Isotropically Gapped Strong-Coupling Superconductivity in the β-Pyrochlore KOs_2O_6: Evidence from Penetration Depth Measurements

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We report on measurements of the temperature dependence of the magnetic penetration depth down to 0.04 K in a high-quality sample of the β-pyrochlore KOs_2O_6 ($T_c = 9.65$ K) with a spin-frustrated lattice. We observe temperature-independent behavior below $T \simeq 0.3T_c$, which is firm evidence for the presence of an isotropic superconducting gap in this material. In the whole temperature range the superfluid density is very well described, without the need of adjustable parameters, by a strong-coupling extension of the BCS model for an isotropic gap. Thus, the penetration depth results indicate that KOs_2O_6 is a strong-coupling superconductor with a fully developed energy gap. No effect of the second phase transition taking place at $T_p = 7.5$ K was observed on the penetration depth, which suggests that the Cooper pairs remain unperturbed across this transition.

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The discovery of superconductivity in the α-pyrochlore rhenium oxide $Cd_2Re_2O_7$ [1,2] attracted so much attention because the geometric spin frustration inherent to its pyrochlore crystal structure was supposed to give rise to unconventional superconductivity via magnetic spin fluctuations [3]. However, $Cd_2Re_2O_7$ turned out to be a conventional s-wave superconductor. Recent observation of superconductivity in the β-pyrochlore osmium oxides $CsOs_2O_6$ ($T_c = 3.3$ K) [4], $RbOs_2O_6$ ($T_c = 6.3$ K) [5], and KOs_2O_6 [6] has renewed interest in the spin-frustrated compounds. The experimental results to date suggest, however, that $CsOs_2O_6$ and $RbOs_2O_6$ are conventional s-wave superconductors. In both compounds the studied thermodynamic and transport properties have temperature-activated behaviors and the zero-temperature upper critical field $H_{c2}(0)$ is below the Pauli limit [7–9].

KOs_2O_6, on the other hand, shows unusual and contrasting behaviors that make its superconducting pairing symmetry unclear. $H_{c2}(0) \approx 31$ T [10–12] exceeds the calculated weak-coupling Pauli limiting field $H_p = 18$ T, which initially was thought to be an indication of unconventional spin-triplet pairing. Recent specific-heat experiments [11,13], however, suggest that KOs_2O_6 lies in the strong-coupling BCS regime, and a recalculation of H_p within this limit and taking into account spin-orbit effects yielded a value of 37 T [13]. Data of NMR-$1/T_1$ down to 2 K show no coherence peak and a power-law temperature dependence that suggests the presence of nodes in the gap [14]. μSR measurements down to 2 K indicate a nodeless anisotropic or multiple gap function [15]. Recent specific-heat data hint at the existence of a second superconducting gap [11]. Thermal conductivity data were interpreted in terms of a fully gapped superconductivity in coexistence with strong electron correlations that normally induce an anisotropic pairing symmetry [16]. Although the most recent experiments appear to point to a conventional-like symmetry in KOs_2O_6, the exact structure of the superconducting gap remains highly controversial. Further studies, in particular, at temperatures below 1 K, are necessary to definitely establish the symmetry and the topology of the superconducting gap.

Another uncommon feature of KOs_2O_6 is the magnetic-field-insensitive phase transition observed in specific-heat measurements at $T_p = 7.5$ K, below T_c [11,13,17]. The origin of this transition was attributed to the freezing of the rattle motion of the K cation, and the transition was found to affect somewhat the superconducting phase. This perturbation of superconductivity is rather intriguing because such a transition involves an ion that does not contribute to the density of states near the Fermi surface. Thus, an effect of this transition on the superconducting state is not expected, unless the low-energy phonons of the rattle motion are involved in the interaction causing superconductivity in KOs_2O_6.

Recently, a dispute emerged over the crystal structure of KOs_2O_6. The structure has been identified by Hiroi and coworkers as a β pyrochlore with space group $Fd\bar{3}m$ at 300 and 5 K [6,18]. On the other hand, Schuck *et al.* [19] identified the space group as noncentrosymmetric $F\bar{4}3m$. Regarding superconductivity the difference between the two groups is quite relevant. If the crystal structure corresponds to $Fd\bar{3}m$ ($F\bar{4}3m$), the superconducting order parameter will be a pure spin-singlet or spin-triplet state (an admixture of spin-singlet and spin-triplet states). This difference in the construction of the order parameter has a significant impact on the analysis of the superconducting properties.

