PHYSICAL REVIEW B VOLUME 49, NUMBER 23 15 JUNE 1994-I

Covalency contributions to the electronic polarizability in dielectric compounds

S. Ishihara and M. Tachiki
Institute for Materials Research, Tohoku University, Sendai 980, Japan

T. Egami
Department of Materials Science and Engineering and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6272

(Received 18 January 1994)

The electron covalency contributions to the polarizability in oxide dielectric compounds are studied in the electron-lattice coupling model by means of the exact diagonalization technique. These contributions originate from the charge transfer between the anion and the cation sites which produces an electric dipole moment extended over the anion-cation bond distance. When a strong on-site Coulomb repulsion between electrons is included, the electronic system is found to undergo a transition between the ionic and Mott insulating phases, and the covalency contributions to the polarizability are largely enhanced near the phase boundary. It is suggested that the present results may explain the high indices of refraction observed in the titanium oxides and the birefringence in the ferroelectric compounds.

I. INTRODUCTION

It is well known that the additivity assumption of the electronic polarizability is invalid even in the alkali halides and is further pronounced in the oxide compounds.[1,2] The values of the polarizability of the oxygen ions in oxides are widely distributed from 0.5–3.2 $\mathring{A}^3$, according to the difference of the crystal structures and the kinds of cations involved.[2,3] In order to explain the lack of the additivity in the polarizability, one of the present authors proposed the covalency mechanism[4] where the electron covalency virtually induces an electronic dipole moment. Since the induced dipole moment is extended over a cation-anion bond distance, even if an amount of the hopping charge is small, the large polarizability is expected. The authors used a perturbational approach for treating the electron covalency on the pair of an anion and a cation and applied the theory to the mono-oxides where systematic changes of the electronic polarizabilities are observed. Independently, Pantelides[5] proposed the interionic mechanism and derived in a perturbational sense a simple formula of the dielectric constant which depends on the interatomic spacing. On the other hand, Phillips and co-workers[6–9] presented a simple model to describe the static dielectric constant in the heteropolar covalent system based on the band scheme. They used a generalized single oscillator model originated from the interband transition, where the band gap has covalent and ionic contributions. The authors applied this model to zinc-blende, wurtzite and rock-salt-type crystals and presented a relation between the dielectric properties and the crystal structures.

Although several approaches were proposed from the different points of view as mentioned above, the nature of the polarizability on the transition-metal oxides has not been adequately described as shown in the following. A recent photoemission experiment[10–12] performed in TiO_2 showed that the Ti ion is considerably hybridized with the surrounding O ions, suggesting a significant amount of reduction of the Ti valence from the formal value. The large covalent characters are also reported in $BaTiO_3$.[10] Thus the perturbational approach for the electron covalency seems to be inadequate in these compounds. On the other hand, the oxides have ionic characters. For example in TiO_2, its static dielectric constant ($\epsilon_0 = 173$).[13–15] is considerably higher than the optical dielectric constant ($\epsilon_\infty = 7.2$),[2,13] indicating a strong ionic character. It seems to be inadequate to apply the simple formulas for the dielectric constant and the energy gap which are not as successful even in the rock-salt-type alkali halides.[8] For the purpose of describing the polarizability in the transition-metal oxides, it is necessary to use an approach without a perturbational approximation.

In the present paper, we study the covalency contributions to the electronic polarizability in dielectric compounds, based on the microscopic electron-lattice model in a linear chain system. The ground-state properties in this model have been studies in the previous papers[16] where the two phases were found by changing the energy parameter, and a dimerization-type lattice distortion was found to decrease greatly the ground-state energy near the phase boundary. In this paper, we introduce an electric field into the model and study the covalency contributions to the polarizability using an exact diagonalization method. Numerical calculations show that considerably large covalency contributions arise in the electronic polarizability. This mechanism is expected to be dominant in the transition-metal oxides, particularly in the titanium oxides. From the polarizability calculated as a function of the lattice displacement, we also expect that the covalency contributes to the birefringence.

In Sec. II, we describe a simple model Hamiltonian for the electron and lattice coupled system and discuss the interaction between the electric field and the covalent charge. We briefly review the previous results without the electric field in this section. In Sec. III, we present

0163-1829/94/49(23)/16123(6)/$06.00

numerical results of the electronic dipole moment and polarizability calculated by the exact diagonalization technique as a function of the lattice displacement. Section IV is devoted to concluding remarks and discussions.

