Laser-excited ultrahigh-resolution photoemission spectroscopy of superconducting $Na_{0.35}CoO_2 \cdot 1.3H_2O$

T. Shimojima [a,*], T. Yokoya [a,1], T. Kiss [a], A. Chainani [b], S. Shin [a,b], T. Togashi [b], C. Zhang [c], C. Chen [c], S. Watanabe [a], K. Takada [d], T. Sasaki [d], H. Sakurai [e], E. Takayama-Muromachi [e]

[a] *Institute for Solid State Physics (ISSP), University of Tokyo, Kashiwa, Chiba 277-8681, Japan*
[b] *The Institute of Physical and Chemical Research (RIKEN), Sayo-gun, Hyogo 679-5143, Japan*
[c] *Beijing Center for Crystal R&D, Chinese Academy of Science Zhongguancun, Beijing 100080, China*
[d] *Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan*
[e] *Superconducting Materials Center, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan*

Abstract

We have studied the electronic structure near the Fermi level of the layered cobaltate superconductor $Na_{0.35}CoO_2 \cdot 1.3H_2O$ using laser-excited ultrahigh-resolution photoemission spectroscopy (PES). In the normal state, we observed the formation of a pseudogap with an energy scale of ~ 20 meV. Across the superconducting transition, we observed the leading-edge shift at 3.5 K compared to that at 10 K, indicating superconducting gap (SC gap) opening having a gap value Δ of 0.5–0.7 meV. The energy scale of the SC gap is ~ 20 times smaller than that of the pseudogap, suggesting the existence of competing order parameters at low temperatures.
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1. Introduction

Recently, Takada et al. has reported the first cobalt oxide superconductor $Na_{0.35}CoO_2 \cdot 1.3H_2O$ (the transition temperature T_c of $\sim$ 4.5 K). [1] It has two-dimensional conductive CoO_2 planes which can be regarded as an electron-doped correlated $S = 1/2$ triangular network of frustrated Co spins, [1] where novel superconductivity emerging from a non-Fermi-liquid ground state has been proposed [2]. In the cuprate high-T_c's, the CuO_2 plain is described in terms of a quasi-two-dimensional correlated system. The characteristics of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ resemble those of high-T_c's, except for the lattice structure of conductive layers: triangular or square. Comparison between the two superconductors will be meaningful for deeper understanding of the unconventional superconductivity in layered transition metal oxides.

After the discovery, extensive experimental and theoretical studies have been made in order to understand the origin of the superconductivity of $Na_{0.35}CoO_2 \cdot 1.3H_2O$.

Theoretically, several order parameters have been proposed depending on the model used [3]. For instance, a d-wave order parameter derived from spin fluctuations using a t–J model on the triangular lattice [4] and a f-wave one derived from charge fluctuations using a single-band extended Hubbard model [5] have been proposed. The former indicates that $d_1 + id_2$ superconductivity is the neighboring phase of spin gap phase. The latter indicates that f-wave superconductivity is realized in the vicinity of charge density wave (CDW) instability in the triangular lattice. Experimentally, while there are some controversial results [6,7], some authors reported no coherence peak in the spin-lattice relaxation rate $(1/T_1)$ curve by nuclear quadrupole resonance (NQR), indicative of the anisotropic pairing symmetry [8,9]. However the pairing symmetry is still under controversy.

On the other hand, a direct observation of a SC gap by PES can provide significant insight into the paring symmetry. Recently, we have constructed a newly designed photoemission spectrometer with a CW ultraviolet laser ($h\nu = 6.994$ eV) as an excitation source. For investigating electronic structure of samples having a very delicate surface and a very small energy scale, PES with a lower photon energy provided by a laser was found to be very powerful, [10] because of the very high energy resolution and the expected large escape depth [11].

In this paper, we report the temperature-dependent electronic structure near E_F of polycrystalline

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* Corresponding author.
E-mail address: t-shimo@issp.u-tokyo.ac.jp (T. Shimojima).
[1] Present address: The Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan.

