Uncommonly high upper critical field of the pyrochlore superconductor KOs2O6 below the enhanced paramagnetic limit

Author(s)
Shibauchi, T; Krusin-Elbaum, L; Kasahara, Y; Shimono, Y; Matsuda, Y; McDonald, RD; Mielke, CH; Yonezawa, S; Hiroi, Z; Arai, M; Kita, T; Blatter, G; Sigrist, M

Citation
PHYSICAL REVIEW B (2006), 74(22)

Issue Date
2006-12

URL
http://hdl.handle.net/2433/49906

Copyright 2006 American Physical Society
Uncommonly high upper critical field of the pyrochlore superconductor KO$_2$O$_6$ below the enhanced paramagnetic limit

T. Shibauchi,1 L. Krusin-Elbaum,2 Y. Kasahara,1 Y. Shimono,1 Y. Matsuda,1,3 R. D. McDonald,4 C. H. Mielke,4 S. Yonezawa,3 Z. Hiroi,3 M. Arai,5 T. Kita,6 G. Blatter,7 and M. Sigrist7

1Department of Physics, Kyoto University, Sakyoku-ku, Kyoto 606-8502, Japan
2IBM T. J. Watson Research Center, Yorktown Heights, New York 10598, USA
3Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
4NHMFL, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
5National Institute for Materials Sciences, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan
6Division of Physics, Hokkaido University, Sapporo 060-0810, Japan
7Theoretische Physik, ETH Zurich, CH-8093 Zurich, Switzerland

(Received 10 March 2006; published 7 December 2006)

The entire temperature dependence of the upper critical field $H_{c2}$ in the β-pyrochlore KO$_2$O$_6$ is obtained from high-field resistivity and magnetic measurements. Both techniques identically give $H_{c2}(T=0 \text{ K})$ not only surprisingly high ($\sim 33 \text{ T}$), but also the approach to it is unusually temperature linear all the way below $T_c (\approx 9.6 \text{ K})$. We show that, while $H_{c2}(0)$ exceeds a simple spin-singlet paramagnetic limit $H_p$, it is well below an $H_p$ enhanced due to the missing spatial inversion symmetry reported recently in KO$_2$O$_6$, ensuring that the pair breaking here is executed by orbital degrees. *Ab initio* calculations of orbital $H_{c2}$ show that an unusual temperature dependence is reproduced if dominant s-wave superconductivity resides on the smaller closed Fermi surfaces.

DOI: 10.1103/PhysRevB.74.220506 PACS number(s): 74.25.Ha, 74.20.Rp, 74.25.Fy, 74.25.Op

Transition metal oxides, with a nexus of strong electron correlations and structural diversity in the ways oxygen tetrahedra and octahedra can be edge and corner linked, are well known to host rather unusual quantum states. High-$T_c$ copper oxide superconductors or manganites are most explored,1 but such quantum phenomena are also in evidence in the “pyrochlore” structure2 where, in addition, geometrical (spin) frustration enters in a crucial way. Superconductivity in the β-pyrochlore oxides AO$_2$O$_6$ discovered not long ago, with relatively high transition temperatures $T_c$ (3.3 K, 6.3 K, and 9.6 K for A=Cs,3 Rb,4,5 and K,6 respectively) and distinctly odd behaviors in the normal state, suggest new physics, perhaps explicitly connected to this structure.

KO$_2$O$_6$, with the highest $T_c$, appears to be more unusual than the rest. The resistivity in the normal state has a pronounced convex temperature dependence down to $T_c$,7 indicating that electron-phonon scattering is strong—likely owing to the rattling motion of “caged” K ions.8 The specific heat has a jump $\Delta C/T_c=185 \text{ mJ} \cdot \text{K}^{-2} \cdot \text{mol}^{-1}$ at $T_c$, but also another (jump) anomaly at a lower temperature $T_p \approx 7.5 \text{ K}$, which has been attributed to freezing of the K rattle.9–11 In addition, strong electron correlations show up in important ways in transport and thermodynamic properties: for example, the thermal conductivity of KO$_2$O$_6$ is enhanced in the superconducting state11 (reminiscent of high-$T_c$ cuprates) and the Sommerfeld coefficient $\gamma$ is also largely enhanced9,10 from the band calculation value.8

