X-ray emission, photoelectron spectra, and electronic structure of $Sr_2CuO_2F_{2+\delta}$

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The electronic structure of the high-T_c superconductor $Sr_2CuO_2F_{2+\delta}$ has been investigated by means of x-ray-emission spectroscopy (O K_α, Cu $L_{\alpha,\beta}$, F K_α), x-ray-photoelectron spectroscopy, and band-structure calculations using the full-potential linear muffin-tin orbital method. The local environment of the F atoms and the valence state of the Cu atoms in $Sr_2CuO_2F_{2+\delta}$ are discussed. On the basis of the x-ray-photoelectron and x-ray-emission spectra it is concluded that the F atoms preferentially bond to Sr atoms in this compound.

I. INTRODUCTION

Relatively high superconducting transition temperatures (T_c=70–100 K) are found in a new family of copper oxide superconductors, $Sr_{n+1}Cu_nO_{2n+1+\delta}$, stabilized at high pressure.[1] In the next member of this superconducting family, $Sr_2Cu_2F_{2+\delta}$ (T_c=46 K), superconductivity was induced via the incorporation of interstitial F atoms.[2] This is the first high-T_c superconductor in which

FIG. 1. Structure of $Sr_2CuO_2F_{2+\delta}$ showing idealized apical (F) and interstitial (F') atoms.

fluorine atoms play an essential role.[2]

It is rather difficult to determine the accurate positions of the O and F atoms in the Sr-Cu-O-F system using x-ray or neutron diffraction because of the similarity of their scattering factors. According to the structural model suggested in Ref. 2 (see Fig. 1), $Sr_2CuO_2F_{2+\delta}$ has orthorhombic structure with $Fmmm$ symmetry and F atoms located at both apical and interstitial positions [near the ideal ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) positions].

It seems very important to check this model with the help of local structure sensitive methods. For this reason, x-ray-emission and photoelectron spectroscopy were recently used for estimating fluorine atom incorporation into Y123 and Bi2212 compounds, for determining their positions in the crystal structure of these cuprates,[3,4] and for analyzing substitution effects in Y123 compounds containing oxyanions groups.[5–7] In this paper we present x-ray-emission valence band spectra (Cu $L_{\alpha,\beta}$, O K_α, F K_α) and x-ray-photoelectron core level and valence band spectra of $Sr_2CuO_2F_{2+\delta}$. These spectra are compared with that of Sr_2CuO_3, CuF_2, and SrF_2 reference compounds. The results of the $Sr_2CuO_2F_2$ band-structure calculation, using the full-potential linear muffin-tin orbital (FLMTO) method, are presented also.

II. EXPERIMENT AND METHOD OF CALCULATION

Sr_2CuO_3 was prepared from $SrCO_3$ and CuO using two heat treatments at 950 °C for 16 h in air. This compound was then annealed in a nickel boat to 210 °C in
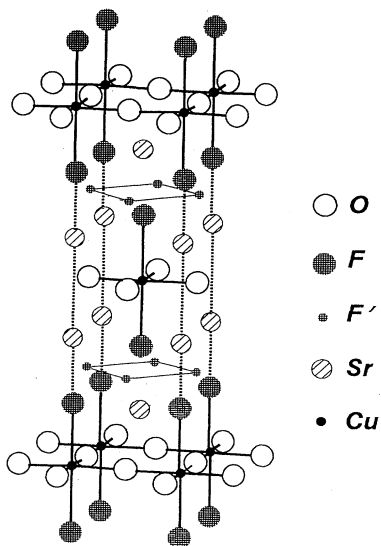
dry N_2 and subjected to a flowing F_2/N_2 atmosphere for 15 min. The resulting samples of $Sr_2CuO_2F_{2+\delta}$ were annealed for approximately 3 h in N_2 at temperatures up to 330 °C. A new orthorhombic ($Fmmm$) phase was found with unit cell dimensions similar to those of La_2CuO_4: $a=5.394(1)$, $b=5.513(1)$, $c=13.468(3)$ Å. The superconducting properties were examined magnetically with a dc superconducting quantum interference device magnetometer using a field of 10^{-3} T. Superconductivity was found for compositions having $\delta=0.25$–0.48 with a maximum $T_c=46$ K for $Sr_2CuO_2F_{2.33}$. A single-phase sample of $Sr_2CuO_2F_{2.6}$ was chosen for the x-ray-emission and photoelectron spectra determinations. As reference samples we also studied a SrF_2 single crystal and CuF_2 powder.

