

## ***Ab-initio* Electronic Structure Calculations of Layered Cuprates with Multiple Fluorite Blocks(Pb-32n2 Phase)**

Masao Arai and Sumio Ikegawa\*

National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305-0044, Japan

Fax: 81-298-52-7449, e-mail: arai@nirim.go.jp

\*Advanced Materials &amp; Devices Lab., Corporate R &amp; D Center,

Toshiba Corp., Kawasaki 212-8582, Japan

Fax: 81-44-520-1801, e-mail: sumio.ikegawa@toshiba.co.jp

Electronic structures of  $(\text{Pb}_2\text{Cu})\text{Sr}_2\text{Eu}_x\text{Ce}_{n-x}\text{Cu}_2\text{O}_{2n+6}$  ( $n = 1, 2, 3$ ) have been studied by using *ab-initio* method. The Fermi velocities calculated from the energy bands indicate that the coupling between two  $\text{CuO}_2$  planes are greatly suppressed with the increase of the thickness of fluorite blocks. For  $n = 3$ , it is also shown that the substitution of Ce by Eu shifts the oxygen p-bands in the fluorite blocks to higher energy region. It may cause the oxygen atoms unstable and increase the oxygen vacancies in the fluorite blocks. This may be the origin of experimentally observed lower carrier density than the value expected from Eu concentration. At  $x = 2$ , our calculation suggests the existence of the hole traps in the fluorite blocks.

Keyword: superconductivity, layered cuprate, electronic structure

### 1. INTRODUCTION

Development of the molecular beam epitaxy (MBE) technology enables the synthesis of various materials by controlling the stacking of atomic layers. One of the authors has reported the synthesis of  $(\text{Pb}_2\text{Cu})\text{Sr}_2\text{Ln}_x\text{Ce}_{n-x}\text{Cu}_2\text{O}_{2n+6}$  ( $n > 2$ , Ln = rare earth elements)<sup>1,2</sup> which is called Pb-32n2. The phases with  $n > 4$  are essentially impossible to obtain in phase pure form with other techniques, since all these phases are energetically very close. As  $n$  increases, the fluorite blocks between the adjacent  $\text{CuO}_2$  layer become thick. Therefore, it may be possible to control the interlayer coupling between adjacent  $\text{CuO}_2$  layers.

In the present paper, we report the electronic structures of Pb-32n2 ( $n = 1, 2, 3$ ). Their anisotropies are quantitatively discussed from the calculated Fermi velocities.

### 2. CALCULATIONS

The crystal structure of Pb-3212 was determined by X-ray and neutron diffractions<sup>3</sup>. It has orthorhombic unit cell with space group symmetry Cmmm. The orthorhombic distortion is accompanied by the disordered displacements of oxygen atoms in the PbO layer. Since such disorder can not be included in the standard electronic structure calculations, we approximate the crystal structure by tetragonal

TABLE I: Internal atomic position parameters (in units of lattice constants  $a = 3.820\text{\AA}$ ,  $c = 15.726\text{\AA}$ ) for  $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$  (space group P4/mmm).

Atom Site	$x$	$y$	$z$	
Pb	$2g$	0	0	0.3883
Sr	$2h$	$\frac{1}{4}$	$\frac{1}{2}$	0.2207
Y	$1c$	$\frac{1}{2}$	$\frac{1}{2}$	0
Cu(1)	$1d$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
Cu(2)	$2g$	0	0	0.1062
O(1)	$2g$	0	0	0.2514
O(2)	$4i$	$\frac{1}{2}$	0	0.0918
O(3)	$2h$	$\frac{1}{2}$	$\frac{1}{2}$	0.3849

unit cell with space group symmetry P4/mmm following the previous work by Mattheiss *et al*<sup>4</sup>. The c-axis coordinates of atomic positions are adjusted by the data in Ref. 3 and is shown in Table I. Compared with the atomic position used by previous calculation<sup>4</sup>, the position of apical oxygen is shifted. As shown later, this shift increases the anisotropy as suggested in Ref. 4.

The crystal structure of Pb-3222 was determined as orthorhombic by neutron diffraction<sup>5</sup>. We ignored small orthorhombic distortion and approximated the structure by body centered tetragonal (bct) unit cell with space group symmetry I4/mmm. The atomic positions are shown in Table II.

TABLE II: Internal atomic position parameters (in units of lattice constants  $a = 3.865\text{\AA}$ ,  $c = 37.0107\text{\AA}$ ) for the calculation of Pb-3222 phase (space group I4/mmm).

