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Electronic structure and Fermi surface of the superconductors LaNiBiO and LaCuBiO from first principles

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Based on first-principle full-potential linearized augmented plane wave generalized gradient approximation calculations, we have investigated electronic structure of synthesized superconductors LaMBiO, where M =Ni or Cu as examples of bismuth-containing compounds in the family of superconducting quaternary oxypnictides. The band structure, density of states, and Fermi-surface features are discussed. Our results indicate that chemical bonding inside La-O and M-Bi layers is covalent while the interlayer binding is mostly ionic. The states of M-Bi layers are found to prevail at the Fermi level. The corresponding Fermi surfaces bear a two-dimensional character thus suggesting strongly anisotropic conduction mostly via M-Bi layers. On the whole, the oxybismuthides may be described as *superconducting nonmagnetic ionic metals*.

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Since the discovery of fluorine-doped quaternary oxyarsenide $LaFeAsO_{1-x}F_x (x\sim 0.05-0.12)$ (Ref. 1) and subsequent demonstration[2] of Sr doped derivatives $La_{1-x}Sr_xFeAsO (x \sim 0.09-0.20)$ with T_C near 26 K, the family of layered pnictides has emerged as a different material platform for further exploration of high-temperature superconductivity.[3,4] Further promising result in search of related superconductors (SCs) has been attained with replacing La atoms by other rare-earth metals [Ln=Gd,[5] Ce,[6] Sm,[7] Pr, and Nd (Refs. 8 and 9)]. These materials demonstrate highest transition temperatures ($T_C\sim 41-55$ K) known except in the high-T_C cuprates. Also, similar T_C values have been achieved by replacing rare-earth atoms for thorium ($Gd_{1-x}Th_xFeAsO$) (Ref. 10) or by introducing oxygen deficiency in $LnFeAsO_{1-\delta}$ (Ln=Sm, Nd, Pr, Ce, and La).[11] Thus, oxyarsenides now represent a whole different group of layered SCs. Their characteristic features such as relatively high critical temperatures, large values of upper critical field H_{c2}, and proximity to magnetic instability are all indicative of unconventional superconductivity.[1–11] On the other hand, these oxyarsenides belong to a broader family of oxypnictides[12] with a layered two-dimensional (2D)-like tetragonal crystal structure (ZrCuSiAs type, space-group $P4/nmm$, $Z=2$). For example, a rich set of quaternary 2D oxyphosphides have been reported including LnFePO and LnRuPO (Ln=La-Nd, Sm, Gd), LnCoPO (Ln=La-Nd, Sm),[12] LnOsPO and LnZnPO,[13,14] LaNiPO,[15,16] LaMnPO,[17] UCuPO,[18] and ThCuPO.[19] It is rather interesting that with the simultaneous synthesis of Fe-containing LaFePO ($T_C=3.2-6.5$ K) (Refs. 20 and 21), the Ni-based analog LaNiPO ($T_C=3.0-4.3$ K) (Refs. 15 and 16) was discovered among quaternary oxyphosphides and later similar oxyarsenide LaNiAsO with bulk superconductivity at $T_C\sim 2.75$ K was found.[22] Further extension of the oxypnictide family was made in Ref. 23 where several oxybismuthides were obtained including Ni-containing LaNiBiO phase with T_C near 4.2 K and the Cu-based oxypnictide LaCuBiO with T_C of 6 K. The Ni(Cu)-Bi sheets in these compounds are sandwiched between La-O layers the same way as Fe-As and Ni-P sheets in LaFeAsO (Refs. 24–35) and LaNiPO,[36] respectively.

In this paper we present a systematic study of electronic properties in the Ni- and Cu-based superconducting oxybismuthides. The results are compared with electronic spectrum features in LaFeAsO and LaNiPO.

Our band-structure calculations were carried out by means of the full-potential linearized augmented plane wave method with mixed basis APW+lo implemented in the WIEN2K suite of programs.[37] The generalized gradient approximation correction to exchange-correlation potential in the PBE form[38] was used. The La($5s^25p^65d^16s^2$), O($2s^22p^4$), Ni($3d^94s^1$), Cu($3d^{10}4s^1$), and Bi($5d^{10}6s^26p^3$) are treated as valence states. The calculations were performed with full-lattice optimization including internal z_{La} and z_{Bi} coordinates. The self-consistent calculations were considered to be converged when the difference in the total energy of the crystal did not exceed 0.01 mRy as calculated at consecutive steps. The densities of states (DOSs) are obtained using a modified tetrahedron method.[39]

The calculations were performed for the nonmagnetic (NM) and magnetic states (in approximation of FM ordering). For both oxybismuthides the calculations of the magnetic states converged into NM states.

