Clarification of Fermi surfaces (FSs) is fundamental to understand the physical properties of functional materials such as superconducting transition metal oxides, heavy fermion systems, and organic conductors. Quantum oscillation measurements by virtue of the de Haas-van Alphen or Shubnikov-de Haas effect are known as useful techniques to detect bulk FSs. However, their electron- or hole-like character and their shape cannot be experimentally revealed by these measurements alone. In addition, these techniques require low temperatures and almost defect-free single crystals, so that they are not easily applicable to doped or partially substituted systems such as the high-temperature superconductors La$_{2-x}$Sr$_x$CuO$_4$, Bi$_2$Sr$_2$CaCu$_2$O$_{8+y}$, or the here reported Sr$_{1.8}$Ca$_{0.2}$RuO$_4$. The number of measurements by using quantum oscillations on oxides is actually very few. On the other hand, low-energy angle-resolved photoemission (ARPES) is known as a tool for probing FSs as well as quasi-particle dispersions of correlated electron systems. However, it is still unclear whether so far reported low-energy ARPES ($\hbar \nu \lesssim 120$ eV) results fully reflect bulk electronic structures because of its high surface-sensitivity. Since high-energy photoemission ($\hbar \nu \gtrsim 500$ eV) has an advantage in probing bulk states, high-energy ARPES with high angular resolution can be a complementary and promising technique for the bulk Fermiology of solids besides the quantum oscillations measurements.

It is known that Sr$_2$RuO$_4$ shows "triplet" superconductivity, which disappears with a very small amount of Ca-substitution. Combination of the quantum oscillation measurements and band-structure calculations suggests one hole-like FS sheet centered at $\pi, \pi$ ($\alpha$ sheet) and two electron-like FS sheets centered at $(0,0)$ ($\beta$ and $\gamma$ sheets) in Sr$_2$RuO$_4$. On the other hand, so far reported results of low-energy ARPES for Sr$_2$RuO$_4$ are controverted although ARPES has an advantage in determining the character of FSs. Yokoya et al. have first concluded two hole-like and one electron-like FSs. However, the following ARPES studies have suggested that the earlier finding originates from surface states, and that the bulk FSs are qualitatively similar to the result of the band-structure calculation. It has also been reported that a lattice distortion takes place at the surface, giving FSs different from the bulk. Thus the characters and shapes of the two-dimensional bulk FSs of Sr$_{1.8}$Ca$_{0.2}$RuO$_4$ are experimentally still unclear because the reported shapes of the FSs from the low-energy ARPES depend on the surface preparation and the excitation photon energies. Low-energy ARPES on Sr$_2$RuO$_4$ has shown that the FSs shapes measured on the " degraded" surface obtained by cleavage at 180 K and fast cooled down seem to be similar to the prediction of the band-structure calculation compared with those on the clean surface prepared by cleavage at 10 K. In general, photoemission data on cleaner surfaces prepared by cleavage at lower temperatures, at which surface desorption and diffusion of atoms from inside are suppressed, are more reliable. Thus the mere similarity of the FSs as obtained by low-energy ARPES and theory cannot guarantee that the genuine bulk FSs of Sr$_2$RuO$_4$ are really established. Besides, the FSs of lightly Ca-substituted Sr$_{1.8}$Ca$_{0.2}$RuO$_4$ are not yet clarified at all.

Compared with low-energy ARPES, high-energy ARPES faces several experimental difficulties regarding the detection of quasi-particle dispersions and FSs. High angular resolution is especially required for high-energy ARPES since the momentum resolution not only depends on the angular resolution but also on the square root of the photoelectron kinetic energy ($\sim \hbar \nu$ in the
case of the valence-band ARPES). Furthermore, a high photon flux is also required for a practical high-energy ARPES measurement because photoionization cross sections decrease exponentially with $h\nu$. Recent improvements in both synchrotron light sources and electron spectrometers allow us to measure high-energy ARPES spectra with high angular and energy resolutions facilitating bulk Fermiology. In this paper, we show the FSs of Sr$_{2-x}$Ca$_x$RuO$_4$ probed for the first time by means of high-energy ARPES.