The coexistence of strong electron correlations that prefer an anisotropic order parameter and strong electron-phonon coupling that favors a fully gapped s-wave ground state may render the workings of superconducting pairing in KO$_2$O$_6$ rather uncommon. Experimentally, the situation appears contradictory: muon spin rotation ($\mu$SR) measurements12 suggest anisotropic gap functions with nodes, in sharp contrast to the nodeless gap in RbO$_2$O$_6$13 while low-temperature thermal conductivity11—based on its magnetic field insensitivity—is consistent with a fully gapped state. Indeed, there has been much speculation about possible (unconventional) modes of pair-breaking in KO$_2$O$_6$ at low temperatures. Based on extrapolated (from low fields) estimates of upper critical field $H_{c2}$ in the $T \rightarrow 0 \text{ K}$ limit, suggestions have been made7,9,10,14 that the spin contribution to the pair breaking must be significant, that $H_{c2}(0)$ in KO$_2$O$_6$ may exceed the Pauli paramagnetic limit expected in a spin-singlet superconductor, that a quantum critical state may enter, and that a state with a spatially modulated order parameter [Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state15] may appear at low $T$ and high magnetic fields.

Here we show that in this pyrochlore system, missing spatial inversion symmetry can uniquely control the pair-breaking process, leading to unconventional behavior of the upper critical field without an unconventional pairing mechanism found in some heavy-fermion systems [e.g., CePt$_3$Si (Ref. 16)] that also lack inversion symmetry.

We have experimentally reached the low-$T$ high-field limit to obtain the full temperature dependence of $H_{c2}$ in KO$_2$O$_6$. We find that $H_{c2}$ in the $T \rightarrow 0 \text{ K}$ limit is not only surprisingly high, but also the approach to it does not display the typical flattening at low $T$. Both high-field resistivity and magnetic penetration measurements gave us an identical $H_{c2}(T)$ growing linearly with temperature and reaching $\sim 32 \text{ T}$ in the subkelvin range. This value is clearly beyond the simple Clogston paramagnetic limit of $H_p \sim 18 \text{ T}$.17 Following a remarkable recent structural finding of broken symmetry in KO$_2$O$_6$,14 we show by relying on experimental inputs how this limit can be hugely enhanced (up to $\sim 54 \text{ T}$). This enhancement leaves orbital pair breaking protected from spin effects up to very high fields, with the observed
Upon the field sweep, a certain amount of broadening is expected since high-field normal state. The resistive transition is relatively from the superconducting sample was inserted in one coil of the pair wound in a gra- range, with the wave form recorded during the pulse. The cal field pulse shown in the inset of Fig.1—the field pulse rise

H

tively determined

Our independent resistive and magnetic measurements de-

fine a unique upper critical field line

\( H_{c2}(T) \) (Fig. 3) which is also consistent with previous low-field data, \( H_{c2}(T) \) has two salient features: (i) its temperature dependence is linear in \( T \), without any visible saturation at low temperatures, and (ii) it reaches 32 T at the lowest temperature measured (0.5 K) and unambiguously extrapolates to 33 T in the zero-temperature limit, which corresponds to the coherence length \( \xi(0) = 3.2 \) nm. To understand the pair-breaking mode, both of these features need to be accounted for.

Since this upper limiting field is so large, let us attempt a more realistic estimate of the Pauli paramagnetic limiting field \( H_p \). At \( H_p \), Cooper pairs are broken apart by the Zeeman splitting produced by the magnetic-field coupling to the electron spins. This takes place when the Zeeman energy reaches the condensation energy

\[ U_c = N(0) \Delta^2 / 2 = H^2_c / 8 \pi [N(0)] \]

which is the density of states at the Fermi level, \( \Delta \) is the superconducting gap, and \( H_c \) is the thermodynamic critical field:

\[ U_c = [\chi_n - \chi_s(T)] H^2_c / 2. \]  

Here \( \chi_n = g^2 \mu_B^2 N(0) / 2 \) is the Pauli spin susceptibility in the normal state (\( \mu_B \) is Bohr magneton) and \( \chi_s(T) \) is the spin susceptibility in the superconducting state. In spin-singlet superconductors, \( \chi_s(T) \) follows the Yoshida function which vanishes at \( T=0 \) K. Simple calculations within the weak-
tering BCS theory with $\Delta C/T_c = 1.85 T_c$ [in kelvin]. In KOs$_2$O$_6$, this limit is 17.8 T, clearly much lower than the observed $H_{c2}(0)$.