$Na_{0.35}CoO_2 \cdot 1.3H_2O$ studied from PES using an ultraviolet laser. We observed SC gap opening across T_c with an unusual reduction of the intensity at E_F in the normal state. We also performed numerical simulations using Dynes function [12] for the spectrum at 3.5 K in order to determine the magnitude and pairing symmetry of the SC gap.

2. Experimental

Polycrystalline samples of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ is synthesized from $Na_{0.7}CoO_2$ through a chemical oxidation process, by which a part of Na ions is removed and water molecules are intercalated between CoO_2 and Na planes [1]. The partial reduction of water easily produces non-superconducting $Na_{0.35}CoO_2 \cdot 0.7H_2O$. Hydrated samples are very sensitive to humidity. PES measurements under an ultrahigh vacuum condition require careful handling of them. We handled hydrated samples as follows. First, the samples are covered with silver paste and mounted on copper substrates to prevent loss of water molecules under vacuum. Then, the prepared samples were cooled to ~ 180 K and are fractured in situ. After the fracturing, they are transferred to a measurement chamber and measured without warming up above ~ 180 K. We chose the temperature of 180 K because no loss of water molecules occurs in $Na_{0.35}CoO_2 \cdot 1.3H_2O$ below 250 K [13].

All PES measurements were performed on a spectrometer built using a GAMMADATA-SCIENTA R-4000 electron analyzer and an ultraviolet laser. The best total energy resolution is 360 μeV [10]. However, the energy resolution for SC gap and near-E_F measurements were set to 1.8 and 6.5 meV,, respectively, in order to get reasonable count rate. Samples are cooled using a flowing liquid He refrigerator with improved thermal shieldings. The base pressure of the measurement chamber was better than 2×10^{-11} Torr. The spectra were all reproducible during the measurement.

3. Results and discussion

Shown in Fig. 1 are (a) the PES spectra near E_F of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ measured as a function of temperature from 3.5 to 150 K, (b) the enlargement of the near E_F region, which highlights the difference in temperature-dependent change at E_F, and (c) the normalized density of state (DOS) of $Na_{0.35}CoO_2 \cdot 1.3H_2O$. In Fig. 1(a), the spectra show systematic temperature dependence with a clear Fermi edge structure at lower temperatures. However, we found that there is an additional decrease within 20 meV binding energy of E_F in the spectrum at 3.5 K (black arrow). In addition, small but important reduction of intensity at E_F is also observed in the raw spectra (Fig. 1(b)). Thus, the raw data shows an unusual normal-state electronic structure change near E_F. In order to see the clear temperature-dependent change in DOS, we extracted the effect of the Fermi–Dirac (FD) function from the raw data as follows. The raw spectrum at each temperature was divided by the corresponding FD function convoluted with a Gaussian with the instrumental resolution. The divided spectra
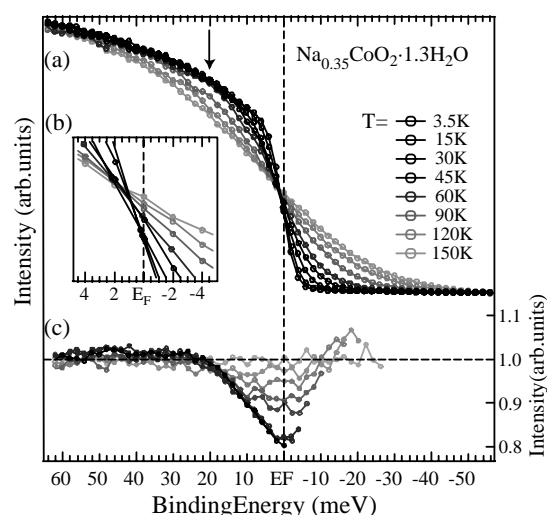

Fig. 1. (a) Temperature-dependent spectra of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ measured with 6.994 eV photon energy. (b) The enlargement of the near E_F region, which highlights the difference in temperature-dependent change at E_F. (c) The normalized DOS of $Na_{0.35}CoO_2 \cdot 1.3H_2O$, showing pseudogap formation at lower temperature.

