

Estimates of Anderson's electron-phonon-coupling constants for nonadiabatic small polarons in n -type BaTiO₃ using a polarizable point-ion shell model

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Using a combination of the attractive potential of a polaron proposed by Anderson and the polarizable point-ion shell model developed by Dienes *et al.*, Anderson's electron-phonon-coupling constants (λ) and changes in interionic spacings (x) due to nonadiabatic small polarons in n -type BaTiO₃ have been estimated by adjusting the calculated values to fit the experimental results, i.e., the polaron binding energy and the deformation energy. Although these values are important for an understanding of the dynamics of small polarons, they are quite difficult to estimate experimentally. In the shell model, the repulsive interactions between ions have been evaluated by the free-ion model constructed by Wedepohl. Though the shell parameters representing the effective numbers of polarizable electrons in ions are determined empirically, they are very close in values to the theoretical ones of Shankar *et al.* Since there is no information on the nature of the electrons localized on Ti ions, two possibilities have been considered, i.e., $3d$ electrons or s -like electrons. The calculations have been carried out in cubic and rhombohedral structures. In the cubic structure, λ and x between Ti³⁺ and Ti⁴⁺ in $\langle 110 \rangle$ are ~ -3.60 eV/Å and ~ -0.01 Å and those between Ti³⁺ and O²⁻ in $\langle 100 \rangle$ are ~ 0.82 eV/Å and ~ 0.03 Å for $3d$ electrons. In the case of s -like electrons, λ and x for the ion pair Ti³⁺ and Ba²⁺ in $\langle 111 \rangle$ and those of Ti³⁺-O²⁻ pairs are ~ -1.29 eV/Å, ~ -0.02 Å and ~ 0.60 eV/Å, ~ 0.03 Å, respectively. In the rhombohedral structure, the values for λ and x are a little different from those in the cubic structure. These calculations suggest clearly that small polarons are stabilized in both the cubic and rhombohedral structures and the polaronic conduction is also confirmed theoretically to take place in n -type BaTiO₃.

I. INTRODUCTION

As majority carriers in crystals of high ionicities, polarons have attracted much interest, and it is important to understand their behavior. A polaron is stabilized through a local deformation of the lattice due to the electron-phonon interaction.¹ From this point of view, Anderson^{2,3} proposed an attractive potential, V , for a polaron. This potential is caused by the drawing together of the ions in the bond *via* the electron-phonon interaction and has the following form:

$$V = \frac{1}{2}cx^2 - \lambda x, \quad (1)$$

where c is the relevant elastic constant, λ is the electron-phonon-coupling constant, and x represents a change in the spacing between ions. This potential indicates that the lattice distortion due to the formation of a polaron leads to an increase in the lattice energy (the first term on the right-hand side), but the electron-phonon interaction decreases the total energy of the crystal (the second term). Consequently, the polaron is stabilized when the attractive potential has a negative value. Based upon this potential, Chakraverty and Schelenker⁴ and Gehlig and Salje⁵ explained polaronic conduction in Ti₄O₇ and WO₃. Thus, the formation of a polaron is associated with a change in the lattice energy due to the local distortion, namely, a polaron relates directly to the lattice energy. This fact calls for a theoretical estimate of the deformation energy due to changes in interionic spacings, which

is indispensable in understanding the dynamics of polarons. Since the deformation energy and displacements of ions are expected to be very small, stringent constraints must be imposed for the required accuracy in making these theoretical estimates. A polarizable point-ion shell model developed by Dienes *et al.*⁶ is certainly one of the most reliable theoretical means which meet such criteria because this is constructed for the purpose of calculating an energy change due to very slight displacements of ions in a crystal.

Though the nature of carriers in n -type BaTiO₃ has still been a subject of discussions as to whether it is a conduction electron or a small polaron, our experiments⁷ measuring the dielectric properties with dc conductivities provide direct evidences for the conduction due to hopping motions of nonadiabatic small polarons with hopping energy $W_H = 0.068$ eV and the coupling constant $\alpha = 5.4$ at low temperatures below the rhombohedral-monoclinic transition point. From the well-known definition¹ [Eq. (2)] and the experimental result⁸ on the longitudinal optical phonon frequency near the zero wave vector in BaTiO₃ ($\omega_{LO} = 7 \times 10^{13}$ /s),

$$\frac{\alpha}{2} = \frac{(\text{deformation energy})}{\hbar\omega_{LO}}, \quad (2)$$

one can assign ~ 0.12 eV to the deformation energy of this small polaron.

