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Authors

Hijmans, TW
Taleb, S
Clark, WG
[et al.](#)

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ESR IN THE SUPERCONDUCTING PHASE OF Gd-DOPED UBe_{13}

T. W. Hijmans, S. Taleb, and W. G. Clark
Dept. of Physics and Solid State Science Center
University of California, Los Angeles, California 90024

Z. Fisk and J. L. Smith
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

and

H. R. Ott
Laboratorium für Festkörperphysik, Eidgenössische Technische
Hochschule Hönggerberg, CH8093 Zürich, Switzerland

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We report ESR measurements in UBe_{13} doped with 1000 ppm Gd, at temperatures down to 0.4 K, which is well below the superconducting transition temperature of this heavy fermion system. Our most important result is the observation that, within the experimental error, the Knight shift of the local Gd moments does not decrease below the normal-state value. The possible implications of this result for the nature of the superconductivity are discussed.

One of the most intriguing aspects of the physics of heavy fermion systems is the fact that some of these compounds exhibit a transition to a superconducting phase. It has often been suggested that the nature of the superconductivity in these systems is of a more complex type than the simple singlet pairing as described by the BCS theory, which applies to ordinary metals and alloys. Although no decisive experiments have been performed to date, many experimental results seem supportive of the idea of non-singlet pairing, or more precisely, of the fact that the wave function of the Cooper pairs is characterized by higher angular momentum quantum numbers than $L = 0$. As an example we quote the NMR data of Maclaughlin et al.¹ on UBe_{13} , which show a power-law dependence of the Be relaxation rate as a function of temperature in the superconducting phase, as opposed to the exponential dependence characteristic of the BCS state. This power law suggests that the gap vanishes on parts of the Fermi surface in a similar way as in superfluid 3He , in which triplet pairing is known to occur. A property which depends in an essential way on the type of pairing is the spin susceptibility. This quantity can in principle be probed by local moments, being either nuclear spins, or magnetic impurities as in the present study. The Knight shift (also called g-shift in the case of electron spins), the shift of the magnetic resonance frequency of the moments with respect to its value in a non-metallic environment due to exchange interaction with the conduction electrons, is a measure of the spin susceptibility.

In this paper we report ESR measurements in UBe_{13} doped with 1000 ppm Gd impurities and discuss several implications of the results. In the temperature range between 4.2 K and 1.5 K a conventional X-band spectrometer was used. In the low temperature region we employed a resonant helix² combined with a 3He cryostat. The microwaves were fed into the resonator through a semi-rigid coax cable. The coupling was accomplished by a small loop near the end of the helix. The helix with the sample and a thermometer were immersed in the evaporating 3He . Although the Q of a helix resonator is much lower than that of a cavity (in our case roughly 200), the filling

factor can be made much larger yielding a comparable sensitivity. The measurements in the X-band cavity were performed on a sample consisting of a large number of grains of UBe_{13} . In the helix we used a small amount of grains. The helix has several resonance frequencies ranging from roughly 7 to 10 GHz.

Gandra et al.³ have reported ESR measurements on Gd-doped UBe_{13} at temperatures above 1.5 K. They found the g-value of the Gd resonance to be 2.07, which is substantially different from the value 1.99 observed in nonmetallic cubic crystals. They also found that the linewidths could be fitted with the relation $\Delta B = a + bT$, where $a = 60$ Gauss and $b = 21$ Gauss/K. The term bT is the usual Korringa relaxation rate. As the shift of the g-value is proportional to the density of states $N(\epsilon_F)$ of the (heavy) conduction electrons, and the Korringa rate is proportional to $N(\epsilon_F)^2$, Gandra et al. expressed surprise that the g-shift and the coefficient b did not reflect the large value of $N(\epsilon_F)$.

There are two main hypotheses to explain the ordinary values for g and ΔB in UBe_{13} in the normal state. As pointed out by Varma,⁴ one can expect the matrix elements involved to be smaller by a factor equal to the enhancement of the density of states, thereby cancelling the effect of the explicit factors $N(\epsilon_F)$. This interpretation relies strongly on the many-body nature of the heavy-fermion state. On the other hand, even in the probably less realistic static hybridization picture, the effect of the large density of states may be cancelled out, as the Gd impurities couple to the U 5f electrons indirectly through the small hybridization matrix element.