The x-ray-emission spectra (XES), Cu $L_{\alpha,\beta}$ ($2p_{3/2,1/2} \rightarrow 3d4s$ transition), O K_α ($1s \rightarrow 2p$ transition), and F K_α ($1s \rightarrow 2p$ transition), were measured with a JCXA-733 electron probe microanalyzer with a fully focused Johan-type spectrometer and a TAP (thallium phtalate) crystal analyzer ($2d=25.76$ Å) curved to $R=280$ mm. The energy resolution was 2.8, 0.5, and 1.8 eV, respectively. A soft operation mode at ($V=5$ keV, $i=100$ nA) was chosen for the x-ray tube and the focused electron beam on the sample surface was changed for every scan to avoid sample decomposition during the measurement.

X-ray-photoelectron spectra (XPS) were recorded using a physical electronics instrument 5600 ci Perkin Elmer electron spectroscopy for chemical analysis (ESCA) spectrometer with monochromatized Al K_α radiation. The samples were studied in pressed pellet form and were cleaved in situ before starting the measurements with an estimated energy resolution of 0.4 eV. The spectra were calibrated using the C $1s$ signal of hydrocarbons ($E_b=284.6$ eV). A small amount of hydrocarbons originated from the residual gas and was accumulated during the measurement time.

In order to calculate the electronic structure density of states (DOS) of $Sr_2CuO_2F_2$, we neglected its orthorhombicity and used an idealized K_2NiF_4 structure with $a=7.322$ a.u. and $c/a=2.455$. The calculations were performed using the FLMTO method[8–10] in a spin-restricted scalar-relativistic mode with atomic Cu $3d^{10}4s^1$, Sr $5s^24p^6$, O $2s^22p^4$, and F $2s^22p^5$ orbitals treated as valence band electrons and Cu $3s^23p^6$, Sr $4s^2$ treated as semicore states (in a second energy window). We used a triple-κ basis set for each type of atom with angular momentum l, up to two for Cu, O, and F, and up to three for Sr for $k^2 = -0.01$ Ry, and up to one for $k^2 = -1.0$ and -2.3 Ry. The charge density was calculated exactly in the muffin-tin spheres. The Brillouin zone integrations were carried out using a 646 k-point mesh corresponding to $24 \times 24 \times 24$ divisions in the $\frac{1}{16}$ irreducible wedge.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the Cu $L_{\alpha,\beta}$ x-ray-emission spectra ($2_{3/2,1/2} \rightarrow 3d4s$ transition) of Sr_2CuO_3 and $Sr_2CuO_2F_{2.6}$. As can be seen, the ratio of integrated in-
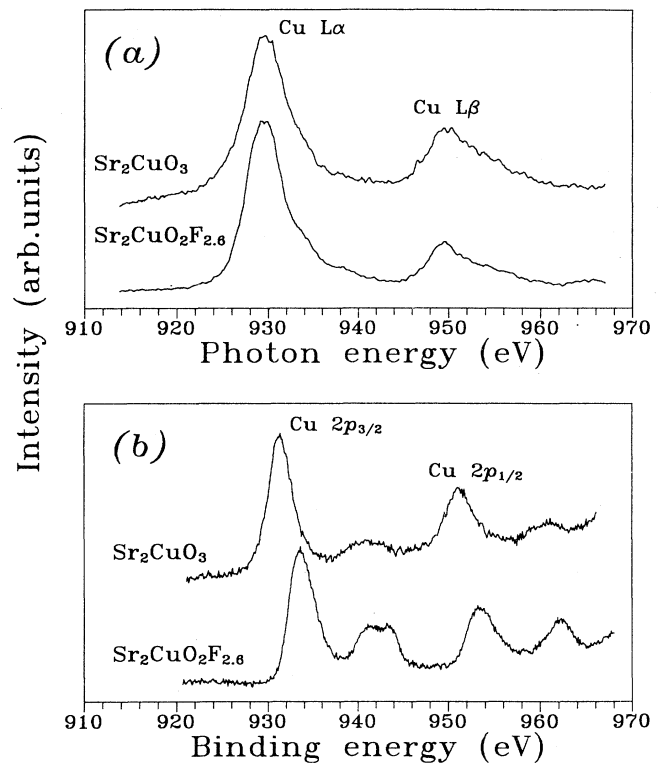