II. MODEL AND FORMULATION

In order to investigate the covalency contributions to the dielectric properties, we set up the following model Hamiltonian which describes the electron and lattice system in a electric field. We consider two kinds of atoms in the unit cell located in a one-dimensional chain and only one electron orbital on each atom. These orbitals are referred as A and B orbitals hereafter which correspond to one of the $3d$ orbitals in the transition-metal ion and the $2p$ orbitals in the oxygen ion, respectively. As for the lattice system, we consider the static dimerization-type lattice distortion and introduce the electron-lattice interaction as a modulation of the electron transfer intensity. We apply the electric field parallel to the chain along the z axis. The model Hamiltonian consists of two parts

$$H=H_0+H_E \ . \tag{2.1}$$

The first term is the electron and lattice Hamiltonian without the electric field and the second term is the interaction term with the electric field. H_0 is given by

$$\begin{aligned} H_0 = &\sum_{i,\sigma} \epsilon_A a^\dagger_\sigma(i) a_\sigma(i) + \sum_{i,\sigma} \epsilon_B b^\dagger_\sigma(i) b_\sigma(i) \\ &+\sum_i U_A n_{a\uparrow}(i) n_{a\downarrow}(i) + \sum_i U_B n_{b\uparrow}(i) n_{b\downarrow}(i) \\ &+\sum_{i,\sigma} t_+ a^\dagger_\sigma(i) b_\sigma(i) + \sum_{i,\sigma} t_- a^\dagger_\sigma(i+1) b_\sigma(i) + \text{c.c.} \\ &+\sum_i V[n_a(i) n_b(i) + n_a(i+1) n_b(i)] \ , \end{aligned} \tag{2.2}$$

where $a^\dagger_\sigma(i)$ and $b^\dagger_\sigma(i)$ are electron creation operators of the Wannier states on A and B sites in the ith unit cell, respectively. The subscript σ is the electron-spin index. The first line on the right-hand side of Eq. (2.2) describes the one electron terms, and ϵ_A and ϵ_B are the level energies on A and B sites, respectively. We define the energy level separation as $\Delta = \epsilon_A - \epsilon_B$ which is kept as a positive value. In the second line, U_A and U_B are the Coulomb interaction energies on the same orbital and $n_{a\sigma}(i)$ and $n_{b\sigma}(i)$ are defined by

$$n_{c\sigma}(i) = c^\dagger_\sigma(i) c_\sigma(i) \quad (c=a \text{ or } b) \ . \tag{2.3}$$

The third line describes the electron hopping processes including the lattice distortion effects between the nearest-neighboring A and B sites. t_+ and t_- are defined by

$$t_\pm = \pm(t \pm \delta t) \ , \tag{2.4}$$

where δt is the contribution from the lattice distortion which is assumed to be proportional to the lattice displacement (δa)

$$\delta t = \beta \delta a \ . \tag{2.5}$$

t_+ represents the hopping intensity for the intradimmer (intracell) orbitals and t_- is for the interdimmer (intercell) orbitals. Signs in front of the right-hand side in Eq. (2.4) come from the phases of the wave functions. The last term represents the intersite Coulomb interactions between the nearest A and B sites. The number operator is defined as

$$n_c(i) = n_{c\uparrow}(i) + n_{c\downarrow}(i) \quad (c=a \text{ or } b) \ . \tag{2.6}$$

The total electron number is fixed as $2N$ where N is the number of the unit cell.