Our work extends the ESR measurements to temperatures below the superconducting transition temperature, which is 0.85 K for this doping concentration and our magnetic field (0.3 T). In fig. 1 the ESR spectra at 4.2 K and 0.43 K are shown. At 4.2 K the lineshape is perfectly Dysonian. The fraction of dispersion in the fit was taken equal to 0.7. The analysis of the lineshape of the low-T data is slightly complicated, because of a small but broad background signal in the helix setup. The fit to the spectrum at 0.43 K is a Dysonian (with a slightly smaller admixture of dispersion),

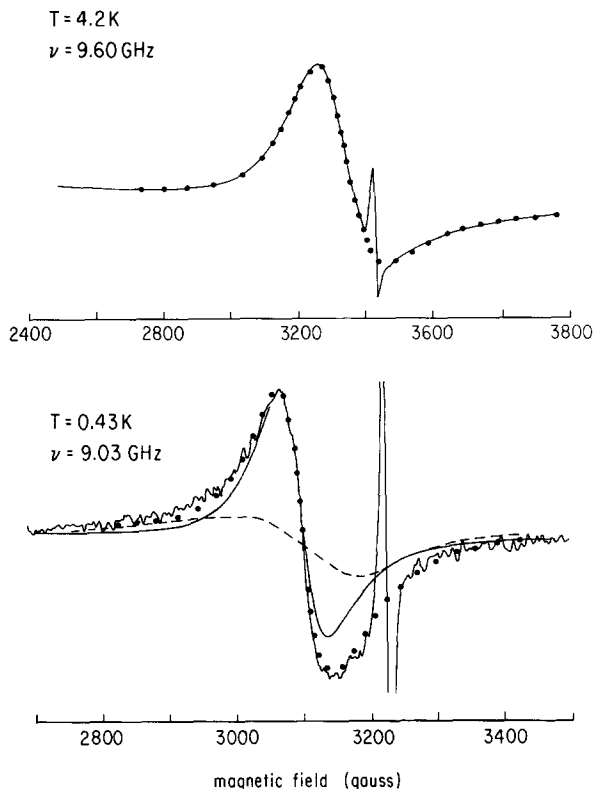


FIG. 1. ESR absorption spectra of $U_{.999}Gd_{.001}Be_{13}$ in the normal (upper) and superconducting (lower) states. The narrow line is a $Qn(TCNQ)_2$ g-marker. Upper: $T = 4.2\text{ K}$; the solid line is the recorded spectrum; the dots are a fit to a Dysonian line shape. Lower: $T = 0.43\text{ K}$; the noisy line is the recorded spectrum; the smooth solid line is the Dysonian component; the dashed line is the background component; the dots are the sum of the Dysonian and background components.

plus the background signal measured in the empty helix. In fig. 2 we show the g-value of the Gd resonance as a function of temperature. The g-values were determined with respect to a $Qn(TCNQ)_2$ marker. Within the experimental accuracy, the g-value remains constant down to the lowest temperature. The error bars on the data at temperatures in the ^3He range are mainly due to the background mentioned above. In fig. 3 we show the line width versus temperature. The data measured with the X-band spectrometer can be fitted with the relation $a + bT$ used above. We find $a = 81 \pm 10\text{ Gauss}$ and $b = 21 \pm 4\text{ Gauss/K}$. The Korringa constant b is in agreement with the value of Gandra et al. The data below 1.5 K show the same temperature dependence but the residual line width a is slightly lower for this sample ($a = 50 \pm 10\text{ Gauss}$, $b = 26 \pm 4\text{ Gauss}$). The difference in the value of a for the two samples may be attributed to different residual line widths of the individual grains. As can be seen from fig. 1, the line shape at 0.43 K can still be fitted reasonably well with a Dysonian, if the background is taken into account. The small deviation in the wings of the line is not very significant in view of slight uncertainties introduced by the correction for the background signal. The error bars in fig. 3 are again mainly related to the background corrections. Other potential corrections to the g-shift are the reduction of

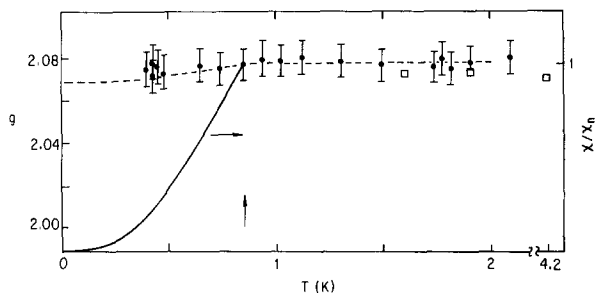


FIG. 2. g-value of the Gd-resonance versus temperature. The solid and broken curves denote the normalized susceptibility of an electron gas in the absence and in the presence of strong spin-orbit interaction respectively (see text). The arrow marks the superconducting transition temperature. Circles and squares refer to data taken with the helix and with the X-band cavity respectively.