Our primary aim is to estimate electron-phonon-coupling constants and changes in spacings between ions

TABLE I. Born-Mayer constants from a segmented fit to the repulsive interactions for ions obtained by Wedepohl's procedure and van der Waals constants in BaTiO₃, where RS represents the range of separation.

RS (Å)	Ti ⁴⁺ -Ti ⁴⁺		Ba ²⁺ -Ba ²⁺		Ti ⁴⁺ -Ba ²⁺		O ²⁻ -O ²⁻		Ti ⁴⁺ -O ²⁻		Ba ²⁺ -O ²⁻	
	A (eV)	B (Å ⁻¹)	A (eV)	B (Å ⁻¹)	A (eV)	B (Å ⁻¹)	A (eV)	B (Å ⁻¹)	A (eV)	B (Å ⁻¹)	A (eV)	B (Å ⁻¹)
1.2 ≤ r < 1.4	1.767 × 10 ⁴	5.618	1.441 × 10 ⁴	3.817	8.911 × 10 ³	4.008	2.529 × 10 ²	3.328	2.202 × 10 ³	3.271	2.396 × 10 ³	3.171
1.4 ≤ r < 1.6	5.123 × 10 ⁴	6.379	1.103 × 10 ⁴	3.626	8.747 × 10 ³	3.995	1.281 × 10 ²	2.842	2.064 × 10 ³	3.225	1.702 × 10 ³	2.927
1.6 ≤ r < 1.8	7.090 × 10 ⁵	8.021	8.358 × 10 ³	3.453	1.255 × 10 ⁴	4.221	8.364 × 10 ¹	2.575	1.953 × 10 ³	3.190	1.464 × 10 ³	2.833
1.8 ≤ r < 2.0	7.090 × 10 ⁵	8.021	7.514 × 10 ³	3.394	2.752 × 10 ⁴	4.657	7.195 × 10 ¹	2.492	1.902 × 10 ³	3.175	1.453 × 10 ³	2.829
2.0 ≤ r < 2.2	7.090 × 10 ⁵	8.021	9.086 × 10 ³	3.489	1.628 × 10 ⁵	5.546	7.687 × 10 ¹	2.525	1.966 × 10 ³	3.192	1.567 × 10 ³	2.867
2.2 ≤ r < 2.4	7.090 × 10 ⁵	8.021	1.650 × 10 ⁴	3.760	1.628 × 10 ⁵	5.546	1.003 × 10 ²	2.646	2.278 × 10 ³	3.259	1.799 × 10 ³	2.929
2.4 ≤ r < 2.6	7.090 × 10 ⁵	8.021	5.747 × 10 ⁴	4.280	1.628 × 10 ⁵	5.546	1.660 × 10 ²	2.856	3.287 × 10 ³	3.412	2.192 × 10 ³	3.012
2.6 ≤ r < 2.8	7.090 × 10 ⁵	8.021	5.747 × 10 ⁴	4.280	1.628 × 10 ⁵	5.546	4.388 × 10 ²	3.230	7.683 × 10 ³	3.738	2.859 × 10 ³	3.114
2.8 ≤ r	7.090 × 10 ⁵	8.021	5.747 × 10 ⁴	4.280	1.628 × 10 ⁵	5.546	4.388 × 10 ²	3.230	6.986 × 10 ⁴	4.527	4.026 × 10 ³	3.236
C (eV Å ⁻⁶)	1.893		41.28		6.583		86.33		10.52		58.92	
RS (Å)	Ti ⁴⁺ -Ti ³⁺		Ba ²⁺ -Ti ³⁺		Ti ³⁺ -O ²⁻							
	A (eV)	B (Å ⁻¹)	A (eV)	B (Å ⁻¹)	A (eV)	B (Å ⁻¹)						
1.2 ≤ r < 1.4	2.618 × 10 ⁴	5.618	1.180 × 10 ⁴	4.008	2.769 × 10 ³	3.271						
1.4 ≤ r < 1.6	8.007 × 10 ⁴	6.379	1.157 × 10 ⁴	3.995	2.587 × 10 ³	3.225						
1.6 ≤ r < 1.8	1.243 × 10 ⁶	8.021	1.686 × 10 ⁴	4.221	2.442 × 10 ³	3.190						
1.8 ≤ r < 2.0	1.243 × 10 ⁶	8.021	3.813 × 10 ⁴	4.657	2.375 × 10 ³	3.175						
2.0 ≤ r < 2.2	1.243 × 10 ⁶	8.021	2.400 × 10 ⁵	5.546	2.458 × 10 ³	3.192						
2.2 ≤ r < 2.4	1.243 × 10 ⁶	8.021	2.400 × 10 ⁵	5.546	2.862 × 10 ³	3.259						
2.4 ≤ r < 2.6	1.243 × 10 ⁶	8.021	2.400 × 10 ⁵	5.546	4.174 × 10 ³	3.412						
2.6 ≤ r < 2.8	1.243 × 10 ⁶	8.021	2.400 × 10 ⁵	5.546	9.981 × 10 ³	3.738						
2.8 ≤ r	1.243 × 10 ⁶	8.021	2.400 × 10 ⁵	5.546	9.591 × 10 ⁴	4.527						
C (eV) Å ⁻⁶	1.893		6.583		10.52							

