

Localization of electrons in  $\text{LaCuO}_{3-\delta}$  and  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{3-\delta}$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 7013

(<http://iopscience.iop.org/0953-8984/6/35/010>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 20:24

Please note that [terms and conditions apply](#).

## Localization of electrons in $\text{LaCuO}_{3-\delta}$ and $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{3-\delta}$

S A Prosandeyev and I M Tennenboun

Department of Physics, Rostov State University, 5 ul Zorge, Rostov-on-Don 344104, Russia

Received 17 February 1994, in final form 5 May 1994

**Abstract.** Changes are considered in the electronic spectrum of crystals caused by their elongation and expansion. Situations are examined when, owing to crystal deformation, the electrons are localized in alternate planes or alternate atomic sublattices. It has been shown that in both cases forbidden gaps may, under certain conditions, arise in the electronic spectrum. The results of the work are discussed in the light of experiments in which it has been found that the increase of  $\delta$  in  $\text{LaCuO}_{3-\delta}$  and  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{3-\delta}$  leads to the metal–semiconductor transition.

### 1. Introduction

Recent experiments on  $\text{LaCuO}_{3-\delta}$  (Darracq *et al* 1993) and  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{3-\delta}$  (Hashimoto and Kawazoe 1993) have revealed that the removal of oxygen from the lattice leads to crystal deformation and to the appearance of dielectric properties in the samples. Darracq *et al* called attention to the fact that the increase of  $\delta$  leads to the tetragonal distortion of the lattice. They carried out the calculation of the band structure of tetragonally distorted  $\text{LaCuO}_3$  and did not find there the presence of a forbidden gap. Thus, it is possible that just partial removal of oxygen atoms will lead to the opening of the gap. However, there exists a possibility of explaining the experiments by the localization of electrons caused by lattice deformation. The present work examines this question in terms of the extended theory of alternating systems.

Originally, this theory was developed in organic chemistry for conjugated hydrocarbons (Coulson and Longuet-Higgins 1947). Rebane extended it to cover the case of disordered crystals of the  $A_nB_m$  type (Rebane 1986). He studied crystals in which the atom A is surrounded by atoms B only and vice versa, and dispersion in the electron-state band is produced by the interaction of nearest neighbours, i.e. A and B. It has been found that there is a gap in the electronic spectrum between the levels of the electron energy  $\varepsilon_A$  and  $\varepsilon_B$  at the atoms A and B. Moreover, the gap in the spectrum is present even in the case when the groups of  $\varepsilon_A$  and  $\varepsilon_B$  levels have their own dispersion, albeit on condition that the corresponding energy intervals do not intersect (Brown 1986). Oxides of the perovskite family of the  $\text{AMO}_3$  type, such as  $\text{BaTiO}_3$ ,  $\text{KNbO}_3$  and  $\text{KTaO}_3$ , are crystals of this type (Wolfram and Ellialtioglu 1982, Harrison 1983, Julien *et al* 1989); however, in  $\text{LaCuO}_{3-\delta}$  and  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{3-\delta}$  the Fermi level lies in the band of antibonding states, which is why both these crystals possess properties typical of metals. Consequently, the fact that the partial withdrawal of oxygen from these crystals triggers a metal–semiconductor transition cannot be accounted for by the above-described model.

Here we consider the possibility of the appearance of a forbidden gap in the electronic spectrum resulting from alternation of the potential in the sublattice of atoms M. The reasons

for such alternation can be different. It may, for example, stem from the freezing of a soft mode (such as the breathing mode), as in  $\text{BaBiO}_3$ , or from magnetic instability, as in  $\text{La}_2\text{CuO}_4$ . Ordering of really different atoms in the lattice is also possible. It should be noted that, in the case of systems with strongly correlated electrons, the alternant model is not quite suitable for the description of magnetic properties, although it can be useful for the investigation of gap formation, the charge-density distribution and the total energy (Oles and Zaanen 1989, Loktev *et al* 1992). For systems with a frozen charge density wave and for complex systems having a superstructure, this model is fully adequate.

The  $\text{LaCuO}_3$  and  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$  crystals may be close to instability even though they exhibit metallic properties. Oxygen vacancies ( $V_{\text{O}}$ ) may through deformation make these crystals unstable, so that they could acquire dielectric properties. Elsewhere we shall examine why  $V_{\text{O}}$  may lead to strong deformation. Here we restrict ourselves to the following qualitative comment.

Owing to the presence in the electronic spectrum of oxides of low-lying electron states of atoms M, the electrons are withdrawn from the centre of  $V_{\text{O}}$  to the nearest M atoms. Therefore, the potential of  $V_{\text{O}}$  is incompletely screened at cations nearest to the vacancy, so that strong forces act on the cations, which strive to shift them away from  $V_{\text{O}}$  (figure 1). Such great atomic displacements were observed near F-centres in the case of alkali-halide crystals in the excited p state. This was the consequence of the fact that such a state proved in large measure delocalized. In the oxides considered here, the effect of crystal expansion takes place even in the ground state.

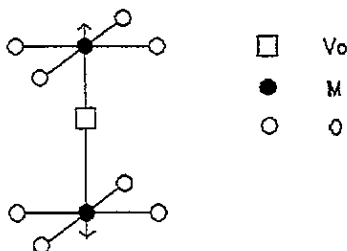


Figure 1. The nearest neighbours of the oxygen vacancy in the  $\text{AMO}_3$  crystals of the perovskite family.

Since the oxygen atom in the lattice is in a non-cubic position (figure 1), the local deformation arising in this case is tetragonal. Obviously, for the macroscopic deformation to have the same character, either the lattice should be unstable or there should occur ordering interactions of defects.