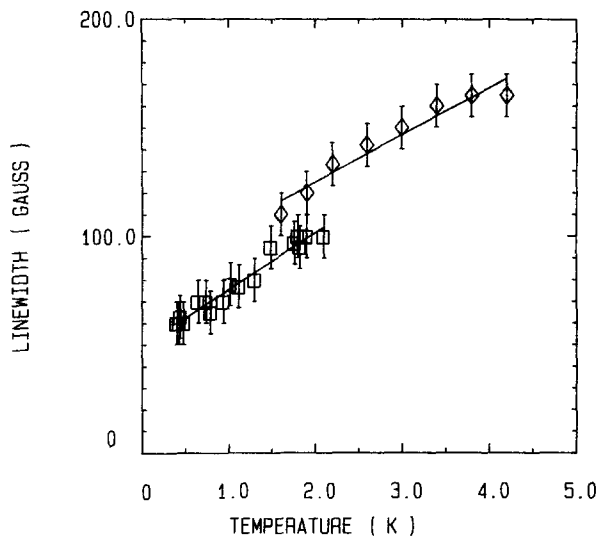


FIG. 3. Linewidth of the ESR absorption of Gd in $U_{.999}Gd_{.001}Be_{13}$ as a function of temperature measured with the cavity spectrometer (diamonds) and the helix (squares). The solid lines are a fit to the relation $\Delta B = a + bT$ (see text).

the field in the vortex state and the demagnetization and Lorentz field corrections in UBe_{13} . Prior NMR experiments^{1,5} can be used to show that these effects are substantially less serious than the errors just described for our measurements; they will not be considered further here. In the remainder of the paper, we shall mainly focus on the implications of the fact that the Knight shift remains unchanged when entering the superconducting phase.

Now we discuss how this result fits current ideas of superconductivity, with emphasis on points related to heavy fermions. The first point is that the lack of a temperature dependence in the Knight shift below T_C is consistent with odd-parity pairing. For comparison we may refer to the superfluid A-phase of ^3He , which is identified with the ABM phase⁶ which is characterized by $L = 1$ (p-wave), triplet pairing. The susceptibility of this phase is very nearly equal to

the normal-state value. However, we must note that odd-parity pairing is not the only possible explanation for the observed phenomenon, and that the large spin-orbit interaction expected of uranium compounds makes comparison with 3He highly questionable.

In an ideal singlet superconductor, the susceptibility will decrease below the transition temperature, becoming zero at $T = 0$. The temperature dependence for a noninteracting Fermi gas is given by the Yosida function⁷ which is plotted in fig. 2 for a transition temperature of 0.85 K. Inclusion of the Fermi liquid parameters will result in an even more rapid decrease of χ below T_c . The part of the resonance shift associated with the susceptibility therefore also vanishes at $T = 0$. There is, however, a physical reason why the g-shift in singlet superconductors may remain finite. As pointed out by Anderson⁸ and by Abrikosov and Gorkov,⁹ in the presence of spin-orbit scattering, the one-electron states are no longer eigenstates of the spin operator. Consequently the Cooper pairs will not be pure singlet states, which results in a finite susceptibility at $T = 0$. In the following we shall analyze the results in UBe_{13} assuming a BCS singlet superconducting state (we shall use the words singlet and triplet rather loosely, i.e., referring to even or odd parity). The error bars on the Knight shift data are approximately 10% of the total value of the shift. Assuming that the shift at $T = 0.4$ K (about $0.5 T_c$) is nearly equal to the value at $T = 0$, we find a lower limit for the ratio χ_s/χ_n of 0.9. Here χ_s and χ_n denote the spin susceptibility in the superconducting and the normal phase, respectively. We can estimate the spin-orbit scattering time τ according to the formula⁸:

$$\chi_s/\chi_n = 1 - (2\Delta\tau/\hbar). \quad (1)$$

Here Δ is the gap which we estimate as given by the BCS value $1.75 k_B T_c$ (i.e., $\Delta/k_B = 1.5$ K for UBe_{13}). This gives $\tau < 2.5 \cdot 10^{-13}$ s. In fig. 2 we plot χ_s/χ_n versus T for this value of τ according to the theory of Abrikosov and Gorkov.⁹ In normal metals, the value found for τ would be quite reasonable, but in a heavy fermion system one encounters a conceptual problem. The spin-orbit scattering rate $1/\tau$ is so large that it is comparable to the (extremely small) effective bandwidth of the heavy quasi-particles. This can be seen in the following physical picture. The fact that the spin-orbit interaction is so large as to retain χ essentially unchanged with respect to the normal-state value implies that the spin operator has to have matrix elements between states whose energy separation is large compared to Δ . In UBe_{13} , however, T_0/T_c (where T_0 is the characteristic temperature in the heavy fermion problem) is not large. That is, the effective bandwidth is not very much larger than k_B times the superconducting transition temperature T_c , which in turn is of the order of the gap energy. Alternatively we can phrase this by noting that the spin-orbit scattering length l_0 , which is given by the relation $l_0 = \tau v_F^*$, where v_F^* is the renormalized Fermi velocity of the heavy quasi-particles, must be anomalously small because of the greatly reduced value of v_F^* . The value of l_0 , consistent with the above derived upper limit, turns out to be of the order of 20 Å (see below); this rules out the possibility of spin-orbit scattering at the boundaries of the sample. The alternative explanation is scattering off the Gd impurities. We shall now argue that the scattering cross section of the Gd impurities may indeed be expected to be very large in heavy fermion materials like UBe_{13} .

