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Jean-Pierre Julien, D. Mayou, F. Cyrot-Lackmann. Tight-binding electronic structure of high Tc superconductors. *Journal de Physique*, 1989, 50 (18), pp.2683-2693. 10.1051/jphys:0198900500180268300 . jpa-00211093

HAL Id: jpa-00211093

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Submitted on 4 Feb 2008

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Classification
Physics Abstracts
71.20C

Tight-binding electronic structure of high T_c superconductors

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(Reçu le 6 juin 1989, révisé le 28 juin 1989, accepté le 29 juin 1989)

Résumé. — Les nouveaux oxydes supraconducteurs ont des similarités importantes au niveau de leur structure cristallographique. Ce sont des perovskites, ou des composés de structure dérivée qui ont en commun une nature alternée : les premiers voisins des atomes d'oxygène sont des atomes métalliques et réciproquement. Nous montrons que cette particularité structurale a des conséquences très importantes sur la structure électronique. Dans ce but, nous présentons d'abord un formalisme général permettant de décrire simplement la structure électronique proche du niveau de Fermi, dès que l'on a un réseau alterné. Dans la seconde partie, nous illustrons la méthode pour différents oxydes en lien avec les supraconducteurs à haute température critique à base de cuivre ou de bismuth. Enfin, nous montrons les résultats obtenus par la méthode du réseau alterné pour le modèle à deux bandes du plan CuO_2 , entité de base des nouveaux supraconducteurs à base de cuivre.

Abstract. — New superconducting oxides have important crystallographic similarities. They are bulk perovskites or structure derived compounds such as the K_2NiF_4 one, with an alternating nature : the oxygen atoms nearest-neighbours are metallic atoms and vice-versa. We show that this structural property has important consequences on the electronic structure. We first present a general formalism allowing us to describe in a simple way the electronic structure as soon as one has an alternating lattice. In a second part, we illustrate this method for different oxides related with the high T_c superconductors. Lastly, we show the results we obtain with the alternating lattice method in the two-band model of the CuO_2 plane which is characteristic of the copper-based new superconductors.

1. Introduction.

Since the discovery of the high T_c superconductivity by Bednorz and Müller in BaLaCuO systems [1], and in other copper compounds [2] and more recently in the copper free $(\text{BaK})\text{BiO}_3$ alloys [3], a lot of attention has been focused on the possible origins of superconductivity. All these compounds have in common typical phase diagrams : the insulating oxide becomes superconducting when it is doped. In copper based systems, the pure compound is antiferromagnetic and in BaBiO_3 there is a charge density wave. Many

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mechanisms have been invoked [4], but the understanding of their electronic structure is crucial.

These materials have a peculiar crystal structure : perovskite, K_2NiF_4 type or derived one, in which oxygen-octahedron with a metallic atom at the centre play an important role. By eliminating one or two oxygen atoms, the octahedron is reduced to a pyramid or a square respectively. In all cases these compounds present a crystal structure having an alternating nature : one kind of atom, like bismuth (oxygen) in $BaBiO_3$ has first nearest neighbours of the other kind, i.e. oxygen (bismuth) (Fig. 1). This alternating nature of the crystal structure will have important consequences on the electronic structure.

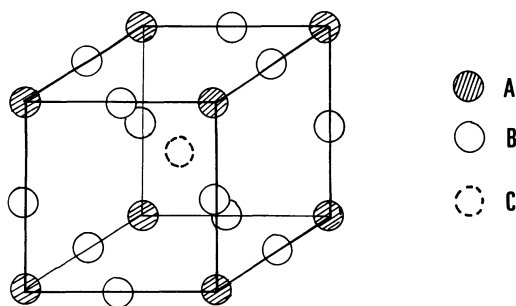


Fig. 1. — Figure showing the alternating nature of the A-B lattice in the perovskite structure. For example in $BaBiO_3$: A = Bi, B = O, and in $SrTiO_3$: A = Ti, B = O'.

The aim of this paper is to discuss the electronic structure of many perovskite type compounds. Although the effect of the correlations is considered by many people to be important, we do not discuss it here specifically. We just point out that, if the interaction parameter U between electrons is not too important as compared with the bandwidth W , the one-electron band structure gives a good starting point to the study of electronic properties. We shall show that in these materials the main features of the electronic structure near the Fermi level involve a small number of orbitals of metal and oxygen atoms and then can be described in a simple way due to their crystal alternating nature. Particularly, the shape of the local densities of states can be analysed in a simple way, and it is possible to scale the difference of the atomic energy levels of the pure elements and thus to study the effects of the covalency. Our results will confirm some of the analysis of Friedel who stressed the importance of the shape of the density of states near the Fermi level. More precisely, he points out that the quasi-two dimensional character of these layered structures leads to a strong density of states near the Fermi level which favors superconductivity [5].

