PHYSICAL REVIEW B VOLUME 44, NUMBER 14 1 OCTOBER 1991-II

Polarized O $K\alpha$ and Cu $L\alpha$ x-ray emission spectra of Bi-Sr-Ca-Cu-O single crystals

J. A. Leiro
Department of Applied Physics, University of Turku, SF-20500 Turku, Finland

F. Werfel and G. Dräger
Fachbereich Physik der Martin-Luther Universität, Halle-4010, Germany

(Received 22 February 1991)

Polarized soft-x-ray emission measurements of the high-temperature superconducting $Bi_{2.2}Sr_{1.8}Ca_{0.7}Cu_{1.9}O_x$ compound are presented. The O $K\alpha$ spectrum shows a strong anisotropy and three main features can be identified. When the c axis of the crystal is nearly perpendicular to the polarization vector $\mathbf{e}(c\perp\mathbf{e})$ of x-ray radiation, the O $K\alpha$ spectrum shows the main peak at 3.8 eV from the Fermi level and a shoulder at about 1.4 eV, correspondingly. It is assumed that this shoulder can be assigned to the $p\sigma_{x,y}$ states in the CuO_2 plane which form a σ bond with the Cu $3d_{x^2-y^2}$ states. In the case of c axis almost parallel to the polarization vector $(c\parallel\mathbf{e})$ the spectrum consists of the main peak at 3.4 eV and a feature at about 6.0 eV from the Fermi level. The possible explanation for this 6.0-eV feature is the $p\sigma_z$ component associated with the Cu $3d_{3z^2-r^2}$ orbital. It should be mentioned that this notation also contains the in-plane $p\sigma_{x,y}$ orbitals. The most striking property of the Cu $L\alpha$ spectrum is the energy shift between the main peaks in the case of the two different polarization directions. It turns out that when $c\perp\mathbf{e}$ the peak energy is larger than that for $c\parallel\mathbf{e}$. This is in accordance with the suggestion that the largely π-bonded Cu $3d_{xy}$ states should have a smaller binding energy than that of the corresponding Cu $3d_{xz,yz}$ states.

INTRODUCTION

One of the copper oxide-based high-transition temperature superconductors with T_c exceeding the temperature of liquid nitrogen is $Bi_2Sr_2CaCu_2O_8$. This compound has the property that it contains two CuO_2 layers whereas the Cu-O chain is missing in contrast with the $YBa_2Cu_3O_7$ metal. Recently, some soft-x-ray emission studies have appeared which give information on the electronic structure of the occupied valence band of the Bi-Sr-Ca-Cu-O system.[1-3] In this paper we study polarized O $K\alpha$ and Cu $L\alpha$ spectra which show strong anisotropic features. As far as the oxygen $2p$ states are concerned our results agree very well with the previous angle-resolved photoemission spectroscopy (ARPES) spectra, which are performed in normal emission.[4-6]

By now there is still some discussion about the effect of the doped holes on the CuO_2 planes. This issue can be studied by using the polarized x-ray emission spectroscopy (PXES), which projects the c axis of the crystal perpendicular to the polarization vector $\mathbf{e}(c\perp\mathbf{e})$ or parallel to the polarization vector $(c\parallel\mathbf{e})$. In the case of $c\perp\mathbf{e}$ the spectra give information about the electronic states in the CuO_2 plane, whereas $c\parallel\mathbf{e}$ is connected with the states normal to the plane (out of plane). Furthermore, the dipole selection rules are applied.

It is found that the polarized O $K\alpha$ spectrum of Bi-Sr-Ca-Cu-O is very similar to the recent ultraviolet-photoemission spectroscopic (UPS) measurements of the same compound. This is because the photoionization cross section of the O $2p$ states is much larger than that of the Cu $3d$ orbitals in the case of the photon energy 21.2 eV.[7,8] The low-binding energy features less than 2 eV below the Fermi energy have been previously interpreted as being due to Cu $3d^9$—O $2p$ hole local singlets in the CuO_2 plane, whereas the larger structures with the binding energy higher than 2 eV have been suggested to be caused by the states in the Bi—O plane.[7] The origin of the above features are now discussed in the light of PXES. It seems that the impurity Anderson model[9] description, which contains the CuO_2 plane, is good as a first approximation. The adjacent Sr-O plane to the CuO_2 plane may give a contribution to the O $K\alpha$ spectrum as well, especially when $\mathbf{e}\parallel c$.