Yafet¹⁰ derived the following expression for the spin-orbit scattering time due to impurities in an ordinary metal:

$$\frac{1}{\tau} = \frac{4\pi^3 n}{3k_F^2} v_F \ell(\ell+1)(2\ell+1) \lambda_{eff}^2 \rho_i(\epsilon_F)^2 \quad (2)$$

Here k_F, v_F , and ϵ_F are the Fermi wavevector, the Fermi velocity, and the Fermi energy; n is the impurity density, ℓ is the orbital quantum number of the virtual bound state associated with the impurity, and $\lambda_{eff} = \lambda/(1 - U\rho_i)$, where λ is the atomic spin-orbit coupling constant and U is the Coulomb integral. In UBe_{13} , the quasi particles which form the narrow band are basically f-like. The f-electrons on the U have a strong spin-orbit interaction ($\lambda \approx 2000 \text{ cm}^{-1}$). Introduction of a Gd impurity on a U site interrupts the translational invariance of the U sublattice and will therefore give rise to spin-orbit scattering, as a result of the large spin-orbit mismatch. In other words, the scattering cross section will be determined by the absence of a U atom rather than by the presence of the Gd. It therefore seems logical to assume that the scattering rate is given by eq. (2), but with the following modifications: we set $\rho_i(\epsilon_F)$ equal to the local density of states per U atom, i.e., $\rho_i(\epsilon_F) = (m^*/14m)\rho(\epsilon_F)$. Here $\rho(\epsilon_F)$ is the bare density of states of the band electrons, m^* is the effective mass of the quasi-particles, and the factor 1/14 is included to take into account that there are 13 Be atoms and 1 U atom, per formula unit. The factor $(1 - U\rho_i)^{-1}$ is of a similar form as the Stoner-like enhancement factor, which enters the calculation of the susceptibility, which is of order unity as may be deduced from the fact that the Wilson ratio is approximately 1 in these systems. Therefore we set λ_{eff} equal to the atomic spin orbit constant of U. Finally we replace v_F in eq. (2) by $v_F m/m^*$, where in the latter expression v_F is the bare Fermi velocity of the band electrons. Using a free electron model for the Be-s electrons, we find the following values for the unrenormalized quantities: $k_F = 1.4 \times 10^{10} \text{ m}^{-1}$, $v_F = 1.4 \times 10^6 \text{ m/s}$, and $\epsilon_F = 8 \text{ eV}$. Using $\ell = 3$, $\lambda \approx 2000 \text{ cm}^{-1}$, and $m^*/m \approx 500$, we find from the modified eq. (2): $\tau \approx 8 \times 10^{-13} \text{ s}$ and $l_0 \approx 24 \text{ Å}$. Due to the crudeness of the approximations, this result is only an estimate of the order of magnitude. The calculated value for τ is therefore reasonably consistent with the above established upper limit.

We have shown that the g-shift data are consistent with either even-parity (singlet) or odd-parity pairing. In the former case, a very strong spin-orbit scattering due to the Gd impurities has to be assumed in order to explain the results. One must conclude that in this case the probe unfortunately destroys the effect one tries to measure. In this light it is interesting to compare the present results with recently presented muon-spin resonance (μ SR) data.¹¹ In that work, it is found that the muon Knight-shift does decrease dramatically below T_c in UBe_{13} but not in $U_{0.97}Th_{0.03}Be_{13}$. An important difference with the present experiment, is the fact that the muons are located interstitially and that there are no impurities substituted on U-sites which can serve as scattering centers. This in turn data appears to support the interpretation in terms of strong spin-orbit scattering given in this paper, and suggests even parity superconductivity. In view of this conclusion, it would be very interesting if the μ SR experiments were repeated in a Gd-doped sample. Be-NMR measurements in pure UBe_{13} are expected to yield results comparable to those using μ SR. Such measurements have been reported in the normal state⁵ of monocrystalline UBe_{13} . Measurements in the superconducting phase have only been performed on polycrystalline samples.¹ The value of the Knight shift is so small that no significant conclusion can be drawn from polycrystal measurements in the superconducting phase.

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