With the aim of shedding light on the symmetry and the structure of the superconducting pairing state and on the effect of the second phase transition at T_p on superconductivity, we measured the temperature dependence of the magnetic penetration depth $\lambda(T)$ in KOs_2O_6 down to 40 mK ($\sim 0.004T_c$). $\lambda(T)$ is a direct response of the Cooper pairs and is perhaps, due to the high resolution with which it can be measured, the most powerful probe for the presence of any kind of anisotropy in the superconducting gap. Precisely because $\lambda(T)$ senses the temperature behavior of the Cooper pairs, any perturbation to the intrinsic superconducting state should be detected in the penetration depth data. In this Letter we report that in high-quality samples of KOs_2O_6 (a) the superconducting gap is isotropic and (b) the second transition around 7.5 K does not seem to affect the Cooper pairs.

We measured a very high quality KOs_2O_6 polycrystal (a block of three single crystals) grown as reported elsewhere [11]. To prevent hydration in air, we took extreme care to keep the sample in a dry atmosphere. The sample, with dimensions about $0.3 \times 0.3 \times 0.1$ mm^3, displays a very sharp transition at the highest reported transition temperature $T_c \simeq 9.65$ K, which confirms the high quality of the sample.

Penetration depth measurements were performed using a 14 MHz tunnel diode oscillator [20]. The magnitude of the ac probing field was estimated to be 5 mOe, and the dc field at the sample was reduced to around 1 mOe. Thus, the field felt by the sample was about 5 orders of magnitude lower than $H_{c1}(0) = 110$ Oe [13], and the possibility of vortex contributions to the measured $\lambda(T)$ is negligible. Such a low field also allowed the study of the intrinsic superconducting behavior of the polycrystalline sample [20]. Because of the cubic symmetry of its crystal structure, KOs_2O_6 has isotropic superconducting properties.

The deviation of the penetration depth from the lowest measured temperature, $\Delta\lambda(T) = \lambda(T) - \lambda(0.04\ \text{K})$, was obtained up to $T \sim 0.99T_c$ from the change in the measured resonance frequency $\Delta f(T)$: $\Delta f(T) = G\Delta\lambda(T)$. Here G is a constant factor that depends on the sample and coil geometries and includes the demagnetizing factor of the sample. To within this calibration factor, $\Delta\lambda(T)$ is raw data. We estimated G by measuring a sample of known behavior and of the same dimensions as the test sample.

Figure 1 shows $\Delta\lambda(T)$ scaled to $\Delta\lambda_0$ as a function of temperature for the KOs_2O_6 sample. Here $\Delta\lambda_0$ is the corresponding total penetration depth shift. For comparison, the figure also depicts data of a pure (99.999%) polycrystalline sample of the s-wave superconductor Nb ($T_c = 9.2$ K). The penetration depth in KOs_2O_6 displays a sharp transition, and its behavior in the entire temperature range below T_c follows closely that of the Nb data. There is no anomaly around the temperature $T_p = 7.5$ K [see a blowup in the inset of Fig. 1(a)], at which a second phase transition was found in specific-heat measurements [13,17]. Such a transition was proven to be nonsuperconducting and nonmagnetic and to have some effects on the superconducting phase [11,17]. In a recent work Hiroi

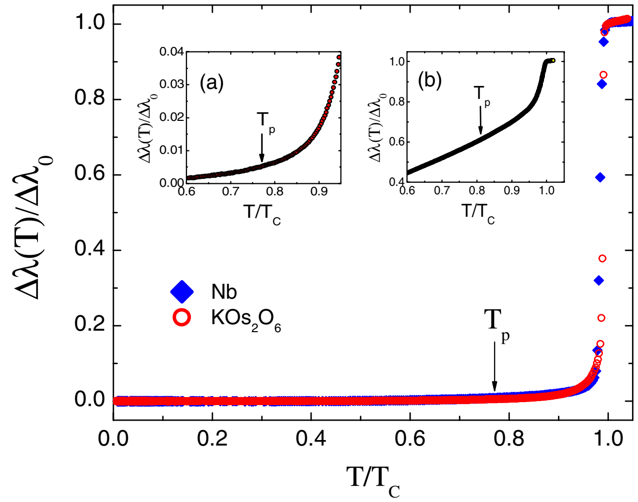

FIG. 1 (color online). Normalized $\Delta\lambda(T)$ vs T/T_c for KOs_2O_6 and conventional superconducting niobium. The insets show the high-temperature region for KOs_2O_6 in (a) the currently studied pure polycrystalline sample and (b) a much lower quality crystal. There is no indication that the structural phase transition taking place at $T_p = 7.5$ K affects the superconducting state (see text).