Also, the Cu $L\alpha$ spectra show a strong anisotropic behavior. The fine structures of the main lines are not so pronounced as for O $K\alpha$. This might be caused by the less covalent character of the Cu $3d$—O $2p$ bond as compared with those of the $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$ compounds, for instance.

EXPERIMENTAL

The nearly polarized Cu $L\alpha$, Cu $L\beta$, and O $K\alpha$ spectra of the Bi-Sr-Ca-Cu-O compound were obtained by using an Applied Research Laboratory (ARL) electron microprobe analyzer (EMX-SM) equipped with a RAP analyzing crystal. The voltage and the current were 5 kV and 200 nA, respectively, at standard vacuum conditions (10^{-3} Pa). The polarized spectra were measured for two special positions of the c axis of the emitting sample relative to the polarization vector $\mathbf{e}$, parallel position $c\parallel\mathbf{e}$ and perpendicular to the plane $c\perp\mathbf{e}$. The polarized O Kα and Cu $L\alpha$ x-ray emission spectra have been registered at

Bragg angles θ of 64.5° and 30.7°, respectively. Both angles deviate from the ideal polarization case of $\theta=45°$. Nevertheless, the essential features can be obtained from the measurements. The energy resolution is about 0.4 and 0.7 eV for O $K\alpha$ and Cu $L\alpha$ respectively.

The sample was made by Easterling *et al.*[10] The size of the single crystal used in our experiment was about 1.0×0.5 mm^2. The stoichiometry and phase purity was checked by electron probe microanalysis (EPMA).

RESULTS

It is assumed that the system contains two holes both in the intermediate and the final state of the x-ray emission process. This means that for the O $K\alpha$ line the relevant transition would be O $1\underline{s}$ Cu $3d^9 \rightarrow 3d^9\underline{L}$ where the hole is transferred from the O 1s level to the O 2p band of the ligand atom in which $\underline{L}$ denotes the ligand hole.[11]. It should be noted that the other hole is located in the Cu 3d band overlapping with the O 2p states.

The nearly polarized O $K\alpha$ spectra of the Bi-Sr-Ca-Cu-O system are shown in Fig. 1. The weak line at about 532 eV is caused by an instrumental effect which is due to the RAP analyzing crystal. The RAP crystal contains oxygen and the O K absorption edge appears at this energy. It is assumed that the position of the Fermi level is at 528.7 eV in Fig. 1. This value has been deduced on the basis of the recent x-ray photoemission (XPS) and x-ray absorption (XAS) measurements.[12,13] The energies of the different features are expressed relative to this Fermi level value. Let us first consider the case $\mathbf{e}\perp c$ in Fig. 1. This means that the polarization vector $\mathbf{e}$ is essentially in the CuO_2 plane. The weak structure at about 1.4 eV from the Fermi level in Fig. 1 coincides quite well with the recent UPS results which show a similar feature for the Bi-Sr-Ca-Cu-O compound including two CuO_2 layers.[7] The origin of this shoulder seems to be the oxygen $2p_{x,y}$ states which is also in agreement with the previous ARPES data.[4–6] It turns out that these O $2p_{x,y}$ states together with the Cu $3d_{x^2-y^2}$ orbitals give rise to local singlets $^1A_1$, which possess the lowest binding energy in the case of the $d^9\underline{L}$ configuration.[9] Also, the main peak at about 3.8 eV shows a good overall agreement with the corresponding UPS result as far as the energy position and the shape of the spectrum are concerned.

Figure 1 shows also the situation when the polarization vector $\mathbf{e}$ is almost parallel to the c axis ($\sim\mathbf{e}\parallel c$). In that case the O $K\alpha$ spectrum gives information mainly on the p_z states (off plane). Indeed, there exists a shoulder at about 6.0 eV. This feature is now largely attributed to local triplets $^3B_1$, where the extra hole can be expressed in terms of the Cu $3d_{3z^2-r^2}$ states combined with the oxygen p_z and $p_{x,y}$ states.[14] Of course, the p_z component will dominate when $\sim\mathbf{e}\parallel c$. It should be noted that the three essential features of the UPS spectrum with the energies at 5.8, 3.3, and 1.6 eV,[15] respectively, can be identified in the polarized O $K\alpha$ spectra of the $Bi_2Sr_2CaCu_2O_x$ compound as well.