FIG. 2. X-ray-emission Cu $L_{\alpha,\beta}$ spectra of $Sr_2CuO_2F_{2.6}$ and Sr_2CuO_3 (a); x-ray-photoelectron Cu $2p$ spectra of $Sr_2CuO_2F_{2.6}$ and Sr_2CuO_3 (b).

tensites $I(L_\beta)/I(L_\alpha)$ in $Sr_2CuO_2F_{2.6}$ (0.27) is lower than that of Sr_2CuO_3 (0.39). In accordance with the estimates given in Refs. 11 and 12, this indicates a decrease of the occupancy of the Cu $3d$ orbitals or a decrease of the covalency of chemical bonding between Cu and its ligands. These data are very similar to those for $Nd_2CuO_{4-\delta}F_x$ (Ref. 12) in which the doping of Nd_2CuO_4 with fluorine leads to decrease of the $I(L_\beta)/I(L_\alpha)$ ratio that was interpreted as the formation of Cu^+ ions. In addition, F doping leads to a decrease in the Cu L_α (Cu $3d$) bandwidth. This can be attributed to the more localized Cu $3d$ states and to a higher ionicity of Cu-O and/or Cu-F bonds.

For the XPS Cu $2p_{3/2}$ spectra [Fig. 2(b)], the intensity ratio (I_s/I_m) of the satellite and the main line for $Sr_2CuO_2F_{2.6}$ is higher with respect to that for Sr_2CuO_3 (0.37 and 0.13, respectively), which is in accordance with Refs. 18 and 19, and shows an increasing influence of the $3d^8$ initial configuration and increasing ionicity of the chemical bonds.

The Cu $2p_{3/2}$ and Cu $2p_{1/2}$ XPS binding energies in $Sr_2CuO_2F_{2.6}$ are closer to those in CuO than in CuF_2 (see Table I). Hence, one can conclude that the contribution of the Cu-F bonds to the Cu $2p$ XPS spectra of $Sr_2CuO_2F_{2.6}$ is very small.

Fluorine K_α x-ray-emission spectra of $Sr_2CuO_2F_{2.6}$, SrF_2, and CuF_2 are shown in Fig. 3(a). A fluorine K_α emission spectrum in general consists of a prominent

TABLE I. Binding energies of the core levels of the some compounds (eV)

Core level	Sr_2CuO_3	$Sr_2CuO_2F_{2.6}$	SrF_2	CuF_2	CuO
Sr $3p_{3/2}$	269.0		269.25		
Sr $3p_{1/2}$	279.2	279.1	279.55		
Sr $3d_{5/2}$	133.2	132.7			
Sr $4s$	36.7	37.3	38.05		
Sr $4p$	18.5	19.2	19.65		
Cu $2p_{3/2}$	931.35	933.5		936.1 (Ref. 17), 937.0 (Refs. 22), 936.8 (Ref. 20)	932.5
Cu $3s$	122.5	124.3			123.1
O $1s$	530.85	530.6			529.3
F $1s$		683.2	684.0	684.5 (Refs. 17, 22), 685.9 (Ref. 20)	
F $2s$		28.4	29.05		
C $1s$	284.6	284.6	284.6		
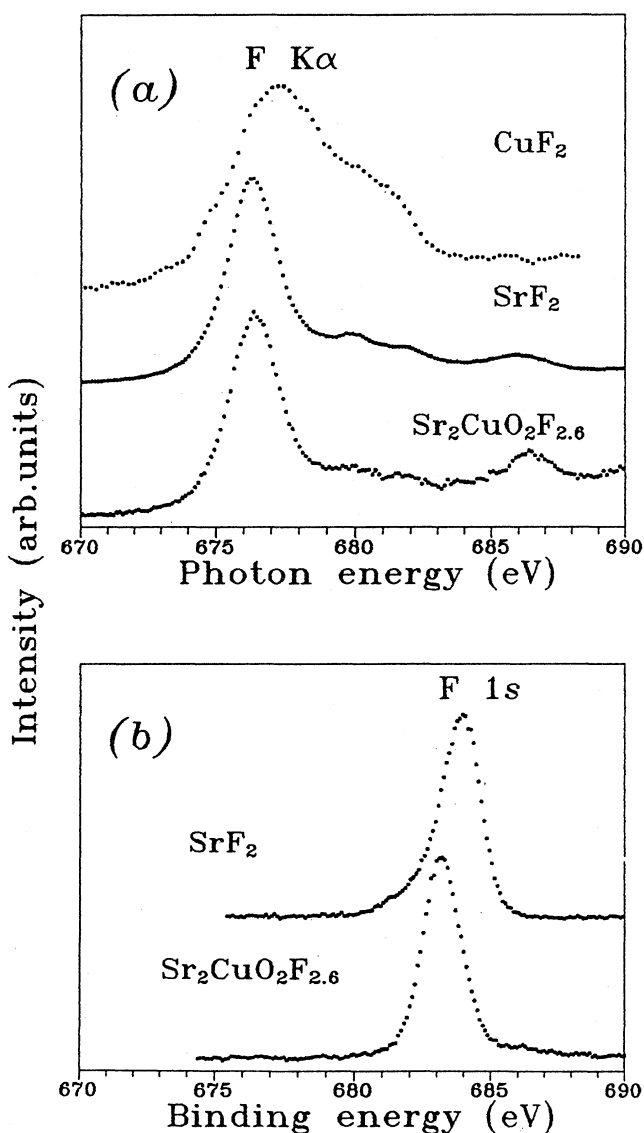
FIG. 3. X-ray-emission F K_α spectra of $Sr_2CuO_2F_{2.6}$, SrF_2, and CuF_2 (a); x-ray-photoelectron F $1s$ spectra of SrF_2 and $Sr_2CuO_2F_{2.6}$ (b).