In the first section, we present the formalism of the method. We show that the real tight-binding Hamiltonian can be transformed in to an effective Hamiltonian acting in a reduced lattice retaining only one kind of orbitals. The density of states (DOS) can be deduced through a « universal » DOS calculated on this effective lattice. We apply this procedure to various cases. We first describe the results obtained for cubic perovskites involving s-orbitals ($BaBiO_3$) or d-orbitals ($SrTiO_3$) on the reduced lattice and we notice that the alternating lattice method results are in good agreement with results obtained by ab initio band structure calculations involving more orbitals. Then we apply the formalism to the case of K_2NiF_4 structure involving d-orbitals on the reduced lattice : Sr_2VO_4 and La_2CuO_4 . We compare both compounds and illustrate the difference of states contributing to the Fermi level (mainly

t_{2g} orbitals in Sr_2VO_4 and e_g orbitals in La_2CuO_4). Finally we show the results of the alternating lattice method in the case of the simplified CuO_2 plane.

2. The alternating lattice method.

The electronic structure near the Fermi level for numerous compounds can be interpreted in a very simple way due to the alternating nature of the perovskite or K_2NiF_4 lattice for which we make the approximation that an A-atom (respectively a B-atom) is just coupled to B-atoms (resp. A-atoms). For example A and B in La_2CuO_4 are respectively the copper and oxygen atoms for which we take into account respectively the d and p orbitals. As we have already exposed the principle of this method elsewhere [6, 8], we only present the outlines of it. Let us recall that this method is valid if the states contributing to the Fermi level are mainly made with the A-orbitals strongly hybridized with the B-orbitals. It is in fact well known from band structure calculations that the other orbitals contributions (like Ba in $BaBiO_3$, La in La_2CuO_4 and Sr in $SrTiO_3$ or $SrVO_4$) are far enough from the Fermi level and that we can neglect them in the tight-binding Hamiltonian.

We start from a Hamiltonian H :

$$H = H_0 + H_c \quad (1)$$

where H_0 is the on-site energy respectively ε_A (ε_B) on a (A|B)-atom and H_c is the hopping energy which just couples, in a first nearest neighbours approximation, the A-orbitals to the B-orbitals. We neglect the direct A-A or B-B coupling as it generally involves parameters which are much smaller.

An eigenstate $|\Psi\rangle$ with energy E obeys the Schroedinger equation

$$H|\Psi\rangle = E|\Psi\rangle \quad (2)$$

and can be decomposed in its components $|\Psi_A\rangle$, $|\Psi_B\rangle$ on the A- or B-sublattice

$$|\Psi\rangle = |\Psi_A\rangle + |\Psi_B\rangle . \quad (3)$$

By projecting the two members of the Schroedinger equation on each sublattice, one obtains

$$H_c|\Psi_A\rangle = (E - \varepsilon_B)|\Psi_B\rangle \quad (4a)$$

$$H_c|\Psi_B\rangle = (E - \varepsilon_A)|\Psi_A\rangle . \quad (4b)$$

By multiplying by H_c one of these equations and inserting the other one, we obtain two formal Schroedinger equations

$$H_c^2|\Psi_A\rangle = (E - \varepsilon_A)(E - \varepsilon_B)|\Psi_A\rangle \quad (5a)$$

$$H_c^2|\Psi_B\rangle = (E - \varepsilon_A)(E - \varepsilon_B)|\Psi_B\rangle \quad (5b)$$

which can be written as

$$\tilde{H}|\Psi_\varepsilon\rangle = \tilde{E}|\Psi_\varepsilon\rangle \quad (6a)$$

with

$$\varepsilon = A \text{ or } B$$

$$\tilde{H} = H_c^2 \quad (6b)$$

and

$$\tilde{E} = (E - \varepsilon_A)(E - \varepsilon_B) . \quad (6c)$$

\tilde{H} is an effective Hamiltonian, homogeneous to the square of an energy, which only couples one kind of orbitals together. Thus, the alternating lattice has been reduced to a lattice with only one kind of orbitals (A or B). One checks easily that $\tilde{H} = H_c^2$ has diagonal as well as off-diagonal elements in the basis of atomic orbitals. The calculations have been made on the metal (Cu, Ti, Bi or V) sublattice which is the easiest one to treat : a simple cubic lattice in the case of the cubic perovskites or square lattice in the case of the K_2NiF_4 -structure.

