

Electronic Structure in Perovskite-Type Oxide Mixtures

Chieko TOTSUJIT† and Takeo MATSUBARA†

†*Department of Applied Physics, Okayama University of Science*

1-1 Ridaicho, Okayama 700, Japan

‡*Okayama Ceramics Research Center*

1406-18 Nishi-Katakami, Bizen-Shi 705, Japan

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Electronic structures of perovskite-type oxide mixtures are studied on the basis of the coherent potential approximation (CPA), one of the most powerful methods for random systems. A multi-band formulation is given for a typical case of mixed perovskites, ABO_3 - $AB'O_3$, and the results are compared with predictions of model calculations.

§1. Introduction

Recently, an electronic theory for the ferroelectric phase transition has been developed and applied to some perovskite type oxides^{1),2)}. The theory is based on the so-called two-band theory and has been successful in explaining the ferroelectric phase transitions in the quantum-paraelectric mixed perovskites. The essential ingredient of the theory may be summarized as follows.

The temperature dependence of the frequency of the soft mode ω_s is expressed as

$$\omega_s^2 = \omega_0^2 \left\{ 1 - \frac{16}{\omega_0 N} \sum_{\mathbf{k}} [G(\mathbf{k})]^2 \frac{f(E_{\mathbf{k}}^v) - f(E_{\mathbf{k}}^c)}{E_{\mathbf{k}}^c - E_{\mathbf{k}}^v} \right\} + B\Theta \coth\left(\frac{\Theta}{T}\right). \quad (1)$$

Here ω_0 is the soft mode bare frequency without perturbation due to electron-phonon coupling. N is the number of unit cell, $G(\mathbf{k})$, the electron-phonon interaction constant, $f(E)$, the Fermi distribution, B , a constant characterizing the strength of the anharmonicity, and Θ , the temperature of a cross-over from the classical high temperature to quantum low temperature behaviors.

The ferroelectric phase appears when the soft mode frequency vanishes. The transition temperature, T_c , is thus determined by

$$\frac{\Theta}{T_c} = \coth^{-1} \left\{ \frac{\omega_0^2}{B\Theta} \left(\frac{16g^2}{\omega_0 \Delta_0} - 1 \right) \right\}. \quad (2)$$

Here the electron-phonon coupling constant g is assumed to have no wave-number dependence and we write the remaining wave-number-dependent part as

$$\frac{1}{\Delta_0} = \frac{1}{N} \sum_k \frac{f(E_k^v) - f(E_k^c)}{E_k^c - E_k^v}. \quad (3)$$

The electronic structure of the crystal plays an important role in determining the phase transition temperature ; it is expected that a small change in $1/\Delta_0$ induces phase transitions either at lower or higher temperatures. In order to analyze the effect of mixing on ferroelectric phase transition it is therefore necessary to calculate the electronic band structure of mixed crystals.

Based on model calculations for mixed crystal, we have shown that the balance between the broadening of the band width and the narrowing of the energy gap is mainly responsible for the modification of the phase diagrams³⁾. When the former effects is large enough to overcome the latter, the phase transition temperature reduces dramatically.

In this paper, we calculate the energy band structure of some mixed perovskites and show that the above model calculations is applicable to real substances.

§2. Tight Binding Hamiltonian for Perovskite-Type Oxide

As in the previous paper²⁾, we follow Wolfram's simple LCAO tight-binding method⁴⁾ to calculate the band structure. In the perovskite structure, which is usually written as ABO_3 , A-site ions at the corner are mostly either alkali metals, alkaline-earth metal, or rare-earth metals. A transition metal atom is at the body center (B-site) and six oxygen atoms are at each face center forming an octahedron. These atoms, metal atoms at B-site and oxygen atoms, mainly determine the electronic band structure related to interesting properties of perovskite-type oxides. We thus have to take into account only nine p-orbitals of three oxygen atoms and five d-orbitals of a transition metal atom in a unit cell in our calculation.

