p-Wave Superconductivity in the Ferromagnetic Superconductor URhGe

F. Hardy and A. D. Huxley

DRFMC/SPSMS, CEA-Grenoble, Grenoble 38054, France

(Received 8 February 2005; published 24 June 2005)

We report that the upper critical field of single crystals of URhGe exceeds the usual paramagnetic limitation for fields applied along all three crystal axes. In detail the temperature dependence of the critical field cannot be reconciled with opposite-spin pairing but is well described by a single component odd-parity polar order parameter with a maximum gap parallel to the a axis.

DOI: 10.1103/PhysRevLett.94.247006 PACS numbers: 74.20.Rp, 74.25.Op, 75.50.Cc

Superconductivity has recently been observed in URhGe and several other ferromagnetic metals [1–3]. Although ferromagnetism and superconductivity are usually considered to be antagonists, the ferromagnetic order in these metals persists in the superconducting state. Moreover, in both URhGe [4] and the high pressure ferromagnetic phase of UGe_2 [5] studies as a function of pressure show that the critical temperature below which superconductivity occurs is higher for larger values of the ordered ferromagnetic moment. These results suggest that, surprisingly, ferromagnetism may actually enhance superconductivity in these compounds. However, the way the electrons are paired to give superconductivity remains controversial. Here we report measurements of the critical field necessary to destroy superconductivity in single crystals of URhGe. The large values of the critical field we find along all three crystal axes establish that equal spins are paired.

It is known from neutron scattering [2,6] that the magnetism in URhGe and UGe_2 is carried by uranium f electrons. However, it is less clear how the different spin-polarized Fermi surfaces are split, and it cannot be excluded that the Fermi-surface sheets for opposite spin almost coincide in some regions. This might occur if the Fermi surface lies in electronic bands formed from orbitals that have little overlap with the magnetically active f orbitals. Alternatively, opposite-spin Fermi surfaces coming from different bands might almost touch along some directions. The pairing of opposite spins therefore cannot be ruled out *a priori*. Indeed, a mechanism in which local moment ferromagnetism stimulates opposite-spin paired (spin-singlet) superconductivity has been suggested by Abrikosov and Suhl [7,8].

In contrast, if the band polarization is everywhere large, opposite-spin pairing cannot occur; a modulated Larkin-Ovchinnikov-Fulde-Ferrel (LOFF) superconducting state [9,10] extends only slightly the maximum polarization that can be accommodated. Equal-spin pairing is then the only possibility, which requires the order parameter to have an odd parity. Although a general odd-parity order parameter has three components, one component measures the pairing of electrons with opposite spins and is expected to be suppressed. The two remaining components correspond to pairing equal spins on the spin-majority and spin-minority Fermi surfaces, respectively. Two possible types of odd-parity superconducting states are compatible with the crystal structure of URhGe (crystal point group mmm with ordered moments parallel to the c axis) and strong spin-orbit coupling [11]. They are distinguished by the directions along which the superconducting energy gap is zero. Symmetry imposes that the gap must either be zero in the plane perpendicular to the ordered moments or be zero in the direction parallel to the ordered moments.

We report here the first measurements on a superconducting single crystal of URhGe. The sample was spark cut from a large Czochralski-grown crystal annealed at high temperature (24 h at 1300 °C). It was then etched and annealed at lower temperature (18 d at 880 °C). The normalized resistivity as a function of temperature of a crystal grown by the Czochralski technique and annealed only at low temperature ($T = 900$ °C) is shown in Fig. 1. The ratio of the room temperature resistance to that at low temperature in the normal state (RRR) is proportional to the defect limited electronic mean-free path, ℓ (if the sample quality varies over its volume, then the RRR value gives a lower bound for ℓ in the highest quality part of the sample). For this sample, RRR $= 5.5$, which is much less than the values (RRR $\gtrsim 100$) found in samples cut from annealed quenched polycrystalline ingots. In the former superconductivity is not observed down to 30 mK, while the latter are superconducting below approximately 270 mK. The single crystal annealed additionally at high temperature has an intermediate RRR of 21 and an intermediate T_c of 220 mK (Fig. 1). For a conventional superconductor, T_c is independent of the electronic mean-free path [12]. However, for an unconventional superconductor, T_c is suppressed and vanishes when ℓ is reduced to a dimension comparable to the superconductor's coherence length [13,14]. The total suppression of superconductivity in lower quality samples provides strong evidence that the superconductivity is unconventional.