The effective density of states \tilde{N} , associated with \tilde{H} , is calculated by recursion on the reduced lattice. \tilde{N} does not depend on ε_A and ε_B but it just depends on the crystal structure and the kind of orbitals. Thus, \tilde{N} , in reduced units, is a universal density of states, characteristic of the structure and the involved orbitals. Some simple relations permit to obtain the total $N(E)$ and projected $N_\alpha(E)$ densities of states from the effective ones \tilde{N} and \tilde{N}_α , which are respectively the total density and the local density on an orbital α in the reduced lattice and for the Hamiltonian \tilde{H} :

$$N(E) = 2|E - (\varepsilon_A + \varepsilon_B)/2|\tilde{N}(\tilde{E}) \quad (7)$$

$$N_A(E) = |E - \varepsilon_B|\tilde{N}(\tilde{E}) \quad (8a)$$

$$N_B(E) = |E - \varepsilon_A|\tilde{N}(\tilde{E}). \quad (8b)$$

We note the following points. First, because $\tilde{H} = H_c^2$ is positive, the energy \tilde{E} must be positive

$$(E - \varepsilon_A)(E - \varepsilon_B) > 0.$$

Thus, one has a gap for $\tilde{E} < 0$ i.e. for E between ε_A and ε_B . Second, if the sublattices A and B contain N_A and N_B orbitals and if $N_A > N_B$ (resp. $N_A < N_B$), there is a delta contribution containing $|N_A - N_B|$ states in the total real density of states which occurs at the energy ε_A (resp. ε_B). If one takes into account the direct interaction, this delta-pike gives rise to a narrow band which can partially or completely fill the gap. Finally, one has

$$N(E) dE = \tilde{N}(\tilde{E}) d\tilde{E}. \quad (9)$$

This relation is interesting to find the position of the Fermi level and its variation with doping. If there are n electrons in the lowest non completely filled band, then one imagines that these n electrons are put in the effective DOS $\tilde{N}(\tilde{E})$. This gives an effective Fermi level \tilde{E}_f and the true Fermi level ε_f is such that

$$(\varepsilon_f - \varepsilon_A)(\varepsilon_f - \varepsilon_B) = \tilde{E}_f. \quad (10)$$

3. Applications.

We now present applications of the method. We recall this *important* result : when two compounds have the same crystal structure, and the same types of orbitals, one obtains the same effective density of states (in reduced units) for each case. The particularity of the compound is just represented by the on-site levels, used to compute the real DOS from the effective one (Eqs. (7) and (8)) and of course, also by the filling of the band. The possibility of varying the on-site levels allows us to study easily the covalency which can change because of the doping. This second aspect has been already studied elsewhere [6] for La_2CuO_4 compound and will not be discussed here.

In this section, we show the differences of singularities for cubic perovskites when there are s (case of BaBiO_3) or d (case of SrTiO_3) type of orbitals. Then, for the K_2NiF_4 structure and in case of d-orbitals, we present the similarities of Sr_2VO_4 with La_2CuO_4 .

3.1 CUBIC PEROVSKITES.

BaBiO_3 . — As a first example of application of the method discussed above, it is interesting to study the case of BaBiO_3 . Its interest is obvious : by substituting the Ba-atom by a K-atom with concentration x , the alloy has been found to be superconducting with a T_c around 30 K for $x \approx 0.4$ [3]. *Ab initio* APW band structure calculations [7] show that the states near the Fermi level are mainly due to the hybridization of the Bi-s orbitals with the O-p ones, with the Slater Koster Parameter $sp\sigma$. Thus, in a first approach, these are the orbitals, we will retain for the application of the alternating lattice method. In a forthcoming paper, we will show how to take into account more orbitals. Because the Bi-atoms are located on a cubic site, the reduced lattice is a simple cubic lattice on which the Bi-s are coupled by the effective Hamiltonian \tilde{H} . The effective density of states $\tilde{N}(\tilde{E})$ is the well-known simple cubic density states (Fig. 2). The real density of states, projected on an s-Bi orbital is shown in figure 3a. The insert is the exact result we obtained by an APW calculation [7] and shows the good agreement. One has to point out that the local s-Bi DOS is a very small part of the total DOS but is the main component at the Fermi level (Fig. 3b).

Experimentally, it is well known that the BaBiO_3 compound is semiconducting with a charge density wave (CDW) leading to formal Bi^{3+} and Bi^{5+} . The explanation of this CDW involves the electron-phonon coupling and is outside the scope of this paper. Let us mention that the condition for the occurrence of this CDW has been studied recently by Nunez Regueiro *et al.* [8] in a simplified model taking into account the s orbitals of Bi and the $p\sigma$ of oxygen.