For the sake of simplicity, we consider p-d coupling and neglect small p-p overlap integrals. This treatment nonetheless reproduces the essential part of the energy bands of perovskite structures. As a result, we have 14×14 Hamiltonian matrix which can be reduced to a 5×5 matrix and three 3×3 matrices.

$$H = \begin{bmatrix} \mathbf{M}_{xyz} & 0 & 0 & 0 \\ 0 & \mathbf{M}_{xy} & 0 & 0 \\ 0 & 0 & \mathbf{M}_{yz} & 0 \\ 0 & 0 & 0 & \mathbf{M}_{zx} \end{bmatrix}, \quad (4)$$

$$\mathbf{M}_{xyz} = \begin{bmatrix} E_e & 0 & -\frac{1}{2} V_{pd\sigma d_x} & -\frac{1}{2} V_{pd\sigma d_y} & V_{pd\sigma d_z} \\ 0 & E_e & \frac{\sqrt{3}}{2} V_{pd\sigma d_x} & -\frac{\sqrt{3}}{2} V_{pd\sigma d_y} & 0 \\ -\frac{1}{2} V_{pd\sigma d-x} & \frac{\sqrt{3}}{2} V_{pd\sigma d-x} & E_{||} & 0 & 0 \\ -\frac{1}{2} V_{pd\sigma d-y} & -\frac{\sqrt{3}}{2} V_{pd\sigma d-y} & 0 & E_{||} & 0 \\ V_{pd\sigma d-z} & 0 & 0 & 0 & E_{||} \end{bmatrix}, \quad (5)$$

$$\begin{aligned} d_x &= 1 - e^{2ik_x d}, \quad d_{-x} = 1 - e^{-2ik_x d}, \\ d_y &= 1 - e^{2ik_y d}, \quad d_{-y} = 1 - e^{-2ik_y d}, \\ d_z &= 1 - e^{2ik_z d}, \quad d_{-z} = 1 - e^{-2ik_z d}, \end{aligned}$$

and

$$\mathbf{M}_{\alpha\beta} = \begin{bmatrix} E_t & V_{pd\pi}(1 - e^{2ik_\alpha d}) & V_{pd\pi}(1 - e^{2ik_\beta d}) \\ V_{pd\pi}(1 - e^{-2ik_\alpha d}) & E_\perp & 0 \\ V_{pd\pi}(1 - e^{-2ik_\beta d}) & 0 & E_\perp \end{bmatrix}, \quad (6)$$

$\alpha, \beta = x, y, z.$

Here $V_{pd\sigma}$ and $V_{pd\pi}$ are overlap integrals between neighboring oxygen and transition metal atoms and d is the lattice constant. E_t and E_e are diagonal matrix elements for d-orbitals: They contain the ionization energy of an electron in the free ion of the transition metal, the Madelung potential at the site of this metal ion, and the electrostatic shift in the energy of the d-levels, t_{2g} and e_g , due to the cubic crystalline field. For p-orbital, we similarly denote the diagonal energies by $E_{||}$ and E_\perp . In this case the electrostatic shift is due to the axial crystalline field.

In Fig. 1, the energy bands of SrTiO₃ are shown as an example and the density of states is given in Fig. 2.

§3. CPA Formulation

Let us now consider the mixture containing B-site randomness. We define the Green's function $F_0(z)$ by

$$F_0(z) = \frac{1}{N} \text{Tr}[z1 - \epsilon(\mathbf{k})]^{-1}, \quad (7)$$

where z is the complex energy, and $\epsilon(\mathbf{k})$ is the energy of unperturbed Hamiltonian. The averaged Green's function is written in terms of the self energy $\mathbf{u}(z)$ in the form

$$F_0(z - \mathbf{u}(z)) = \frac{1}{N} \text{Tr}[z1 - \mathbf{u}(z) - \epsilon(\mathbf{k})]^{-1}. \quad (8)$$

The random potential w_l at l -th site appears to have the effective potential \tilde{w}_l written by

$$\tilde{w}_l = w_l - \mathbf{u}(z). \quad (9)$$

This potential works as a perturbation in the uniform substance giving the scattering expressed by t -matrix as

$$t_l = \frac{\tilde{w}_l}{1 - \tilde{w}_l F_0}. \quad (10)$$

The t -matrix describes the effect of the scattering of an electron due to an atom on site l embedded in the effective medium F_0 . We therefore require, on the average,

$$\begin{aligned} \langle t_i \rangle &\equiv \frac{\tilde{w}_i}{1 - \tilde{w}_i F_0} \\ &\equiv \int \frac{\{w - \mathbf{u}(z)\} P(w) dw}{1 - \{w - \mathbf{u}(z)\} F_0(z - \mathbf{u}(z))} = 0. \end{aligned} \quad (11)$$