We may improve on this estimate by making use of experimental parameters for the susceptibility $\chi_a$ and in the determination of the condensation energy $U_c$: the normal-state Pauli susceptibility $\chi_a = 4.2 \times 10^{-4}$ emu/mol has been measured just above $T_c$. The specific heat jump $\Delta C/T_c = 185$ mJ K$^{-2}$ mol$^{-1} = |dH_c/dT_c|^2 / 4\pi$ at $T_c$ (Refs. 9 and 23) gives an estimate for the $T = 0$ K thermodynamic critical field $H_c_0 = 0.26$ T. Using Eq. (1), this results in a larger value $H_{c2} \approx 31$ T, somewhat higher than the estimate $H_{c2} = 27$ T by Brühlwiler et al. using strong-coupling corrections. These values are near but still below the experimental $H_{c2}(0) = 33$ T. We point out that in the usual spin-singlet superconductors $H_{c2}(T)$ tends to saturate below $H_{c2}$, which appears to contradict our data.

At first glance, this would suggest spin-triplet superconductivity for which $\chi(T)$ remains of the order of the normal-state value, pushing the Pauli limit towards higher fields. Rather than invoking unconventional pairing, an alternative scenario providing a finite $\chi(T = 0)$ K derives from the recently reported noncentrosymmetric crystal structure of KOs$_2$O$_6$ by Schuck et al.: they found a volume deviation from an ideal $\beta$-pyrochlore lattice in Os tetrahedral and O octahedral networks and found the structure to be cubic with $F\overline{4}3m$ space group. The lack of inversion symmetry (visualized by the Os network in the inset of Fig. 3) affects the electronic properties through the appearance of an antisymmetric spin-orbit coupling (ASOC) term $\Delta \Sigma_{k,k'} g^2(\bar{k}) \sigma_{i\alpha} c^\dagger_{i\alpha} c_{i\alpha}'$, in the Hamiltonian, where $\alpha$ denotes the spin-orbit coupling strength, $\sigma$ is the Pauli matrix vector, $c^\dagger_{i\alpha}$ creates (annihilates) an electron with momentum $\bar{k}$ and spin $s$, and $g(\bar{k})$ is a dimensionless vector with $\bar{g}(\bar{k}) = -g(\bar{k})$. Such a term will admix spin-singlet and spin-triplet pairings and hence modify the spin susceptibility $\chi_s(t)$ in the superconducting state.

The effect has been extensively studied for the noncentrosymmetric superconductor CePt$_3$Si (Ref. 16); there the susceptibility $\chi_s(t)$ of the spin-singlet state assumes the form of a spin-triplet material with the $\bar{d}(\bar{k})$ vector of the triplet order parameter replaced by the spin-orbit coupling vector $\bar{g}(\bar{k})$. With a simple $s$-wave superconductivity found in the sister compounds RbOs$_2$O$_6$ and CsOs$_2$O$_6$, it appears natural to start from an $s$-wave scenario also in the present case. Given the $F\overline{4}3m$ symmetry in KOs$_2$O$_6$ (as in zinc blende), the spin-orbit coupling vector $\bar{g}(\bar{k})$ has a form

$$\bar{g}(\bar{k}) = \left[ k_x(k_x^2 - k_y^2), k_y(k_y^2 - k_z^2), k_z(k_z^2 - k_x^2) \right] / \hbar k_F,$$  

with $k_F$ the Fermi wave vector.

In KOs$_2$O$_6$, we expect a fairly large $\alpha$ from the heavy Os atoms, allowing us to use the spin-triplet state expression in the determination of $\chi_a(t)$, with the replacement $\bar{d}(\bar{k}) \rightarrow \bar{g}(\bar{k})$ as noted above. Following the calculations formulated in Ref. 28 with $\bar{g}(\bar{k})$ in Eq. (2), we obtain the value $\chi_a(t) = (2/3)\chi_a$. The right-hand side of our Eq. (1) then is reduced by a factor of $1/3$, resulting in a paramagnetic limiting field $H_p$ enhanced by a factor of $\sqrt{3}$. Taking our above estimate of 31 T based on experimental values for $U_c$ and $\chi_a$, we find an enhanced limiting field $H_p \approx 54$ T, way beyond the observed value of $H_{c2}(0)$. This large $H_p$ then resides sufficiently far above the measured value $H_{c2}(0) = 33$ T and thus protects the orbital upper critical field $H_{c2}(T)$ from spin effects.