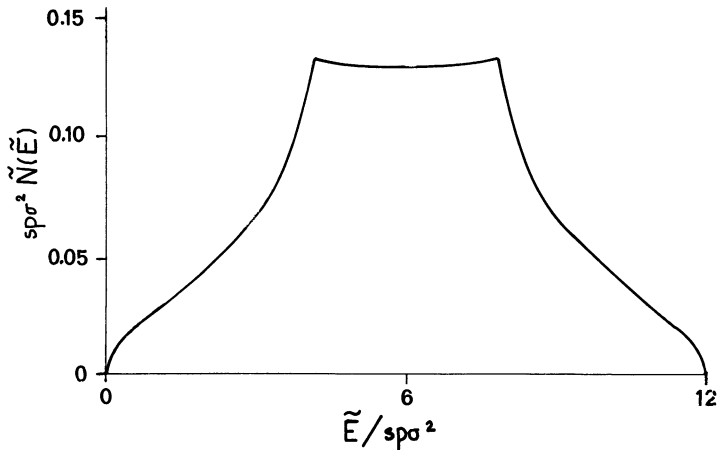


Fig. 2. — Density of states of the simple cubic lattice with s-orbitals.

SrTiO_3 . — Another compound having a perovskite structure is the semiconducting SrTiO_3 which becomes superconducting when it is doped. Its electronic structure has been already studied but we present it to illustrate the difference due to the orbital symmetry : in this case, the hybridizations are mainly between the Ti-d orbitals and the O-p orbitals involving the parameter $pd\pi$ (for hybridization between $\text{Ti-}t_{2g}$ orbitals with $\text{O-p}\pi$ orbitals, i.e. orbitals

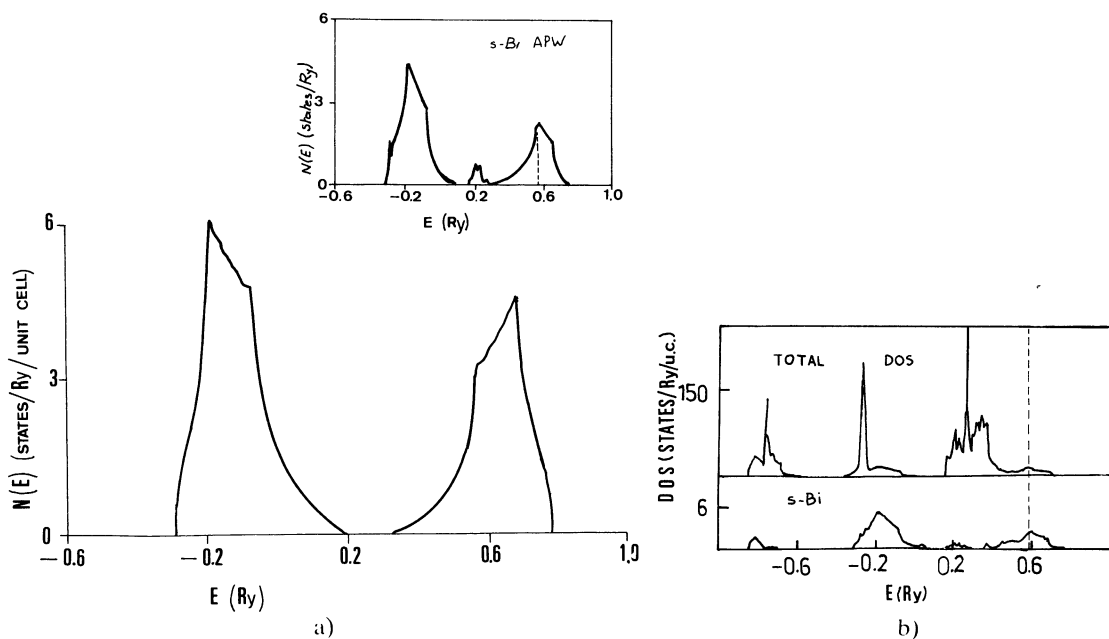


Fig. 3. — Local s-Bi density of states of BaBiO₃ obtained by the alternating lattice method. (a) Insert : exact result obtained by APW-calculation (after Ref. [7]). (b) APW densities of states of BaBiO₃. Upper panel : total density of states, lower panel : partial s-Bi density of states.

having their lobes perpendicular to the bond Ti-O) and the parameter $pd\sigma$ (for the hybridization between Ti- e_g orbitals with O- $p\sigma$ orbitals, i.e. orbitals having their lobes parallel to the bond Ti-O). In a cubic structure, the bonds are perpendicular and the sets of orbitals Ti- t_{2g} -O- $p\pi$ and Ti- e_g -O- $p\sigma$ are not coupled, and for each set it is possible to apply the alternating lattice method. Let us recall that the only role of the Sr atom is to provide electrons to the system and in our calculation, we neglect its bands since they are higher than the Fermi level.