The tetragonal distortion of the lattice may give rise to the localization of electrons in planes perpendicular to the  $c$  axis and, consequently, to the dielectrization of the spectrum. This hypothetical possibility will be dealt with in section 2 in terms of the model of alternating planes. Section 3 moves on to examine the electronic spectrum for the case when alternation of the potential occurs not only between the planes, but also in the planes themselves. Localization of electrons in this case may be explained by the overall expansion of the lattice caused by  $V_{\text{O}}$ . In section 4 the theory will be applied to the  $\text{LaCuO}_3$  and  $\text{BaBiO}_3$  crystals. Section 5 proposes the model of three alternating sublattices. Section 6 discusses the results obtained, which, in particular, will be generalized for the  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{3-\delta}$  crystal, and section 7 will be devoted to conclusions.

## 2. A model of alternating planes

The tetragonal distortion of the crystal leading to its elongation means that the hopping integrals are reduced along the  $c$  axis. This may cause localization of electrons in atomic planes perpendicular to the  $c$  axis. Let us examine the electronic spectrum that is obtained in this case.

A unit cell of the  $\text{AMO}_3$  crystal comprises in the cubic phase one M atom and three atoms of oxygen. The atom A may ordinarily be regarded as simply a donor of electrons for the sublattice  $\text{MO}_3$ . Thus, the atom La donates three electrons, and the Ba atom two.

Let us double the unit cell (figure 2) and assume that the electron at the atoms  $M_1$  and  $M_2$  can possess different energies. This means that we admit the possibility of the alternating planes  $(M_1)\text{O}_2\text{-O-(}M_2)\text{O}_2\text{-O-(}M_1)\text{O}_2\text{-...}$  being formed in which the one-electron potentials are, generally speaking, different. This may result from the situation when  $M_1$  and  $M_2$  have somewhat different nearest surroundings, but it can likewise be a consequence of the correlation effects. Of interest also is the case when the atoms  $M_1$  and  $M_2$  are actually different.

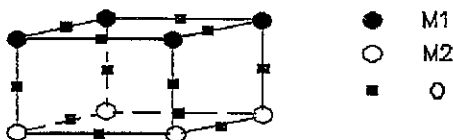


Figure 2. The  $\text{AMO}_3$  crystal of the perovskite family with two alternating planes.

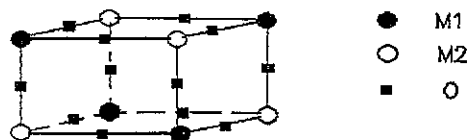


Figure 3. The  $\text{AMO}_3$  crystal of the perovskite family with two alternating sublattices.

The secular equation of the tight-binding method will be written with the interaction of only the nearest neighbours taken into account:

$$\begin{aligned}
 (\varepsilon_1 - \varepsilon)C_1 + \mathbf{t}_1 C_0^{(1)} + \mathbf{v}_1 C_0^{(1,2)} &= 0 \\
 (\varepsilon_2 - \varepsilon)C_2 + \mathbf{t}_2 C_0^{(2)} + \mathbf{v}_2 C_0^{(1,2)} &= 0 \\
 \mathbf{t}_1^+ C_1 - \varepsilon C_0^{(1)} &= 0 \\
 \mathbf{t}_2^+ C_2 - \varepsilon C_0^{(2)} &= 0 \\
 \mathbf{v}_1^+ C_1 + \mathbf{v}_2^+ C_2 - \varepsilon C_0^{(1,2)} &= 0.
 \end{aligned} \tag{1}$$

Here  $\mathbf{t}_1$ ,  $\mathbf{t}_2$ ,  $\mathbf{v}_1$  and  $\mathbf{v}_2$  are the matrices of the hopping integrals;  $C_1$  and  $C_2$  are the components of the vector of states for the atoms  $M_1$  and  $M_2$ ,  $C_0^{(1)}$ ,  $C_0^{(2)}$  for oxygen atoms in the corresponding planes and  $C_0^{(1,2)}$  for interplanar atoms; and  $\varepsilon_1$  and  $\varepsilon_2$  are the electron energies at the atoms  $M_1$  and  $M_2$ , respectively, with the energy zero set at oxygen atoms.

Next we remove from (1) the vectors of state of the oxygen atoms. The result for  $\varepsilon \neq 0$  looks like

$$\begin{aligned}
 \hat{\mathbf{A}}_1 C_1 + \mathbf{V}_{12} C_2 &= 0 \\
 \hat{\mathbf{A}}_2 C_2 + \mathbf{V}_{12}^+ C_1 &= 0
 \end{aligned} \tag{2}$$

where  $\hat{\mathbf{A}}_i = \varepsilon(\varepsilon_i - \varepsilon)\mathbf{I} + \mathbf{W}_i$ ,  $\mathbf{W}_i(k_x, k_y) = \mathbf{t}_i \mathbf{t}_i^+ + \mathbf{v}_i \mathbf{v}_i^+$ ,  $\mathbf{V}_{12} = \mathbf{v}_1 \mathbf{v}_2^+$ ,  $\mathbf{I}$  is the identity matrix. Thus, the three-band model has been reduced to the two-band one whose matrix

of the effective Hamiltonian depends on the energy  $\varepsilon$ . By going the same way we simplify the problem further still, reducing it to the one-band type. For this purpose the vector  $C_2$  is removed from (3). On condition that  $\det \|\varepsilon(\varepsilon_2 - \varepsilon)\mathbf{I} + \mathbf{W}_2\| \neq 0$  we arrive at

$$(\hat{\mathbf{A}}_2 \hat{\mathbf{A}}_1 - \mathbf{Y})C_1 = 0 \quad (3)$$

where  $\mathbf{Y} = \mathbf{V}_{12} \mathbf{V}_{12}^\dagger$ .

