Electronic structure of the superconducting layered perovskite niobate

Izumi Hase*
Electrotechnical Laboratory, Tsukuba, 305, Japan

Yoshikazu Nishihara†
Electrotechnical Laboratory, Tsukuba, 305, Japan
and Faculty of Science, Ibaraki University, Mito, 310, Japan
(Received 21 April 1998)

The electronic energy-band structure for $RbLaNb_2O_7$, which is closely related to the layered perovskite niobate superconducting $KCa_2Nb_3O_{10}$ and metallic $KLaNb_2O_7$ with Li intercalation, has been calculated by using the scalar-relativistic full-potential linearized augmented-plane-wave method within the local-density approximation. The result of the calculation shows that this compound is a band insulator with a small gap, and its conduction band is a typical two-dimensional one and the valence band is rather three dimensional. We can conclude that the layered perovskite niobate $KCa_2Nb_3O_{10}$ is a band insulator that can be superconducting with electron doping, and have the highly two-dimensional electronic structure. [S0163-1829(98)51228-3]

After the great discovery of superconductivity in $La_xBa_{2-x}CuO_4$ (LBCO),[1] many high-T_c superconducting cuprates have been synthesized. Their most common feature is the presence of CuO_2 layers, however, it is still not clear why only the CuO_2 plane can be superconducting and the other MO_2 plane (M=transition metal element) cannot. The recent discovery of superconductivity in Sr_2RuO_4, which is isostructural with LBCO,[2] shows us a new frontier in the sense that the presence of copper is not a necessary condition for superconductivity in this type of structure. Very recently, triple-layered perovskite $KCa_2Nb_3O_{10}$ has been found to be superconducting by intercalating Li ($T_c \sim 5$ K).[3,4] Double-layered perovskite $KLaNb_2O_7$ has also been found to be metallic by intercalating Li, though it shows no superconducting signal down to 0.5 K.[4] These compounds are good insulators without intercalation.

In order to investigate this new type of superconducting oxides, we have performed the *ab initio* full-potential linearized augmented-plane-wave (FLAPW) band-structure calculation for $RbLaNb_2O_7$, which has the simplest crystal structure among the series of $ALaNb_2O_7$ (A=Li, Na, K, Rb, Cs, NH$_4$).[5] Our results show that there is large hybridization between the Nb $4d$ states and the O $2p$ states in $RbLaNb_2O_7$, as well as in the case of La_2CuO_4 and Sr_2RuO_4. We also show that $KCa_2Nb_3O_{10}$+Li is a superconductor whose mother material is a two-dimensional band insulator.

We have carried out this calculation by using the computer code KANSAI-94. For the one electron exchange-correlation potential in the local-density approximation (LDA) scheme, we adopted the prescription of Gunnarson and Lundqvist.[6] The lattice constants we used are a =3.885 Å and c=10.989 Å, taken by the experimental data.[5] The space group is $P4/mmm$. The schematic crystal structure and the definition of the oxygen site indices are shown in Fig. 1. $KLaNb_2O_7$ has a similar crystal structure but has an eight times larger unit cell. We took the muffin-tin (MT) sphere radii of each atom as $0.40a$ for Rb and La, $0.278a$ for Nb, and $0.198a$ for O. At each self-consistent

step, the core states are reconstructed from the potential. The calculation of these core states and the valence states are carried out by the scalar-relativistic scheme.[7] Inside the MT spheres, the wave functions were expanded in terms of spherical harmonics with the angular momentum $l \leqslant 7$. For the charge densities and potential, the angular momentum expansion was used up to $l=4$. The basis functions with the wave vector $|\mathbf{k}+\mathbf{G}| < K_{max} = 4.50(2\pi/a)$, where $\mathbf{k}$ is a wave vector in the Brillouin zone and $\mathbf{G}$ is a reciprocal-lattice vector used resulting in about 1100 basis LAPW's. The self-consistent potentials are calculated at 12 points in the 1/16 irreducible Brillouin zone (IBZ). Final eigenstates are obtained at 75 points in the same IBZ. The density of states (DOS) has been deduced from the final eigenstates by using the ordinary tetrahedron method.