peak (K^1L^0) and high-energy satellites K^1L^1 and K^1L^2 (due to K^1L^1 double-hole and K^1L^2 triple-hole states, respectively).[13,14] The relative intensities of the K^1L^1 satellites to that of the main peak correlate strongly with the ionic character of the bonds to the fluorine atoms in fluorides. The anomalously low intensity of the K^1L^1 satellite peak observed for SrF_2 is explained by a resonant transfer of an electron between the $4p$ level of Sr^{2+} ion and the $2p$ level of the F^- ion.[15,16] The full width at half-maximum (FWHM) of the main F K_α peak is closely related to the difference in the electronegativity of the metal and fluorine atoms: the FWHM decreases with increasing electronegativity (in other words, with increasing ionicity).[16]

The F K_α spectrum of $Sr_2CuO_2F_{2.6}$ is very similar to that of SrF_2 but quite different from that of CuF_2. Since the contribution of the F-Cu bonds to the F K_α spectrum of $Sr_2CuO_2F_{2.6}$ seems to be very small, the fluorine atoms in the crystal structure of $Sr_2CuO_2F_{2.6}$ appear to preferentially bond to Sr atoms rather than to Cu atoms. Such a conclusion is consistent with the Cu $2p$ XPS data and with the structural model of the compound in question[2] given in Fig. 1 for which the number of Sr-F bonds is larger than that of the F-Cu bonds and the length of the F-Sr bonds (2.5–2.6 Å) is shorter than that of the F-Cu bonds (2.5–3.4 Å).

The F $1s$ XPS spectra of $Sr_2CuO_2F_{2.6}$ and the reference compound SrF_2 are presented in Fig. 3(b). The F $1s$ signal of $Sr_2CuO_2F_{2.6}$ is rather symmetric and there is no second peak that could be associated with the presence of the two types of F atoms. The XPS F $1s$ binding energy of $Sr_2CuO_2F_{2.6}$ is 683.2 eV, which is closer to that of SrF_2 (684.0 eV) than to that of CuF_2 [684.5 eV (Refs. 17 and 22) or 685.9 eV (Ref. 20)]. This is also in agreement with the results of the x-ray-emission spectra.