Let us now examine the electron energy dependence on  $k_z$  at unchanged  $k_x$  and  $k_y$ . It will be assumed that all the operators in the parentheses in (3) can be diagonalized simultaneously. This is trivial in the case when the basis includes one electron state at the atoms  $M_1$  and  $M_2$ , since in this case the matrices  $\mathbf{W}_1$ ,  $\mathbf{W}_2$  and  $\mathbf{Y}$  have one eigenvalue each. The eigenvalues of the operator  $\mathbf{Y}(k_z)$ , judging from its construction, cannot take on negative values. Hence

$$\lambda_1 \lambda_2 \geq 0 \quad (4)$$

where  $\lambda_i = \varepsilon(\varepsilon_i - \varepsilon) + w_i$ ,  $w_i$  is the eigenvalue of the operator  $\mathbf{W}_i$ . The lower boundary of inequality (4) is reached at

$$\begin{aligned} \varepsilon^{(1,2)} &= \varepsilon_1/2 \pm (\varepsilon_1^2/4 + w_1)^{1/2} \\ \varepsilon^{(3,4)} &= \varepsilon_2/2 \pm (\varepsilon_2^2/4 + w_2)^{1/2}. \end{aligned} \quad (5)$$

Let us place the four values (5) in order of increasing energy  $u_1$ ,  $u_2$ ,  $u_3$  and  $u_4$ . It is now not difficult to show that the inequality (4) is violated between  $u_1$  and  $u_2$  as well as  $u_3$  and  $u_4$ . In other words, there are gaps in the electronic spectrum in these energy intervals. The gaps are absent only when  $u_1$  and  $u_2$  or when  $u_3$  and  $u_4$  coincide. When the Fermi level lies in the said energy intervals, the electrical conductivity must acquire two-dimensional character.

The other boundaries of the electronic spectrum can be obtained from the condition

$$\max w_1 \max w_2 \geq y. \quad (6)$$

It follows from (3) and (6) that

$$\varepsilon[\varepsilon(\varepsilon_1 - \varepsilon)(\varepsilon_2 - \varepsilon) + \max w_1(\varepsilon_2 - \varepsilon) + \max w_2(\varepsilon_1 - \varepsilon)] \leq 0. \quad (7)$$

It can be seen that the energy  $\varepsilon = 0$  is always a possible boundary of the spectrum. Note that in our model this is the energy of the 2p state of oxygen. For example, on the condition that  $\varepsilon_1 = \varepsilon_2 = \varepsilon_M$ , one will conclude from (7) that there is a gap in the electronic spectrum between the energy  $\varepsilon_M$  and the energy of the oxygen 2p level ( $\varepsilon = 0$ ). This is an ordinary charge-transfer gap, which was carefully studied by Rebane for  $A_n B_m$  alloys (Rebane 1986). This gap exists in all the dielectric cubic oxides of e.g.  $\text{SrTiO}_3$  type (Wolfram and Ellialtioglu 1982, Julien *et al* 1989). The forbidden gap in  $\text{SrTiO}_3$  amounts to 3.2 eV. This gap most closely corresponds to the difference between energies of Ti 3d and O 2p levels (Harrison 1983), which confirms the theory described above.

The electronic energy spectrum can be represented in analytical form in the following cases:

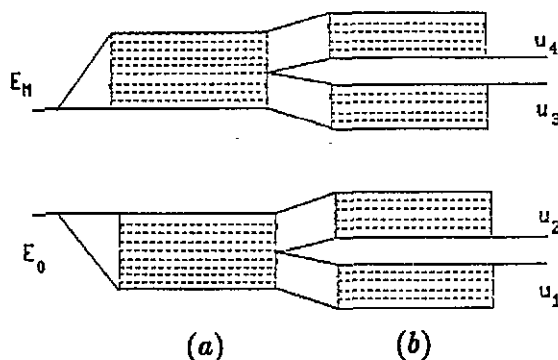


Figure 4. The electronic structure schemes for the ordinary alternant systems (a) and for the generalized ones (b).

$$(i) \varepsilon_1 = \varepsilon_2$$

$$\varepsilon = \varepsilon_1/2 \pm \{ \varepsilon_1^2/4 + (w_1 + w_2)/2 \pm [(w_1 + w_2)^2/4 - w_1 w_2 - y]^{1/2} \}^{1/2} \quad (8)$$

$$(ii) \varepsilon_1 = \Delta, \varepsilon_2 = -\Delta, w_1 = w_2 = w$$

$$\varepsilon = \pm \{ (\Delta^2 + 2w)/2 \pm [(\Delta^2 + 2w)^2/4 - w^2 + y]^{1/2} \}^{1/2} \quad (9)$$

as well as in the exotic case of  $\varepsilon_1 w_2 + \varepsilon_2 w_1 = 0$ , which we do not consider here.

The examination has shown that the alternation of planes in a tetragonally distorted crystal may produce a strongly anisotropic forbidden gap in the electronic spectrum, which, in turn, may render the character of the electrical conductivity two-dimensional. Obviously, there are no reasons in this case for the complete localization of electrons.