In an applied field the resistive transitions remain sharp and show no hysteresis. The applied field at which superconductivity is destroyed (taken to be the midpoint of the transition) in the superconducting single crystal with RRR $= 21$ is shown as a function of temperature in Fig. 2. The temperature dependence of the resistance close

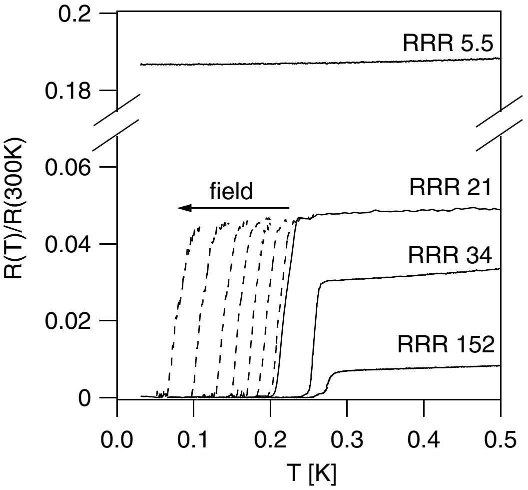

FIG. 1. The solid curves show the resistivity normalized to its value at 300 K in zero field for the single crystal with RRR = 21, another crystal with RRR = 34, a crystal annealed only at low temperature (RRR = 5.5), and a small piece from an annealed quenched melt (RRR = 152). The dashed lines show the resistive transitions of the RRR = 21 sample in applied fields of 0.11, 0.32, 0.53, 0.74, 0.95, 1.27, and 1.59 T applied parallel to the crystal's a axis.

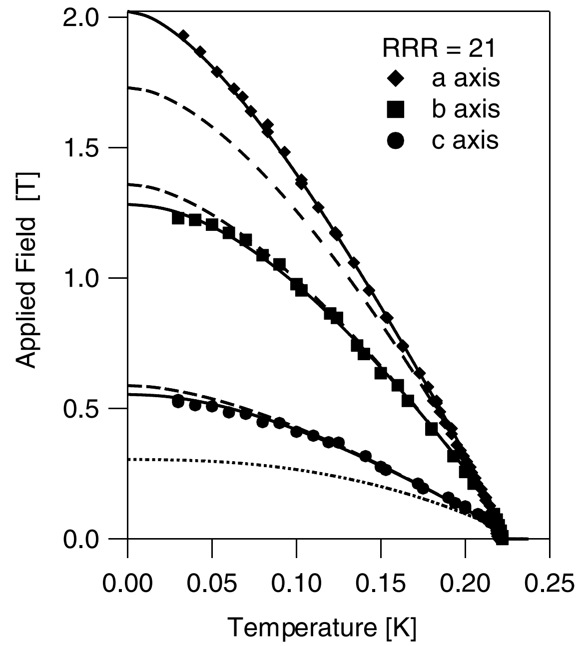

FIG. 2. The temperature dependence of the applied field at which superconductivity is destroyed is shown for fields applied along the three different crystal axes of the single crystal with RRR = 21. The solid lines show the calculated dependence for a completely broken symmetry polar state considered in the text. The dashed lines show the calculated BCS dependence without paramagnetic limitation. The dotted line is the BCS dependence for the c axis including paramagnetic limitation. The data for the c axis is shown in more detail in Fig. 3.

to T_c is found to be independent of the applied field parallel to the c axis, $H_c^{\rm app}$, for $\mu_0 H_c^{\rm app} < 50$ mT (the subscript c refers to the crystal axis). This is more clearly seen in Fig. 3, where the data for the c axis are shown on an expanded scale, and compared with measurements made on a second single crystal (prepared similarly to the first) that has a higher RRR of 34. To understand the origin of the vertical slope of the critical field at T_c, it is necessary to consider the sample geometry: both crystals were rectangular bars with the magnetic c axis perpendicular to their length. A demagnetizing field therefore has to be included in addition to the field due to ferromagnetism in the analysis. For the long time scales of the present measurements, it is reasonable to assume that the magnetic domain structure relaxes almost to equilibrium. The magnetic domain walls then move in response to a small applied field so that the total field inside the sample is zero. The magnetic induction acting on the conduction electrons is then $B_c/\mu_0 \approx \pm\alpha M_s$, independent of $H_c^{\rm app}$ (M_s is the magnetization in a single domain and α is a constant in the spirit of the Clausius-Mossotti equation). This is true as long as $H_c^{\rm app} < NM_s$, where the demagnetization factor $N \approx 0.55$ is determined from the sample geometry. For $H_c^{\rm app} > NM_s$, the sample is monodomain and any further increase in the applied field cannot be compensated by changes in the domain structure; the magnetic induction acting on the conduction electrons is then $B_c/\mu_0 = \alpha M_s - NM_s + H_c^{\rm app}$.