The x-ray-emission O K_α spectra of $Sr_2CuO_2F_{2.6}$ and Sr_2CuO_3 are presented in Fig. 4(a). Both spectra are very similar and show a high-energy subband in the energy region between 526 and 529 eV. This subband may be particularly due to the strong hybridization of the O $2p$ states with Cu $3d$ states. But on the other hand, such satellites can also be seen in the O K_α spectra of YOF, $YBa_2Cu_3O_{6.5-x}F_x$ (Ref. 3), and in other oxides with strong ionic bonds. The nature of this satellite is
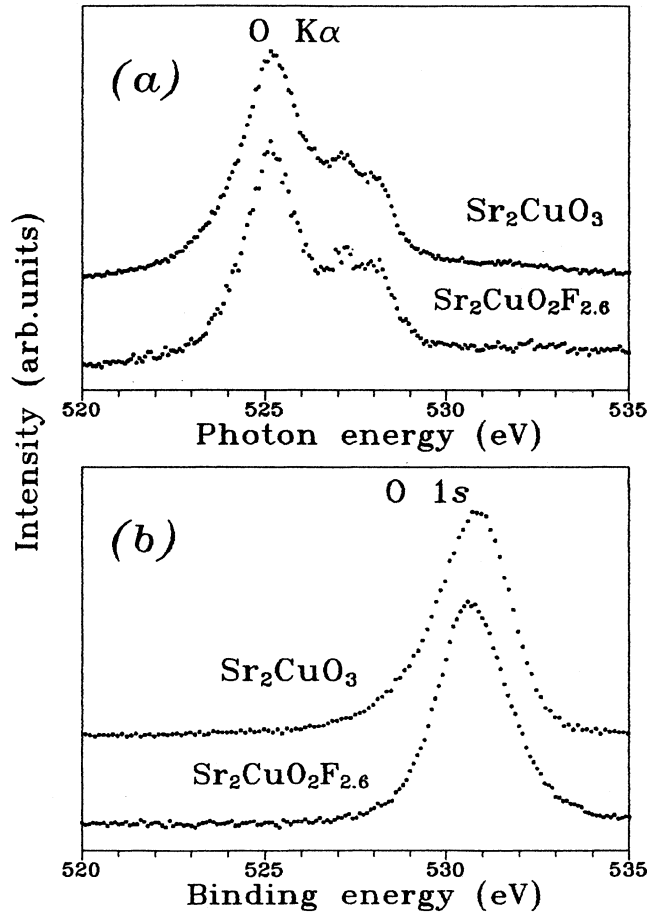
FIG. 4. X-ray-emission O K_α spectra of $Sr_2CuO_2F_{2.6}$ and Sr_2CuO_3 (a); x-ray-photoelectron O $1s$ spectra of $Sr_2CuO_2F_{2.6}$ and Sr_2CuO_3 (b).

FIG. 5. X-ray-emission and photoelectron valence band spectra of $Sr_2CuO_2F_{2.6}$.

binding energies of the F $1s$, O $1s$, and Cu $2p_{3/2}$ core levels. According to the dipole selection rules, the F K_α, O K_α, and Cu L_α x-ray-emission spectra probe F $2p$, O $2p$, and Cu $3d4s$ partial DOS, respectively, in the valence band whereas the intensity of the XPS valence band is proportional to the contribution of the total den-

probably the same as for the F K_α spectra. The intense satellites indicate that certain of the chemical bonds in $Sr_2CuO_2F_{2.6}$ and Sr_2CuO_3 are more ionic than that in other high-T_c superconductors.

The O $1s$ binding energies in $Sr_2CuO_2F_{2.6}$ and Sr_2CuO_3 [see Fig. 4(b)] are found to be very similar: 530.6 and 530.8 eV, respectively, which is in agreement with the XES data and the proposed structural model of $Sr_2CuO_2F_{2.6}$.[2]

In accordance with the structural model, F atoms both substitute oxygen atoms in the Sr-O chains of Sr_2CuO_3 and occupy some interstitial positions. The substitution of O atoms by F atoms increases the ionicity of the chemical bonding. This means that oxygen-copper bonds in $Sr_2CuO_2F_{2.6}$ are similar to those in Sr_2CuO_3, which is confirmed by the O K_α x-ray-emission spectra of $Sr_2CuO_2F_{2.6}$ and Sr_2CuO_3, which are very similar [see Fig. 4(a)].