In the two-component system, $AB_cB'_{1-c}O_3$, the probability distribution of w can be

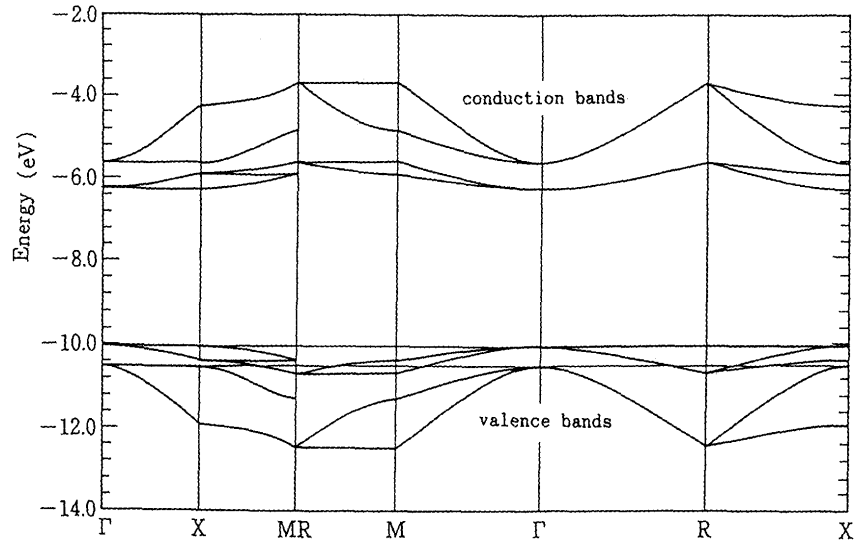


Fig. 1 Energy bands for SrTiO₃ given by simple tight binding method.

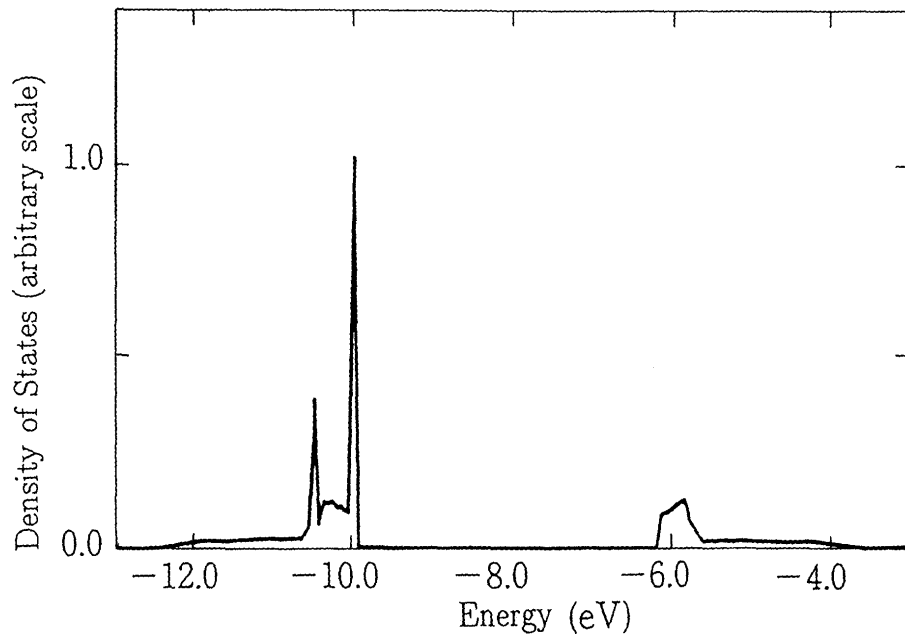


Fig. 2 Density of states calculated from energy bands shown in Fig. 1.