Let us now turn to the Cu $L\alpha$ spectra of the Bi-Sr-Ca-Cu-O high-temperature superconducting oxide. It is assumed the main contribution to this line comes from the transition Cu $2\underline{p}d^{10}\underline{L} \rightarrow d^9\underline{L}$[16], in which the intermediate state[16] corresponds to the final state of the XPS Cu 2p core line. The final-state configurations d^8 and $d^{10}\underline{L}^2$ are also possible in addition to the $d^9\underline{L}$ one for the XES spectrum in the case of the two-hole state.[17] Also, the configuration Cu $2\underline{p}d^9$, which is associated with high-binding energy satellite of the Cu 2p XPS spectrum, can contribute to the final result. Because the energy difference between this satellite and the (XPS) valence-band satellite with the configuration Cu $3d^8$ is somewhat larger ($\sim$1 eV) than the corresponding energy difference of the main peaks for the 2p core level and valence band, respectively, the high-binding energy satellite is missing in the case of Cu $L\alpha$ spectrum as seen in Fig. 2, although it is observed in the XPS valence-band spectrum. Instead, on the basis of the above considerations, high-energy satellite features are expected. Indeed, some structures can be observed on the high-energy side of the main line. In Fig. 2 the energy of the Fermi level is supposed to be 933.1 eV according to the recent XPS measurements for the Cu $2p_{3/2}$ core line.[15] The striking property for the nearly polarized Cu $L\alpha$ spectra is the energy shift of the main line. It turns out that when $\sim\mathbf{e}\perp c$ the energy difference between the peak and the Fermi level is about

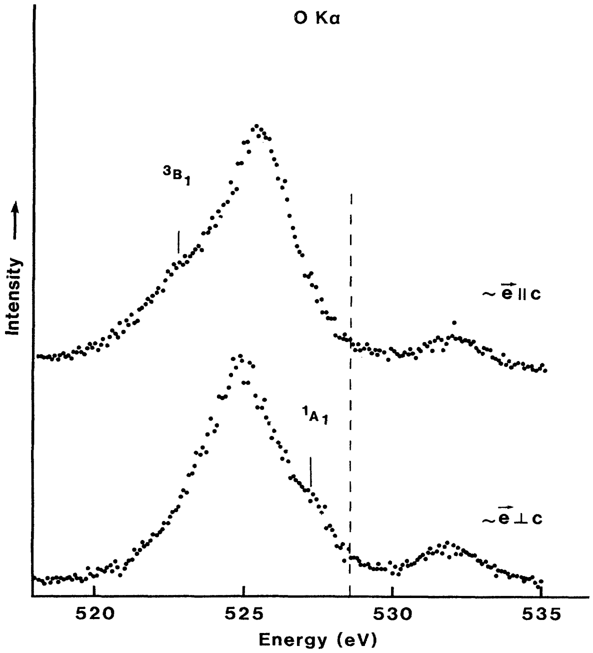

FIG. 1. The upper O $K\alpha$ spectrum shows the situation when the polarization vector $\mathbf{e}$ is nearly parallel to the c axis. The shoulder at about 6.0 eV is associated with local triplets $^3B_1$. In this case the Cu 3d-O 2p band with $3d_{3z^2-r^2}$ and $3d_{x^2-y^2}$ symmetry orbitals has $p\sigma_z$ holes mainly in the Sr-O plane. The lower spectrum corresponds to the case when the polarization vector $\mathbf{e}$ is almost perpendicular to the c axis. The 1.4 eV feature is attributed to local singlets $^1A_1$ where the Cu 3d-O 2p band consists of two $3d_{x^2-y^2}$ symmetry orbitals. The $p\sigma_{x,y}$ holes are now in the CuO_2 plane. The assumed energy position of the Fermi level is described by a dashed vertical line.

3.5 eV which is considerably smaller than the corresponding energy difference 4.4 eV for $\sim \mathbf{e} \| c$. The possible reason for this is that the component Cu $3d_{xy}$ ($\mathbf{e} \perp c$) has a smaller binding energy than the components Cu $3d_{xz,yz}$ ($\mathbf{e} \| c$) in the ground state.[18] It should be noted that these states are π bonded to the O $2p_{x,y}$ states.[14] Furthermore, the hybridization is weak for this $3d$-$2p$ band, which would partly explain the deviation of the shape between the Cu $L\alpha$ and O $K\alpha$ spectra.

DISCUSSION

The ground state of the undoped system is usually supposed to have one hole which is shared between the Cu $3d$ and the O $2p$ states. This state is a linear superposition of the $3d^9$ and $3d^{10}\underline{L}$ configuration. There is a hybridization (mixing) between these two configurations. The weight of the former case ($3d^9$) has generally been assumed to be about two times larger than that of the later one ($3d^{10}\underline{L}$)[17].

