Photoemission Spectroscopic Evidence of Gap Anisotropy in an f-Electron Superconductor

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We used low-temperature ultrahigh-resolution (360 μeV) photoemission spectroscopy with a laser as a photon source (Laser-PES) to study the superconducting (SC) gap of an f-electron superconductor $CeRu_2$. The unique combination of the large escape depth expected from the known universal behavior and extremely high-energy resolution has enabled us to directly measure the bulk SC gap of an f-electron superconductor for the first time. The present study provides direct evidence for an anisotropic SC gap in $CeRu_2$, and also demonstrates the potential of Laser-PES in investigating unconventional superconductivity realized in correlated d- and f-electron superconductors.

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It is well known that the variety of properties that conducting materials display stems from the electronic structure (ES) at and near the Fermi level (E_F). One of the most fascinating examples is superconductivity, in which the pairing of two electrons makes a tiny energy gap at E_F, leading to unexpected physical properties [1]. Tunneling and photoemission spectroscopies (PES) are experimental probes that directly measure superconducting (SC) energy gaps for low and high temperature superconductors [2–8]. However, being sensitive to surfaces, such studies have not been able to provide reliable data for f-electron superconductors which exhibit a surface ES different from the bulk [9]. Nonetheless, they exhibit intrinsic but anomalous normal- and SC-state properties [10]. Moreover, the extremely small energy scale of the f-electron superconductors has made it difficult to be studied in detail.

In this Letter, we present PES using a vacuum-ultraviolet laser ($h\nu = 6.994$ eV) (Laser-PES) with sub-meV resolution that can measure the SC gap of $CeRu_2$. Consistent with bulk thermodynamic measurements but in contrast to tunneling, the results indicate an anisotropic SC gap for $CeRu_2$. Hence, Laser-PES has a strong potential for directly and precisely studying intrinsic bulk SC ESs of correlated f- as well as d-electron superconductors with energy scales less than 1 meV.

Most intermetallic materials containing cerium and uranium show anomalous properties originating from an interplay of the localized and itinerant nature of the f electrons. Even below the SC transition temperature (T_c), the f-electron systems show unconventional SC properties that cannot be explained by the simple BCS theory assuming an isotropic energy gap, most likely due to the strong correlation between f electrons. Indeed, anomalous SC properties suggestive of anisotropic order parameters have been reported for f-electron superconductors from thermodynamic and magnetic studies [10]. Among the f-electron correlated superconductors, $CeRu_2$ has the highest T_c of 6.2 K (Ref. [11]) and exhibits dominantly Ce $4f$ character states at E_F [9] which are hybridized with Ru $5d$ states [12]. The symmetry of the order parameter as suggested from SC properties is controversial. While early specific heat measurements have suggested an axial symmetry with a line node [13], later studies reported an isotropic s-wave gap [14]. More recently, from specific heat and magnetization measurements, Hedo *et al.* concluded that $CeRu_2$ is a BCS type superconductor, with magnetic field dependence of the specific heat at 0.5 K exhibiting a $H^{0.5}$-like behavior in low fields [15]. The specific heat behavior is similar to Ni borocarbide superconductors, but for which existence of a line node has been discussed [16]. From measurements of the nuclear lattice relaxation rate, Matsuda *et al.* [17] and Ishida *et al.* [18] have suggested that $CeRu_2$ is an s-wave superconductor with a finite gap having $2\Delta/k_BT_c = 3.8$–4.0, where Δ is the SC gap value and k_B the Boltzmann constant. However, Mukuda *et. al.* [19] have shown from impurity effects that the superconductivity is better described in terms of an anisotropic s-wave gap. Tunneling studies have provided scattered gap values of 0.8–3.1 meV, corresponding to $2\Delta/k_BT_c = 3.3$–6.6 (Refs. [20–23]). This is most likely due to fast degradation of sample surfaces and/or different electronic states in the surface region [23], as shown by soft x-ray PES [9]. Thus, a bulk sensitive technique that directly measures the ES with an extremely high-energy resolution is essential to know the SC ESs of $CeRu_2$.