Atom	Site	$x$	$y$	$z$
Pb	4e	0	0	0.0475
Sr	4e	0	0	0.3816
Ce/Ln	4e	0	0	0.2854
Cu(1)	4e	0	0	0.1665
Cu(2)	2b	0	0	$\frac{1}{2}$
O(1)	8g	0	$\frac{1}{2}$	0.1717
O(2)	4e	0	0	0.4509
O(3)	4e	0	0	0.1050
O(4)	4d	0	$\frac{1}{2}$	$\frac{1}{4}$

The precise atomic positions of Pb-32n2 compound with  $n > 2$  have not been reported. We guessed them from observed lattice constants and crystal structures of related compounds. We created the prototype of the structure model by replacing Y layers in Pb-3212 with fluorite blocks. The atomic layer spacings of the fluorite blocks are taken from those of double fluorite blocks in (Pb,Cu)-1232 determined by Wada *et al*<sup>6</sup>. The resultant c-axis lattice constant is still  $0.2\text{\AA}$  smaller than the observed value. We modified atomic positions as follows. First, the (Pb,Cu)-1232 in Ref. 6 uses Ho as lanthanide element while the Pb-32n2 phase synthesized in Ref. 2 uses Eu. The atomic layer spacing is adjusted to compensate the difference of ionic radii between Ho and Eu. Namely, we enlarged the distance between O(4) layer and Ce(1)/Ln(1) and that between O(3) and Ce(1)/Ln(1) about  $\frac{1}{\sqrt{2}}$  times ionic radius difference. Next, the distance between Pb and Cu(1) are enlarged to adjust the residual difference with observed c-axis lattice constants since the excess oxygens usually extend the spacing. The obtained atomic positions for Pb-3232 are summarized in Table III.

We calculated the bulk electronic structures of Pb-32n2 within the local density approximation,<sup>7</sup> using the WIEN97 package<sup>8</sup> which is based on the full-potential linear augmented plane wave method. The self-consistent calculations were performed by using 15, 11, and 21 k-points in an irreducible Brillouin zone for Pb-3212, Pb-3222, and Pb-3232, respectively.

Quantitative estimates of anisotropy have been performed by calculating the Fermi velocities. In such a calculation, we increased the k-points and obtained the energy eigenvalues on finer mesh points. The energy bands were fitted by the linear combination of symmetrized and periodic function in the Brillouin

TABLE III: Internal atomic position parameters (in units of lattice constants  $a = 3.845\text{\AA}$ ,  $c = 21.465\text{\AA}$ ) for the calculation of Pb-3232 phase (space group P4/mmm).

Atom	Site	$x$	$y$	$z$
Ce(2)	1a	0	0	0
O(4)	4i	$\frac{1}{2}$	0	0.06329
Ce(1)/Ln(1)	2h	$\frac{1}{2}$	$\frac{1}{2}$	0.12413
O(3)	4i	$\frac{1}{2}$	0	0.19781
Cu(2)	2g	0	0	0.20836
Sr	2h	$\frac{1}{2}$	$\frac{1}{2}$	0.29229
O(2)	2g	0	0	0.31479
O(1)	2h	$\frac{1}{2}$	$\frac{1}{2}$	0.41264
Pb	2g	0	0	0.41514
Cu(1)	1d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$

Zone as described in Ref. 9 and 10. Then, the average of Fermi velocity was calculated.

The detailed calculations were performed for the Pb-3212 and Pb-3232 since they have same symmetry and, thus, suitable to compare the difference of electronic structures.

### 3. RESULTS

#### 3.1 Pb-3212

The energy bands of Pb-3212 are presented in Fig. 1 with the Fermi energy ( $E_F$ ) chosen at 0. The circles indicate the calculated eigen energies and their sizes are proportional to the weights of wavefunctions projected to the Cu(2)  $d_{x^2-y^2}$  orbitals. As coinciding with other high-Tc superconductors, the two bands crossing  $E_F$  are anti-bonding states of Cu(2)  $d_{x^2-y^2}$  and O(2)  $p_x$  and  $p_y$  orbitals. The most significant difference with the previous calculation<sup>4</sup> is that these  $\text{CuO}_2$  derived bands are less dispersive along  $\Gamma$ -Z and M-R, indicating more anisotropic electronic structures.

#### 3.2 Pb-3232

We calculated the electronic structures of Pb-3232 with two different concentrations of Eu atoms. The first model (model I) does not contain any Eu atoms. In the second model (model II), all Ce atoms at the nearest layers of  $\text{CuO}_2$  planes are substituted by Eu atoms. Assuming the valence of Ce and Eu as +4 and +3, The Cu atoms in  $\text{CuO}_2$  planes have the valence of +1.5 and +2.5 for model I and II, respectively. Namely, the model I is considered to be doped by 0.5 electrons per copper atom and model II to be doped by 0.5 holes.