The remaining question is how the orbital effects can enforce the observed linear temperature dependence. The orbital depairing is usually well described by the WHH theory, where the reduced critical field $h^*(t) = \frac{H_{c2}(0)}{T/T_c}$ saturates to $h^*(0) = 0.727$ in the clean limit. This $h^*(t = T/T_c)$, plotted as a solid line in Fig. 3, clearly deviates from the experimental data at low $T$.

Recently Kita and Arai provided a theoretical framework that allows for ab initio calculations of orbital $H_{c2}$ accounting for electronic band-structure effects. Band-structure calculations for the AOs$_2$O$_6$ compounds unveil two kinds of FS’s: one is the connected FS with necks along the threefold axis, while the other involves closed sheets centered on the $\Gamma$ point. Taking these Fermi surface shapes into account, we performed ab initio calculations of $h^*(t)$. We find that the FS anisotropy gives a maximum $H_{c2}$ in the [111] direction, which we compare with the experimental $H_{c2}$ taken as the field where the whole sample becomes normal.
The calculated results including all Fermi surfaces (connected and closed) are shown in Fig. 3. This $h^*(t)$ still deviates from the $H_{c2}(T)$ data at low temperatures. In contrast, if we ignore the connected surface and calculate $h^*(t)$ for the closed surfaces alone, we obtain an essentially $T$-linear $h^*(t)$ without saturation at low $T$, in very good agreement with the data. We conclude, then, that depairing at the upper limiting closed surfaces alone, we obtain an essentially nodeless gap is possible for the superconductivity suggested by thermal conductivity measurements. In the simple spin-triplet case, a nodeless gap is possible for the superconducting state. This strongly suggests that the $\tilde{a}=(k_x, k_y, k_z) = \tilde{a}_{BW}$ (known as the Balian-Werthamer state). This state, however, is easily suppressed by the ASOC term that satisfies $\tilde{g}(\tilde{k}) \tilde{a}_{BW} = 0$. This strongly suggests that the $s$-wave full-gap component is dominant (with small possible anisotropic component) in $\text{KO}_2\text{O}_6$, which is likely mediated by the strong electron-phonon coupling that wins over the electron correlations.

Last, we comment on new vortex phases that can arise. In CePt$_3$Si, the ASOC forms a helical vortex phase, analogous to the FFLO state with a finite net momentum of Cooper pairs. Thus, there is an intriguing expectation that a new vortex state may also appear in $\text{KO}_2\text{O}_6$. So, in summary, our results highlight a profound influence of broken spatial inversion symmetry on the nature of pair-breaking in $\text{KO}_2\text{O}_6$.

Note added. Recently, we became aware of high-field penetration depth by Ohmichi et al. corresponding to similarly high $H_{c2}$.

We acknowledge fruitful discussions with S. Fujimoto, M. Takigawa, Y. Yanase, P. A. Frigeri, B. Batlogg, M. Brühwiler, J. Karpinski, and K. Rogacki. This work was partly supported by Grants-in-Aid for Scientific Research from MEXT and by the Swiss National Fonds, including the NCCR MaNEP.

7 Z. Hiroi et al., J. Phys. Soc. Jpn. 74, 1682 (2005); 74, 3400 (2005). The weakly anisotropic crystallites in the sample block are most likely randomly aligned. In our study we use a similar sample block, so we experimentally define $H_{c2}$ as the maximum field where the superconducting current has completely vanished.
9 Z. Hiroi et al. (unpublished).
16 E. Bauer et al., Phys. Rev. Lett. 92, 027003 (2004). CePt$_3$Si has $P4mm$ space group and a Rashba-type coupling $\tilde{g}(\tilde{k}) \propto (k_y, -k_x, 0)$.
24 Here, in evaluating $\xi_0$ a possible orbital susceptibility is ignored and consequently the Wilson ratio $R_W$ close to 1 is obtained (Ref. 10). Taking $R_W \sim 2$, as widely observed for strongly correlated materials, the $H_T$ estimates are reduced only by a factor of $\sqrt{2}$, not affecting our conclusions.
26 T. Tayama et al., Phys. Rev. B 65, 180504(R) (2002). In the heavy-fermion CeCoIn$_5$ superconductor, the Pauli-limited $H_{c2}(T)$ is markedly flatter relative to WHH result (Ref. 29).
31 The antisymmetric spin-orbit coupling suppresses odd pairing states with $\tilde{a}$ vectors not parallel to $\tilde{g}$; see Ref. 28.