et al. [11] point out that after hydration of the samples the second specific-heat anomaly, attributed to the structural transition, goes away and that the superconducting transition slightly broadens. In preliminary penetration depth measurements (unpublished) in much lower quality single crystals of KOs_2O_6, with T_c's around 9.1–9.2 K and with hydration-prevented treatments, we found broad superconducting transitions and no anomalies at T_p [see an example in the inset of Fig. 1(b)]. Thus, from our penetration depth data it appears that Cooper pairs are not affected by the second phase transition at T_p.

We believe that it is unlikely that surface damage covered up any anomaly in $\lambda(T)$ arising from the second transition. First, the samples look clean, shiny, and without surface defects under the microscope. In our experience, such a surface effect is mostly seen in nonetched and unpolished samples. Second, in KOs_2O_6 $\lambda(0) = 270$ nm [15] is much larger than the BCS coherence length $\xi_0 \sim 3.3$ nm [10,11] [in clean superconductors ξ_0 is approximately the same as the zero-temperature Ginzburg-Landau coherence length $\xi(0)$]. We therefore expect our probe to be sensitive to the bulk superconducting state.

The second phase transition at T_p was suggested to be due to the freezing of the rattle motion of the K cation. In KOs_2O_6 the density of states near the Fermi surface is mainly due to the strong hybridization of the Os $5d$ and O $2p$ states [21]. Thus, from an electronic viewpoint any change in the K cation would hardly influence the superconducting state. On the other hand, there is a possibility that the low-energy phonons caused by the rattle motion of the K cation are involved in the electron-phonon interaction [11] that could be responsible for superconductivity in

KOs_2O_6. In such a case, the freezing of the rattle motion should perturb the superconducting phase. This latter view is not supported by the present penetration depth data.

From resistivity data the mean free path l was found to significantly increase (27%) at the second transition [11], implying that the rattle motion acts as a scatter of the conduction electrons. This conclusion is supported by thermal conductivity results [16] which suggest that below T_p the electron-phonon scattering suddenly decreases and that electron transport becomes dominated by electron-electron scattering. Thus, the reduction of the electron-phonon scattering rate causes an increase in l which in turn leads to an enhancement of the thermal conductivity at T_p. A change in the mean free path may influence the penetration depth in the dirty limit. For a local (London) superconductor with $\lambda(0) > \xi_0$ $\lambda(T) = \lambda_L(T) \times (1 + c\xi_0/l)^{1/2}$. Here $\lambda_L(T)$ is the London penetration depth of a pure system and c a constant. Since KOs_2O_6 is in the clean limit ($l \approx 640$ nm $\gg \xi_0$), basically no variation in $\lambda(T)$ due to a 27% change in l should be expected. This is confirmed by our penetration depth results.

It seems that the mechanism driving the second phase transition at 7.5 K neither disturbs the Cooper pairs nor modifies fundamental superconducting parameters as T_c and H_c [11]. The changes observed at T_p in some physical variables can be reasonably ascribed to the enhancement of the mean free path of the conduction electrons.

Figure 2 displays the low-temperature region of the data in the main body of Fig. 1. The penetration depth of KOs_2O_6 as well as that of Nb clearly flattens below $0.3T_c$, just as theoretically expected for a superconductor with a fully developed superconducting gap. Invariably, in the low-temperature limit $\lambda(T)$ follows for an isotropic energy gap Δ_0 an exponential function $\propto \exp(-\Delta_0/k_BT)$, and for an anisotropic (with nodes) gap a power law T^α. In nodeless anisotropic gaps $\lambda(T)$ displays an exponential behavior only below the gap minimum.