### 3. Model of two alternating sublattices

Next we turn to the electronic spectrum in the case when the atoms alternate, not only between planes, but also in the planes themselves. Thus, if we have a simple cubic lattice of atoms  $M$  in an  $\text{AMO}_3$  crystal, it can be represented as two alternate FCC sublattices. Assume that one of these accommodates  $M_1$  atoms, and the other  $M_2$  atoms. Evidently,  $M_1$  will be surrounded by  $M_2$  only and vice versa (figure 3). Assuming further that the electron energies at these atoms are different, we can write the secular equation of the tight-binding method as

$$\begin{aligned} (\varepsilon_1 - \varepsilon)C_1 + \mathbf{t}_1 C_0 &= 0 \\ (\varepsilon_2 - \varepsilon)C_2 + \mathbf{t}_2 C_0 &= 0 \\ \mathbf{t}_1^+ C_1 + \mathbf{t}_2^+ C_2 - \varepsilon C_0 &= 0 \end{aligned} \quad (10)$$

where  $\mathbf{t}_1$  and  $\mathbf{t}_2$  are the hopping integrals, and  $C_1$ ,  $C_2$ ,  $C_0$  the components of the vector of states. Reducing the problem to the one-band type, we again obtain equation (3); however, the quantities contained in it are defined differently as  $\mathbf{W}_1 = \mathbf{t}_1 \mathbf{t}_1^+$ ,  $\mathbf{W}_2 = \mathbf{t}_2 \mathbf{t}_2^+$ ,  $\mathbf{Y} = |\mathbf{t}_1 \mathbf{t}_2^+|^2$ . Hence, all conclusions drawn earlier for the problem (1) are equally valid for the problem (10); in particular, there are gaps between the energies  $u_1$  and  $u_2$ , and between  $u_3$  and  $u_4$ . Unlike the case of the alternating planes, here the gap in the electron spectrum exists for any  $k_x$ ,  $k_y$  and  $k_z$ . Thus, if the Fermi level is located in this gap, the crystal must exhibit dielectric properties (figure 4). The other boundaries of the electronic spectrum including the charge-transfer gap can be obtained from the inequality (7).

In the alternant model the direct interaction of the second nearest neighbours is neglected. However, this interaction, relatively weak as it is, does still exist, which provides conditions for the existence of a semimetallic state of the crystal when the bands do not intersect, but the direct gap is absent. From this it follows that the conditions for the formation of a gap in the electronic spectrum obtained by us should be determined more exactly. Let us assume that, owing to possible changes in the potential of the atoms M, the groups of levels  $u_1$ ,  $u_2$ ,  $u_3$  and  $u_4$  have their own dispersion. Then the gap in the spectrum arises only in the case when the corresponding energy intervals do not intersect. Otherwise, one should expect the appearance of the metallic or semimetallic state.

It is interesting to note that all the results obtained in this section are valid not only for ordered alternate sublattices but also for disordered crystals  $(M_1)_x(M_2)_{1-x}O_n$ . Indeed, in the foregoing we never made use of any attributes of the ordered phase. It was only important that the atoms  $M_1$  and  $M_2$  be surrounded by oxygen atoms and vice versa, and that the matrices  $\mathbf{W}_1$ ,  $\mathbf{W}_2$  and  $\mathbf{Y}$  be diagonalized simultaneously. However, in the case of an ordered cubic alternate lattice of  $A(M_1)_{1/2}(M_2)_{1/2}O_3$  type, the matrices  $\mathbf{W}_1$  and  $\mathbf{W}_2$  are proportional to the identity matrix (see section 4). In the disordered lattice this is no longer valid. In the latter case  $\mathbf{W}_1$  and  $\mathbf{W}_2$  have several eigenvalues and, consequently, the quantities  $u_1$ ,  $u_2$ ,  $u_3$  and  $u_4$  have their own dispersion.

Let us now take up the question of a possible change in the electron spectrum produced by  $V_O$ . The removal of an oxygen atom from the lattice results in the breaking of the chemical bonds Cu-O. The energy of the levels in the forbidden gap associated with this breaking can in this case be estimated in the approximation of remote orbitals (Bernholm and Pantelides 1978) from the equation

$$g_0(\varepsilon) = 0 \quad (11)$$

where  $g_0$  is the diagonal element of the electron Green function. For the problem (10), on the condition that  $\varepsilon_1 = -\varepsilon_2 = \delta$ ,  $w_1 = w_2 = w$ , this element can be expressed via a universal function depending on the dimensionless parameter (Prosandeyev and Tarasevich 1992)

$$g_0 = [\varepsilon(\varepsilon^2 - w - \delta^2)/w^2]f(e) + 1/[2(\varepsilon + i0)] \quad (12)$$

where

$$f(e) = \frac{1}{\Omega} \sum_{\lambda} \int d^3k [e - y^\lambda/w + i \operatorname{sgn}(\mu)0]^{-1} \quad (13)$$

$$\mu = (2\varepsilon/w^2)(2\varepsilon^2 - 2w - \delta^2)$$

$$e = 1 + \varepsilon^2(\varepsilon^2 - 2w - \delta^2)/w^2.$$

Here  $y^\lambda$  is the  $\lambda$ th eigenvalue of the operator  $\mathbf{Y}$ . The general analysis of the function (12) has shown that it changes its sign in the forbidden gap. This means that in the forbidden gap there exists a solution to equation (11) and, consequently,  $V_O$  has its eigenstates. Their presence in the spectrum leads to the situation in which an increase in the  $V_O$  concentration in the dielectric phase does not produce metallic properties in the crystal. However, this is valid so long as  $V_O$  can be regarded as isolated defects.

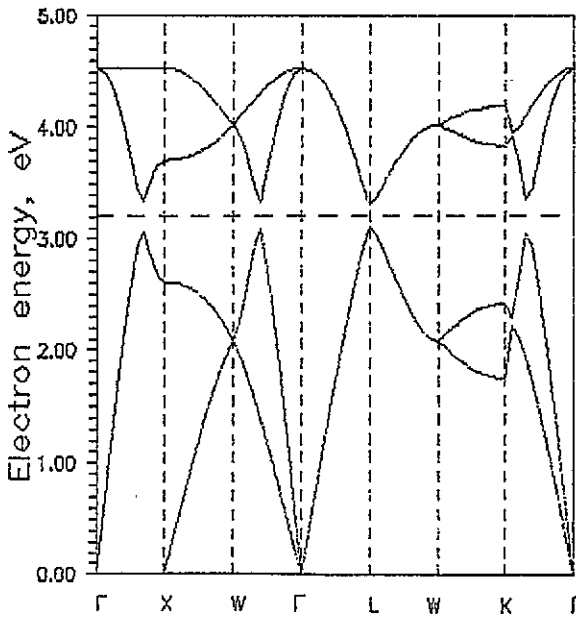


Figure 5. The band structure of  $\text{LaCuO}_3$  obtained within the alternant model.