In terms of energy resolution, tunneling spectroscopy is better than PES. However, escape depth of photoelectron shows strong photon-energy dependence [24] and the increase of escape depth using soft x rays has been demonstrated with a resolution of $\sim$100 meV [9]. But the value is 100 times larger than the energy scale for the SC gap (less than 1 meV) of f-electron systems. The energy resolution using synchrotron radiation with 20–30 eV photon energy is at most ~5 meV for solid-state studies [3,4], which is again not enough for studying f-electron systems. PES using a He I resonance line (21.2 eV) can produce a nearly ~1–2 meV resolution. But the escape depths using a photon energy of ~20 eV are less than 10 Å, and may not be suitable for studying f-electron systems having a surface ES completely different from the bulk, as in $CeRu_2$. To overcome these limitations, we have constructed a new PES spectrometer using a laser as a photon source, as illustrated in Fig. 1(a). The spectrometer system is built using a newly-developed hemispherical electron analyzer and a laser system producing a high-flux (2.2×10^{15} photons/sec) quasi-continuous-wave (quasi-CW, a repetition rate of 80 MHz) with the highest photon energy of 6.994 eV [25]. Though the use of a laser as a photon source for PES spectroscopy is not new, the combination of a high-resolution electron analyzer and the quasi-CW laser system using a nonlinear crystal is unique, making it possible to study the very small SC gap of a sample susceptible to surface degradation. Since the escape depth of $CeRu_2$ for 6.994 eV is not known, we estimated the escape depth to be ~200 Å by using the universal curve [24]. It is known that the escape depth for low energies mainly depends on electron-phonon scattering and, therefore, shows a strong material dependence. The fact that the obtained results are consistent with that obtained from the bulk measurements, as shown later, ensures that the present study indeed probes the bulk SC ES of $CeRu_2$. The use of the quasi-CW laser is essential for preventing space-charging effects that broaden energies of photoelectrons [26]. As shown in Fig. 1(b), an ultrahigh-resolution measurement of a gold Fermi-edge spectrum measured at 2.9 K shows a good correspondence to the convolved Fermi-Dirac (FD) function, indicating the energy resolution of 360 μeV.

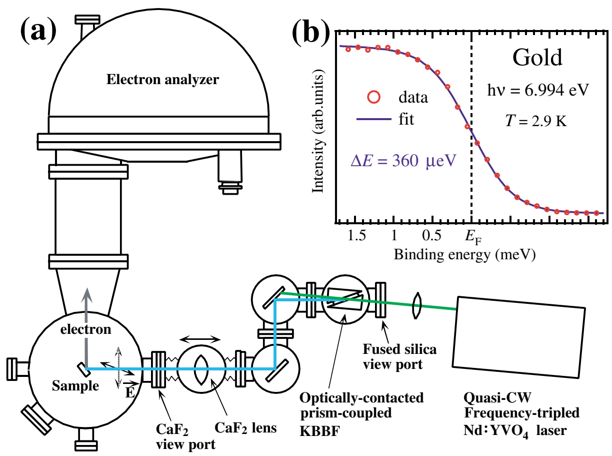

FIG. 1 (color). (a) Schematic diagram of the PES spectrometer system using a laser as a photon source (Laser-PES) and a demonstration of the sub-meV energy resolution. The second harmonic of a quasi-CW frequency-tripled $Nd:YVO_3$ laser by using an optically-contacted prism-coupled $KBe_2BO_3F_2$ (KBBF) crystal is focused on a sample with a CaF_2 lens [25]. The kinetic energies of electrons emitted from the sample are measured with a high-precision hemispherical electron analyzer (GAMMADATA-SCIENTA R-4000). The PES spectrometer and the laser systems are vacuum-separated by a CaF_2 view port, through which the produced 6.994 eV light can be transmitted. (b) Ultrahigh-resolution PES spectrum of an evaporated gold film measured at 2.9 K (red circles), together with the FD function at 2.9 K convolved by a Gaussian with full width at half maximum of 360 μeV (a blue line). Total energy resolution of 360 μeV was confirmed from the very good match between the experimental and calculated spectra.