Let us focus first on the t_{2g} -orbitals. Despite the cubic nature of the perovskite, a t_{2g} -orbital (xy , yz or zx) is only coupled with its neighbouring $p\pi$ -orbitals in a plane (xy , yz or zx). Thus, the effective DOS $\tilde{N}(\tilde{E})$ (Fig. 4) is the square-lattice DOS with a characteristic two-

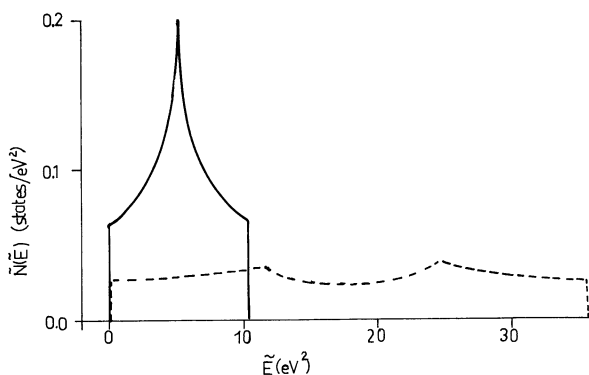


Fig. 4. — Effective density of states for SrTiO₃-like compounds. Full line : t_{2g} -band ; dotted line : e_g -band.

dimensional Van Hove singularity. Due to the degeneracy of t_{2g} orbitals in this symmetry, we obtain the same features for xy , yz or zx -orbitals.

The e_g orbitals are also degenerated. Because a $3z^2 - r^2$ orbital is coupled with $p\sigma$ orbitals in three directions, the effective DOS (Fig. 4) $\tilde{N}(\tilde{E})$ presents three dimensional Van Hove singularities, analogous to those pictured in figure 2. However, because of the mixing of the $x^2 - y^2$ and $3z^2 - r^2$ orbitals, this effective DOS is more complicated than the simple cubic DOS of figure 2.

In figure 5, we have reconstructed the real DOS of SrTiO_3 , in good agreement with the exact APW result obtained by Mattheiss [9], shown in the insert. The peak just below E_F in the exact result can be interpreted as the delta peak of the non-bonding p-oxygen states (three $p\pi$ states at $\varepsilon_{p\pi}$ and one $p\sigma$ state at $\varepsilon_{p\sigma}$), widened by direct oxygen-oxygen interaction.

The same method would apply to any other cubic perovskite involving transitional metal, such as SrVO_3 , LaNiO_3 ... The main differences would be the values of the levels and the position of the Fermi level. It is also possible with this method to study the axial distortion of this cubic lattice leading for example to a tetragonal or orthorhombic lattice. The main effect is to split the two-dimensional Van Hove singularity peak in two or three peaks respectively, as one lifts the degeneracy of the t_{2g} and e_g orbitals.

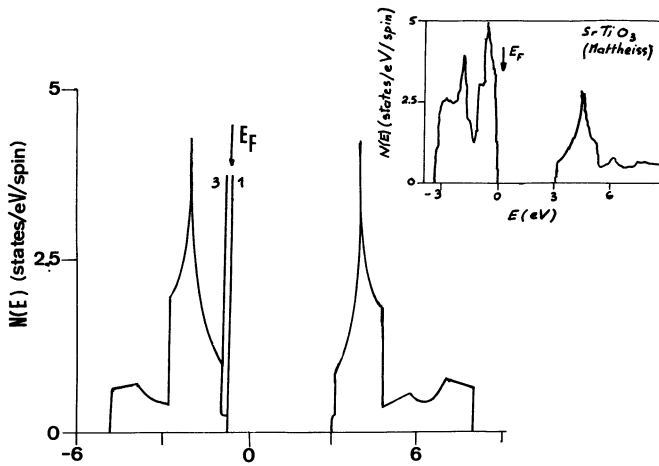


Fig. 5. — Total density of states of SrTiO_3 obtained by the alternating lattice method. Insert : exact result obtained by APW-calculation (after Ref. [9]).

3.2 COMPOUNDS WITH K_2NiF_4 STRUCTURE. — In this section we present two cases : Sr_2VO_4 and the widely studied La_2CuO_4 . Sr_2VO_4 is a new insulating compound studied in Grenoble [10]. For both compounds the orbitals taken into account are the d-orbitals of the transition metal (Vanadium or Copper) which are strongly hybridized with the p-orbitals of oxygen. As mentioned above, we neglect the La or Sr orbitals which are mainly above the Fermi level. In this tetragonal symmetry, there is also no mixing between the sets $t_{2g}\text{-Op}\pi$ and $e_g\text{-Op}\sigma$, as in the previous case but only yz and zx -orbitals are degenerated, all other degeneracies are lifted. In this structure, the reduced lattice of d-orbitals is a square plane. For both compounds, the parameters that we use are listed in table I and have been deduced from *ab initio* calculations [11, 12].