#### 4. Electronic structure of $\text{LaCuO}_3$ and $\text{BaBiO}_3$ after the application of the alternating potential

The theory described in the preceding section will now be applied to  $\text{LaCuO}_3$  (for the case of  $\text{La}_2\text{CuO}_4$ , see Oles and Zaanen (1989) and Loktev *et al* (1992)). The doubled unit cell of the  $\text{LaCuO}_3$  crystal consists of two La, two Cu and six O atoms. The basis for each copper atom includes the orbitals  $d_{x^2-y^2}$  and  $d_{z^2}$ , and for the oxygen atom the orbital  $p\sigma$ . In this case  $\mathbf{W}_1 = \mathbf{W}_2 = 3V_\sigma^2\mathbf{I}$ ,

$$y = (Y_{11} + Y_{22})/2 \pm [(Y_{11} + Y_{22})^2/4 + Y_{12}^2]^{1/2} \quad (14)$$

where

$$\begin{aligned} Y_{11} &= 3V_\sigma^4 \{3 \cos^2(k_1 a/2) \cos^2[(k_3 - k_2)a/2] + \sin^2(k_1 a/2) \sin^2[(k_3 - k_2)a/2]\} \\ Y_{22} &= V_\sigma^4 \{3 \sin^2(k_1 a/2) \sin^2[(k_3 - k_2)a/2] + \{\cos(k_1 a/2) \cos[(k_3 - k_2)a/2] \\ &\quad + 2 \cos[(k_1 - k_2 - k_3)a/2]\}^2\} \\ Y_{12} &= 2\sqrt{3}V_\sigma^4 \sin(k_1 a/2) \sin[(k_3 - k_2)a/2] \{2 \cos(k_1 a/2) \cos[(k_3 - k_2)a/2] \\ &\quad + \cos[(k_1 - k_2 - k_3)a/2]\}. \end{aligned} \quad (15)$$

Here  $V_\sigma$  is the integral of the  $(pd\sigma)$  interaction. The results of the electronic spectrum calculation by means of formula (9) are given in figure 5. As follows from the general analysis in section 3, in the electronic spectrum at  $\Delta \neq 0$  there is a gap, the width of which is  $\Delta$ . Thus, we may conclude that the dielectrization of the electronic spectrum occurring in  $\text{LaCuO}_3$  crystals with increasing  $\delta$  is caused by the localization of electrons in alternate sublattices of copper atoms. This, in turn, results from the expansion of the lattice produced by  $V_O$ .



Similar results were obtained for BaBiO<sub>3</sub> whose basis of electronic states included 6s states of Bi and p $\sigma$  states of O (for a more complicated model whose basis contains also 6p states, see Mattheiss and Hamann (1983)). In this case we have  $w = 6V_{sp\sigma}^2$  where  $V_{sp\sigma}$  is the integral of the (sp $\sigma$ ) interaction

$$y = V_{sp\sigma}^4 \{6 + 4 \cos(k_1 a) + 4 \cos(k_2 a) + 4 \cos(k_3 a) + 4 \cos[(k_1 - k_2) a] \\ + 4 \cos[(k_2 - k_3) a] + 4 \cos[(k_1 - k_3) a] + 2 \cos[(k_3 + k_1 - k_2) a] \\ + 2 \cos[(k_1 + k_2 - k_3) a] + 2 \cos[(k_1 - k_2 - k_3) a]\}. \quad (16)$$

Calculation results obtained by means of formula (9) are given in figure 6. As expected, there is a gap in the electronic spectrum at  $\Delta \neq 0$ . However, here it results from the ordering of the charge density, which occurs on account of the freezing of the breathing mode.

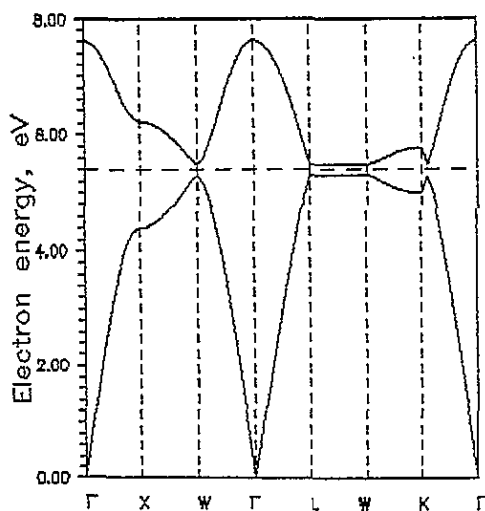


Figure 6. The band structure of BaBiO<sub>3</sub> obtained within the alternant model.

