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Uncommonly high upper critical field of the pyrochlore superconductor KOs_2O_6 below the enhanced paramagnetic limit

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The entire temperature dependence of the upper critical field H_{c2} in the β-pyrochlore KOs_2O_6 is obtained from high-field resistivity and magnetic measurements. Both techniques identically give $H_{c2}(T \simeq 0\ K)$ not only surprisingly high ($\sim$33 T), but also the approach to it is unusually temperature *linear* all the way below T_c(=9.6 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 KOs_2O_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.

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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" structure[2] where, in addition, geometrical (spin) frustration enters in a crucial way. Superconductivity in the β-pyrochlore oxides AOs_2O_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, suggests new physics, perhaps explicitly connected to this structure.

KOs_2O_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 $\Delta C/T_c = 185\ \mathrm{mJ\,K^{-2}\,mol^{-1}}$ at T_c, but also another (jump) anomaly at a lower temperature $T_p \sim 7.5$ 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 KOs_2O_6 is enhanced in the superconducting state[11] (reminiscent of high-T_c cuprates) and the Sommerfeld coefficient γ is also largely enhanced[9,10] 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 KOs_2O_6 rather uncommon. Experimentally, the situation appears contradictory: muon spin rotation (μSR) measurements[12] suggest anisotropic gap functions with nodes, in sharp contrast to the nodeless gap in $RbOs_2O_6$,[13] while low-temperature thermal conductivity[11]—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 KOs_2O_6 at low temperatures. Based on *extrapolated* (from low fields) estimates of upper critical field H_{c2} in the $T \to 0$ K limit, suggestions have been made[7,9,10,14] that the spin contribution to the pair breaking must be significant, that $H_{c2}(0)$ in KOs_2O_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) state[15]] 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., $CePt_3Si$ (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 KOs_2O_6. We find that H_{c2} in the $T \to 0$ 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 T in the subkelvin range. This value is clearly beyond the simple Clogston paramagnetic limit of $H_P \sim 18$ T.[17] Following a remarkable recent structural finding of broken symmetry in KOs_2O_6,[14] we show by relying on experimental inputs how this limit can be hugely enhanced (up to $\sim$54 T). This enhancement leaves orbital pair breaking protected from spin effects up to very high fields, with the observed

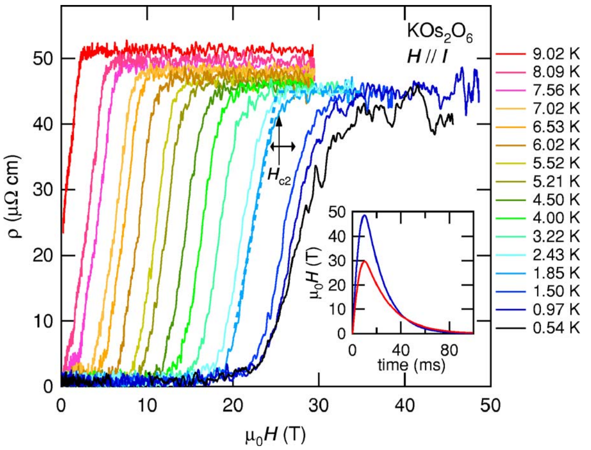

FIG. 1. (Color online) Field dependence of the resistivity in KOs_2O_6. In the experiments, a block of small single crystals was cut into two pieces: one was used for resistivity and the other for magnetic measurements, as those in Fig. 2. Inset: typical field-pulse profiles used. Magnetic fields up to $\sim$50 T were applied in the current direction.