Before discussing H_E, we briefly review the previous results for the system of H_0. At first when we consider the limiting case as $t=0$, $\delta t=0$, and $V=0$, the electronic states is described as follows. The ground-state properties are qualitatively interchanged by changing parameters U_B and Δ. For the $\Delta > U_B$ case, two electrons in each unit cell are located in the B site and the system becomes the ionic state described as $A^{2+}B^{2-}$. On the other hand, for the $\Delta < U_B$ case, each A and B site possesses one electron and the system is transferred to the Mott insulating state described as $A^{1+}B^{1-}$. The many-body Hamiltonian including t and δt is solved by the exact diagonalization method in the finite-size chain system. The above two phases are still found even in the finite t case and significant changes in the spin and charge characters are observed by crossing the phase boundary. The critical value of U_B, at which the system changes from one phase to another with a fixed value of Δ, is termed as U_{B_c}. A dimerization-type lattice distortion strongly decreases the total energy around the crossover region. A similar phase change is investigated intensively in one-dimensional organic compounds of the charge-transfer type, termed as the neutral-ionic transition.[17-20] Detailed results and implications to the ferroelectrics are presented in the previous papers.[16]

Let us consider the second term in Eq. (2.1). The interaction between the electronic charge and the electric field parallel to the z direction is represented as follows:

$$H_E = eE \sum_\sigma \int dz\, \psi^\dagger_\sigma(z) z \psi_\sigma(z) \ , \tag{2.7}$$

where e is defined as the positive value. Since we consider a higher-frequency component in the electric field than the vibration of the ion, the interaction with the electronic charge is only taken into account in Eq. (2.7). $\psi_\sigma(z)$ is an electron field operator which is expanded by the Wannier functions and we rewrite H_E as follows:

$$H_E = H_E^{\text{diag}} + H_E^{\text{off}} \ . \tag{2.8}$$

H_E^{diag} is a site-diagonal part defined by

$$H_E^{\text{diag}} = eE \sum_{i,\sigma} [z_i^a a^\dagger_\sigma(i) a_\sigma(i) + z_i^b b^\dagger_\sigma(i) b_\sigma(i)] \ . \tag{2.9}$$

This site-diagonal part is interpreted as the usual interaction between the on site electronic charge $n_{c\sigma}(i)$ $(c=a$ or $b)$ and the electric-field potential eEz_i^c. When the electric-field potential is smaller than the energy gap, we introduce the electrochemical potential $\mu_E(z)$ defined by

$$\mu_E(z)=\mu_0-eEz \ , \tag{2.10}$$

where μ_0 is the chemical potential in no electric field. We assume that the electron energy levels ϵ_A and ϵ_B in the Eq. (2.2) are measured from the electrochemical potential.

The second part in Eq. (2.8) is a site-off-diagonal part given by

$$H_E^{\rm off}=eE\sum_{i,\sigma}[v_+(i)a_\sigma^\dagger(i)b_\sigma(i)+v_-(i)a_\sigma^\dagger(i+1)b_\sigma(i)+\text{c.c.}] \ . \tag{2.11}$$

v_+ and v_- in Eq. (2.11) are the site-off-diagonal matrix elements of the position z defined by

$$v_+=\int dz\,\phi_a^*\left[z+\frac{a_+}{2}\right]z\phi_b\left[z-\frac{a_+}{2}\right] , \tag{2.12a}$$

and

$$v_-=\int dz\,\phi_a^*\left[z-\frac{a_-}{2}\right]z\phi_b\left[z+\frac{a_-}{2}\right] , \tag{2.12b}$$

where $\phi_a(z)$ and $\phi_b(z)$ are the Wannier functions on A and B sites, respectively. a_+ and a_- are the distances between the A and B sites given by

$$a_\pm=\frac{a}{2}\mp\delta a \ , \tag{2.13}$$

a being the lattice constant. We assume that the correction on $v_\pm$ due to the lattice distortion is small and neglect δa dependence of $v_\pm$ in this paper, so that we obtain the following relation between v_+ and v_-:

$$v_-=v_+ \ . \tag{2.14}$$

In Eq. (2.11), v_+ is interpreted as the interaction intensity between the electric field and the intracell covalent charge $a_\sigma^\dagger(i)b_\sigma(i)$, and v_- is the interaction with the intercell covalent charge $a_\sigma^\dagger(i+1)b_\sigma(i)$, both having the same sign as shown in Eq. (2.14). Since δt also has the same sign in the interunit and intraunit cells shown in Eq. (2.4), $Ev_\pm$ is expected to play a similar role with δt on the electronic system.