Let us now turn to the O $K\alpha$ spectra. It is now plausible to suggest the transition O $1\underline{s}$ Cu $3d^9 \rightarrow$ Cu $3d^9\underline{L}$ for this line which means that the Cu $3d^9$ configuration remains essentially unchanged during the x-ray process. This is supported by the fact that XPS O $1\underline{s}$ line exhibits no strong satellite structure on the high-binding energy side of the main line.[12] Of course there is a mixing of the d^8, $d^9\underline{L}$ and $d^{10}\underline{L}^2$ configurations in the final state of the O $K\alpha$ spectrum but it seems likely that $3d^9\underline{L}$ is dominating. It should be mentioned that the above configurations are characteristic for the ground state of the high-T_c system, in which an extra hole is doped.[17]

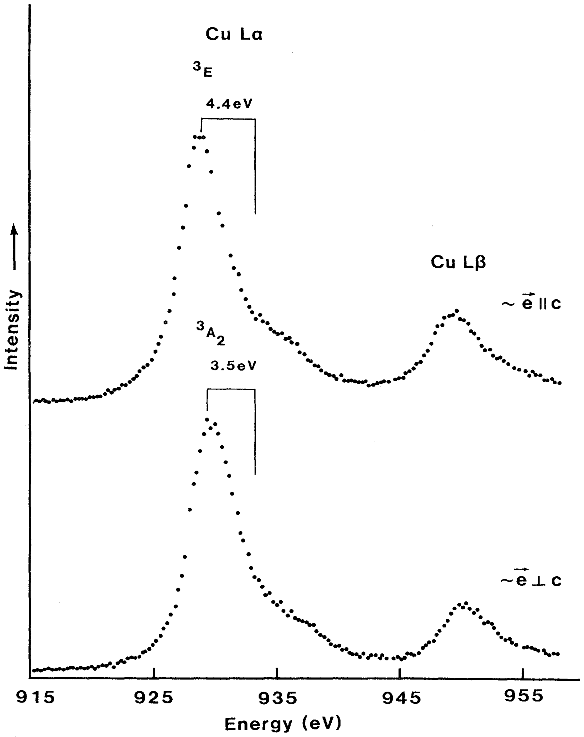

FIG. 2. The upper spectrum contains the Cu $L\alpha$ line when the polarization vector $\mathbf{e}$ is nearly parallel to the c axis. Now, the dominating state is suggested to be ^3E in which the relevant symmetries are $d_{xz,yz}$ and $d_{x^2-y^2}$ whereas the $p\pi_{x,y}$ states are in the Sr-O plane. It should be noted that the $3d$ character of the hole is more pronounced than the oxygen $2p$ contribution. The lower spectrum has the polarization vector $\mathbf{e}$ almost perpendicular to the c axis. The state $^3A_2$ is now the strongest component consisting of $3d_{x^2-y^2}$ and $3d_{xy}$. The corresponding $p\pi_{x,y}$ orbitals are in the CuO_2 plane. The energy separation of the nearly polarized Cu $L\alpha$ lines from the Fermi level is also shown.

Recently, Eskes and Sawatzky have performed an Anderson impurity model calculation for the CuO_2 plane.[9] In this model the Cu $3d$ band is assumed to be a localized state whereas the O $2p$ band possesses a strong dispersion. The local symmetry was D_{4h} in square planar coordination. They showed that the doped holes can be expressed in terms of local singlets $^1A_1$ largely in the $d^9\underline{L}$ configuration for the charge transfer high-T_c oxides. The feature at about 1.4 eV below the Fermi level in Fig. 1, when $\sim c \perp \mathbf{e}$ is a good candidate for singlets $^1A_1$ in the CuO_2 plane. It should be noted that the oxygen character is dominating for this state instead of the Cu $3d$, which further supports the above assignment. In practice, the $^3B_1$ state contains a hole both in p_z and $p_{x,y}$ symmetries. This state has two main features at about 6.0 eV and 2.5 eV below the Fermi level in which the latter one is more intense.[9] The O $K\alpha$ spectrum in Fig. 1 shows a clear shoulder at about 6.0 eV when $\sim c \| \mathbf{e}$. Indeed, triplets $^3B_1$ should be expected for $c \| \mathbf{e}$.[19] Furthermore, the small energy shift (~ 0.4 eV) of the main peak might be due to the stronger 2.5-eV component of triplets $^3B_1$. This would explain the energy difference of the O $K\alpha$ spectra, because the 2.5-eV component shifts the peak energy closer to the Fermi surface when $c \| \mathbf{e}$. It seems that there is a good overall agreement between the polarized O $K\alpha$ spectrum and the calculation.