expressed as $P(w) = c$ or $1 - c$. In this case, we have

$$\langle t_i \rangle = \frac{c(E_B - \mathbf{u}(z))}{1 - F_0(z - \mathbf{u}(z))(E_B - \mathbf{u}(z))} + \frac{(1 - c)(E_{B'} - \mathbf{u}(z))}{1 - F_0(z - \mathbf{u}(z))(E_{B'} - \mathbf{u}(z))}. \quad (12)$$

Then CPA requires average t -matrix to vanish as

$$\langle t_i \rangle = 0. \quad (13)$$

Now we apply the above formalism to the mixed perovskite containing B-site randomness. We assume that the mixing does not affect the electronic energy of oxygen ions nor interaction energy between the electrons on B-sites and those on oxygen sites. Hamiltonian of our system is written as

$$\hat{H} = \hat{K} + \sum_j |j\rangle [\xi_j(E_B - \mathbf{u}(z)) + (1 - \xi_j)(E_{B'} - \mathbf{u}(z))] \langle j|. \quad (14)$$

where $|j\rangle$ is the Wannier wave functions. The diagonal part of Eq. 6 in each material is given by

$$E_{B,B'} = \begin{pmatrix} E_t^{B,B'} & 0 & 0 \\ 0 & E_\perp & 0 \\ 0 & 0 & E_\perp \end{pmatrix}, \quad (15)$$

and that of Eq. 5, by

$$E_{B,B'} = \begin{pmatrix} E_e^{B,B'} & 0 & 0 & 0 & 0 \\ 0 & E_e^{B,B'} & 0 & 0 & 0 \\ 0 & 0 & E_{||} & 0 & 0 \\ 0 & 0 & 0 & E_{||} & 0 \\ 0 & 0 & 0 & 0 & E_{||} \end{pmatrix}. \quad (16)$$

In Eq. 14, \hat{K} contains the off-diagonal components without randomness or

$$\epsilon(\mathbf{k}) = \begin{pmatrix} 0 & \alpha & \beta \\ -\alpha & 0 & 0 \\ -\beta & 0 & 0 \end{pmatrix}, \quad (17)$$

$$\alpha = 2i V_{pd\pi} \sin k_x d, \quad \beta = 2i V_{pd\pi} \sin k_y d,$$

and

$$\epsilon(\mathbf{k}) = \begin{pmatrix} 0 & 0 & -\alpha & -\beta & -\gamma \\ 0 & 0 & \sqrt{3}\alpha & -\sqrt{3}\beta & 0 \\ \alpha & -\sqrt{3}\alpha & 0 & 0 & 0 \\ \beta & \sqrt{3}\beta & 0 & 0 & 0 \\ \gamma & 0 & 0 & 0 & 0 \end{pmatrix}, \quad (18)$$

$$\alpha = -i V_{pd\sigma} \sin k_x d, \quad \beta = -i V_{pd\sigma} \sin k_y d, \quad \gamma = 2i V_{pd\sigma} \sin k_z d.$$

Since we take into account the randomness only in B-sites, we define unknown

functions with self energy as follows ;

$$\mathbf{u}(z) = \begin{pmatrix} u + E_{\perp} & 0 & 0 \\ 0 & E_{\perp} & 0 \\ 0 & 0 & E_{\perp} \end{pmatrix}, \quad (19)$$

and

$$\mathbf{u}(z) = \begin{pmatrix} u + E_{\parallel} & 0 & 0 & 0 & 0 \\ 0 & u + E_{\parallel} & 0 & 0 & 0 \\ 0 & 0 & E_{\parallel} & 0 & 0 \\ 0 & 0 & 0 & E_{\parallel} & 0 \\ 0 & 0 & 0 & 0 & E_{\parallel} \end{pmatrix}. \quad (20)$$

We now apply above functions to obtain density of states (DOS) in mixed crystal. Since σ -band states can be treated in the same manner, only π -band states are shown hereafter.