In order to study a response to the electric field, we adopt the exact diagonalization method for a finite-size chain system; a one-dimensional three unit cell $(3A+3B)$ chain with the periodic boundary condition. The ground-state energy and the wave functions are obtained by the modified Lanczos method with good precision.[21,22] In the present one-dimensional small chain, we interpret E in Eq. (2.7) as the local electric field in the crystal and the polarization p and the polarizability α per molecule are given by

$$p=-\lim_{E\to 0}\frac{1}{N}\frac{\partial\langle H\rangle}{\partial E} \tag{2.15a}$$

and

$$\alpha=-\lim_{E\to 0}\frac{1}{N}\frac{\partial^2\langle H\rangle}{\partial E^2} \ , \tag{2.15b}$$

where $\langle H\rangle$ is the ground-state energy as a function of E.

III. NUMERICAL RESULTS

In this section, we present numerical results obtained by the computational calculation. We consider the following two cases. The first case is for $\delta a=0$. In the second case, the lattice is deformed in the static sense and we calculate the electronic polarizability as a function of δa.

Let us present numerical results for the $\delta a=0$ case. ΔE_G is a reduction of the ground-state energy due to the electric field defined by $\Delta E_G=E_G(E)-E_G(E=0)$. The electric-field dependence of ΔE_G are shown in Fig. 1 for several U_B cases. Parameter values are chosen as $\Delta=2$ eV, $t=1$ eV, $U_A=5$ eV, and $V=1$ eV, and the critical U_B value (U_{B_c}) is about 4.7 eV. Figure 1(a) is for the $U_B<U_{B_c}$ region (the ionic region) and Fig. 1(b) is for the $U_B>U_{B_c}$ region (the Mott region). With increasing U_B in the ionic region, the ΔE_G curve becomes gradually steep and at last the system is transformed to the Mott phase where the curvature is gradually reduced with increasing U_B. Although for all values of U_B the electric field decreases the ground-state energy, the energy reduction becomes prominent near the phase boundary. The decrease in the energy originates from the interaction between the electric field and the electronic polarization which is easily induced by the electron hopping near U_{B_c}. To calculate the electric polarization (p) and the electric polarizability (α), we interpolate the numerical data using the spline method. In Fig. 2, the electronic polarizability is presented as functions of U_B. The parameter values are chosen as $\Delta=2$ eV, $t=1$ eV, and $U_A=5$ eV, and the critical U_B values U_{B_c} are approximately 3.2 eV

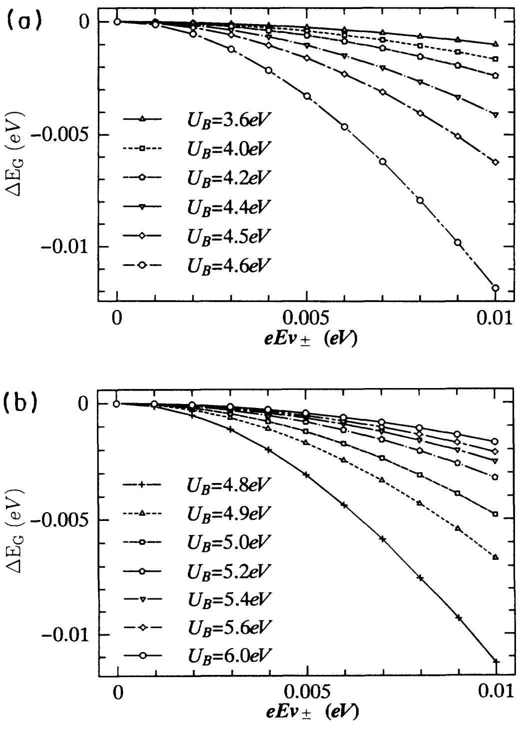

FIG. 1. Deviation of the ground-state energy from the $E=0$ case. (a) is for the ionic phase and (b) is for the Mott phase.

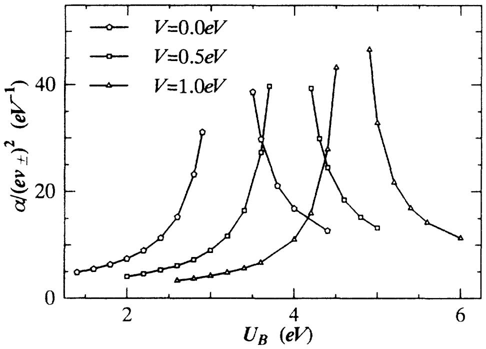

FIG. 2. The polarizability as a function of U_B in the $\delta a = 0$ case.