High-quality single crystals of $CeRu_2$ with the residual resistivity ratio of ~270 were grown with the Czochralski pulling method in a tetra-arc furnace, with details described in Ref. [15]. The T_c of 6.2 K was determined from magnetization measurements. The spectra were measured using the Laser-PES system with 6.994 eV photon energy, as illustrated in Fig. 1(a). The total energy resolution (analyzer and light) for $CeRu_2$ measurements was set to 520 μeV. The vacuum inside the chamber during measurement was less than 1×10^{-11} Torr. Clean surfaces were obtained by fracturing samples *in situ* at 3.8 K and resulted in uneven surfaces. The spectra did not show any angular as well as polarization (vertical and horizontal) dependence, indicating obtained spectra reflect angle-, or k-, integrated ESs. Measured work functions of $CeRu_2$ are 3.6 ± 0.15 eV. Using this value, the maximum momentum of electrons emitted from E_F is 0.94 ± 0.02 Å^{-1} [$= 0.51 \cdot \mathrm{sqrt}(E_K) \cdot \sin(90°)$], where E_K is the kinetic energy of electrons. These are larger than the size of the Brillouin zone of $CeRu_2$ [$2\pi/a = 0.83$ Å^{-1}, a is the lattice constant (7.5364 Å)], indicating that the present measurement with 6.994 eV probes the whole Brillouin zone of $CeRu_2$. Samples were cooled using a liquid helium continuous flow cryostat with an improved thermal shielding, and temperatures were measured using a silicon-diode sensor mounted close to samples. E_F of samples was referenced to that of a gold film evaporated onto the sample substrate and its accuracy is better than 50 μeV as estimated from a possible shift of E_F during measurement of 2 h.

In Fig. 2(a), temperature (T)-dependent ultrahigh-resolution PES spectra of high-quality single crystal $CeRu_2$ across T_c measured with a total energy resolution of 520 μeV are shown. While the spectrum at 8.0 K, normal phase, has a Fermi edge, the spectrum at 3.8 K in the SC phase shows a sharp peak at 1.35 meV with a leading-edge shift to higher binding energy, indicative of the opening of the SC gap. The small peak above E_F of the SC spectrum corresponds to thermally excited electrons across the gap. The formation of a gap across T_c is more clearly seen in the inset showing symmetrized spectra, which removes the effects of the FD function [4]. These results constitute the first PES measurement of SC ESs of an f-electron superconductor. It is believed that the sudden approximation, which provides the foundation for the interpretation of the PES spectra from a many-body system in terms of the single particle spectral function, holds only