In the case of the Cu $L\alpha$ spectrum the situation differs from the previous one. Because of the core ionization the valence electron moves from the ligand atom to the Cu atom for charge transfer oxides such as $Bi_2SrCa_2Cu_2O_8$. That is why the dominating transition should be Cu $2\underline{p}d^{10}\underline{L} \rightarrow d^9\underline{L}$ for the Cu $L\alpha$ line. If we compare the energy position of the main peak with that of the O $K\alpha$ spectrum it can be observed that the energy distance from the Fermi level is larger for the Cu $L\alpha$ line. This is in agreement with the fact that the XPS valence band possesses a slightly larger binding energy than the corresponding UPS spectrum.[15,20] In the case of the XPS valence-band spectrum the d character of the photoionization cross section increases at the expense of the O $2p$ states when the energy of the ionizing radiation will be larger. Furthermore, the polarized Cu $L\alpha$ spectra in Fig. 2 are peaked, which suggests that the Cu $3d$-$2p$ hybridization is not so strong for the copper line. It is therefore tempting to assume that when the polarization vector $\mathbf{e}$ is nearly parallel to the c axis ($\sim \mathbf{e} \| c$) then the largest contribution to the Cu $L\alpha$ spectrum comes from the ^3E symmetry whereas the component $^3A_2$ would dominate in the case of the situation when the polarization vector $\mathbf{e}$ is almost perpendicular to the c vector ($\sim \mathbf{e} \perp c$). This is also in accordance with the recent theoretical estimates based on the Anderson impurity model which were made for the La_2CuO_4 compound.[21] A considerable energy shift was calculated between these two symmetries, the state ^3E possessing a larger binding energy than the state $^3A_2$.[21] The trend is therefore the same as in Fig. 2 for the Bi-Sr-Ca-Cu-O compound. This indicates that the main features of the polarized Cu $L\alpha$ spectra could be largely explained in terms of the Anderson impurity model as well. It seems that the d character is dominating for the $d^9\underline{L}$ configuration in the case of the Cu $L\alpha$ final state whereas the oxygen $2p$ states are more pronounced as far as the O $K\alpha$ spectrum is concerned which would be expected.

Finally, let us consider the O $K\alpha$ spectra in terms of the one-electron approximation. It is evident that in the case of the $Bi_2Sr_2CaCu_2O_8$ compound there exist three different oxygen layers consisting of Cu-O1, Sr-O2, and Bi-O3 planes:[22,23] Provided the calculated O $2p$ densities of states by Krakauer and Pickett[24] are shifted about 1 eV to higher binding energy[15] a good overall agreement between theory and experiment is achieved as far as the energy position of the three essential features of the polarized O $K\alpha$ spectra in Fig. 1 is concerned. The shoulder closest to the Fermi level when the polarization vector e is nearly perpendicular to the c axis $(\sim \mathbf{e} \perp c)$ coincides very well with the main structure of the O $2p$ states calculated in the Cu-O(1) plane. This supports the assumption that the 1.4 eV feature in Fig. 1 is due to local singlets $^1A_1$ in the CuO_2 plane. Furthermore, the O $2p$ band of the Sr-O 2 plane possesses two essential features. The stronger one has a slightly smaller binding energy than the main peak of the O $K\alpha$ spectrum whereas the structure with the higher binding energy agrees well with the 6.0- eV shoulder ($^3B_1$) in Fig. 1 when the polarization vector $\mathbf{e}$ is almost parallel to the c axis $(\sim \mathbf{e} \| c)$. This suggests that the p_z component of the $^3B_1$ symmetry would be in the Sr-O plane rather than in the CuO_2 plane. On the basis of the band calculations[23,24] one could also expect that the oxygen in the Bi-O plane would to some extent affect the main feature of the O $K\alpha$ spectrum.

In conclusion we can say that our experimental results for the Bi-Sr-Ca-Cu-O compound are consistent with the assumption that the first ionization state would correspond to local singlets $^1A_1$ in the CuO_2 plane. Furthermore, some features in the O $K\alpha$ spectrum could be assigned to local triplets $^3B_1$ which would indicate that the Sr-O plane gives a contribution to the spectrum as well. The polarization dependence of the Cu $L\alpha$ spectra shows that there might be a clear energy splitting between the $3d_{xy}$ and the $3d_{xz}$, $3d_{yz}$ states of copper.