Let us now consider in some detail the selection of the model parameters. The integrals of the (pd $\sigma$ ) and (sp $\sigma$ ) interactions have been found from the condition of the best approximation of calculation results for the band structure of non-alternated LaCuO<sub>3</sub> and BaBiO<sub>3</sub>. For LaCuO<sub>3</sub> this work was based on calculations by Darracq *et al* (1993), while in the case BaBiO<sub>3</sub> the results were taken from Mattheiss and Hamann (1983):  $V_{pd\sigma} = -1.1$  eV,  $V_{sp\sigma} = -2.2$  eV. The alternation of the potential in the sublattice of Cu (Bi) was performed through varying the diagonal elements of the Hamiltonian:  $\varepsilon_{d1} = -\Delta$ ,  $\varepsilon_{d2} = \Delta$ , where  $\Delta = 0.2$  eV for LaCuO<sub>3</sub> and for BaBiO<sub>3</sub>. The choice of the value of  $\Delta$  for LaCuO<sub>3</sub> was not dictated by any conditions since, according to the results of section 3, a gap in the spectrum must exist for any  $\Delta \neq 0$ . This follows from the fact that, in the case of the approximations used, there is a nesting on the Fermi surface, which causes the Peierls instability. The data given in figure 5 merely serve to illustrate this effect. As regards BaBiO<sub>3</sub>, the value of  $\Delta$  for this crystal was selected with the condition taken into account that the calculated value of the forbidden gap must coincide with that obtained by experiment (0.2 eV).

In more exact models that account for interactions between the second—and so on—nearest neighbours, the nesting condition will obviously be violated. However, as follows from the results of section 3, the gap in the electron spectrum can be presented in this case also, albeit on condition that the groups of levels  $u_1$  and  $u_2$ , and  $u_3$  and  $u_4$  do not intersect. Calculation carried out by Mattheiss and Hamann (1983) using the linear augmented plane-wave (LAPW) method has shown that in the case of  $\text{BaBiO}_3$  the gap does open when the cell is doubled. We expect that the same approach may be helpful in verifying also our data for the volume-expanded  $\text{LaCuO}_3$ .

### 5. Three alternating sublattices

Let us consider the more complicated case of lattice M that consists of three sublattices  $M_1$ ,  $M_2$  and  $M_3$ , the atoms of the first two of which are surrounded by atoms of the third. In a manner similar to that used in section 3, one may obtain the equation

$$[(\hat{A}_1\hat{A}_3 - \mathbf{Y}_1)(\hat{A}_2\hat{A}_3 - \mathbf{Y}_2) - |\mathbf{Y}_{12}|^2]C_1 = 0 \quad (17)$$

where  $\mathbf{Y}_1 = \mathbf{V}_{13}\mathbf{V}_{13}^+$ ,  $\mathbf{Y}_2 = \mathbf{V}_{23}\mathbf{V}_{23}^+$ ,  $\mathbf{Y}_{12} = \mathbf{V}_{13}\mathbf{V}_{23}^+$ ,  $\mathbf{V}_{ij} = \mathbf{t}_i\mathbf{t}_j^+$ . Taking into account that all the eigenvalues of the operator  $|\mathbf{Y}_{12}|^2$  are positive, we have

$$(\lambda_1\lambda_3 - y_1)(\lambda_1\lambda_3 - y_2) \geq 0 \quad (18)$$

where  $y_1$  and  $y_2$  are the eigenvalues of the matrices  $\mathbf{Y}_1$  and  $\mathbf{Y}_2$ . We have assumed here that all the matrices in (17) can be diagonalized simultaneously.

The lower boundary of inequality (18) can be easily found from the equation

$$(\lambda_1\lambda_3 - y_1)(\lambda_2\lambda_3 - y_2) = 0. \quad (19)$$

The eight values obtained can be placed in order of increasing energy  $u_1, u_2, \dots, u_8$ . Evidently, there are gaps in the electronic spectrum between  $u_1$  and  $u_2$ , between  $u_3$  and  $u_4, \dots, u_7$  and  $u_8$ . All that was said in section 3 regarding the dispersion of  $w_1$  and  $w_2$  can now be repeated for the quantities  $y_1$  and  $y_2$ .

As in section 2, we can now obtain the other boundaries from the following inequalities:

$$\begin{aligned} \max y_1 \max y_2 - z &\geq 0 \\ \max w_1 \max w_3 - y_1 &\geq 0 \\ \max w_2 \max w_3 - y_2 &\geq 0 \end{aligned} \quad (20)$$

where  $z$  is an eigenvalue of the operator  $|\mathbf{Y}_{12}|^2$ .

In the foregoing we considered the models of alternating planes, as well as of two and three sublattices. Clearly, this theory can be evolved further, i.e. four and more sublattices may be invoked. For example, if a simple cubic lattice is represented in the form of two FCC lattices, each of these may again be divided into four equivalent simple cubic lattices and so on. Thus, one may expect that not only the electronic spectrum of  $\text{AM}_{1/2}^{(1)}\text{M}_{1/2}^{(2)}\text{O}_3$ -type crystals can contain forbidden gaps caused by the localization of electrons, but that this will be valid also in the case of  $\text{AM}_{1/2}^{(1)}\text{M}_{1/8}^{(2)}\text{M}_{1/8}^{(3)}\text{M}_{1/8}^{(4)}\text{M}_{1/8}^{(5)}\text{O}_3$ .

We wish now to sum up the discussion, highlighting its important aspects. First, analytical expressions have been derived that define the boundaries of the electronic

spectrum and account for both the charge transfer and the Peierls instability. We did that for a large number of oxides with alternant structures, making use of reasonable approximations based on an analysis of calculation results for band structure. Of course, the correctness of the analytical description of the electronic spectrum rests on the assumption that the inclusion of the interaction between only the nearest neighbours is sufficient and valid. However, we can point out that this assumption has already been scrupulously examined for  $AMO_3$ -type crystals (Harrison 1983, Julien *et al* 1989, Mattheiss and Hamann 1983, Wolfram and Ellialtioglu 1982) and shown to be satisfactory.

Another point we should like to emphasize is the following. When dielectric oxides of the perovskite family are reduced, they, as a rule, acquire some metallic attributes. For example, strongly reduced  $SrTiO_3$  has black colour and a relatively high electrical conductivity. The transition of metallic oxides  $LaCuO_{3-\delta}$  and  $BaPb_{0.75}Bi_{0.25}O_3$  into the dielectric state experimentally observed (Darracq *et al* 1993, Hashimoto and Kawazoe 1993) with increase in  $\delta$  was therefore an unexpected phenomenon calling for a theoretical explanation.