Table I. — *Slater-Koster parameters used for the K₂NiF₄-type compounds.*

	Sr ₂ VO ₄	La ₂ CuO ₄
t _{2g} on-site	8.3	4.9
e _g on-site	10.7	6.25
Oxygen p on-site	5.9	4.5
pdσ	-2.4	-1.4
pdπ	1.3	0.8

Sr₂VO₄. — We have calculated the DOS of Sr₂VO₄ by taking the VO₆ octahedron distortion predicted by Pickett *et al.* [11] and experimentally observed by Lambert [10] (the distance V-O in plane is equal to 1.92 Å, as the distance V-O out of plane is 1.99 Å). For Sr₂VO₄ the states contributing near the Fermi level are mainly V-t_{2g} orbitals hybridized with Opπ orbitals. The xy-orbital is coupled in the xy plane, *via* the effective Hamiltonian \tilde{H} with its four surrounding xy-orbitals. Thus the effective DOS is still the well-known square lattice DOS shown as in cubic perovskite of figure 4. The yz (or zx) orbital is just coupled along a chain with its two neighbouring yz(zx) orbitals in the direction y(x). Thus, one obtains the effective DOS which is that of a chain (Fig. 6) with one dimension singularities, the role of the out of plane oxygens is to give a contribution to the effective on-site energy of yz and zx orbitals. This explains the fact that the effective DOS yz(zx) is displaced towards higher energies than the effective DOS of xy. By adding all contributions (including also the e_g-Opσ states) and coming back to the real density of states (Fig. 7) one obtains a good agreement in the region of the Fermi level with an APW result [11] pictured in the insert. We stress that the Fermi level is very close to a one dimension Van Hove singularity.

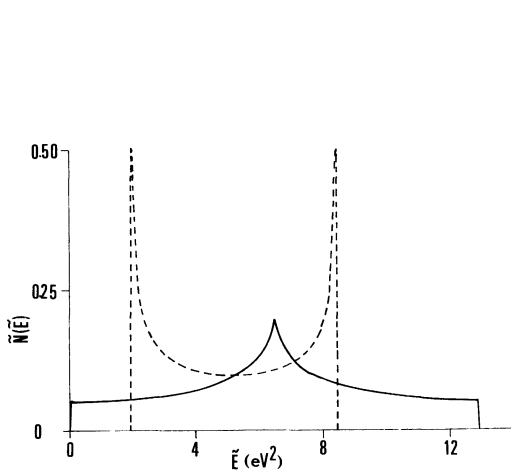


Fig. 6.

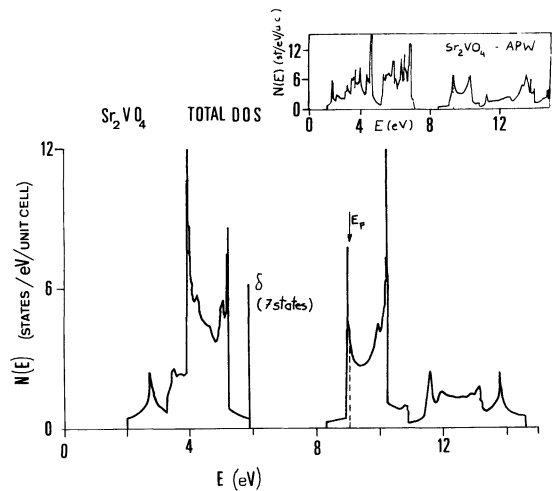


Fig. 7.

Fig. 6. — Effective densities of states for Sr₂VO₄-like compounds. Full line : xy-band ; dashed line : yz or zx-band.

Fig. 7. — Total density of states of Sr₂VO₄ obtained by the alternating lattice method. Insert : exact result obtained by APW-calculation (after Ref. [11]).

La_2CuO_4 . — Doped La_2CuO_4 was the first high T_c material [1] and it has been intensively studied. Some features of its electronic structure have been described elsewhere [6] and we present it here to illustrate the similarity with Sr_2VO_4 as can be seen by comparing the total densities of states in figures 7 (Sr_2VO_4) and 8 (La_2CuO_4). Let us point out the importance of the Jahn-Teller distortion of the octahedron (the distance Cu-O in plane is equal to 1.89 Å, whereas the distance Cu-O out of plane is 2.43 Å). The differences between the two compounds are due to the Jahn-Teller distortion and the separation of atomic levels ε_p and ε_d . Of course, the filling is different : for La_2CuO_4 the states contributing to the Fermi level are e_g -orbitals hybridized with $p\sigma$ ones (instead of t_{2g} and $p\pi$ -orbitals in Sr_2VO_4). By projecting the e_g -DOS on $x^2 - y^2$ and $3z^2 - r^2$, one sees that the $3z^2 - r^2$ band is lower in energy than the $x^2 - y^2$ one (Figs. 9 and 10). This is due to the Jahn-Teller distortion as can be seen in figure 11, where we present $x^2 - y^2$ and $3z^2 - r^2$ DOS for a « pseudo » La_2CuO_4 without octahedron distortion.