The calculated lattice parameters (Table I) are in reasonable agreement with the available experiments; some divergence between calculated and experimentally observed parameters should be attributed to oxygen nonstoichiometry in the prepared samples.[23] As can be seen, a(LaNiBiO) $>a$(LaCuBiO) whereas c(LaNiBiO)$<c$(LaCuBiO), i.e., *anisotropic deformation* of crystal structure takes place through replacement of Ni for Cu. Namely, when going from LaNiBiO to LaCuBiO, the interlayer distances (La-O)-(Ni,Cu-Bi) increase with simultaneous compression of the layers in xy planes. This mechanism can be understood using the data presented in Table I, which demonstrate that replacement of nickel (atomic radius $R^{at}=1.24$ Å) for larger Cu atom ($R^{at}=1.28$ Å) results in stretching of all chemical bonds. At the same time the angle for Cu-O-Cu bonds (64.7°) in LaCuBiO becomes smaller than the respective angle for Ni-Bi-Ni bonds (73.2°) in LaNiBiO. This change in LaCuBiO results in contraction of Cu-Bi tetrahedra (as compared to Ni-Bi tetrahedra) and in some decrease in the lattice parameter a.

Figure 1 shows the total and atomic-resolved l-projected

TABLE I. The optimized lattice parameters (a and c in Å), internal coordinates (z_{La} and z_{Bi}), and some interatomic distances (d in Å) for tetragonal oxybismuthides LaNiBiO and LaCuBiO.

Phase/parameter	a	c	z_{La}	z_{Bi}
LaNiBiO	4.3138	8.9619	0.1265	0.6573
LaCuBiO	4.1151	10.3850	0.1168	0.6711
Phase/parameter	d(La-Bi)	d(Ni,Cu-Bi)	d(Bi-Bi)	d(La-Ni)
LaNiBiO	3.61	2.57	4.13	3.94
LaCuBiO	3.65	2.72	4.59	4.48

DOSs in LaNiBiO and LaCuBiO as calculated for equilibrium geometries. The valence bands (VBs) include three subbands A, B, and C and occupy energy intervals from Fermi level down to −5.4 and −5.2 eV in LaNiBiO and LaCuBiO, respectively.

The subband A in LaNiBiO is formed predominantly from O 2p states and it ranges from −5.4 to −3 eV. The band B within −3 and −1 eV contains two intense peaks (Fig. 1) that comprise mainly Ni 3d states with some admixture of Bi 6p states. Finally, the topmost part C of the VB is derived basically from Ni 3d states. This band intersects with the Fermi level and continues up to +1.5 eV. Thus, the region of DOS near the Fermi level in LaNiBiO is formed mainly from states of (Ni-Bi) planes.

The increase in the number of electrons per unit cell and of the band filling in LaCuBiO results in respective shift of the Fermi level so that E_F in LaCuBiO occurs in the region of relatively small DOSs values. Additionally, some changes in contributions from Cu 3d and Bi 6p to subband C can be observed in Fig. 1.

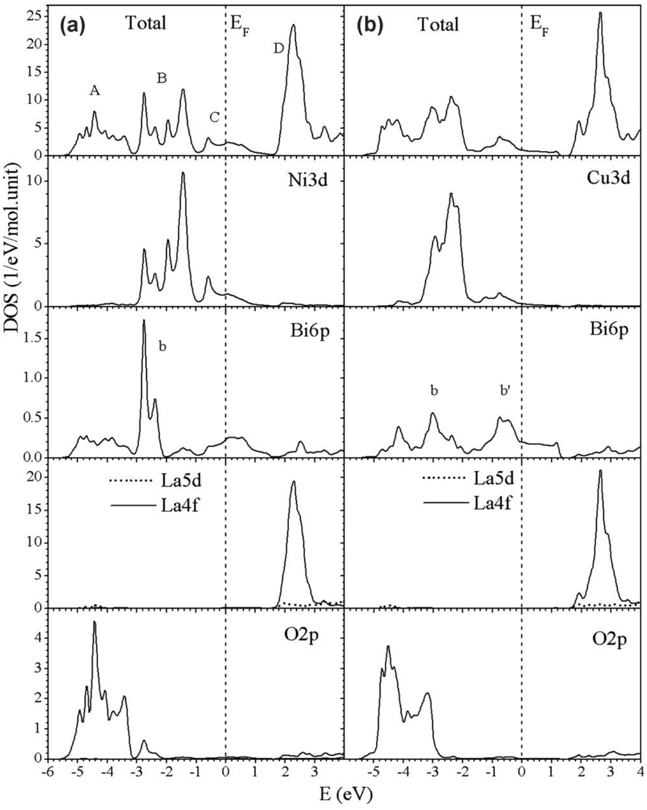

FIG. 1. Total and partial densities of states (DOSs) of (a) LaNiBiO and (b) LaCuBiO.