Darracq and co-workers observed experimentally that the increase in  $\delta$  leads to distortion of the crystal and assumed that this distortion was the cause of the localization of electrons in  $LaCuO_{3-\delta}$ . Under the same assumption, we found that the electrical conductivity may acquire two-dimensional character as a result of the potential being alternated in the planes. This finding has to be verified. The total localization of electrons is practicable in terms of our model only on condition that the volume expansion of the crystal taking place with the increase of  $\delta$  is included. Such an expansion provides for the localization of electrons, not only in alternant planes, but also in alternant sublattices.

Thus, the main idea that can help to rationalize the experimental data discussed here may be put as follows. The removal of oxygen atoms from the lattice leads to its volume expansion, and this expansion is precisely the factor that triggers the transition of the crystal into the dielectric state.

In deriving the formulae, we by no means intended simply to demonstrate once again the general conditions of the appearance of gaps in the electronic spectrum produced by the Peierls instability of electrons. Rather, these formulae allow one to describe analytically the electronic spectra of a large class of oxides in the approximation of interaction between the nearest neighbours and under conditions of an alternating potential. The formulae in question have already been used by us to explain some recent experiments in which uncommon results were obtained.

## 6. Discussion

We have carefully examined the comparatively simple cases of  $LaCuO_3$  and  $BaBiO_3$  and applied the alternant theory to explain the increasing dielectrization of the electronic spectrum with increasing oxygen deficiency. Unfortunately, too little is known about the energy level positions in  $BaPb_{0.75}Bi_{0.25}O_3$ , which does not allow us to calculate its electronic structure within the alternant theory. However, we wish to offer a qualitative judgment on this topic using the three alternant sublattices model described in section 5.

It follows from the theory developed in section 5 that the electrons in  $BaPb_{0.75}Bi_{0.25}O_3$  can be localized due to a difference between the energies of Pb and Bi levels as well as because of the alternation of the potential in the Bi sublattice (differences in hopping integrals are also possible). The electrons of  $V_O$  fill the bands up to the full dielectrization of the electronic spectrum.

Let us consider more closely the first eventuality. Imagine that the Pb energy level lies so much higher than the Bi level (and the oxygen one) that the electrons of  $V_O$  fill only the Bi-O bands. Then to fill this band completely it is necessary to have 0.25 electrons per atom M. Thus, 0.125  $V_O$  will fill the band since each  $V_O$  has two electrons. This may explain why at  $\delta = 0.15$  the sample has dielectric properties.

A different possible cause of dielectrization could be the alternation of the potential in the Bi sublattice. If the Pb level lies much higher than the Bi level (and the oxygen one), then there is no need for additional electrons since the ordered phase with the alternate Bi sublattice has dielectric properties anyway (section 4).

Thus, both these possible causes could explain the experiment when the 6s level of Pb has a high energy. However, we may reasonably assume that the Pb level has a higher energy than the Bi level but it cannot lie too much higher than the oxygen 2p level because it is known that the  $\text{BaPbO}_3$  crystal has a semimetallic property owing to a slight intersection between the 6s band of lead and 2p band of oxygen (Mattheiss and Hamann 1983). Possibly, in  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$  such an intersection is no longer present, but more probably, both factors are important to explain the experiment. It can be fairly well illustrated by the model of three sublattices (section 5). Indeed, a gap can exist in this model not only because of a difference between  $\epsilon_1(\text{Bi}^{3+})$  and  $\epsilon_2(\text{Bi}^{5+})$  but also as a result of a difference between  $\epsilon_1$  and  $\epsilon_3(\text{Pb})$  as well as  $\epsilon_2$  and  $\epsilon_3$ . It is important only that the quantities  $u_1$  and  $u_2$ ,  $u_3$  and  $u_4, \dots, u_7$  and  $u_8$  should not coincide.

The localization of electrons can also occur in a different manner, for example, (i) in virtue of the electrons being bound near  $V_O$ , (ii) because of the widening of dielectric intergranular layers in ceramics due to a great number of  $V_O$ , (iii) following the formation of the dielectric superstructure, etc. At the same time, the above-mentioned version as to the localization of electrons resulting from the alternation of the potential in the sublattice of Bi and from the difference between the energies of the Pb and Bi levels seems to us quite sensible. It is the more so as this approach gives the same qualitative results as those obtained by Sofu *et al* (1989) through calculations using the coherent-potential method. In this work the electronic structure of  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  was examined making use of methods that are ordinarily applied in the case of disordered alloys with the cubic structure of the  $\text{A}_{1-x}\text{B}_x$  type. It was assumed in this case that if the Bi atoms in the lattice lie close to one another, their potential alternates. The energy of the atomic level of Pb lay higher by approximately 3 eV than the level of Bi. These conditions proved sufficient to show that there is, in accordance with the experiment, a certain critical value of the concentration  $x$  above which the samples exhibit dielectric properties. Our hypothesis is that this critical value will get lower upon the appearance of  $V_O$ . Note that, in order to obtain a result coinciding with the experiment, the authors of this work had to make the same assumption regarding the level of Pb as we did, namely, that these levels do not coincide with those of Bi. The 2p states of oxygen were not considered in this work at all, but in our model they are present.

Unfortunately, we do not know whether there is a disorder in the Pb-Bi positions or the crystal is ordered. It is interesting to note that, if the Bi atom is not present in all the layers (figures 7(a) and (b)), there arises the possibility of quasi-two-dimensional conductivity similar to that in the layered copper oxides (section 2). This could be the case for the tetragonal metal phase ( $\delta = 0.09$  and  $\delta = 0.11$ ). In the cubic phase ( $\delta = 0.15$ ) we could have a transition into a disordered dielectric phase, containing Bi in all the layers (figure 7(c)). It would be interesting to check this possibility experimentally.