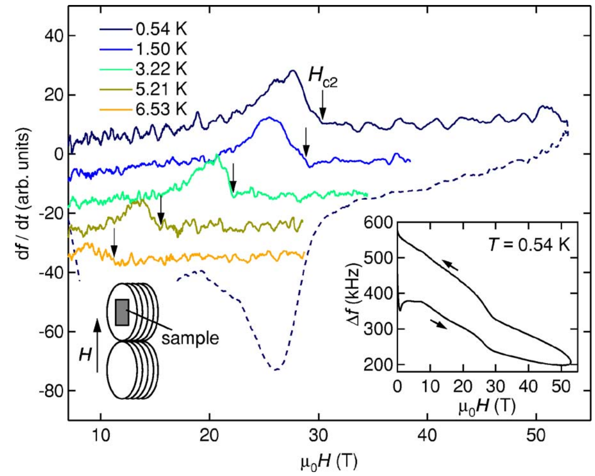

FIG. 2. (Color online) Time derivative df/dt of the frequency shift of the tunnel diode oscillator containing the KOs_2O_6 sample. The full up-field (dashed line) and down-field cycle is shown for T=0.54 K, for which the frequency shift Δf vs field is also displayed in the inset. At other temperatures (color coded as in Fig. 1), only down-field sweeps are shown and each curve is vertically shifted for clarity.

T-linear H_{c2} fully consistent with the orbital contributions from the closed Fermi surfaces.

In this study, we used a block containing several single crystals of cubic KOs_2O_6 grown by the technique described in Ref. 7. The resistivity was recorded using a 100-kHz lock-in technique in a 65-T maximum field, 60-ms pulsed magnet[18] at the National High Magnetic Field Laboratory (NHMFL in Los Alamos). The magnetic penetration was measured by a tunnel diode oscillator (TDO) operating at $f \sim 55$ MHz in an LC tank circuit.[19] A heterodyne technique was used to beat down the frequency to the hundreds of kHz range, with the wave form recorded during the pulse. The sample was inserted in one coil of the pair wound in a gradiometer configuration (sketched in Fig. 2), and the inductance change due to the change in the penetration depth was detected by the shift of the resonance frequency Δf.

Figure 1 shows the field dependence of the resistivity ρ in KOs_2O_6. Upon the field sweep, $\rho(H)$ evolves, as expected, from the superconducting (vortex) state at low fields to the high-field normal state. The resistive transition is relatively sharp; a certain amount of broadening is expected[20,21] since the crystals in a block are weakly connected. The upper critical field H_{c2} can therefore be determined in the usual way from the field at which $\rho(H)$ is fully restored to its normal-state value. In order to remove any ambiguity in the resistively determined H_{c2} (Ref. 21) we have further corroborated our results by magnetic measurements. The inset of Fig. 2 displays the frequency shift Δf of the TDO as a function of H. The observed hysteresis is related to the asymmetry of the field pulse shown in the inset of Fig. 1—the field pulse rise time (10 ms) is much shorter than the fall time (50 ms). The field direction is perpendicular to the axis of the coils; in our setup, one coil detects the change in the sample and the other is for the cancellation of the voltage signal from dB/dt. To bypass the somewhat imperfect cancellation, we plot df/dt as a function of field in the main panel of Fig. 2, where the anomaly (peak) due to the change in the penetration depth is clearly articulated. The high-field end point of the peak in df/dt corresponds to the field where the whole sample becomes normal, and hence it is the value of the upper critical field. The H_{c2} values determined from the up and down sweeps of the field pulse coincide with each other, which is a solid indication that our measurements are free from eddy-current heating $\propto (dB/dt)^2$.

Our independent resistive and magnetic measurements define a unique upper critical field line $H_{c2}(T)$ (Fig. 3) which is also consistent with previous low-field data;[7,9,10,14] we surmise then that this temperature dependence is intrinsic to KOs_2O_6. $H_{c2}(T)$ 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 $U_c=N(0)\Delta^2/2=H_c^2/8\pi$ [$N(0)$ is the density of states at the Fermi level, Δ is the superconducting gap, and H_c is the thermodynamic critical field]:

$$U_c = [\chi_n - \chi_s(T)]H_P^2/2. \tag{1}$$

Here $\chi_n=g^2\mu_B^2 N(0)/2$ is the Pauli spin susceptibility in the normal state (μ_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-

