, $T_c < 0.015$ K. The model is that in the undisturbed HFS lattice, the incipient $5f$ electron local moment (seen in the Curie-Weiss behavior of χ at higher temperatures) is compensated at lower temperatures by exchange coupling to the surrounding conduction electron cloud. When defects are introduced into the lattice, if J, the exchange coupling parameter, decreases, then the compensation of the local moment decreases. This simple Kondo-lattice model would then argue that the evidence for increased magnetic behavior in neutron-irradiated HFS's reported here is simply a result of a decrease in the exchange coupling brought on by lattice defects. Although it may be argued that doping experiments[15] have amply proven the nearness to magnetic behavior of UPt_3, our observed increase of χ and increased nonlinearity in M versus H after irradiation, though less pronounced, is the first observation[21] of the nearness to a magnetic instability in UBe_{13}.

If this simple line of reasoning presented above is correct, then one may postulate that the reason T_c is totally suppressed by minimal Cu doping on the Be site in UBe_{13} ($UBe_{12.94}Cu_{0.06}$) is that the Cu, by disturbing the local environment of the U $5f$ electrons, lowers the exchange coupling J, thus creating magnetic impurities which suppress T_c. Thus the above results and arguments would predict a larger χ and a larger nonlinearity in M versus H in $UBe_{12.94}Cu_{0.06}$ compared to pure UBe_{13}.

We have made χ and M versus H measurements to see if this prediction is born out. The value of $\chi(1.7\text{ K})$ for $UBe_{12.94}Cu_{0.06}$ is $17.0 \pm 0.1 \times 10^{-3}$ emu/mol, versus $15.0 \pm 0.1 \times 10^{-3}$ emu/mol for pure UBe_{13}. M versus H is more linear in UBe_{13} than in UPt_3, and no detectable difference was found in the linearity of M versus H up to 5.5 T. Measurements to 20 T, however, show a clear difference, with $[M^* - M(20\text{ T})]/M(20\text{ T})$ as defined in Table I equal to 0.066 for pure UBe_{13} and 0.148 in $UBe_{12.94}Cu_{0.06}$.

In summary, neutron irradiation of UPt_3 and UBe_{13} has shown that these HFS's are more sensitive to neutron damage than any other known superconductor. Due to the low amount of ^{235}U (0.2 at. %) in the depleted U used, it is thought that this is not due to the presence of U. Specific-heat measurements have shown that the spin fluctuations and low-temperature enhanced γ in UPt_3 are sensitive to damage. Susceptibility and magnetization measurements indicate the magnetic behavior of neutron-induced defects in HFS's. In particular, we have used a simple model based on our irradiation results to predict a larger $\chi(T \rightarrow 0)$ and a greater nonlinearity in M versus H at low temperatures for nonsuperconducting $UBe_{12.94}Cu_{0.06}$ compared with the HFS UBe_{13}. This prediction has been checked and is shown to be correct.

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