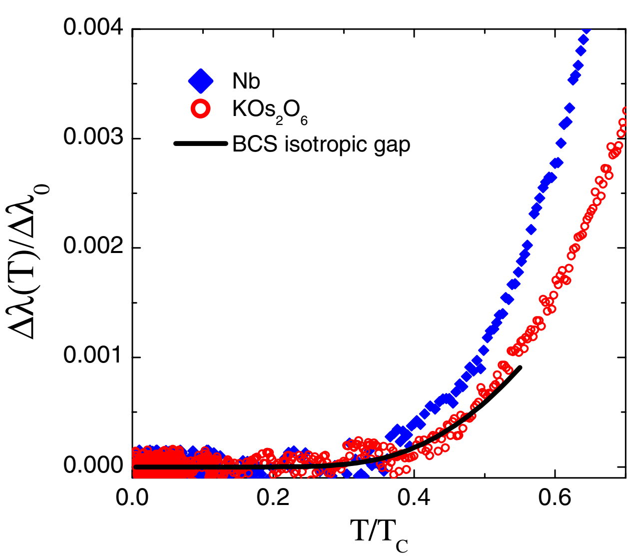

FIG. 2 (color online). (a) Normalized $\Delta\lambda(T)$ against T/T_c for KOs_2O_6 and niobium in the low-temperature region. The solid line is a fit to the strong-coupling BCS model for an isotropic pairing symmetry.

At low temperatures $T < 0.5T_c$, the data of KOs_2O_6 are very well fitted to the BCS model

$$\Delta\lambda(T) \propto \sqrt{\frac{\pi\Delta_0}{2k_BT}}\exp(-\Delta_0/k_BT), \tag{1}$$

with $\Delta_0 = 2.4k_BT_c$, which is much larger than the standard BCS value of $1.76k_BT_c$ and implies large corrections to the weak-coupling theory. Such a high value places KOs_2O_6 in the strong-coupling regime, in agreement with conclusions drawn from specific-heat measurements [11,13]. The penetration depth value $\Delta_0/k_BT_c = 2.4$ compares quite well with the specific-heat values of 2.29–2.35.

The low-temperature response of the penetration depth down to $0.004T_c$ is unequivocal evidence for an isotropic superconducting energy gap in KOs_2O_6. This contrasts suggestions of both an anisotropic or multiple gap structure from μSR [15] and specific heat [11] and nodes in the gap from NMR-$1/T_1$ [14]. It agrees with the conclusion of an isotropic gap from the intriguing thermal conductivity measurements [16], which also provide evidence for strong electron correlations that usually favor an anisotropic gap.

Next, we compare the temperature dependence of the experimental superfluid density $n_s(T)$ with several models. In the local limit of the electrodynamics the normalized BCS superfluid density $\rho(T) = n_s(T)/n = \lambda^2(0)/\lambda^2(T)$, where n is the total density and

$$\frac{\lambda^2(0)}{\lambda^2(T)} = \left\langle 1 + 2\int_0^\infty d\epsilon \frac{\partial f}{\partial E}\right\rangle. \tag{2}$$

Here $\langle\cdots\rangle$ represents an angular average over the Fermi surface and f is the Fermi function. The total energy $E(\mathbf{k}) = \sqrt{\epsilon^2(\mathbf{k}) + |\Delta(T,\mathbf{k})|^2}$, where ϵ is the single-particle energy measured from the Fermi surface, $\Delta(T,\mathbf{k}) = \Delta^t(T)\Delta^k(\mathbf{k})$, and $\mathbf{k}$ is the wave vector. We considered a spherical Fermi surface and used the standard interpolation formula for the gap $\Delta^t(T)$. We evaluated (a) the isotropic s-wave BCS model in the weak-coupling ($\Delta C/C_n = 1.43$ and $\Delta_0 = 1.76k_BT_c$) and strong-coupling ($\Delta C/C_n = 2.8$ and $\Delta_0 = 2.3k_BT_c$) limits, (b) a weak-coupling two-gap model $\rho = N\rho_l + (1 - N)\rho_s$, with the normalized density of states in the large-gap band $N = 0.8$ and the value of the small gap one-fifth of the large gap, (c) a model with the symmetry-allowed 3D anisotropic s-wave gap $\Delta^k \propto [a + \sin^2(\theta)\cos(4\phi)]$, with $a = 1.2$, and (d) the 3D d-wave model. Figure 3 displays the results of the numerical evaluations along with the experimental data (circles). We note that the values of $\Delta C/C_n$ and Δ_0 used in the strong-coupling isotropic gap model were those