We first calculate the right hand side of Eq. 8 as

$$\begin{aligned} & z\mathbf{1} - \mathbf{u}(z) - \varepsilon(\mathbf{k}) \\ &= \begin{pmatrix} z & 0 & 0 \\ 0 & z & 0 \\ 0 & 0 & z \end{pmatrix} - \begin{pmatrix} u + E_{\perp} & 0 & 0 \\ 0 & E_{\perp} & 0 \\ 0 & 0 & E_{\perp} \end{pmatrix} + \begin{pmatrix} 0 & \alpha & \beta \\ -\alpha & 0 & 0 \\ -\beta & 0 & 0 \end{pmatrix} \\ &= \begin{pmatrix} z - E_{\perp} & 0 & 0 \\ 0 & z - E_{\perp} & 0 \\ 0 & 0 & z - E_{\perp} \end{pmatrix} - \begin{pmatrix} u & \alpha & \beta \\ -\alpha & 0 & 0 \\ -\beta & 0 & 0 \end{pmatrix}. \end{aligned} \quad (21)$$

The inverse of Eq. 21 is given as

$$[z\mathbf{1} - \mathbf{u}(z) - \varepsilon(\mathbf{k})]^{-1} = \mathbf{U} \begin{pmatrix} \frac{1}{z - E_{\perp}} & 0 & 0 \\ 0 & \frac{1}{z - E_{\perp} - \lambda_{-}} & 0 \\ 0 & 0 & \frac{1}{z - E_{\perp} - \lambda_{+}} \end{pmatrix} \mathbf{U}^{-1}, \quad (22)$$

where $\lambda_{\pm} = \frac{1}{2}(u \pm \sqrt{u^2 - 4(\alpha^2 + \beta^2)})$, and

$$\mathbf{U} = \begin{pmatrix} 0 & \sqrt{\frac{\lambda_{+}}{\sqrt{u^2 - 4(\alpha^2 + \beta^2)}}} & \sqrt{\frac{\lambda_{-}}{\sqrt{u^2 - 4(\alpha^2 + \beta^2)}}} \\ -\frac{\beta}{\sqrt{\alpha^2 + \beta^2}} & \cdots & \cdots \\ \frac{\alpha}{\sqrt{\alpha^2 + \beta^2}} & \cdots & \cdots \end{pmatrix}. \quad (23)$$

Averaged Green's function, Eq. 8, can then be expressed as

$$F_0(z - \mathbf{u}(z)) = \frac{1}{N} \text{Tr}[z\mathbf{1} - \mathbf{u}(z) - \varepsilon(\mathbf{k})]^{-1}$$

$$\begin{aligned}
&= \frac{1}{N} \sum_{\mathbf{k}} \mathbf{U} [z \mathbf{1} - \mathbf{u}(z) - \boldsymbol{\varepsilon}(\mathbf{k})]^t \mathbf{U} \\
&= \begin{pmatrix} f_{11} & f_{12} & f_{13} \\ f_{21} & f_{22} & f_{23} \\ f_{31} & f_{32} & f_{33} \end{pmatrix}, \tag{24}
\end{aligned}$$

and

$$1 - F_0(z - \mathbf{u}(z)) \cdot (E_{B,B'} - \mathbf{u}(z)) = \begin{pmatrix} 1 - f_{11}(E_t^{B,B'} - u - E_{\perp}) & 0 & 0 \\ -f_{21}(E_t^{B,B'} - u - E_{\perp}) & 1 & 0 \\ -f_{31}(E_t^{B,B'} - u - E_{\perp}) & 0 & 1 \end{pmatrix}.$$

Using the inverse of the right hand side of this equation, we have

$$\begin{aligned}
&\frac{E_t^{B,B'} - \mathbf{u}(z)}{1 - F_0(z - \mathbf{u}(z)) \cdot (E_{B,B'} - \mathbf{u}(z))} \\
&= \begin{pmatrix} E_t^{B,B'} - u - E_{\perp} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{1 - f_{11}(E_t^{B,B'} - u - E_{\perp})} & 0 & 0 \\ \frac{-f_{21}(E_t^{B,B'} - u - E_{\perp})}{1 - f_{11}(E_t^{B,B'} - u - E_{\perp})} & 1 & 0 \\ \frac{-f_{31}(E_t^{B,B'} - u - E_{\perp})}{1 - f_{11}(E_t^{B,B'} - u - E_{\perp})} & 0 & 1 \end{pmatrix} \\
&= \frac{(E_t^{B,B'} - u - E_{\perp})}{1 - f_{11}(E_t^{B,B'} - u - E_{\perp})}.
\end{aligned}$$