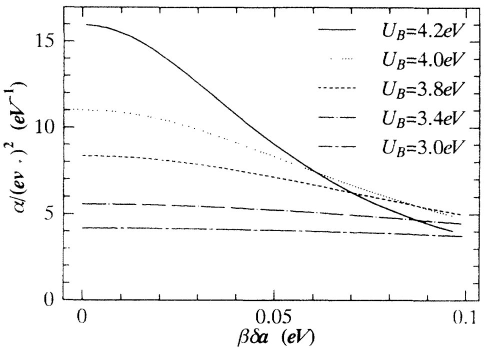

FIG. 4. The polarizability as a function of δa for the ionic phase.

(for $V=0.0$ eV), 4.1 eV (for $V=0.5$ eV), and 4.7 eV (for $V=1.0$ eV). In order to investigate the size effect on numerical values, we compare the results obtained in $(2A+2B)$, $(3A+3B)$, and $(4A+4B)$ chain systems. Because U_{B_c} slightly depends on the chain size, the calculated data is compared as a function of $(U_B - U_{B_c})$. Although about 20% deviations are found near U_{B_c} $(U_B - U_{B_c} = -0.2$ and $0.3)$, away from the crossover region $(U_B - U_{B_c} < -0.3$ and $U_B - U_{B_c} > 0.5)$ the size effect rapidly disappears and the obtained values in each case differ only by a few percent or less. Therefore, the numerical data in the above region and the whole features in Fig. 2 are reliable. In Fig. 2, the peak structure is observed around the crossover region, originating from the steepness of the curvature around U_{B_c} in Fig. 1. Near the phase boundary, the energy levels in the two phases become close to each other and the electron easily hops from one site to other. Therefore, the system becomes sensitive to the electric field and the electric polarizability gradually increases here. The U_B dependence of the polarizability is approximately proportional to the function of $1/(U_{B_c} - U_B)^{\gamma}$ in the ionic region. In $U_{B_c} - U_B > (t \sim 2t)$ region, the curve is fitted by the function with $\gamma = 1$ which is consistent with the behavior predicted in the perturbational approach[4,5] by assuming that $U_{B_c} - U_B$ is proportional to the energy gap. On the other hand, when $U_{B_c} - U_B$ is smaller than $(t \sim 2t)$, the component of $\gamma > 1$ appears and thus the perturbational approach seems to be inappropriate. Also the simple form used in the heteropolar semiconductors[6-9] is not adequate in fitting the present results. In the Mott phase each site has nearly one electron and the nearest-neighbor spin coupling decreases the energy due to the interaction between the electric field and the covalent charge. Therefore, α keeps a higher value even in the large $U_B - U_{B_c}$ region in this phase. The long-range Coulomb interaction stabilizes the ionic state and shifts U_{B_c} to a higher value. The peak structure in the polarizability becomes sharp and narrow in the large V case where the phase change abruptly occurs between the ionic and the Mott insulating phases.

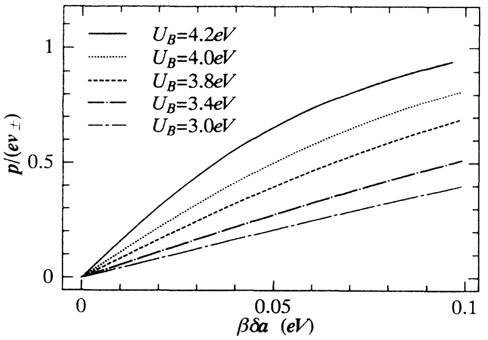

FIG. 3. The polarization as a function of δa for the ionic phase.