We show the energy bands of Pb-3232 (model II) in Fig. 2 with the Fermi energy ( $E_F$ ) chosen at 0. Like the Pb-3212, the dominant bands which cross the  $E_F$  is anti-bonding

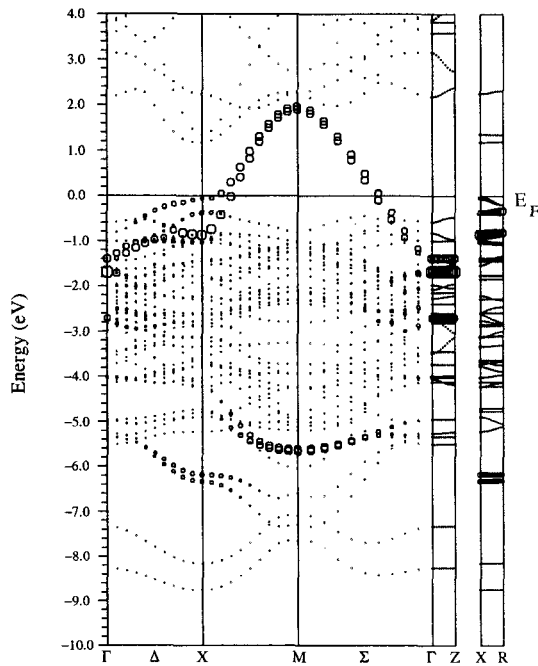


FIG. 1: Energy bands of Pb-3212

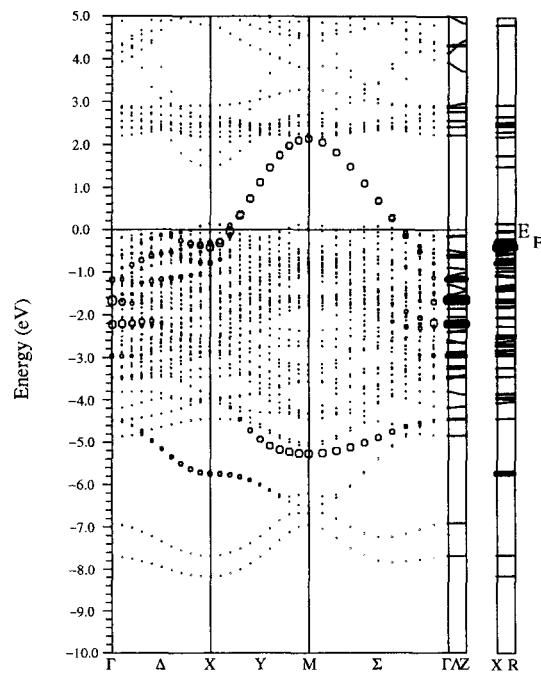


FIG. 2: Energy bands of Pb-3232 (model II)

states of Cu(2)  $d_{x^2-y^2}$  and O(3)  $p_x$  and  $p_y$  orbitals. In Fig. 3 and 4, we show total and partial densities of states (DOS) of model I and II, respectively. The most significant difference between two models is the partial DOS of oxygen in fluorite blocks. The substitution of Ce by Eu shifts them to higher energy region. This behavior seems to be natural since part of the surrounding  $Ce^{4+}$  ions are substituted by  $Eu^{3+}$  and electrostatic potential for electrons increases at oxygen atoms. It may cause the oxygen atoms unstable and increase the oxygen vacancies in the fluorite blocks.

Even if the oxygen vacancies are absent, the oxygen 2p orbitals in fluorite blocks may affect the transport properties at high concentration of Eu (model II) since they slightly contribute to the density of states at Fermi energy. As a consequence, a portion of doped holes are not released to the  $CuO_2$  planes but are trapped in the fluorite blocks. This may be one of the reason why the experimentally observed carrier density is lower than the value expected from the Eu concentration<sup>1</sup>. It should be noted, however, that experimentally synthesized compounds are intermediate of model I and II. Namely, about 70% of Ce atoms nearest to  $CuO_2$  planes are substituted by Eu atoms. At present, it is not clear whether the oxygen 2p orbitals in fluorite blocks affect the electronic structure at Fermi energy for such experimental Eu concentration.

TABLE IV: Fermi velocities of Pb-32n2 ( $n = 1, 2, 3$ ) in units of  $10^8$  cm/s. Those of  $YBa_2Cu_3O_7$  and  $Nd_2CuO_4$  are calculated using the same programs and presented for comparison.