Finally, CPA condition of Eq. 12 is written as

$$\frac{c(E_t^B - u - E_{\perp})}{1 - f_{11}(E_t^B - u - E_{\perp})} + \frac{(1-c)(E_t^{B'} - u - E_{\perp})}{1 - f_{11}(E_t^{B'} - u - E_{\perp})} = 0. \tag{25}$$

From Eqs. 22, 23, and 24, we obtain f_{11} as

$$\begin{aligned}
f_{11} &= \frac{1}{N} \sum_{\mathbf{k}} \frac{z - E_{\perp}}{(z - E_{\perp})^2 - u(z - E_{\perp}) + (\alpha^2 + \beta^2)} \\
&= \left(\frac{d}{2\pi}\right)^2 \iint_{-\pi/d}^{\pi/d} \frac{(z - E_{\perp}) dk_x dk_y}{(z - E_{\perp})^2 - u(z - E_{\perp}) - 2V_{pd}^2(-\cos 2k_x d - \cos 2k_y d + 2)}. \tag{26}
\end{aligned}$$

From Eq. 25, f_{11} is also given by

$$f_{11} = \frac{c}{E_t^{B'} - u - E_{\perp}} + \frac{1-c}{E_t^B - u - E_{\perp}}. \tag{27}$$

To obtain the electronic density of states in mixed crystal, we only have to calculate the imaginary part of f_{11} using Eqs. 26 and 27 : The imaginary part of Green's function is precisely the electronic density of states.

§4. A Simple Example and Results

Since it is difficult to execute numerical computations in the form presented in the previous section, we now confine ourselves within the analysis of mixing effect by