Next, we present numerical results in the finite δa case. The δa dependence of the polarization is presented in Fig. 3 for the ionic insulating side. The parameter values are chosen as $t=1$ eV, $\Delta=2$ eV, $U_A=5$ eV, and $V=1$ eV. The polarization due to the electron hopping is induced by the lattice dimerization and its intensity linearly increases with δa. Near the phase boundary it rises up abruptly and saturates to a certain value in the large δa region. In Fig. 4, the δa dependence of the polarizability is presented as a function of U_B for the ionic insulating region. The polarizability smoothly decreases with increasing δa and it is also most prominent near the phase boundary. In the large δa region, the polarizability does not depend as strongly on U_B any longer. The decrease in the polarizability originates from the stabilization of the system due to the lattice distortion. As we have investigated in the previous papers, the system is barely stable under the lattice dimerization, and the smaller the lattice displacement is, the larger the influences on the system is. However, once the lattice is distorted, the system settles to a stable state and is not as sensitive to the electric field any longer.

IV. CONCLUDING REMARKS AND DISCUSSION

In the present paper, we studied the covalency effects on the electronic polarizability in the dielectric compounds by using the electron-lattice coupling model including the electron covalency and the electron correlations. The virtual electron hopping induces the electric dipole moment extended over the interatomic distance which interacts with the electric field. This interaction induces a similar effect on the electronic system with the alternative modulation of the electron transfer intensity due to the lattice dimerization. The numerical results are summarized as follows. Without the electric field, the system undergoes the phase change between the ionic insulating phase and the Mott insulating phase when the energy parameters are changed. Near the phase boundary, the system becomes barely stable against a small perturbation like the electric field, so that the electronic polarizability is strongly enhanced. By introducing the lattice distortion the system ceases to be sensitive to the electric field, and the electronic polarizability smoothly decreases as the distortion increases.

There are important implications for the present results. First, large refractive indices and electronic polarizabilities were observed in the titanium oxides. Tessman and co-workers[2,23] have estimated the electronic polarizabilities of the oxygen ion in the several oxides from the experimental refractive indices and shown that the oxygen polarizabilities ($\alpha_{\rm ox}$) were found to be strongly dependent on its surrounding. In Be, Mg, Ca, Sr, and Ba mono-oxides, $\alpha_{\rm ox}$ shows a linear dependence on the oxygen volume in the crystal. The linear dependence of $\alpha_{\rm ox}$ has been explained by the volume dependence of the intraatomic oxygen polarizability evaluated from the Hartree-Fock wave functions for O^{2-} ion in a potential well.[24–26] On the other hand, the values of $\alpha_{\rm ox}$ estimated for $CaTiO_3$ and TiO_2 by using the Lorentz-Lorenz formula are about 80 percent higher than the line of the volume dependence in the mono-oxides. Since this formula is not rigorously valid for their crystal structures, we reexamine $\alpha_{\rm ox}$ for the perovskite-type titanium oxides by adopting the Slater formula[27] including the Lorentz corrections. It was found that the deviation from the Lorentz-Lorenz formula is smaller than a few percent. The higher values of $\alpha_{\rm ox}$ compared with the case of the mono-oxides suggest that the existence of additional contributions to the electronic polarizability in the case of the titanium oxides. In the present paper, U_B dependence of the polarizability are shown in Fig. 2. While only one orbital is considered on A and B sites in the present calculation, the effect of the orbital degeneracy in the titanium oxides contributes to the polarizability. From the small energy gap in the actual titanium oxides, for example 3.0 eV for TiO_2,[28] 3.2 eV for $BaTiO_3$,[29] and 3.4 eV for $SrTiO_3$,[30–32] it seems that the actual titanium oxides are not situated in the region as far away from the phase boundary in the ionic side where the perturbational approach tends to become inadequate as discussed in Sec. III. The numerical values for the polarizability presented in this paper evaluated by assuming that $v^2=0.03$ are $\alpha/(4\pi\epsilon_0)=1.03$ Å^3 at $U_B=3$ eV, 1.59 Å^3 at $U_B=3.4$ eV, and 2.83 Å^3 at $U_B=4.0$ eV for $V=1.0$ eV. These values are comparable to the atomic ion contributions estimated from the experimental refractive indices, for example 0.24 Å^3 for Ti^{4+}, 1.68 Å^3 for Ba^{2+}, and 0.51 Å^3 for Ca^{2+} by Ref. 33 and 2.45 Å^3 for O^{2-} in $BaTiO_3$ by present authors. It is concluded from the above that the covalency mechanism is a dominant contribution to the observed large electronic polarizabilities in the titanium oxides. Long ago, van Santen and de Boer[34] and Shockley[23] qualitatively discussed the high refractive index observed in the titanium oxide. van Santen and de Boer assumed the small distance between the excitation and ground levels. In contrast, Shockley stressed the large oscillator strength due to the Ti 4*s* and 4*p* orbitals. On the other hand, we propose that the induced dipole moment extended over the cation-anion distance due to charge transfer plays an important role on the high refractive index.