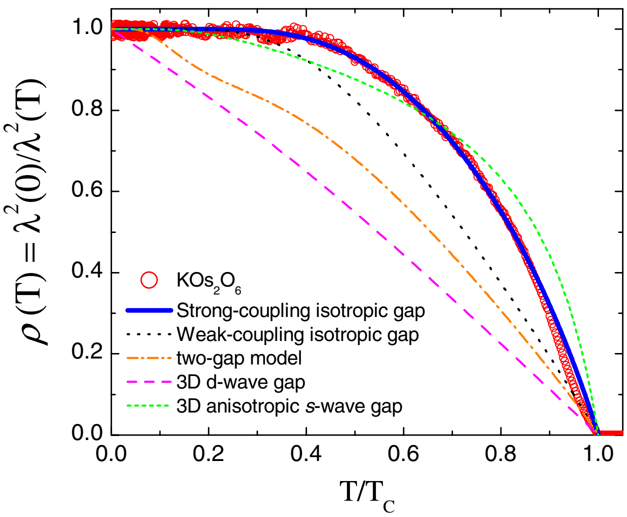

FIG. 3 (color online). Results of the numerical evaluations of local BCS models compared with the experimental data of KOs_2O_6 (see text for details).

obtained from specific-heat measurements [11,13] and that there is no adjustable parameter. The excellent agreement with the strong-coupling model gives forceful support for isotropically gapped superconductivity in the strong-coupling limit.

In light of the present magnetic penetration depth result we conclude that KOs_2O_6 is unambiguously an isotropically gapped strong-coupled superconductor. Since thus far there are no experimental indications in KOs_2O_6 for the realization of a superconducting state with orbital angular momentum $l \neq 0$, our result implies that the gap function in this compound has an s-wave symmetry. If this is confirmed, and given the previous results of s-wave symmetry in $CsOs_2O_6$ and $RbOs_2O_6$, it will mean that spin-frustrated geometries do not lead to unconventional superconductivity.

We now consider the penetration depth data in the context of a possible noncentrosymmetric KOs_2O_6. Without the spatial inversion symmetry, the spatial component of the wave function has no definite parity. To preserve the antisymmetry of the pairing, the same is true for the spin component. The direct implication of parity violation is that the pairing symmetry should, in principle, be a mixture of spin-singlet and spin-triplet states. This admixture can be theoretically obtained by assuming that the lack of the inversion symmetry in a crystal structure causes the appearance of an antisymmetric spin-orbit coupling that breaks the spin degeneracy of normal superconducting states [22]. A large coupling strength lifts the spin degeneracy by originating two energy bands, $\Delta_{\pm}(\mathbf{k}) = \psi \pm t|\mathbf{g}(\mathbf{k})|$, with different spin structure. Here ψ and $t|\mathbf{g}(\mathbf{k})|$ are the spin-singlet and spin-triplet components, respectively, and $\mathbf{g}(\mathbf{k})$ a dimensionless vector parallel to the vector $\mathbf{d}(\mathbf{k})$ of the spin-triplet order parameter.

In KOs_2O_6 the penetration depth data indicate an isotropically gapped superconductivity; therefore, any possible mixing of spin-singlet and spin-triplet states in $\Delta_{\pm}$ is ruled out—any mixture yields a two-gap order parameter. The pairing state then should consist of either the spin-singlet or the spin-triplet component of $\Delta_{\pm}$. But even the simplest isotropic spin-triplet state, $\mathbf{d}(\mathbf{k})_{A_{1u}} = \hat{x}k_x + \hat{y}k_y + \hat{z}k_z$, is suppressed by the spin-orbit coupling term: $\mathbf{g}(\mathbf{k}) \cdot \mathbf{d}(\mathbf{k})_{A_{1u}} = 0$. Here $\mathbf{g}(\mathbf{k}) \propto [k_x(k_y^2 - k_z^2), k_y(k_z^2 - k_x^2), k_z(k_x^2 - k_y^2)]$ [22]. Thus, the penetration depth result implies that only the spin-singlet component, specifically the isotropic s-wave state, is allowed in KOs_2O_6.

In summary, we reported on magnetic penetration depth measurements in KOs_2O_6. The results unquestionably indicate that this material is a strong-coupled superconductor with an isotropic (possibly s-wave) gap. No evidence was found that the second phase transition at T_p affects the penetration depth and, therefore, the Cooper pairs.

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