Since the internal parameters $z[O(2)]$, $z[O(3)]$, and $z[Nb]$ have not yet been experimentally determined, we first assumed that the NbO_6 octahedra are not distorted. Then we allowed only the elongation of NbO_6 octahedra along the c
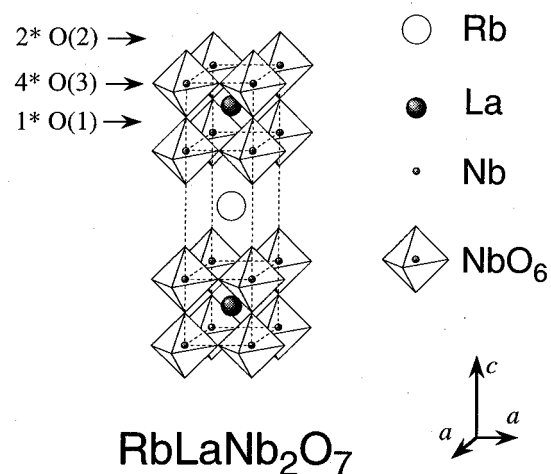

FIG. 1. Schematic of the crystal structure of $RbLaNb_2O_7$ used in the calculation. The cubes indicate NbO_6 octahedra.
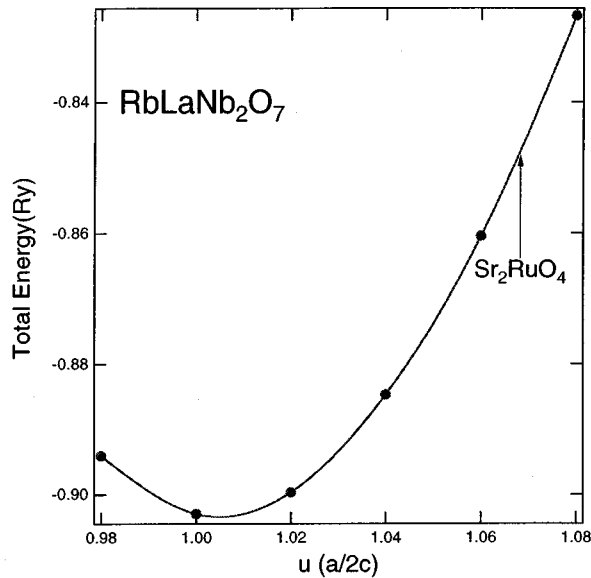
FIG. 2. Total energy with changing the internal parameter u. The filled circles are the points of which the total energy was calculated, and the line is the simple cubic spline fitting curve. The origin of the total energy is shifted by $+39249$ Ry. The lattice constants a and c are fixed during this calculation.

axis, from the similarity to the structure of Sr_2RuO_4. Under this assumption, the only one independent internal parameter is $u = r[O(1) - Nb] = z[Nb] = z[O(3)]$, and now $z[O(2)]$ is determined as $2u$. In the case where NbO_6 octahedra are not elongated, $u = 1.00(a/2c)$. To determine u, we have estimated the total energy as the function u by calculating the electronic states for each u (Fig. 2). We have obtained the value of $u = 1.005(a/2c)$ for minimizing the total energy as the function of u. This means that the NbO_6 octahedra are almost not elongated statically in $RbLaNb_2O_7$ in contrast to the case of Sr_2RuO_4 [$u = 1.068(a/2c)$, shown in Fig. 2]. Hereafter we show the calculational result only for the value of $u = 1.00(a/2c)$.

Figure 3 is the energy dispersion curve for $RbLaNb_2O_7$

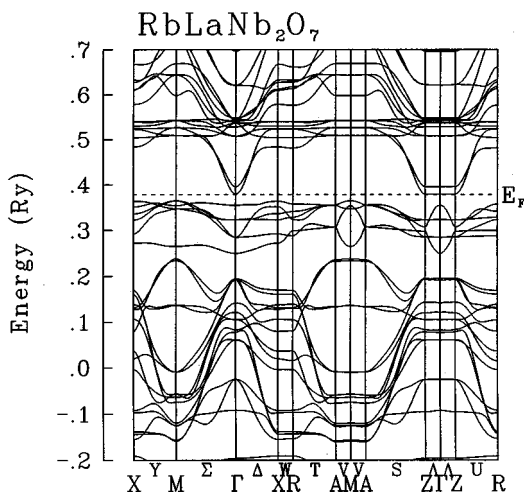FIG. 3. Energy-band structure of $RbLaNb_2O_7$ along some symmetry axes. The Fermi energy is denoted by E_F. Calculated Nb $4p$, La $5p$, Rb $4p$, and O $2s$ bands are not shown for clarity.