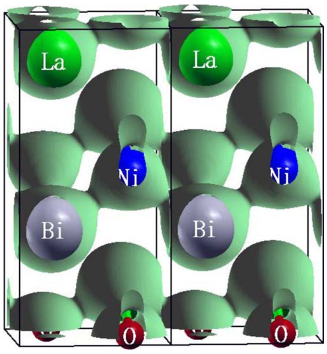

FIG. 2. (Color online) The isosurface (0.36 $e/\text{Å}^3$) of charge density for LaNiBiO.

La f states form intensive unoccupied DOS peak D near the bottom of the conduction band in both oxybismuthides. The quasicore DOS peaks at large binding energies occupy intervals from −10.0 to −11.3 eV (Bi 6s states), −14.8 to −16.7 eV (overlapping La 5p and O 2s states), −18.6 to −20.1 eV (mainly O 2s states), and −21.9 to −22.3 eV (mainly Bi 5d states).

Thus, we can conclude from our calculations that (i) electronic bands around the Fermi level are formed mainly by the states of (Ni(Cu)-Bi) layers and (ii) the general bonding mechanism in both oxybismuthides does not correspond to "pure" ionic picture, rather it includes covalent interactions inside of 2D (La-O) and (Ni(Cu)-Bi) layers.

In order to gain further understanding about the bonding situation in La(Ni,Cu)BiO, we turn our attention to the charge-density distribution (Fig. 2). It is evident that the highest charge density resides inside the above mentioned 2D (La-O) and (Ni(Cu)-Bi) layers. Moreover, the charge distributions are not spherically symmetric but are strongly deformed along (Ni,Cu)-Bi and La-O bond directions inside the corresponding layers and, hence, it can be concluded that considerable covalent interactions are present between (Ni,Cu)-Bi and La-O. In contrast, in intervals between (Ni,Cu)-Bi and La-O layers, the appreciable electronic density is absent (i.e., the hybridization effects should be very small), therefore, the corresponding interlayer bonding mechanism is mostly of the ionic type.

In an attempt to quantify the amount of electrons, redistributed between the adjacent (Ni,Cu)-Bi and La-O layers, we have made a Bader[40] analysis. In this approach each atom of a crystal is surrounded by an effective surface that runs through the minima of the charge density and the total charge of an atom (so-called Bader charge Q^B) is determined by integrating within this region. The calculated atomic Q^B as well as the corresponding charges as obtained from purely ionic model (Q^i) and their differences ($\Delta Q = Q^B - Q^i$) are presented in Table II. The obtained results show that the charge transfer from (La-O) to (Ni(Cu)-Bi) layers is about 0.46 and 0.44 electron per formula unit for LaNiBiO and LaCuBiO, accordingly. Naturally, taking into account the metalliclike