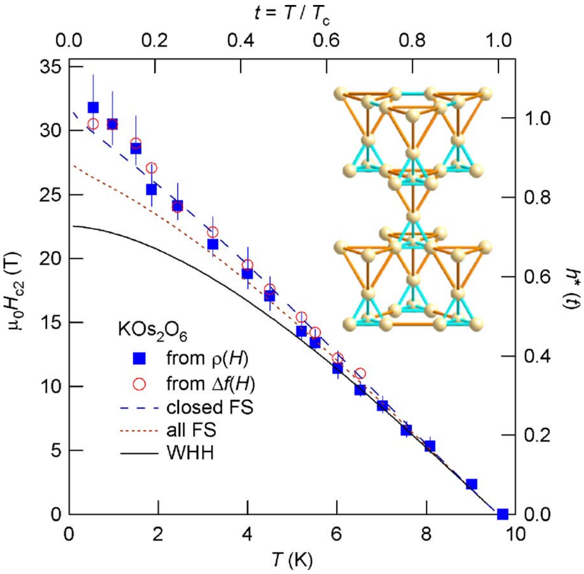

FIG. 3. (Color online) Temperature dependence of the upper critical field determined by the resistivity (solid squares) and magnetic (open circles) measurements. The solid line is the expected orbital $h^{*}(t)$ from the conventional Werthamer-Helfand-Hohenberg (WHH) formulation. The dotted and dashed lines are *ab initio* calculations for the maximum $h^{*}(t)$ ([111] direction) by fitting the initial slope at T_c and taking into account all the Fermi surfaces (FS) and the closed FS only, respectively. Inset: schematic Os network in the noncentrosymmetric ($F\bar{4}3m$) structure.

coupling BCS theory with $\Delta=1.76k_{\mathrm{B}}T_{\mathrm{c}}$ and the assumption $g=2$ give the well-known result[17] H_{P} [in tesla]$=1.85T_{\mathrm{c}}$ [in kelvin]. In $\mathrm{KOs_2O_6}$, this limit is 17.8 T, clearly much lower than the observed $H_{\mathrm{c2}}(0)$.

We may improve on this estimate by making use of experimental parameters[22] for the susceptibility χ_{n} and in the determination of the condensation energy U_{c}: the normal-state Pauli susceptibility $\chi_{\mathrm{n}}\approx 4.2\times 10^{-4}$ emu/mol has been measured[9,10] just above T_{c}. The specific heat jump $\Delta C/T_{\mathrm{c}}$ $=185$ mJ K^{-2} mol^{-1}$=[\mathrm{d}H_{\mathrm{c}}/\mathrm{d}T]^2_{T_{\mathrm{c}}}/4\pi$ at T_{c} (Refs. 9 and 23) gives an estimate for the $T=0$ K thermodynamic critical field $H_{\mathrm{c}}(0)\approx 0.26$ T. Using Eq. (1), this results in a larger value $H_{\mathrm{P}}\approx 31$ T,[24] somewhat higher than the estimate $H_{\mathrm{P}}\approx 27$ T by Brühwiler *et al.*[10] using strong-coupling corrections.[25] These values are near but still below the experimental $H_{\mathrm{c2}}(0)\approx 33$ T. We point out that in the usual spin-singlet superconductors $H_{\mathrm{c2}}(T)$ tends to saturate below H_{P},[26] which appears to contradict our data.

At first glance, this would suggest spin-triplet superconductivity for which $\chi_{\mathrm{s}}(T)$ 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 $\chi_{\mathrm{s}}(T=0\ \mathrm{K})$ derives from the recently reported noncentrosymmetric crystal structure of $\mathrm{KOs_2O_6}$ by Schuck *et al.*;[14] they found a volume deviation from an ideal β-pyrochlore lattice in Os tetrahedral and O octahedral networks and found the structure to be cubic with $F\bar{4}3m$ 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 $\alpha\Sigma_{\vec{k},s,s'}\vec{g}(\vec{k})\vec{\sigma}_{ss'}c^{\dagger}_{\vec{k}s}c_{\vec{k}s'}$ in the Hamiltonian, where α denotes the spin-orbit coupling strength, $\vec{\sigma}$ is the Pauli matrix vector, $c^{\dagger}_{\vec{k}s}$ ($c_{\vec{k}s}$) creates (annihilates) an electron with momentum $\vec{k}$ and spin s, and $\vec{g}(\vec{k})$ is a dimensionless vector with $\vec{g}(-\vec{k})=-\vec{g}(\vec{k})$. Such a term will admix spin-singlet and spin-triplet pairings[27] and hence modify the spin susceptibility $\chi_{\mathrm{s}}(T)$ in the superconducting state.[28]