along the principal symmetry axes in the Brillouin zone. We obtained a small gap 0.20 eV in this calculation and the ground state is insulating. The Fermi level is fixed at the bottom of the conduction band for convenience. We have also obtained the insulating ground state when the internal parameter u is changed up to $u = 1.06(a/2c)$, though the semiconducting gap collapses when $u = 1.08(a/2c)$. Since the formal valence of Nb is $5+$, the formal number of $4d$ electron of Nb within the ionic model is zero. In this sense $RbLaNb_2O_7$ is a band insulator, while the La_2CuO_4 is known to be a charge-transfer insulator, though the LDA calculations predict La_2CuO_4 as a metal.[8,9] It also shows a sharp contrast to the case of Sr_2RuO_4, which is a compensated metal without doping.[10–12] The conduction bands mainly correspond to Nb $4d$ bands, and the valence bands are mainly O $2p$ bands. The very narrow bands around 0.52 Ry are the La $4f$ bands. Likewise the band structure of La_2CuO_4 and Sr_2RuO_4, which has the single MO_2 layer ($M =$ Cu, Ru), has a conduction band that is highly two dimensional.[8–12] To see this, we can compare the energy dispersion curves of the Σ axis and S axis, which are parallel and within the different $k_z =$ const plane. The dispersion of conduction bands along these two axes are almost the same and this means the lightly electron-doped system will have electron Fermi surfaces that are very two dimensional. On the other hand, the top of the valence band is not as two dimensional, easily seen by the different dispersion curves of Σ and S axes. Therefore we can see that the Fermi surfaces of this system can be either two dimensional or three dimensional, depending on the different carrier doping. This behavior is also seen in the electronic structure of La_2CuO_4.[9] Experimentally, the intercalation of Li may supply electrons to the system, thus the metallic $RbLaNb_2O_7 +$ Li is expected to have highly two-dimensional Fermi surfaces, e.g., highly anisotropic electronic conductivity.

Figures 4 and 5 are the DOS curves of $RbLaNb_2O_7$. The ''in-plane'' O(3) $2p$ states form broad bands by hybridizing the Nb $4d$ bands at the range from -0.2 to 0.25 Ry, mainly. On the other hand, the ''out-of-plane'' O(1) and O(2) $2p$ states form relatively narrow bands near the Fermi level. Since these oxygens have the nearest-neighbor Nb along the c axis, these states form the bands with relatively wide dispersion along the c axis. For the bottom of the conduction band, the mainly contributing orbitals are Nb $4d_{xy}$ states with t_{2g} symmetry, strongly hybridized with O(3) $2p$ π orbitals. These orbitals form widely dispersive bands within the ab plane.

A good insight into electronic structure can be achieved by a crude fitting of the bonding and antibonding bands made of Nb $4d\varepsilon$ and O $2p\pi$ orbitals by the nearest-neighbor tight-binding (TB) model. It is sufficient for reproducing the overall dispersion of the lower part of the conduction band and the ''in-plane'' part of the valence band to consider only the NbO_2 layer and include two adjustive parameters: the orbital energy difference $E(d\varepsilon) - E[O(3) - p\pi] = 1.9$ eV, and the transfer integral $pd\pi[d\varepsilon, O(3) - p\pi] = 1.6$ eV. This simple model makes a large gap 1.9 eV ($= 0.14$ Ry) between the conduction band and the valence band, and the further inclusion of ''out-of-plane'' O(1) and O(2) orbitals will reproduce the narrow bands within this gap, found in the FLAPW calculation. The value of transfer integral $pd\pi$
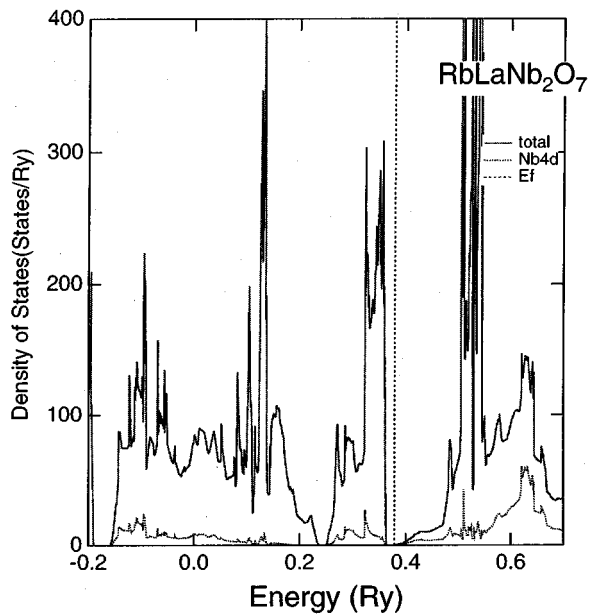
FIG. 4. Calculated density of states for $RbLaNb_2O_7$. Shown are the total density of states (solid line), and partial density of states for Nb d states (dotted line). Note that the ordinate is per one $RbLaNb_2O_7$.
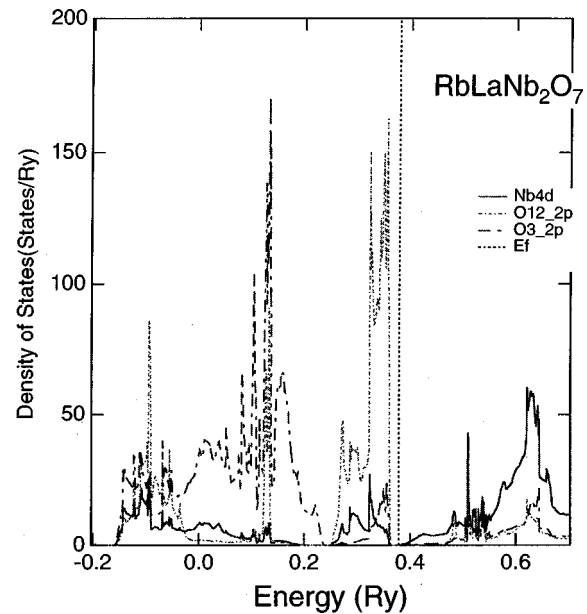