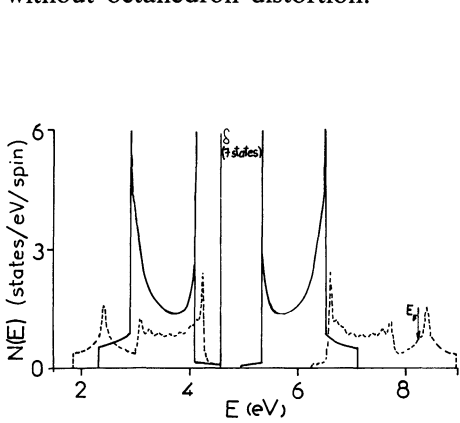


Fig. 8.

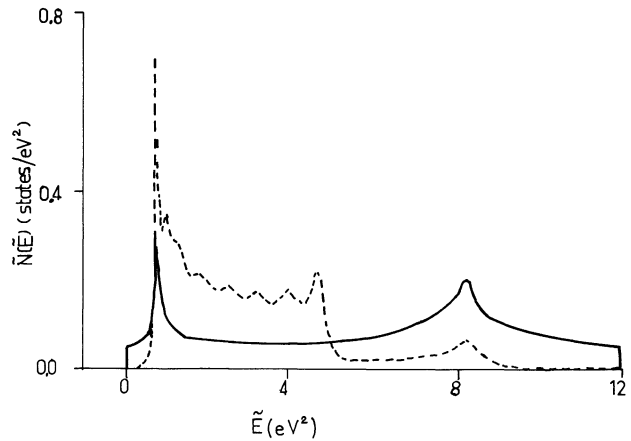


Fig. 9.

Fig. 8. — Total density of states of La_2CuO_4 decomposed in t_{2g} - $p\pi$ band (full line) and e_g - $p\sigma$ band (dotted line).

Fig. 9. — Effective density of states of the Jahn-Teller distorted La_2CuO_4 compound. Full line : $x^2 - y^2$ band ; dotted line : $3z^2 - r^2$ band.

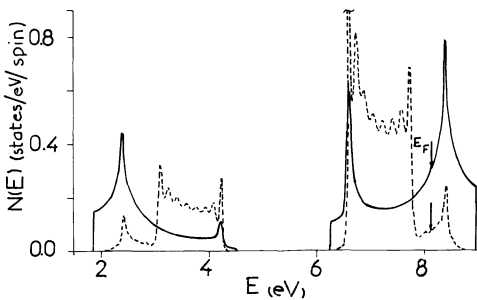


Fig. 10.

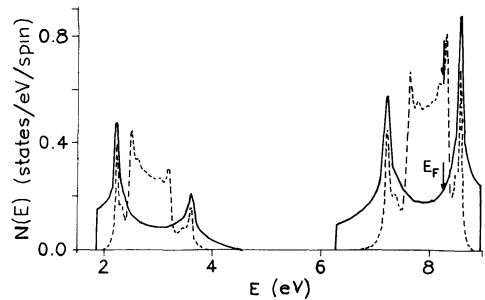


Fig. 11.

Fig. 10. — Local density of states of the Jahn-Teller distorted La_2CuO_4 . Full line : on a $x^2 - y^2$ orbital ; dotted line : on a $3z^2 - r^2$ orbital.

Fig. 11. — Local density of states of La_2CuO_4 without Jahn-Teller distortion. Full line : on a $x^2 - y^2$ orbital ; dotted line : on a $3z^2 - r^2$ orbital.

As a consequence of this energy lowering of $3z^2 - r^2$, the hole above the Fermi level is mainly located on $x^2 - y^2$ and $p\sigma$ -orbitals. This allows a simple description of La_2CuO_4 by retaining only the $x^2 - y^2$ and $p\sigma$ -orbitals in the CuO_2 plane.