Varma and co-workers[35] proposed that the charge-transfer excitation enhances the electronic charge fluctuations in high-T_c cuprates. They predicted the large charge fluctuations occur in a metallic phase near the charge-transfer instability. The barely stable electronic state due to the Coulomb interaction is important for the enhancement of the electronic polarizability commonly in both Varma's case and our case for the insulating phase.

Also, our calculation has an implication with respect to a change in the refractive index due to the ferroelectric transition, which is experimentally evaluated by the birefringence. The measurements of the temperature dependence of the refractive indices[36–39] show that with the ferroelectric transition in $BaTiO_3$ from the cubic to the tetragonal phase, the refractive index in the a direction n_a shows no measurable anomaly at the Curie point. On the other hand, n_c rapidly decreases below T_c and n_c/n_a becomes 0.97 in the tetragonal phase. This is called the negative birefringence. Also, a similar temperature dependence of the refractive indices is observed in several ferroelectric compounds.[40–42] In this paper, we present the δa dependence of the polarizability in Fig. 4, where the polarizability smoothly decreases with increasing δa. Since the calculated polarizability in the finite δa case is considered the refractive index in the direction of the spontaneous polarization, the present mechanism contributes to the negative birefringence. The decreasing rate of the polarizability, defined as

$$[\alpha(\beta\delta a=0.0\ \text{eV})-\alpha(\beta\delta a=0.1\ \text{eV})]/\alpha(\beta\delta a=0.0\ \text{eV})\ ,$$

is about 40.3% at $U_B=3.8$ eV, 21.0% at $U_B=3.4$ eV, and 10.3% at $U_B=3.0$ eV. Kinase, Kobayashi, and Yamada[41] theoretically evaluated the birefringence from the atomic ion approach in the tetragonal $BaTiO_3$ taking account of the actual lattice distortion. The refractive indices were computed from the electronic polarizability data of each ions and the Lorentz field corrected by the lattice distortion, however, their result shows $n_c > n_a$ in the ferroelectric phase which is inconsistent with the experimental results. Kinase, Kobayashi, and Yamada attributed the discrepancy to the contribution from the electro-optic effect. The negative birefringence may also be explained from the present covalency mechanism.

ACKNOWLEDGMENTS

The authors would like to thank Professor K. Inoue, Professor A. Yamanaka, Professor A. Fujimori, Professor H. Matsumoto, Dr. T. Koyama, and Dr. S. Takahashi for useful discussions. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area, "Science of High-T_c Superconductivity" given by the Ministry of Education, Science and Culture, Japan, the National Science Foundation through Grant No. DMR91-20668, and the Office of Naval Research through Grant No. N00014-91-J-1036.

---

[1] K. Fajans and G. Joos, Z. Physik. **23**, 1 (1924).

[2] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

[3] R. Kirsch, A. Gérard, and M. Wautelet, J. Phys. C **7**, 3633 (1974).

[4] M. Tachiki and Z. Sroubek, J. Chem. Phys. **48**, 2383 (1968).

[5] S. T. Pantelides, Phys. Rev. Lett. **35**, 250 (1975).

[6] J. C. Phillips, Phys. Rev. Lett. **20**, 550 (1968); J. C. Phillips and J. A. Van Vechten, *ibid.* **22**, 705 (1969).

[7] J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973); Rev. Mod. Phys. **42**, 317 (1970).

[8] J. A. Van Vechten, Phys. Rev. **182**, 891 (1969).

[9] S. H. Wemple and M. DiDomenico, Jr., Phys. Rev. Lett. **23**, 1156 (1969); Phys. Rev. B **3**, 1338 (1971).

[10] L. T. Hudson, R. L. Kurtz, S. W. Robey, D. Temple, and R. L. Stockbauer, Phys. Rev. B **47**, 1174 (1993).

[11] T. Uozumi, K. Okada, and A. Kotani, J. Phys. Soc. Jpn. **62**, 2595 (1993).