The effect has been extensively studied for the noncentrosymmetric superconductor $\mathrm{CePt_3Si}$ (Ref. 16); there the susceptibility $\chi_{\mathrm{s}}(T)$ of the spin-singlet state assumes the form of a spin-triplet material with the $\vec{d}(\vec{k})$ vector of the triplet order parameter replaced by the spin-orbit coupling vector $\vec{g}(\vec{k})$.[28] With a simple s-wave superconductivity found in the sister compounds $\mathrm{RbOs_2O_6}$ and $\mathrm{CsOs_2O_6}$, it appears natural to start from an s-wave scenario also in the present case. Given the $F\bar{4}3m$ symmetry in $\mathrm{KOs_2O_6}$ (as in zinc blende), the spin-orbit coupling vector $\vec{g}(\vec{k})$ has a form[28]

$$\vec{g}(\vec{k})=[k_x(k_y^2-k_z^2),k_y(k_z^2-k_x^2),k_z(k_x^2-k_y^2)]/k_{\mathrm{F}}^3, \qquad (2)$$

with k_{F} the Fermi wave vector.

In $\mathrm{KOs_2O_6}$, we expect a fairly large α from the heavy Os atoms, allowing us to use the spin-triplet state expression in the determination of $\chi_{\mathrm{s}}(0)$, with the replacement $\vec{d}(\vec{k})$ $\rightarrow\vec{g}(\vec{k})$ as noted above. Following the calculations formulated in Ref. 28 with $\vec{g}(\vec{k})$ in Eq. (2), we obtain the value $\chi_{\mathrm{s}}(0)=(2/3)\chi_{\mathrm{n}}$. 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 χ_{n}, we find an enhanced limiting field $H_{\mathrm{P}}\sim 54$ T, way beyond the observed value of $H_{\mathrm{c2}}(0)$.[24] This large H_{P} then resides sufficiently far above the measured value $H_{\mathrm{c2}}(0)\simeq 33$ T and thus protects the orbital upper critical field $H_{\mathrm{c2}}(T)$ 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,[29] where the reduced critical field $h^{*}(t)=\frac{H_{\mathrm{c2}}(t)}{-\mathrm{d}H_{\mathrm{c2}}(t)/\,\mathrm{d}t|_{t=1}}$ saturates to $h^{*}(0)=0.727$ in the clean limit. This $h^{*}(t=T/T_{\mathrm{c}})$, 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.[30] Band-structure calculations for the $A\mathrm{Os_2O_6}$ compounds[8] 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 Γ 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.[7]

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 field is enforced by the orbital degrees of freedom, without interferences from the Pauli limit, and that the superconducting pairing mainly occurs on the closed Fermi surfaces.

Our finding of orbitally limited H_{c2} is compatible with the fully gapped superconductivity suggested by thermal conductivity measurements.[11] In the simple spin-triplet case, a nodeless gap is possible for the $\vec{d}=(k_x,k_y,k_z)=\vec{d}_{\mathrm{BW}}$ (known as the Balian-Werthamer state). This state, however, is easily suppressed by the ASOC term that satisfies $\vec{g}(\vec{k})\cdot\vec{d}_{\mathrm{BW}}=0$.[31] This strongly suggests that the s-wave full-gap component is dominant (with small possible anisotropic component) in KOs_2O_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 $CePt_3Si$, the ASOC forms a helical vortex phase,[32] analogous to the FFLO state with a finite net momentum of Cooper pairs.[15] Thus, there is an intriguing expectation that a new vortex state may also appear in KOs_2O_6.[28] So, in summary, our results highlight a profound influence of broken spatial inversion symmetry on the nature of pair-breaking in KOs_2O_6.

Note added. Recently, we became aware of high-field penetration depth data by Ohmichi *et al.*[33] corresponding to similarly high H_{c2}.

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