For a superconductor sufficiently close to T_c, the critical magnetic induction at which superconductivity is suppressed, B_{c2}, is expected to vary linearly with temperature. Including the intrinsic induction due to ferromagnetism and the demagnetizing field as described above, it is then possible to define T_{c*} the critical temperature for the hypothetical state with $B = 0$ and the slopes $(dB_{c2}/dT)_{T_{c*}}$ along all the axes. We find that such a description is valid near T_c, simultaneously for all three axes, if $\alpha \approx 2/3$.

The theoretical temperature dependence of B_{c2} as the temperature is lowered further depends on many factors, including (i) Pauli paramagnetic limitation, (ii) the coupling strength of the pairing interaction, (iii) impurity scattering, and (iv) any anisotropy of the gap and Fermi surface beyond that described by an anisotropic effective mass tensor. When paramagnetic limitation is ignored, the theoretical critical field is referred to as the orbital limit. This has a universal temperature dependence in the BCS theory when (ii)–(iv) are weak [15]. Remarkably, the data for the b and c axes approximately follow this dependence (dashed lines in Fig. 2) down to the lowest temperature measured.

We now examine whether the upper critical field can be reconciled with theoretical models that predict opposite-spin pairing. Theoretically, Pauli paramagnetic limitation must then be included in the analysis. For a spin-singlet superconductor in the absence of spin-orbit scattering and ignoring the orbital limit, the zero temperature critical field is given by the Pauli limit $B_{c2}^{\rm Pauli} = 1.84 T_c$ (T/K) [16]. For the case when both orbital and Pauli limits are comparable the actual critical field is considerably lower. For the value

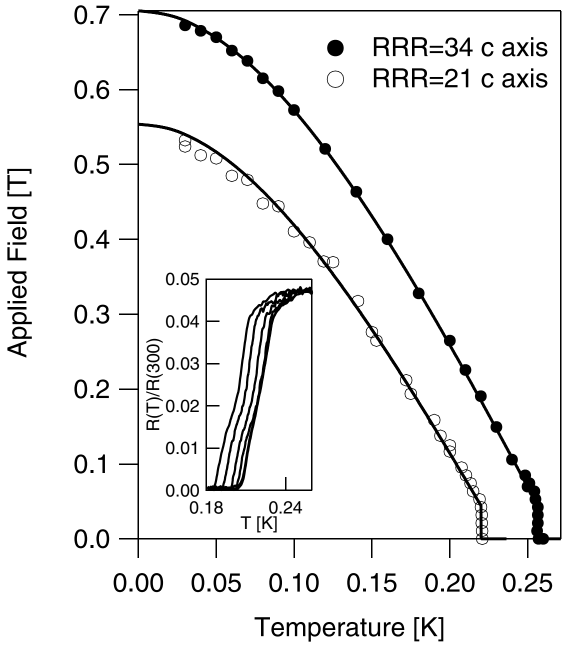

FIG. 3. The temperature dependence of the applied field at which superconductivity is destroyed for two crystals with RRR ≈ 34 and RRR ≈ 21 for fields applied parallel to the c axis. The solid lines show the theoretical dependences for a completely broken symmetry polar state described in the text. The inset shows in detail the resistive transition of the sample with RRR $= 21$ in fields of 0, 0.021, 0.042, 0.063, 0.085, and 0.11 T (the data for the lowest fields superimpose).

of $(dB_{c2}/dT)_{T_{c*}}$ found for the c axis of the RRR $= 21$ crystal the theoretical applied field necessary to suppress superconductivity at low temperature is calculated to be 0.30 T (almost unchanged if an eventual LOFF spatial modulation of the superconductivity is considered). This is much less than the measured value which exceeds 0.5 T. Strong coupling can, however, lead to an increase of the paramagnetic limit for a conventional superconductor [17]. A large value of the coupling constant, $\lambda_c \approx 2$, would be necessary to sufficiently increase the paramagnetic limit to be compatible with singlet pairing (even larger values are required for the other axes). Increasing λ_c, however, also leads to a decrease of the normal state quasiparticle lifetime, τ, at finite temperature that should be reflected in a reduction of the electron mean-free path, ℓ, at T_c [18,19]. The strong dependence of T_c on the sample quality found for URhGe establishes that the superconductivity is unconventional, and that $\ell(T = 0) > \xi$. Above T_c the resistance has a quadratic temperature dependence characteristic of a well behaved Fermi liquid. The magnitude of this dependence relative to the residual resistance establishes that any contribution to $1/\tau$ at T_c from the pairing interaction is several orders of magnitude less than $k_B T_c/\hbar$. Thus the coupling strength does not appear to be sufficiently strong to reconcile the high critical field with singlet pairing. The normal state properties of URhGe do not appear to be strongly modified over the field range spanned by B_{c2}; thus there is additionally no evidence that the pairing interaction changes with the applied field in this range. These observations are in contrast to those for UBe_{13} [20], a material with a critical field that also exceeds the usual paramagnetic limit. For UBe_{13}, strong-coupling effects are important and the normal state properties depend strongly on field. For UBe_{13}, unlike for URhGe, both of these effects afford an explanation of its unusually high critical field.