at all temperatures were further divided with the smoothed spectrum at 150 K [14]. As shown in Fig. 1(c), the normalized DOS of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ within 20 meV binding energy of E_F are gradually suppressed with decreasing temperature, indicative of formation of a pseudogap with an energy scale of 20 meV. Further, the reduced spectral weight around E_F seems to be compensated by a slight increase beyond 20 meV binding energy. It indicates that spectral weight is transferred from the near-E_F region to the higher-binding energy region. Recently, temperature-dependent pseudogap in non-hydrated samples Na_xCoO_2 ($x = 0.5$, 0.25) was reported from optical spectroscopy [15]. The energy scales of half of the pseudogap measured by optical spectroscopy are 6–25 meV depending on the Na concentration. These values are consistent with the pseudogap size of present study. However, the reduction of normalized DOS in hydrated samples is smaller (10–20% of the spectrum at 150 K) than the optical data. It may indicate that the pseudogap formation is partially suppressed due to the difference in Na concentration and/or inclusion of the water molecules.

Fig. 2 shows the ultrahigh-resolution PES spectra measured at 3.5 K (superconducting phase, black circle) and 10 K (normal phase, gray circle). The broken lines denote the FD functions at 3.5 and 10 K, convoluted with the Gaussian corresponding to the instrumental resolution. We found that, while the spectrum at 10 K is well reproduced by the FD function at 10 K, spectrum of 3.5 K shows a slight leading-edge shift and seems not to be fitted by the FD function. Spectral difference between the spectrum at 3.5 and 10 K is also shown as gray area on a lower part of Fig. 2. Assuming that the both spectra are well reproduced by the FD function at each temperature, the difference should be zero at E_F. However, the spectral difference at E_F is not zero, and the crossing point between the difference spectra and the horizontal line indicating intensity zero shifts to higher binding energy. This
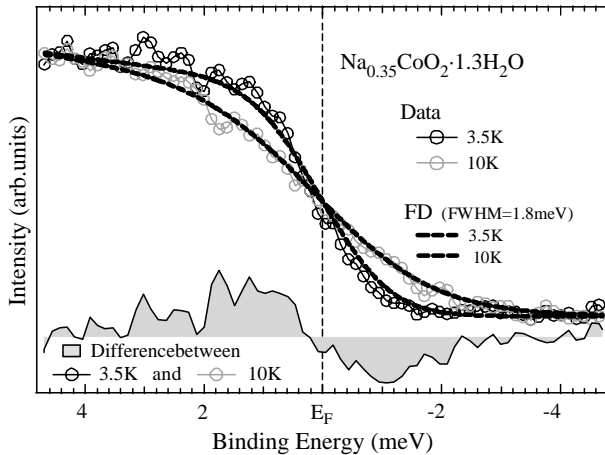
Fig. 2. Ultrahigh-resolution spectrum of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ measured at 3.5 K (superconducting phase, black circles) and 10 K (normal phase, gray circles). The broken lines denote the FD functions at 3.5 and 10 K, convoluted with the Gaussian with the instrumental resolution of 1.8 meV. Gray area is shown as a spectral difference between spectrum at 3.5 and 10 K.

indicates that there is SC gap opening. Absence of a sharp peak is due to the relatively smaller SC gap compared with the energy resolution used as confirmed below.

In order to obtain the magnitude of the SC gap and determine the pairing symmetry, we have done numerical simulations using Dynes functions as shown in Fig. 3. Fig. 3 shows the ultrahigh-resolution spectra of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ measured at 3.5 K (open circle), the FD function at 3.5 K (broken line), and fitting curves with Dynes function (black and gray lines). From Fig. 3, it seems that the FD function failed to reproduce the spectrum at 3.5 K. We used Dynes functions with s-wave and d-wave symmetry to fit the spectra. Better fittings have been obtained with $\Delta = 0.5 \pm 0.1$ meV and $\Gamma = 0.05$ meV for s-wave (black line), $\Delta = 0.7 \pm 0.1$ meV and $\Gamma = 0.05$ meV for d-wave (gray line), where Δ is SC gap size, Γ a term of quasi-particle lifetime. It is difficult to determine the pairing symmetry from the fitting curves, since they give little difference due to the insufficient energy
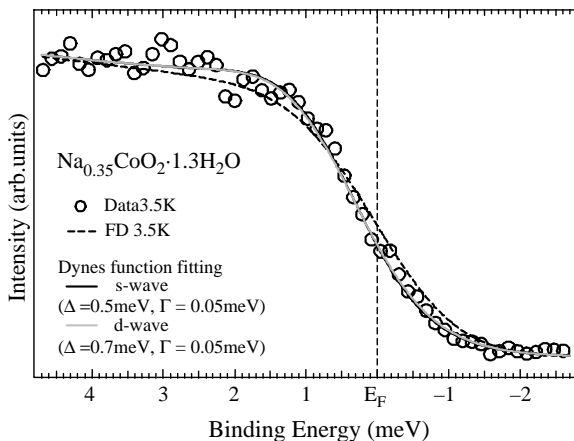