[12] Y. Tezuka, S. Shin, T. Ishii, T. Ejima, S. Suzuki, and S. Sato, J. Phys. Soc. Jpn. **63**, 347 (1994).

[13] F. A. Grant, Rev. Mod. Phys. **31**, 646 (1959).

[14] G. A. Samara and P. S. Peercy, Phys. Rev. B **7**, 1131 (1973).

[15] S. Roberts, Phys. Rev. **76**, 1215 (1949).

[16] T. Egami, S. Ishihara, and M. Tachiki, Science **261**, 1307 (1993); S. Ishihara, T. Egami, and M. Tachiki, Phys. Rev. B **49**, 8944 (1994).

[17] J. B. Torrance, J. E. Vazquez, J. J. Mayerle, and V. Y. Lee, Phys. Rev. Lett. **46**, 253 (1981).

[18] J. Hubbard and J. B. Torrance, Phys. Rev. Lett. **47**, 1750 (1981).

[19] N. Nagaosa and J. Takimoto, J. Phys. Soc. Jpn. **55**, 2735 (1986); **55**, 2745 (1986); N. Nagaosa, *ibid.* **55**, 2754 (1986); **55**, 3488 (1986).

[20] M. Avignon, C. A. Balseiro, C. R. Proetto, and B. Alascio, Phys. Rev. B **33**, 205 (1986).

[21] E. Dagotto and A. Moreo, Phys. Rev. D **31**, 865 (1985).

[22] E. R. Gagliano and C. A. Balseiro, Phys. Rev. Lett. **59**, 2999 (1987).

[23] W. Shockley, Phys. Rev. **73**, 1273 (1948).

[24] R. E. Watson, Phys. Rev. **111**, 1108 (1958).

[25] J. Thorhallsson, C. Fisk, and S. Fraga, Theoret. Chim. Acta **10**, 388 (1968).

[26] A. Bussmann, H. Bilz, R. Roenspiess, and K. Schwarz, Ferroelectrics **25**, 343 (1980); H. Bilz, G. Benedek, and A. Bussmann-Holder, Phys. Rev. B **35**, 4840 (1987).

[27] J. C. Slater, Phys. Rev. **78**, 748 (1950).

[28] J. B. Goodenough, in *Progress in Solid State Chemistry,* edited by H. Reiss (Pergamon, London, 1971), Vol. 5.

[29] S. H. Wemple, Phys. Rev. B **2**, 2679 (1970).

[30] M. Cardona, Phys. Rev. **140**, A651 (1965).

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

[32] A. Fujimori, I. Hase, M. Nakamura, H. Namatame, Y. Fujishima, Y. Tokura, M. Abbate, F. M. F. de Groot, M. T. Czyzyk, J. C. Fuggle, O. Strebel, F. Lopez, M. Domke, and G. Kaindl, Phys. Rev. B **46**, 9841 (1992).

[33] H. Stuart, in *Atome und Ionen,* edited by A. Eucken, Landolt-Börnstein, Vol. 1, Pt. 1 (Springer-Verlag, Berlin, 1950).

[34] J. H. van Santen and F. de Boer, Nature **163**, 957 (1949).

[35] C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Solid State Commun. **62**, 681 (1987); P. B. Littlewood, C. M. Varma, and E. Abrahams, Phys. Rev. Lett. **63**, 2602 (1989); P. B. Littlewood, C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Phys. Rev. B **39**, 12 371 (1989).

[36] D. Meyerhofer, Phys. Rev. **112**, 413 (1958).

[37] H. F. Kay and P. Vousden, Philos. Mag. **40**, 1019 (1949).

[38] W. N. Lawless and R. C. deVries, J. Appl. Phys. **35**, 2638 (1964).

[39] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, New York, 1962).

[40] E. Wiesendanger, Ferroelectrics **1**, 141 (1970).

[41] W. Kinase, J. Kobayashi, and N. Yamada, Phys. Rev. **116**, 348 (1959).

[42] M. DiDomenico, Jr. and S. H. Wemple, J. Appl. Phys. **40**, 720 (1969); S. H. Wemple and M. DiDomenico, Jr., *ibid.* **40**, 735 (1969).