The XPS valence band spectrum and F K_α, O K_α, and Cu L_α x-ray-emission spectra of $Sr_2CuO_2F_{2.6}$ are shown in Fig. 5. The position of the Fermi level of the x-ray-emission spectra is determined with the help of the
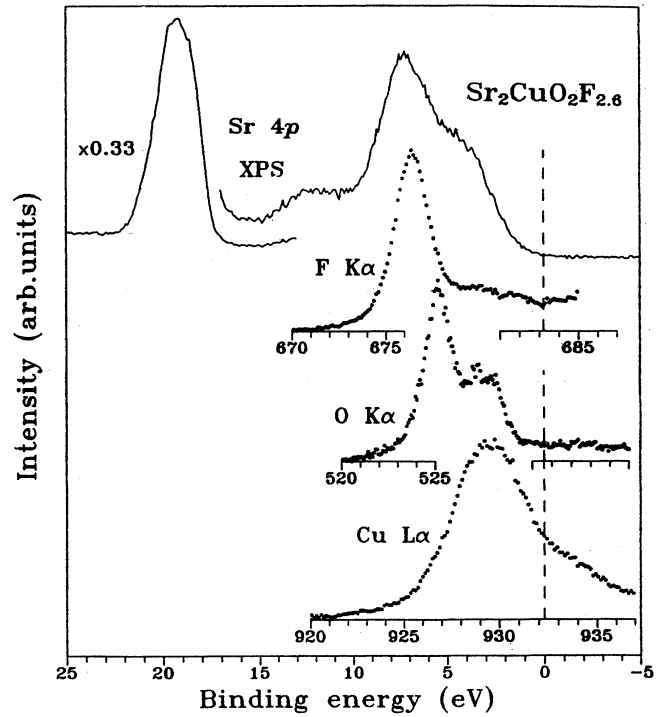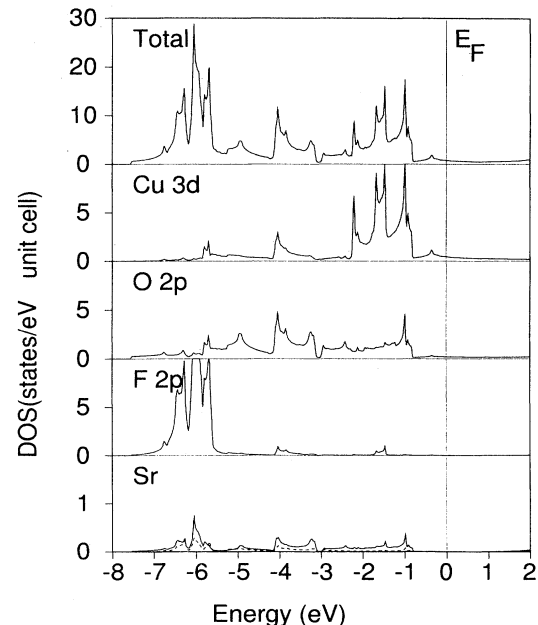

FIG. 6. Total and projected densities of states of $Sr_2CuO_2F_2$.

sity of states weighted with atomic photoionization cross sections. Based on the analysis of these data, one can conclude that Cu $3d$ states are mostly concentrated at the top of the valence band and are strongly hybridized with O $2p$ states, which prevail in the middle part of the valence band. F $2p$ states dominate at the bottom of the valence band and form the most intensive peak of the XPS valence band spectrum. The structure of the energy bands of $Sr_2CuO_2F_{2.6}$ (see Fig. 5) is found to be rather different in respect to that of F-free superconducting cuprates for which a stronger Cu $3d$–O $2p$ hybridization takes place and the reverse mutual position of Cu $3d$ and O $2p$ bands is established.[21]

The interpretation of the XPS and XES data of the valence band of $Sr_2CuO_2F_{2.6}$ is in agreement with the results of the FLMTO calculations, which are presented in Fig. 6. The feature near Fermi level (at -0.36 eV) is caused by a Van Hove saddle point singularity.[10] The main contribution to the total DOS near the Fermi level comes from the Cu $3d$ and O $2p$ orbitals and is almost three times larger than that at E_F for the undoped compound. The main contribution of the F $2p$ states is at about -6 eV. The results of the calculations reflect the strong hybridization between the Sr and F electron states (the maximum of the Sr DOS is at the same energy as that of the F $2p$ DOS). On the other hand, the Cu $3d$–F $2p$ hybridization is small. These calculations are consistent with the details of the electronic structure determined from x-ray-emission and photoelectron spectroscopy, and support the structural model for $Sr_2CuO_2F_{2.6}$.[2]

IV. CONCLUSION

X-ray-emission and photoelectron spectra of $Sr_2CuO_2F_{2.6}$ and Sr_2CuO_3 have been investigated. According to the analysis of these spectra and their comparison with spectra of reference compounds, it is concluded that fluorine atoms are really incorporated into Sr_2CuO_3 lattice and form strong bonds primarly with Sr atoms, which is in accordance with the structural model of this compound suggested in Ref. 2. The valence band structure of $Sr_2CuO_2F_{2.6}$ is analyzed and compared with one calculated by the FLMTO method. Differences between the electronic structure of alkaline earth copper oxyfluorides and the corresponding oxides have been highlighted.