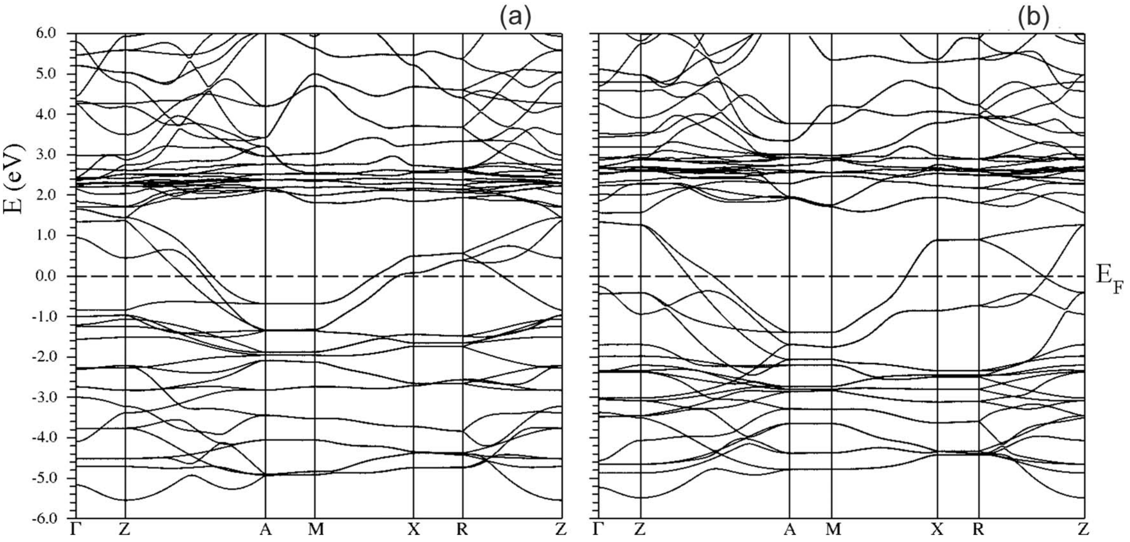

FIG. 3. Electronic band structures of (a) LaNiBiO and (b) LaCuBiO.

type of the both oxybismuthides, these values are much smaller than the assumed values for idealized ionic picture. Therefore, the oxybismuthides can be characterized as *NM ionic metals*.

The calculated band-structure pictures are shown in Fig. 3 for LaNiBiO and LaCuBiO along some high-symmetry directions of Brillouin zone (BZ) in the range of energies from −6 to +6 eV. The most interesting feature is a 2D-like behavior of quasiflat electronic bands along Γ-*Z* and A-M directions, which is also found for all other tetragonal oxypnictides.[24–36] It is seen for four bands cross the Fermi level in LaNiBiO and because of the increase in the band filling only three bands intersect the Fermi level in LaCuBiO.

The corresponding Fermi surfaces (FSs) in the first BZ are shown in Fig. 4. Due to the 2D electronic structure, all FSs consist of sheets parallel to the k_z direction. These sheets are cylindrical in LaNiBiO and the first sheet is centered along the *R*-*X* direction. Three other ones are centered along the *A*-*M* high-symmetry line. Comparing with the FS in LaFeAsO,[24,28] we can see a number of differences. Namely, while the cylindrical FSs centered along the *A*-*M* direction exist in both phases, the tubelike FS centered in LaFeAsO along the *Z*-Γ direction and the three-dimensional hole pocket around Γ (Refs. 24 and 28) disappear in LaNiBiO. On the other hand, isoelectronic LaNiPO (Ref. 36) and LaNiBiO exhibit similar FS topologies.

TABLE II. Atomic charges (in e) quaternary oxybismuthides La*M*BiO (where *M*=Ni and Cu) as obtained from purely ionic model (Q^i), from Bader (Ref. 39) analysis (Q^B), and their differences ($\Delta Q = Q^B - Q^i$).

Atom	Q^i	Q^B	ΔQ	Atom	Q^i	Q^B	ΔQ
La	8(+3)	9.156	1.156	La	8(+3)	9.146	1.146
O	8(−2)	7.303	−0.697	O	8(−2)	7.292	−0.708
Ni	8(+2)	10.129	2.129	Cu	15(+2)	16.994	1.994
Bi	18(−3)	15.412	−2.588	Bi	18(−3)	15.568	−2.432

The FS is composed of three sheets connected in LaCuBiO where just three bands intersect the Fermi energy and two of them have the crossing point, which is located at E_F (Fig. 3). Two sheets are cylindrical and centered along the *R*-*X* and *A*-*M* high-symmetry lines (parallel to the k_z direction) while the third sheet is tubular and aligned along the *Z*-Γ direction (Fig. 4).

As electrons near the FS are involved in formation of superconducting state, it is important to figure out their nature. The total and orbital decomposed partial DOSs at the Fermi level, $N(E_F)$ are shown in Table III. It is seen that the regions of DOSs near the Fermi level in both oxybismuthides are formed by states of (Ni(Cu)-Bi) layers. Therefore, the conduction in these systems is expected to be strongly anisotropic, i.e., happening mainly in these layers. Notice also that in addition to Ni(Cu) d_{xy} and Ni(Cu) $d_{x^2\text{-}y^2}$ orbitals, the contribution from Ni(Cu) d_{xz}, d_{yz}, and d_z^2 orbitals is also present at $N(E_F)$ (Table III). The contribution from Bi is noticeable but smaller than the contribution from Ni(Cu) orbitals; the main contribution to $N(E_F)$ is formed from Bi $6p_{x,y}$ orbitals and it increases considerably at the shift from LaNiBiO to LaCuBiO.