ACKNOWLEDGMENT

We are grateful to Dr. Staffan Bergwall for providing the samples.

---

[1] E. Barnole, J.-M. Mariot, C. F. Hague, C. Michel, and B. Raveau, Phys. Rev. B **41**, 4262 (1990).

[2] D. R. Mueller, D. E. Ederer, J.-E. Rubensson, R. Shuker, J. Wallace, C. H-Zhang, J. Jai, T. A. Callcott, Ring-Yi Dang, L. E. Toth, R. Rayne, and M. Osofsky, Phys. Scr. **41**, 979 (1990).

[3] V. R. Galakhov, S. M. Butorin, L. D. Finkelstein, E. Z. Kurmaev, Yu. M. Yarmoshenko, V. A. Trofimova, and V. L. Kozhevnikov, Physica C **160**, 267 (1989).

[4] B. O. Wells, P. A. P. Lindberg, Z.-X. Shen, D. S. Dessau, W. E. Spicer, I. Lindau, D. B. Mitzi, and A. Kapitulnik, Phys. Rev. B **40**, 5259 (1989).

[5] T. Takahashi, H. Matsuyama, H. Katayama-Yoshida, Y. Okabe, S. Hosoya, K. Saki, M. Sato, and H. Inouchi, Nature (London) **334**, 691 (1988).

[6] C. G. Olson, R. Liu, D. W. Lynch, B. W. Veal, Y. C. Chang, P. Z. Jiang, J. Z. Liu, A. P. Paulikas, A. J. Arko, and R. S. List, Physica C **162- 164**, 1697 (1989).

[7] H. Eisaki, H. Takagi, S. Ushida, H. Matsubara, S. Suga, M. Nakamura, K. Yamaguchi, A. Misu, H. Namatame, and A. Fujimori, Phys. Rev. B **41**, 7188 (1990).

[8] P. Marksteiner, S. Massidda, Jaejun Yu, A. I. Freeman, and J. Redinger, Phys. Rev. B **38**, 5098 (1988).

[9] H. Eskes and G. A. Sawatzky, Phys. Rev. Lett. **61**, 1415 (1988).

[10] K. Easterling, Guo Shi-ju, Dou S. X., and Liu H. K. (unpublished).

[11] G. Dräger, F. Werfel, and J. A. Leiro, Phys. Rev. B **41**, 4050 (1990).

[12] Z.-X. Shen, P. A. P. Lindberg, B. O. Wells, D. B. Mitzi, I. Lindau, W. E. Spicer, and A. Kapitulnik, Phys. Rev. B **38**, 11 820 (1988).

[13] N. Nücker, H. Romberg, X. X. Xi, J. Fink, B. Gegenheimer, and Z. X. Zhao, Phys. Rev. B **39**, 6619 (1989).

[14] A Fujimori, Phys. Rev. B **39**, 793 (1989).

[15] F. U. Hillebrecht, J. Fraxedas, L. Ley, H. J. Trodahl, J. Zaanen, W. Braun, M. Mast, H. Petersen, M. Schaible, L. C. Bourne, P. Pinsukanjana, and A. Zettl, Phys. Rev. B **39**, 236 (1989).

[16] S. Tanaka, K. Okada, and A. Kotani, J. Phys. Soc. Jpn. **58**, 813 (1989).

[17] K. Okada and A. Kotani, J. Phys. Soc. Jpn. **58**, 1095 (1989).

[18] A. K. McMahan, R. M. Martin, and S. Satpathy, Phys. Rev. B **38**, 6650 (1988).

[19] O. Gunnarsson *et al.*, Phys. Rev. B **41**, 4811 (1990).

[20] A. Fujimori, S. Takekawa, E. Takayama-Muromachi, Y. Uchida, A. Ono, T. Takahashi, Y. Okabe, and H. Katayama-Yoshida, Phys. Rev. B **39**, 2255 (1989).

[21] A. Kotani, K. Okada, S. Tanaka, and Y. Seino, Phys. Scr. **41**, 569 (1990).

[22] M. S. Hybertsen and L. F. Mattheiss, Phys. Rev. Lett. **60**, 1661 (1988).

[23] S. Massidda, Jaejun Yu, and A. J. Freeman, Physica C **152**, 251 (1988).

[24] H. Krakauer and W. Pickett, Phys. Rev. Lett. **60**, 1665 (1988).