Fig. 3. Ultrahigh-resolution spectrum of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ measured at 3.5 K (open circles) compared with fitting results. The FD functions at 3.5 K convoluted with Gaussian (broken line), fitting curves with Dynes function for s-wave (black line), and for d-wave (gray line) are shown.

resolution. However, both fitting curves reproduce the raw spectrum better than the FD function. The obtained values of Δ (3.5 K) = 0.5 meV (s-wave) and Δ (3.5 K) = 0.7 meV (d-wave) correspond to $2\Delta(0)/k_BT_c \sim 3.4$ and $2\Delta(0)/k_BT_c \sim 4.8$, respectively, (the known mean field relation of $2\Delta/k_BT_c = 3.54$ according to BCS theory, where k_B is the Boltzmann constant). From NQR measurements, the $1/T_1$ curve was reproduced by the calculation using the two-dimensional line-node model $\Delta(\theta) = \Delta(0)\cos(2\theta)$. The appropriate fitting parameters were reported to be $2\Delta(0)/k_BT_c = 3.5$ by Ishida et al. [9] and $2\Delta(0)/k_BT_c = 5.2$ by Fujimoto et al. [8], respectively. The present PES value from the d-wave model is located between these two values. This is the first observation of SC gap of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ measured by ultrahigh-resolution PES. In the present study, we could not use the highest resolution due to the very low count rate near E_F, which is inherent to the cobalt oxides. We are now preparing laser PES studies of single crystal samples, and this will give more detailed information on the pairing symmetry.

Lastly we discuss the relation between the superconducting gap and pseudogap. The energy scale of the obtained SC gap (0.5–0.7 meV) is smaller than the pseudogap (20 meV) of $Na_{0.35}CoO_2 \cdot 1.3H_2O$. This indicates that the pseudogap is the different phenomena from superconductivity. Such a large pseudogap is also reported on high-T_c's [16,17], where it is found that pseudogap formation is related to the growth of magnetic correlations. On the other hand, a temperature-dependent pseudogap has been observed in $Ba_{0.67}K_{0.33}BiO_3$ [18], where the energy scale of the pseudogap correlated with the energy of the breathing mode phonon. In the Co oxides, the energy scale of 20 meV is comparable to the nearest neighboring magnetic coupling constant $J = 10$–20 meV [19] which has been also concluded from angle-resolved PES measurements [20,21]. This J value is smaller than the highest phonon energies [15]. Thus, while additional studies are needed to clarify the relation between the superconductivity and the formation of the pseudogap, there is a possibility of existence of another ground state competing with and/or cooperating the superconductivity at low temperature in the new layered Co oxide superconductor.

In conclusion, we performed ultra-high resolution PES and observed pseudogap formation with the energy scale of ~ 20 meV in normalized DOS of $Na_{0.35}CoO_2 \cdot 1.3H_2O$. We also observed the leading-edge shift of $Na_{0.35}CoO_2 \cdot 1.3H_2O$ at 3.5 K, indicating SC gap opening. Numerical simulation with Dynes function gives the SC gap size of 0.5 (s-wave) and 0.7 meV (d-wave), corresponding to $2\Delta(0)/k_BT_c \sim 3.4$ and 4.8, respectively.

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