Compounds	$v_{\parallel}$	$v_{\perp}$	$v_{\perp}/v_{\parallel}$
Pb-3212	0.39	0.05	0.13
Pb-3222	0.37	0.016	0.043
Pb-3232	0.35	0.013	0.031
$YBa_2Cu_3O_7$	0.21	0.05	0.22
$Nd_2CuO_4$	0.38	0.02	0.04

### 3.3 Anisotropy of Pb-32n2

From the calculated energy bands, we estimated average Fermi velocities which are classified to those parallel to the  $CuO_2$  plane ( $v_{\parallel}$ ) and perpendicular to the plane ( $v_{\perp}$ ). The ratio  $v_{\perp}/v_{\parallel}$  is a measure of anisotropy of the present compounds. As shown in Table IV, the anisotropy of Pb-3212 is comparable to that of  $YBa_2Cu_3O_7$ . As the thickness of fluorite blocks increases, the anisotropy is enhanced systematically. These results show that the thickness of fluorite blocks has strong influence of the anisotropy of Pb-32n2 compounds.

## 4. CONCLUSION

In this paper, we presented the electronic structures of series of compounds Pb-32n2, in which fluorite blocks with different thicknesses are inserted between two adjacent  $CuO_2$  planes. For Pb-3232, it is found that the substitution of Ce by Eu shifts the states derived

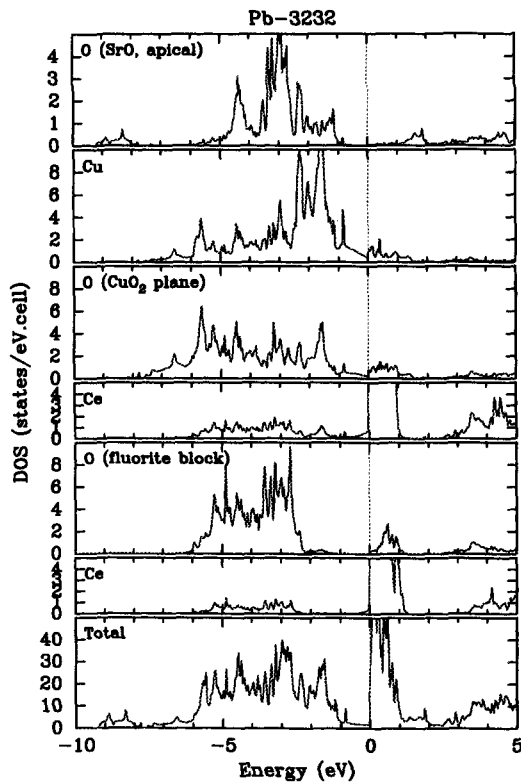


FIG. 3: Total and partial densities of states (DOS) of Pb-3232(model I)

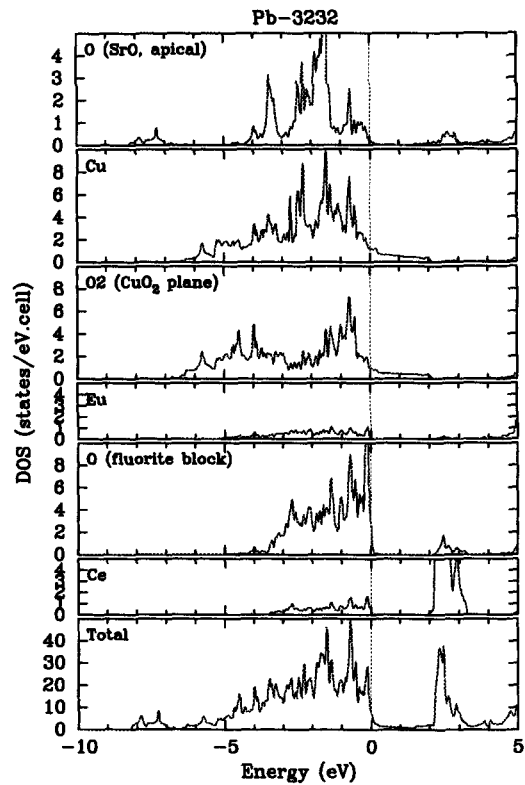


FIG. 4: Total and partial densities of states (DOS) of Pb-3232(model II)

from the oxygen p-orbitals in fluorite blocks to higher energy region. It may cause the oxygen atoms unstable and increase the oxygen vacancies in the fluorite blocks. This may be the origin of lower carrier density than the value expected from Eu concentration<sup>1</sup>. At high concentration of Eu, our calculation suggests the existence of the hole traps in the fluorite blocks, which also decrease the carrier density.

From the calculated Fermi velocities, we found that the anisotropy increases systematically with the thicknesses. This suggests that these materials are suitable to design artificial lattice with desired anisotropy.

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