The expansion of the crystal and its tetragonal distortion are, apparently, the main factors determining the phenomenon under discussion. At the same time, the following

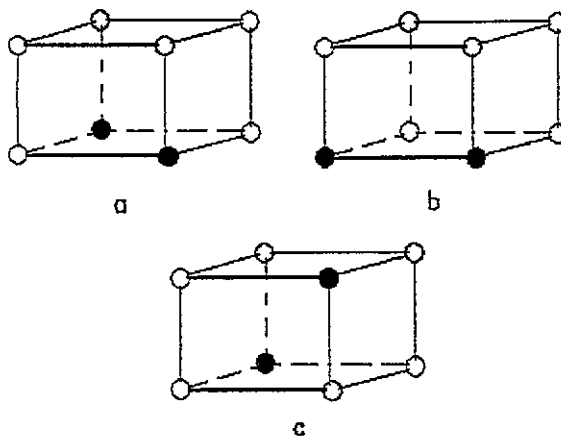


Figure 7. The possible crystal structures of  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ .

is to be noted. If the  $V_{\text{O}}$  vacancies could be regarded as independent, then, even though the local deformation near the  $V_{\text{O}}$  is tetragonal, the macroscopic deformation would be isotropic (on condition that the lattice is stable with respect to the tetragonal distortion). Thus, the tetragonal distortion of the lattice observed in experiments (Darracq *et al* 1993, Hashimoto and Kawazoe 1993) with increase of  $\delta$  could result either from the ordering of  $V_{\text{O}}$  along the  $c$  axis or from the instability of the lattice. In the former case  $V_{\text{O}}$  appear to produce a strong anisotropic potential. Similarly to the case of  $V_{\text{O}}$ , the substitution of La with smaller rare-earth atoms equally leads to the localization of electrons (Tresse *et al* 1991). These substitutions are, apparently, non-central and, consequently, dipolar. The anisotropic potential of microscopic dipoles in a lattice of polarizable ions is known to increase manifold, which may bring about observed deformations of crystals and the subsequent localization of electrons. We wish to point out that, in the case of two alternate lattices,  $V_{\text{O}}$  can also be a dipole centre. For example, in  $\text{BaBiO}_3$  the ions  $\text{Bi}^{3+}$  and  $\text{Bi}^{5+}$  are the nearest to the O atom. Two electrons of  $V_{\text{O}}$  are pulled to the  $\text{Bi}^{5+}$  ion, so that  $V_{\text{O}}$  acquires a large dipole moment.

The instability of the lattice with respect to the tetragonal distortion can also be caused by the Jahn–Teller effect. Thus, it is known that the cluster  $(\text{CuO}_6)^{10-}$  must have tetragonal distortion because precisely such a distortion removes the degeneration of  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals. The  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  crystals are also susceptible to tetragonal distortion in a certain range of concentration  $x$ . It is possible that  $V_{\text{O}}$  broadens the lattice and thereby creates conditions for lattice distortion. It is similar to the action of a negative pressure.

## 7. Conclusions

Finally, we summarize the main points of the work. We associated the dielectrization of the electronic spectrum of  $\text{LaCuO}_{3-\delta}$  and  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{3-\delta}$  observed experimentally when  $\delta$  is increasing with the alternation of the potential in the sublattice of Cu (Pb–Bi). The metal–dielectric transition is, in our view, caused by the general widening (and elongation) of crystals, which is due to considerable displacement of the nearest-to- $V_{\text{O}}$  cations away from the centre of  $V_{\text{O}}$ . The widening of the crystal lowers the covalent degree of chemical bonds, whereby the conditions are eased in which the alternation of the potential takes

place. The alternation of the potential in the sublattice of atoms M produces forbidden gaps in the electronic spectrum, which, generally speaking, cannot be classified as gaps with charge transfer, although for a large width of the gaps the difference is not significant. We believe that further band-structure calculations carried out self-consistently and with accurate exchange and correlation approximations to the potential and charge density will confirm the results obtained in the simple tight-binding model.

### Acknowledgment

This work was supported by the Russian National Scientific Program on HTSC through the project No 92068.

### References

- Barnholm J and Pantelides S T 1978 *Phys. Rev.* **18** 1780  
Brown P A 1986 *Fiz. Tverd. Tela* **28** 1914  
Coulson C A and Longuet-Higgins H C 1947 *Proc. R. Soc. A* **191** 39  
Darracq S, Matar S and Demazeau G 1993 *Solid State Commun.* **85** 961  
Harrison W A 1983 *Electronic Structure and Properties of Solids* (Moscow: MIR)  
Hashimoto T and Kawazoe H 1993 *Solid State Commun.* **87** 251  
Julien J P, Mayou D and Cyrot-Lackmann F 1989 *J. Physique* **50** 2683  
Loktev V M, Prosandeyev S A and Tarasevich Yu Yu 1992 *Phys. Status Solidi b* **174** 141  
Mattheiss L F and Hamann D R 1983 *Phys. Rev. B* **28** 4227  
Oles A M and Zaanen J 1989 *Phys. Rev. B* **39** 9175  
Prosandeyev S A and Tarasevich Yu Yu 1992 *Ferroelectrics* **131** 141  
Rebane T K 1986 *Fiz. Tverd. Tela* **28** 1368  
Sofa J O, Aligia A A and Nunez Regueiro M D 1989 *Phys. Rev.* **39** 9701  
Tresse F, Demazeau G and Muller K A 1991 *High Pressure Res.* **7** 61  
Wolfram T and Ellialtioglu S 1982 *Phys. Rev. B* **25** 2697