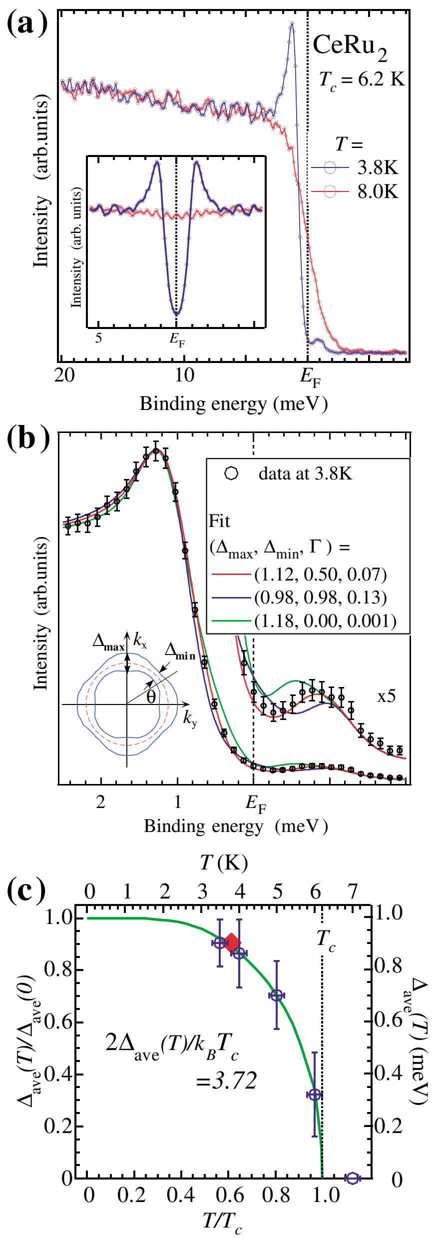

FIG. 2 (color). Ultrahigh-resolution PES data of $CeRu_2$. (a) T-dependent ultrahigh-resolution spectra near E_F with an inset showing the symmetrized spectra from the same data. (b) Normalized SC DOS at 3.9 K compared with calculated spectra. Error bars correspond to square root of intensity. Blue, red, and green lines are results of fittings with anisotropic gaps of a form $\Delta(\theta) = \Delta_{min} + (\Delta_{max} - \Delta_{min}) \times \cos(2\theta)$ of $(\Delta_{max}, \Delta_{min}, \Gamma)$ = (0.98, 0.98, 0.13), (1.12, 0.50, 0.07), and (1.18, 0.00, 0.001) in units of meV, where Γ is a thermal broadening parameter and θ the polar angle ($0 \leq \theta \leq \pi/4$). The inset schematically illustrates the anisotropic gap, where a red broken circle represents FS and the distance between blue lines corresponds to a gap value. (c) T-dependent SC gap values. The red diamond is the averaged gap value ($\Delta_{ave} = \langle\Delta(\theta)\rangle$) determined from the anisotropic s-wave gap fitting for the data shown in (b), while circles are Δ_{ave} determined from the same fitting for another high-quality sample ($T_c = 6.2$ K) with an energy resolution of 1.15 meV assuming the same $\Delta_{min}/\Delta_{max}$ ratio.

if the kinetic energy of the photoelectrons is larger than the relaxation energy of solid. In the present case, with photoelectrons of a few eV kinetic energy, one may not expect the sudden approximation to hold. However, contrary to such an expectation, we could measure the SC transition of f-electron compound $CeRu_2$ with a 6.994 eV photon energy. The present results thus provide validity of the sudden approximation for states near E_F of correlated compounds measured with very low photon energy.

The SC spectrum is analyzed with Dynes function including a thermal broadening parameter (Γ) [27,28]. We used gap forms $\Delta(\theta) = \Delta_{min} + (\Delta_{max} - \Delta_{min}) \times \cos(2\theta)$, where θ is the polar angle and Δ_{max} and Δ_{min} are the maximum and minimum gap values [8], respectively, in order to estimate the SC gap value and study the suggested SC gap anisotropy [13,15,19]. Figure 2(b) shows the normalized SC spectrum, compared with three calculated spectra with $(\Delta_{max}, \Delta_{min}, \Gamma)$ = (0.98, 0.98, 0.13; isotropic case), (1.12, 0.50, 0.90; anisotropic case), and [1.18, 0.00, 0.001; maximum anisotropy (nodal) case, which corresponds to a point or line node case] in units of meV. The normalized spectrum (circles) is obtained from the SC spectrum of Fig. 2(a) by dividing normal-state density of states (DOS), which is obtained from the normal-state spectrum at 8.0 K divided by an energy resolution convoluted FD function at 8.0 K, in order to remove the shape of the normal-state DOS. The BCS functions were multiplied with a FD function at 3.8 K and convoluted with a Gaussian representing the known resolution to reproduce the spectrum measured at 3.8 K (circles). The parameter sets are determined by giving a first priority to reproduce the experimental spectrum for the regions of the peak and second for the leading edge. However, around the region near E_F, while the calculated results using an isotropic gap and the highest anisotropic gap show clear deviations from the experimental data, calculated spectrum using an anisotropic gap reproduces the experimental one very well. These analyses indicate that the SC gap of $CeRu_2$ has an anisotropy with $\Delta_{min}/\Delta_{max}$ ratio of 0.446. Since PES measurements using polarized photon with a low energy may probe some portions of the Fermi surface (FS), we may observe a part of anisotropy [29]. The present result gives a maximum anisotropic ratio $\Delta_{min}/\Delta_{max} = 0.446$, indicating that $\Delta_{min}/\Delta_{max}$ can vary between 0 (node situation) to 0.446 (observed anisotropy) [29]. This clearly excludes a simple isotropic gap. From the anisotropic s-wave fit using the same $\Delta_{min}/\Delta_{max}$ ratio for spectra measured with another sample we obtained T-dependent average gap ($\Delta_{ave} = \langle\Delta(\theta)\rangle$) [Fig. 2(c)] and found that it follows the T dependence expected from the BCS theory [1] well. The reduced gap value defined with $2\Delta_{ave}(0)/k_B T_c = 3.72$ locates between the weak-coupling BCS value of 3.54 and that obtained for the strong-coupling superconductor Pb ($\sim$ 4.5–4.9) (Refs. [2,5]), classifying $CeRu_2$ into a moderately strong-coupling superconductor.