ACKNOWLEDGMENTS

[1] Z. Hiroi, M. Takano, M. Azuma, and Y. Takeda, Nature **364**, 315 (1993).

[2] M. Al-Mamouri, P. P. Edwards, C. Greaves, and M. Slaski, Nature **369**, 382 (1994).

[3] V. V. Fedorenko, V. R. Galakhov, L. V. Elokhina, L. D. Finkelstein, V. E. Naish, S. M. Butorin, E. J. Nordgren, A. K. Tyagi, U. R. K. Rao, and R. M. Iyer, Physica C **221**, 71 (1994).

[4] E. Z. Kurmaev, V. V. Fedorenko, L. V. Elokhina, L. D. Finkelstein, and T. B. Popova, Physica C **226**, 58 (1994).

[5] Yu. M. Yarmoshenko, V. A. Trofimova, E. Z. Kurmaev, P. R. Slater, and C. Greaves, Physica C **224**, 317 (1994).

[6] E. Z. Kurmaev, S. N. Shamin, P. R. Slater, and C. Greaves, Physica C **227**, 309 (1994).

[7] E. Z. Kurmaev, V. V. Fedorenko, V. R. Galakhov, S. Bartkowski, S. Uhlenbrock, M. Neumann, P. R. Slater, C. Greaves, and Y. Miyazaki, J. Supercond. (to be published).

[8] M. Springborg and O. K. Andersen, J. Chem. Phys. **87**, 7125 (1987).

[9] M. Methfessel, Phys. Rev. B **38**, 1537 (1988).

[10] D. L. Novikov, A. J. Freeman, and J. D. Jorgensen, Phys. Rev. B **51**, 6675 (1995).

[11] S. M. Butorin, V. R. Galakhov, E. Z. Kurmaev, and V. I. Glazyrina, Solid State Commun. **81**, 1003 (1992).

[12] S. M. Butorin, V. R. Galakhov, E. Z. Kurmaev, S. M. Cheshnitsky, S. A. Lebedev, and E. F. Kukovitzki,

Phys. Rev. B **47**, 9035 (1993).

[13] V. F. Demekhin and V. P. Sachenko, Izv. Akad. Nauk SSSR, Ser. Fiz. **31**, 900 (1967) [Bull. Acad. Sci. USSR, Phys. Ser. **31**, 921 (1967)].

[14] T. Åberg, G. Graeffe, J. Utriainen, and M. Linkoaho, J. Phys. C **3**, 1112 (1970).

[15] O. Benka, R. L. Watson, and R. A. Kenefick, Phys. Rev. Lett. **47**, 1202 (1981).

[16] C. Sugiura, W. Konishi, S. Shoji, and S. Kojima, J. Phys. Soc. Jpn. **59**, 4049 (1990).

[17] S. W. Gaarenstroom and N. J. Vinograd, J. Chem. Phys. **67**, 3500 (1977).

[18] N. Merrien, F. Studer, C. Michel, P. Srivastava, B. R. Swkhar, N. L. Saini, K. B. Garg, and G. Tourillon, J. Phys. Chem. Solids **54**, 499 (1993).

[19] F. Parmigiani and L. Sangaletti, J. Electron Spectrosc. Relat. Phenom. **66**, 223 (1994).

[20] G. Van der Laan, C. Westra, C. Haas, and G. A. Sawatzky, Phys. Rev. B **23**, 4369 (1981).

[21] S. M. Butorin, V. R. Galakhov, L. D. Finkelstein, E. Z. Kurmaev, Yu. A. Teterin, M. I. Sosulnikov, S. M. Cheshnitsky, S. A. Lebedev, and A. I. Akimov, Physica C **177**, 8 (1991).

[22] C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, and G. E. Mullenburg, *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer Corporation, Eden Prairie, MN, 1979).