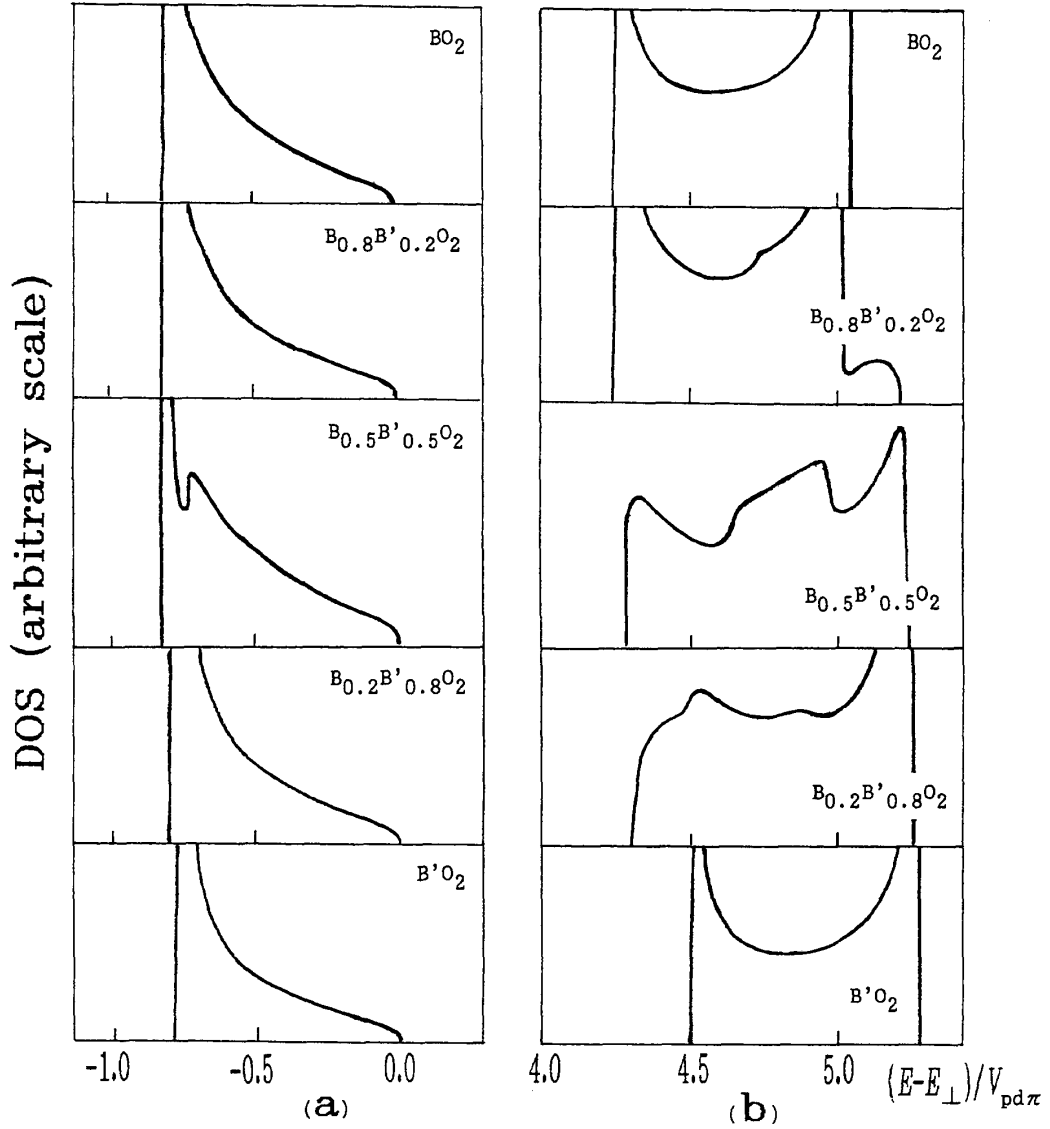


Fig. 3 Electronic density of states in $B_c B'_{1-c} O_2$.
 $(E_t^B - E_\perp) / V_{pd\pi} = 4.25$, $(E_t^{B'} - E_\perp) / V_{pd\pi} = 4.50$, and $E_\perp = 0.0$.
 (a) valence bands and (b) conduction bands.

simplified model of two-dimensional BO_2 system. The problem reduces to 2×2 matrices with one conduction band (out of five d-orbitals of a transition metal ion) and one valence band (out of six p-orbitals of two oxygen ions). In this case, Eq. 26 becomes

$$f_{11} = \frac{d}{2\pi} \int_{-\pi/d}^{\pi/d} \frac{1}{u} \left\{ -2 + \frac{2(z - E_\perp)^2 - (z - E_\perp)u}{(z - E_\perp)^2 - (z - E_\perp)u - 2V_{pd\pi}^2(1 - \cos 2kd)} \right\} dk. \quad (28)$$

With dimensionless variables

$$\frac{z - E_\perp}{V_{pd\pi}} = \epsilon, \quad \frac{u}{V_{pd\pi}} = v, \quad V_{pd\pi} f_{11} = F, \quad \frac{E_t^B - E_\perp}{V_{pd\pi}} = e^b \quad \text{and} \quad \frac{E_t^{B'} - E_\perp}{V_{pd\pi}} = e^{b'},$$

Eqs. 27 and 28 reduce to

$$ce^b + (1-c)e^{b'} - v - F(e^b - v)(e^{b'} - v) = 0, \quad (29)$$

and

$$(vF + 2)^2(\epsilon^2 - v\epsilon - 4)(\epsilon - v) = \epsilon(2\epsilon - v)^2. \quad (30)$$

The imaginary part of the solution F of Eqs. 29 and 30 gives the electronic density of states (DOS). We illustrate some examples in Fig. 3. Since the oxygen p-orbital energy is assumed to be the same in both component, the valence band DOS is slightly affected by mixing. The DOS of conduction band, on the contrary, is considerably changed; the band width are apparently broadened. We also observe that energy gaps in mixed crystal has become narrower than those in pure crystals.

§5. Discussions

We have calculated the electronic band structures of mixed perovskites taking the randomness in B-site into account. It has been shown that the mixing has an effect on the electronic structure inducing such changes in the phase diagrams as we have predicted in Ref. 3.

In order to compare the results of this scheme with phase transitions of real substances in more detail, we may have to take into account the randomness in both conduction and valence bands. In this case, the CPA analysis requires much more complicated computation and we also need further data on energy bands of pure perovskite materials. These detailed treatments are left as a problem in the future.

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