The obtained data allow us also to estimate the Sommerfeld constants (γ) and the Pauli paramagnetic susceptibility (χ) for oxybismuthides under assumption of the free-electron model as $\gamma = (\pi^2/3)\mathrm{N}(E_F)k_B^2$ and $\chi = \mu_B^2 N(E_F)$. It is seen from Table III that both γ and χ decrease approximately twice at replacement of nickel for copper. Moreover, these values

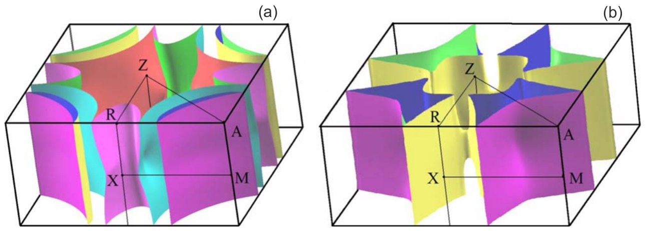

FIG. 4. (Color online) The FSs of (a) LaNiBiO and (b) LaCuBiO .

TABLE III. Total $N^{\mathrm{tot}}(E_F)$ and partial $N^{l}(E_F)$ densities of states at the Fermi level (in states/eV atom^{-1}), electronic heat capacity γ (in mJ K^{-2} mol^{-1}), and molar Pauli paramagnetic susceptibility χ (in 10^{-4} emu/mol) of quaternary oxybismuthides LaMBiO (where M=Ni and Cu).

Phase/parameter	$N^{M3dxy}(E_F)$	$N^{M3dx2-y2}(E_F)$	$N^{M3dxz}(E_F)$	$N^{M3dyz}(E_F)$	$N^{M3dz2}(E_F)$	$N^{Bi6pz}(E_F)$
LaNiBiO	0.205	0.231	0.199	0.199	0.207	0.096
LaCuBiO	0.015	0.055	0.065	0.065	0.036	0.026
Phase/parameter	$N^{Bi6px+y}(E_F)$	$N^{M3d}(E_F)$	$N^{Bi6p}(E_F)$	$N^{\mathrm{tot}}(E_F)$	γ	χ
LaNiBiO	0.137	0.982	0.233	2.287	5.39	0.74
LaCuBiO	0.172	0.236	0.198	1.037	2.44	0.34

also occur appreciably smaller than in Fe-containing oxypnictides [e.g., γ=81 mJ K^{-2} mol^{-1} in $\mathrm{SmO}_{1-x}\mathrm{F}_x\mathrm{FeAs}$ (Ref. 41) and γ=12.5 mJ K^{-2} mol^{-1} in LaFePO (Ref. 42)], which follows from the differences in band-structure features.

In summary, we have systematically studied the band structures, DOS, and FSs in SCs—quaternary oxybismuthides LaNiBiO and LaCuBiO. Our results indicate that these phases consist of alternately stacked insulating (La-O) and conductive (Ni(Cu)Bi) layers; the binding between them is mostly ionic. Thus, the discovered oxybismuthides may be described as quasi-2D NM ionic metals where the conduction is strongly anisotropic—happening mostly in (Ni(Cu)-Bi) layers. Finally, the present discussion is focused only on ideal oxybismuthides and numerous issues are to be resolved yet. For example, further in-depth studies are necessary in order to understand the influence of oxygen nonstoichiometry on the properties of these materials. Additionally, these oxybismuthides may be of interest as a different material platform for further exploration of relationships between magnetism and superconductivity. Really, in the presently synthesized quaternary oxyarsenide high-temperature SCs, an increase in T_C up to ~55 K is observed exclusively as a result of electron or hole doping through ion substitutions (or creation of oxygen vacancies) in the Ln-O insulating layers.[1–11] In turn, these high-T_C superconducting phases exist near a magnetic instability in oxyarsenides and magnetic spin fluctuations should play an important role in possible scenarios of superconducting coupling mechanisms, which are proposed for these systems.[24–39] It is possible that for discussed oxybismuthides, the balance between their NM and magnetic states may be achieved as a result of doping through substitutions of magnetic 3d ions (e.g., Fe or Co) in conductive (Ni(Cu)Bi) layers. Therefore, these materials may be used as model systems in order to clarify the pairing mechanism in oxypnictides.

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