In Fig. 3 the critical field parallel to the c axis of two different quality single crystals is shown. It is known that spin-orbit scattering from defects can give rise to critical fields in excess of the paramagnetic limit in conventional superconductors [21]. Paramagnetic limitation is then reestablished in better quality samples, resulting in a lower critical field. Even if we overlook the fact that superconductivity occurs only in clean samples of URhGe, the observation that the upper critical field increases with the sample quality, with $B_{c2}(T = 0) \propto T_c^2$, shows that the absence of paramagnetic limitation in URhGe cannot be due to this mechanism. The observed relationship between $B_{c2}(T = 0)$ and T_c is instead that expected for unconventional superconductivity in the clean limit without paramagnetic limitation.

So far we have considered the gyromagnetic ratio of the electrons to have the standard value, $g = 2$. A different smaller value might, however, be relevant. For our data to be consistent with paramagnetic limitation, we require that $g < 0.2$ along all three crystal axes. Although it is possible by judicial choice of crystal field levels to have a g factor that is small along certain crystal directions, it cannot have such a small value simultaneously along all three principal axes. We therefore conclude that the paramagnetic limit must be exceeded along at least one crystal direction. Singlet pairing is thereby excluded.

We now examine whether the upper critical field can be explained by equal-spin pairing. For a triplet superconductor, Pauli limitation suppresses only the component of the order parameter corresponding to Cooper pairs composed of opposite spins projected along the field direction [22]. It has no effect on states with equal-spin pairing, and the absence of Pauli limitation is therefore easily reconciled with such states.

Odd-parity nonconventional states have been put forward to account for superconductivity in other nonferromagnetic metals, such as UPt_3. For UPt_3 there is no paramagnetic limitation for fields in the basal plane, but there is for fields applied along the c axis [23]. This is consistent with spin-triplet Cooper pairs with opposite spins paired along the c axis. Large critical fields exceeding the BCS Pauli limit have also been observed in organic superconductors, although the resistive transitions are often rather wide and the critical fields very anisotropic. For example, the large upper critical field in the plane of $(TMTSF)_2ClO_4$ has been interpreted as evidence in favor of a triplet state [24]. However, the low dimensional character of these materials requires special consideration since

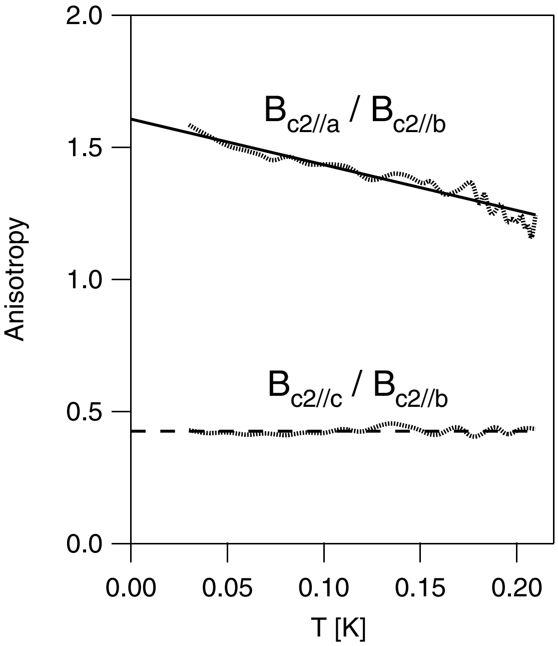

FIG. 4. The temperature dependence of the ratio of B_{c2} parallel to different axes. The straight lines are a guide to the eye.

it is so extreme that structural layers might decouple; much larger critical fields than the Pauli limit (even for opposite-spin pairing) are possible under these special conditions [25,26]. For URhGe the normal state anisotropy of, for example, the resistivity is only of the order of 3, similar to that of the upper critical field, and the consideration of such two-dimensional physics appears unlikely to be appropriate.