Single crystals of Sr$_{2-x}$Ca$_x$RuO$_4$ ($x = 0, 0.2$) were used for the measurements. The high-energy ARPES measurements at $h\nu = 700$ eV were performed at BL25SU in SPring-8. The base pressure was about 4 x $10^{-8}$ Pa. The (001) clean surface was obtained by cleaving the samples in situ at the measuring temperature of 20 K. The photoelectrons within polar angles of about $\pm 6^\circ$ with respect to the normal of the sample surface were simultaneously collected by using a GAMMADATA-SCIENTA SES200 analyzer, thereby covering more than a whole Brillouin zone along the direction of the analyzer slit. The overall energy resolution was set to $\sim 120$ and $\sim 200$ meV for high-resolution measurements and Fermi surface-mapping, respectively. The angular resolution was $\pm 0.1^\circ$ ($\pm 0.15^\circ$) for the perpendicular (parallel) direction to the analyzer slit, which was experimentally confirmed at BL25SU. These values correspond to the momentum resolution of $\pm 0.024$ Å$^{-1}$ ($\pm 0.035$ Å$^{-1}$) [6 and 9 % of $\pi/a$, where $a$ is the lattice constant of Sr$_2$RuO$_4$, 3.87 Å[Ref. 3]] at $h\nu = 700$ eV. The surface cleanliness was confirmed by means of the angle-integrated photoemission by the absence of additional spectral weight on the higher binding energy side of the intrinsic O 1$s$ contribution, absence of the possible C 1$s$ signal, and no peak or hump structure at 9 – 10 eV from $E_F$ in the spectra. We also measured core-level spectra with an energy resolution of 200 meV.

Figure 1 shows the polar-angle ($\theta$) dependence of the Sr 3$d$ core-level spectra of Sr$_2$RuO$_4$ (filled circles). The spectra are well deconvoluted into three components corresponding to the contributions from the top-most SrO surface layer (S1), the second SrO surface layer (S2) placed just below the top RuO$_2$ layer, and the bulk layers.

![FIG. 1: Polar-angle ($\theta$) dependence of the Sr 3$d$ core-level photoemission spectra of Sr$_2$RuO$_4$ (filled circles). The spectra are well deconvoluted into three components corresponding to the contributions from the top-most SrO surface layer (S1), the second SrO surface layer (S2) placed just below the top RuO$_2$ layer, and the bulk layers.](image)

The surface spectral weight is expected at higher binding energies away from $E_F$ in the spectrum of various transition metal oxides. Likewise the surface spectral weight is expected at higher binding energies away from $E_F$ in the spectrum of various transition metal oxides. The peak width becomes narrower near $E_F$. This quasi-particle forms the hole-like FS sheet as shown in Fig. 2(b). A similar behavior is observed in Sr$_{1.8}$Ca$_{0.2}$RuO$_4$ as shown in Fig. 2(b).

However, the peak is broader in the spectra for $x = 0.2$ near the Fermi wave vector ($k_F$) compared with those for $x = 0$. The ARPES spectra of Sr$_{2-x}$Ca$_x$RuO$_4$ along the $(\pi,0)$-$(\pi,\pi)$ cut are shown in Figs. 2(c) and 2(d). They are rather complicated because there are three quasi-particle bands below $E_F$ in this direction. For both compounds, the band forming the $\alpha$ sheet is located at $\sim 0.5$ eV, which shifts hardly between $(0,0)$ and $(\pi,0)$, while the other two bands forming the $\beta$ and $\gamma$ sheets show dispersion and
cross $E_F$. The behavior of the $E_F$ crossing of the $\beta$ and $\gamma$ branches (hereafter abbreviated as $\beta$ and $\gamma$ crossing) is also confirmed by the momentum distribution curves (MDCs) as shown in Figs. 2(c) and 2(f), and the symmetrized EDCs with respect to $E_F$ (not shown in this paper, a similar procedure was used in Ref. 11). The behavior of the ARPES spectra for Sr$_{1.8}$Ca$_{0.2}$RuO$_4$ is qualitatively similar to that of Sr$_2$RuO$_4$ whereas subtle differences can be recognized as the quasi-particle of the $\beta$ sheet is more prominent for Sr$_{1.8}$Ca$_{0.2}$RuO$_4$ than for Sr$_2$RuO$_4$ whereas the $E_F$ crossing of the $\gamma$ sheet is less prominent than for $x = 0$.

The photoemission intensity at $E_F$ for Sr$_{2-x}$Ca$_x$RuO$_4$ and estimated Fermi wave vectors are displayed in Fig. 2. One can clearly identify the one hole-like ($\alpha$) and the two electron-like ($\beta$ and $\gamma$) FS sheets. We find that the shapes of the $\alpha$ and $\beta$ sheets are square-like while the shape of the $\gamma$ sheet is rather circular-like for both compounds. These shapes reflect that the $\gamma$ sheet is mainly composed of a rather ideally two-dimensional $d_{xy}$ band while the other square-shaped sheets are due to the $d_{yz}$ and $d_{zx}$ bands, which are to some extent one-dimensional in the electronic states. The estimated area of each sheet is comparable to the results from the quantum oscillations for Sr$_2$RuO$_4$. The obtained FSs of Sr$_{1.8}$Ca$_{0.2}$RuO$_4$ are similar to those of Sr$_2$RuO$_4$. The two-dimensional topology of the FSs is also consistent with the prediction from band-structure calculations.