Two bands model of CuO_2 plane. — This model, which takes into account $\text{Cu-}dx^2 - y^2$ and $\text{O-}p\sigma$ orbitals, has been widely used as a starting point to study antiferromagnetism [13] and correlations [14] or superconductivity [15]. Some authors have treated the Cu-O hopping integral t as a perturbation. This approach leads to two subbands, having a square lattice DOS. The upper band is the Copper band with an effective Cu-Cu hopping integral $t^2/\varepsilon_d - \varepsilon_p$. This perturbative approach does not give the right band edges and it is no longer valid if the Cu-O hopping is not small compared with $\varepsilon_d - \varepsilon_p$. Let us recall that band calculations [16] actually show that the covalency is important, i.e. $t/\varepsilon_d - \varepsilon_p$ is large, and thus the perturbative approach is not very good.

With no loss of simplicity, the alternating lattice method leads to an exact result whatever the parameter $t/\varepsilon_d - \varepsilon_p$. In figure 12, we show the densities of states obtained by the alternating lattice method and it appears that for realistic parameters, the oxygen partial DOS is not negligible in the upper band. Let us recall that in the limit of small $t/\varepsilon_d - \varepsilon_p$ (perturbative approach) the upper band would be purely made of copper states.

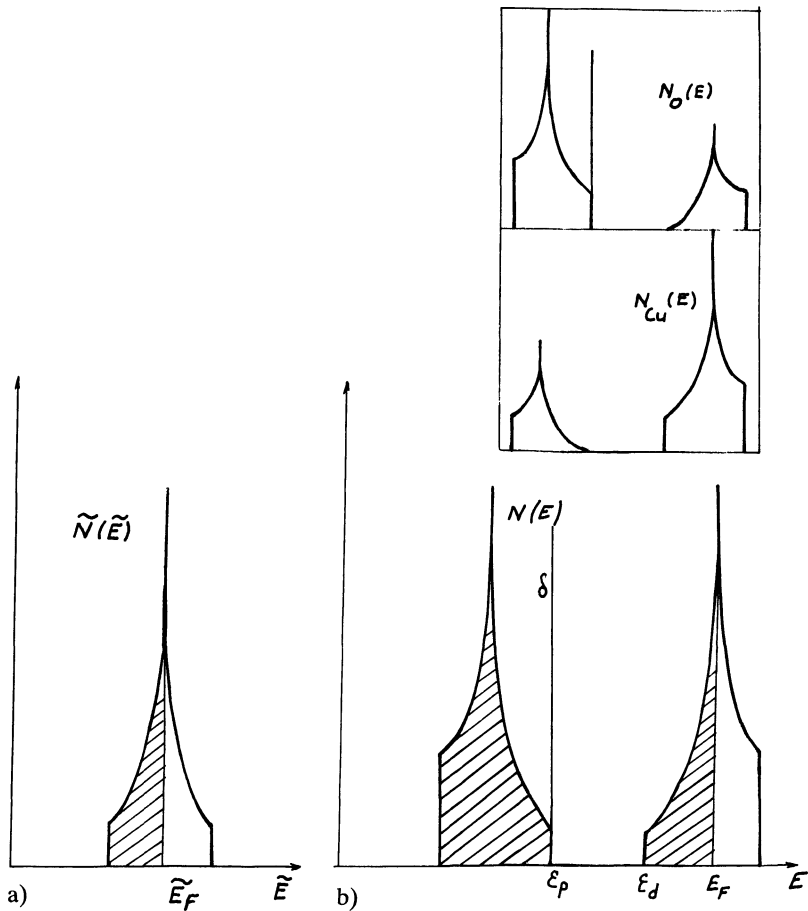


Fig. 12. — (a) Effective density of states. (b) Total density of states of the $\text{Cu}(x^2-y^2)\text{-O}_2(p\sigma)$ plane. Insert : copper and oxygen projected densities of states.

Finally, the alternating lattice method allows us to show an important result concerning the position of the Fermi level using equations (9) and (10). For the stoichiometric compound (one electron in the copper band) the Fermi level is exactly in the Van Hove singularity for all values of $t/\varepsilon_d - \varepsilon_p$. This confirms Friedel's proposition [15] that the Fermi level is close to the two dimensional Van Hove singularity for the doped superconducting phase, and could explain the high values of T_c .

Conclusion.

Let us conclude with some general remarks. We have shown that a reliable description of the electronic structure, near the Fermi level, of various perovskite type compounds is achieved with a small set of orbitals of the metal and of oxygen. We have shown the importance of the alternating structure of the perovskite compounds. It allows a simple description of their electronic structure in term of a DOS which depends on the geometry and the type of the involved orbitals, but not on metal-oxygen covalency. We have applied this method to various oxides. Let us mention that this method is applicable to study various other physical properties such as the antiferromagnetism of the CuO_2 plane and the phonon spectrum in alternating structures.

Acknowledgements.

This article has been written in honour of Professor Jacques Friedel. From him we have benefitted of many advices and encouragements of invaluable help.

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