For our data, further progress can be made by examining the temperature dependence of the anisotropy of the critical field. The ratio of B_{c2} along the c axis to that along the b axis is independent of temperature. However, the ratio of B_{c2} parallel to the a axis divided by the value along the b axis (or c axis) increases linearly by approximately 20% as the temperature is decreased from T_c to zero (Fig. 4). This temperature dependence is much stronger than can be explained by Fermi-surface anisotropy. It is, however, consistent with a choice of an equal-spin-paired gap having a line node in the bc plane. To test further whether such a gap could explain our results, we considered the particular choice of pairing potential $V_{\sigma\sigma'}(k, k') \propto \delta_{\uparrow\sigma}\delta_{\uparrow\sigma'}k_a k'_a$ that gives rise to the paired state $k_a|\uparrow\uparrow\rangle$. This state obeys the symmetry requirements for states with a gap node parallel to the magnetic moments. The temperature dependence of B_{c2} for such an order parameter has been previously analyzed theoretically [27]. The calculated temperature dependence of the critical field over the complete temperature range (the solid lines in Fig. 2) is determined entirely from the linear temperature dependence of the critical field close to T_c. The agreement of the calculated form with the experimental data at low temperature is surprisingly good, including the apparent weakness of the low temperature saturation of B_{c2} parallel to the a axis. Equal-spin pairing can therefore *de facto* describe the observed critical field. Future work is required to determine why the pairing interaction might have this particular form, with pairing effectively confined to the a-axis direction.

We acknowledge useful discussions with J.-P. Brison, J. Flouquet, I. Fomin, F. Lévy, V. Mineev, C. Paulsen, J. Sauls, and S. Yates.

[1] S. S. Saxena *et al.*, Nature (London) **406**, 587 (2000).
[2] D. Aoki *et al.*, Nature (London) **413**, 613 (2001).
[3] T. Akazawa *et al.*, J. Phys. Condens. Matter **16**, L29 (2004).
[4] F. Hardy *et al.* (to be published).
[5] A. Huxley *et al.*, Phys. Rev. B **63**, 144519 (2001).
[6] N. Kernavanois *et al.*, Phys. Rev. B **64**, 174509 (2001).
[7] A. A. Abrikosov, J. Phys. Condens. Matter **13**, L943 (2001).
[8] H. Suhl, Phys. Rev. Lett. **87**, 167007 (2001).
[9] P. Fulde and R. A. Ferrell, Phys. Rev. **135**, A550 (1964).
[10] A. I. Larkin and Y. N. Ovchinnikov, Zh. Eksp. Teor. Fiz. **47**, 1136 (1964) [Sov. Phys. JETP **20**, 7621 (1965)].
[11] V. P. Mineev and T. Champel, Phys. Rev. B **69**, 144521 (2004).
[12] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).
[13] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960) [Sov. Phys. JETP **12**, 1243 (1961)].
[14] A. I. Larkin, Pis'ma Zh. Eksp. Teor. Fiz. **2**, 205 (1965) [JETP Lett. **2**, 130 (1965)].
[15] E. Helfand and N. R. Werthamer, Phys. Rev. **147**, 288 (1966).
[16] A. M. Clogston, Phys. Rev. Lett. **9**, 266 (1962).
[17] J. P. Carbotte, Rev. Mod. Phys. **62**, 1027 (1990).
[18] A. J. Millis, S. Sachdev, and C. M. Varma, Phys. Rev. B **37**, 4975 (1988).
[19] K. Levin and O. T. Valls, Phys. Rev. B **20**, 105 (1979).
[20] J.-P. Brison *et al.*, Physica (Amsterdam) **280B**, 165 (2000).
[21] T. P. Orlando, E. J. McNiff, Jr., S. Foner, and M. R. Beasley, Phys. Rev. B **19**, 4545 (1979).
[22] V. P. Mineev and K. V. Samokhin, *Introduction to Unconventional Superconductivity* (Gordon and Breach, Amsterdam, 1999).
[23] C. H. Choi and J. A. Sauls, Phys. Rev. Lett. **66**, 484 (1991).
[24] J. I. Oh and M. J. Naughton, Phys. Rev. Lett. **92**, 67 001 (2004).
[25] A. G. Lebed and K. Yamaji, Phys. Rev. Lett. **80**, 2697 (1998).
[26] I. J. Lee, P. M. Chaikin, and M. J. Naughton, Phys. Rev. Lett. **88**, 207002 (2002).
[27] K. Scharnberg and R. A. Klemm, Phys. Rev. Lett. **54**, 2445 (1985).