The Δ_{ave} value is consistent with the known bulk SC properties reported from the specific heat [15] and the nuclear quadrupole resonance (NQR) measurements [18,19], which provide indirect information on the ES. The existence of anisotropy also agrees with the NQR studies [19,30]. On the other hand, present results are different from the tunneling measurements [20–23] in terms of the spectral shape and the reproducibility. As shown in the inset of Fig. 2(a), the residual intensity at E_F compared with that of normal-state of the present Laser-PES studies is $\sim$0.12 compared to the normal-state intensity, much smaller than the values obtained (0.4–0.9) from tunneling measurements. In addition, the obtained Δ_{ave} values for different samples in the present studies agree well with each other within the experimental accuracy [Fig. 2(c)], also different from the tunneling studies that provide wide variation in gap values from 0.81 to 3.1 meV. These differences can be attributed to the fact that the tunneling studies measure the local surface ESs, and therefore can be easily affected by the condition of the surface, which may lead to uncertainties in discussion of bulk ESs. On the other hand, the present Laser-PES study overcomes all such disadvantages and directly probes bulk ES of very small energy scales.

The present success in probing the bulk SC ES of an f-electron superconductor, $CeRu_2$ having a delicate surface, opens up important opportunities in solid-state physics. First, the technique can be applied to any other material displaying differing surface and bulk electronic states. Second, the laser has a great advantage in the small natural width of light (260 μeV) without sacrificing total photon numbers, indicating a great potential for further increase of the energy resolution. This feature is in contrast to other light sources where increasing resolution inherently reduces the intensity. Third, utilizing the k-resolving capability of PES, one can measure k-dependent ESs, especially for the k-dependent SC gap. These characteristics indicate that Laser-PES is a unique experimental probe to study the anisotropic SC order parameter of correlated materials, like f-electron superconductors [10], d-electron superconductors [Sr_2RuO_4 (Ref. [31]) and recently discovered $Na_xCoO_2 \cdot yH_2O$ (Ref. [32]], and organic superconductors [33], with energy scales less than 1 meV. Such studies will reveal the origin of unconventional superconductivity originating in the interplay of localized and itinerant electrons, which is one of the fundamental questions in the condensed matter physics.

In conclusion, we used ultrahigh-resolution PES using a laser as a photon source to measure the bulk SC gap of f-electron superconductor $CeRu_2$. The present study provides PES evidence of anisotropic gap of $CeRu_2$. These results indicate that Laser-PES can be a powerful tool to study the SC ESs of correlated materials.