The combination of the observed two square-like FS sheets, the $\alpha$ and $\beta$ sheets, can also be regarded as two
one-dimensional FSs located at $k_x = \pm Q$ and $k_y = \pm Q$, where $Q$ is estimated as $\sim 0.65\pi$ from our high-energy ARPES. It has been theoretically predicted that FS nesting effect occurs with wave vectors $q = (\pm 2\pi/3, k_y')$, $q = (k_y', \pm 2\pi/3)$ and especially at $q = (\pm 2\pi/3, \pm 2\pi/3)$ where $k_y'$ and $k_x'$ are arbitrary\textsuperscript{22} An inelastic neutron scattering study indeed detected magnetic fluctuations for $q_0 = (\pm 0.6\pi, \pm 0.6\pi)$, which could be due to the nesting properties\textsuperscript{22}. As shown in Fig.\textsuperscript{2} the observed FSs give direct evidence for the nesting instability with $q = (\pm 2\pi/3, \pm 2\pi/3)$.

For Sr\textsubscript{1.4}Ca\textsubscript{0.6}RuO\textsubscript{4}, the $\gamma$ crossing cannot be resolved in some $k$-regions whereas the $\beta$ crossing is clearly detected almost everywhere in reciprocal space [Figs. \textsuperscript{3}(c) and \textsuperscript{3}(d)]. This is somewhat different from our FS map of Sr\textsubscript{2}RuO\textsubscript{4}, where also the $\gamma$-crossing can be resolved almost everywhere [Figs. \textsuperscript{4}(a) and \textsuperscript{4}(b)] and the spectral weight at $k_F$ is comparable between the $\beta$ and $\gamma$ sheets in most of the $k$-regions. As for the $\alpha$ sheet, a reduced quasi-particle weight at $E_F$ is observed for $x = 0.2$ compared with that for $x = 0$ as shown in Fig.\textsuperscript{4}. From these facts we conclude that the electron correlations become stronger for the $\alpha$ and $\gamma$ sheets by the small amount of Ca-substitution ($x < 0.5$), which does not lead any lattice distortion\textsuperscript{24}.

Although the electron correlation strengths seem to be changed depending on the individual band between the superconducting Sr\textsubscript{2}RuO\textsubscript{4} and the non-superconducting Sr\textsubscript{1.8}Ca\textsubscript{0.2}RuO\textsubscript{4}, the electronic structures are found to be qualitatively unchanged. On the other hand, it has been reported that the superconductivity in Sr\textsubscript{2}RuO\textsubscript{4} is easily suppressed by impurities and/or defects\textsuperscript{23,24}. From these facts, we can conclude that the superconductivity disappears with the Ca-substitution because the substituted Ca ions behave as "impurity" and/or induce disorder in Sr\textsubscript{2-x}Ca\textsubscript{x}RuO\textsubscript{4}, and therefore break the superconductivity, as proposed by Nakatsuji and Maeno\textsuperscript{2}. To conclude, the bulk-sensitive high-energy ARPES study of Sr\textsubscript{2-x}Ca\textsubscript{x}RuO\textsubscript{4} has revealed the character and the shape of FS sheets, and the nesting instability. We are convinced that high-energy ARPES measurements are crucial for really revealing the bulk FSs of many transition metal oxides.

We thank T. Satonaka, H. Fujiwara, A. Higashiyama, P. T. Ernst, A. Shigemoto, and T. Sasabayashi for supporting the experiments. This work was supported by a Grant-in-Aid for COE Research (10CE2004) and Creative Scientific Research (15GS0213) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. M.S. is grateful for financial support by the Japan Society for the Promotion of Science (JSPS). The ARPES measurements were performed under the approval of the Japan Synchrotron Radiation Research Institute (2001A0128-NS-np, 2002B3009-LS-np, and 2003A4009-LS-np).

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\textsuperscript{16} For the analysis of core-level spectra, a symmetric line shape (Lorentzian with Gaussian broadening) is used for each component. The Lorentzian width is assumed to be independent of components ($\sim 0.06$ eV) while the Gaussian width is changed depending on components. Origins of the different Gaussian widths among components are not clear at present. Asymmetry of the core-level line shapes originates generally from excited electron-hole pairs in the vicinity of $E_F$ due to the core-level excitation on the same sites. Since there is no Sr-derived conduction electron near $E_F$, the line shapes of the Sr 3d core level should be almost symmetric. The Shirley-type background is also added in the fitted spectra.
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We have determined $k_F$'s by the criteria listed below, which are commonly used in ARPES studies: (1) peak dispersion extrapolated to $E_F$, (2) intensity maxima in the MDCs at and slightly above ($\leq 0.1$ eV) $E_F$, (3) momentum where the peak closest to $E_F$ drastically changes its intensity and disappears.

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