FIG. 5. Calculated density of states for $RbLaNb_2O_7$. Partial density of states of Nb d states (solid line), O(1)+O(2) p states (dotted line), and O(3) p states (one-dot-dashed line). Note that the ordinate is per one $RbLaNb_2O_7$.

=1.6 eV is comparable to the case of Sr_2RuO_4 ($pd\pi$ =1.5 eV),[10] and larger than the case of La_2CuO_4 ($pd\sigma$ $= -1.85$ eV, $pd\pi = 0.75$ eV).[8,13] It is also larger than the case of the three-dimensional band insulator $SrTiO_3$ ($pd\pi$ =1.0 eV).[14] Thus we can say that the Nb $4d$ orbitals are more delocalized than Cu or Ti $3d$ orbitals, as expected from the extending nature of its atomic wave function. The inclusion of the double-layer nature and the transfer integrals such as $pp\sigma$ and $pp\pi$ between the O $2p$ states are necessary for a more accurate description of the conduction and valence bands. However, it is quite hopeful that a simple single-layer NbO_2 TB model can describe the conduction bands obtained by the FLAPW calculation for the double-layer $RbLaNb_2O_7$. Thus we can safely say that the triple-layered perovskite $KCa_2Nb_3O_{10}$ has almost the same electronic structure, at least the bottom of the conduction band that is relevant to the superconductivity.

In summary, we have performed the *ab initio* band-structure calculation of $RbLaNb_2O_7$, which has the layered

perovskite structure and is closely related the new superconducting niobate $KCa_2Nb_3O_{10}$+Li. In this calculation we have found that the semiconducting ground state and the bottom of conduction bands that are relevant to the superconductivity are highly two dimensional, while the tops of the valence bands have the three-dimensional character. This type of electronic structure is also seen in La_2CuO_4, while the symmetry of orbitals are different. We insist that this system is a band insulator that can be superconducting with electron doping, and have the highly two-dimensional electronic structure.

Note added in proof. It has also been found that the triple-layered perovskite $RbCa_2Nb_3O10$ is to be superconducting with intercalation.[15]

*Electronic address: hase@etl.go.jp

†Electronic address: ynishi@mito.ipc.ibaraki.ac.jp

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, Nature (London) **372**, 532 (1994).

[3] Y. Takano, H. Taketomi, H. Tsurumi, T. Yamadaya, and N. Môri, Physica B **237-238**, 68 (1997).

[4] Y. Takano, S. Takayanagi, S. Ogawa, T. Yamadaya, and N. Môri, Solid State Commun. **103**, 215 (1997).

[5] J. Gopalakrishnan, V. Bhat, and B. Raveau, Mater. Res. Bull. **22**, 413 (1987).

[6] O. Gunnarson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[7] D. D. Koelling and B. N. Harmon, J. Phys. C **9**, 3107 (1977).

[8] L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[9] K. Takegahara, H. Harima, and A. Yanase, Jpn. J. Appl. Phys., Part 2 **26**, L352 (1987).

[10] T. Oguchi, Phys. Rev. B **51**, 1385 (1995).

[11] D. J. Singh, Phys. Rev. B **52**, 1358 (1995).

[12] I. Hase and Y. Nishihara, J. Phys. Soc. Jpn. **65**, 3957 (1996).

[13] A. K. McMahan, R. M. Martin, and S. Satpathy, Phys. Rev. B **37**, 7482 (1988).

[14] L. F. Mattheiss, Phys. Rev. B **6**, 4718 (1972).

[15] Y. Takano, Y. Kimishima, Y. Yamadaya, S. Ogawa, and N. Mori, Rev. High Press. Sci. Tech. (to be published).