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[1] J.R. Schrieffer, *Theory of Superconductivity* (Preseus Books, Reading, MA, 1983).
[2] W.L. McMillan, and J.M. Rowell, in *Superconductivity*, edited by R.D. Parks (Marcel Dekker, Inc., New York, 1969).
[3] A. Damascelli, Z.-X. Shen, and Z. Hussain, Rev. Mod. Phys. **75**, 473 (2003).
[4] J.C. Campuzano, M.R. Norman, and M. Randeria, cond-mat/0209476.
[5] A. Chainani *et al.*, Phys. Rev. Lett. **85**, 1966 (2000).
[6] R. Hesper *et al.*, Phys. Rev. Lett. **85**, 1970 (2000).
[7] F. Reinert *et al.*, Phys. Rev. Lett. **85**, 3930 (2000).
[8] T. Yokoya *et al.*, Phys. Rev. Lett. **85**, 4952 (2000).
[9] A. Sekiyama *et al.*, Solid State Commun. **121**, 561 (2002).
[10] M. Sigrist and K. Ueda, Rev. Mod. Phys. **63**, 239 (1991).
[11] S.B. Roy and P. Chaddah, Pramana- J. Phys. **53**, 659 (1999).
[12] M. Higuchi and A. Hasegawa, J. Phys. Soc. Jpn. **65**, 1302 (1996).
[13] J.G. Sereni *et al.*, Mod. Phys. Lett. B **3**, 1225 (1989).
[14] A.D. Huxley *et al.*, J. Phys. Condens. Matter **5**, 7709 (1993).
[15] M. Hedo *et al.*, J. Phys. Soc. Jpn. **67**, 272 (1998).
[16] M. Nohara *et al.*, J. Phys. Soc. Jpn. **66**, 1881 (1997).
[17] K. Matsuda, Y. Hohori, and T. Hohara, J. Phys. Soc. Jpn. **64**, 2750 (1995).
[18] K. Ishida *et al.*, Z. Naturforsch., A: Phys. Sci. **51**, 793 (1996).
[19] H. Mukuda *et al.*, J. Phys. Soc. Jpn. **67**, 2101 (1998).
[20] W. Schmitt and G. Guntherodt, J. Magn. Magn. Mater. **47-48**, 542 (1985).
[21] T. Ekino *et al.*, Phys. Rev. B **56**, 7851 (1997).
[22] H. Sakata *et al.*, J. Phys. Soc. Jpn. **69**, 1970 (2000).
[23] A. V. Moskalenko *et al.*, Low Temp. Phys. **27**, 613 (2001).
[24] M.P. Seah and W.A. Dench, Surf. Interface Anal. **1**, 2 (1979).
[25] T. Togashi *et al.*, Opt. Lett. **28**, 254 (2003).
[26] P. Balzers (private communication).
[27] R. C. Dynes, V. Narayanamurti, and J. P. Garno, Phys. Rev. Lett. **41**, 1509 (1978).
[28] We do not exclude more complicated nonmonotonic gap structures. To address this issue, measurements at extremely lower T compared to the present study ($T =$ 3.8 K) may be essential.
[29] In low-energy PES, one can measure direct transitions that would enhance emission for a particular energy and momentum. This, combined with other matrix element effects, could enhance (or suppress) the emission for some parts of the Brillouin zone.
[30] The anisotropy ratio obtained from the NQR results [19] $[(\Delta_{max} - \Delta_{min})/\Delta_{min}$ determined as in Ref. [19]] is 0.15, significantly lower than 1.24 from the present study. However, the nearly isotropic value obtained by Mukuda *et al.* [19] does not explain the coherence peak at T_c and higher anisotropy is necessary to explain the coherence peak, as pointed out by the authors, consistent with our results.
[31] Y. Maeno *et al.*, Nature (London) **372**, 532 (1994).
[32] K. Takada *et al.*, Nature (London) **422**, 53 (2003).
[33] T. Ishiguro, K. Yamaji, and G. Saito, *Organic Superconductors* (Springer, Berlin, 1998).