of a nonadiabatic small polaron in n -type BaTiO₃ using these experimental results. The combination of Anderson's attractive potential and the polarizable point-ion shell model enables such estimations. A calculation like this is of great importance from the scientific point of view because these values are still difficult to estimate experimentally. In addition, they are necessary in order to clarify the nature of nonadiabatic small polarons responsible for the conduction in n -type BaTiO₃. The results of these calculations are presented in this paper.

II. LATTICE ENERGIES OF PERFECT CRYSTALS

The shell model starts from calculations of lattice energies of perfect crystals (cohesive energies). Based upon a fully ionic model (ionicity of BaTiO₃ ≈ 0.9),⁹ the lattice energy per BaTiO₃ formula unit, E_L , has the form of the summation of the long-range Coulombic interaction energy (Madelung energy, E_M), the short-range repulsive energy (E_R), van der Waals energy (E_{vdw}), and the zero-point energy (E_0) in the following way:^{10,11}

$$E_L = \frac{1}{2} \sum_i \left[q_i \phi_i(0) + \sum_j' \left(A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} \right) \right] + \frac{9nk_B \Theta_D}{8}, \quad (3)$$

where $\phi_i(0)$ is the self-potential of the i th ion with the charge q_i , as developed from Ewald's method¹² by Van Gool and Piken,¹³ A_{ij} and B_{ij} are the Born-Mayer constants of the repulsive interaction between the particular ion pair, r_{ij} is the spacing between ions i and j , C_{ij} represents the van der Waals constant of the ion pair, n is the number of ions per formula unit, Θ_D is the Debye temperature (450 K) (Ref. 14), and k_B is Boltzmann's constant. In Eq. (3), \sum_i represent the summation of ions per unit cell and \sum_j' indicates the summation over all ions

in a crystal except the i th ion.

The Born-Mayer parameters are determined, in general, from perfect-crystal properties. In ternary systems, however, such determinations are difficult because of too many combinations of ion pairs. Alternatively, these interactions have been calculated from the Wedepohl procedure¹⁵⁻¹⁷ using the Hartree-Fock wave functions of free ions as we did on several oxides.¹⁸⁻²⁰ The wave function obtained by Watson²¹ for O²⁻ and those of Ti⁴⁺ and Ba²⁺ calculated using the short Herman-Skillman programs²² were used. The Born-Mayer parameters A and B relevant to particular ion pairs and designated ranges of separations, r_{ij} , have been obtained by fitting the numerical results calculated by Wedepohl's procedure. These parameters are collected in Table I but some of them, Ba²⁺-Ba²⁺, Ba²⁺-O²⁻, and O²⁻-O²⁻, were already reported together with the discussion on their reliability.¹⁹ In order to test the appropriateness of the Born-Mayer parameters of Ti⁴⁺-O²⁻ and Ti⁴⁺-Ti⁴⁺, calculations have been made on the lattice energy of TiO₂ (rutile), the force constants in tetragonal BaTiO₃, and the lattice constant of the cubic structure. These values are compared with the results in other literature^{10,23-26} in Table II. The calculation of the lattice energy in TiO₂ has employed the values for Madelung, van der Waals, and zero-point energies which were evaluated in the previous reports.^{10,23}

The van der Waals constant between ions consists of electronic polarizabilities α^e and some average exciting energies of ions.²⁷ The values for these parameters are quoted from literature^{10,28,29} and collected in Table III, together with free-ion polarizabilities α^0 and ionic polarizabilities α^i . The van der Waals constants determined with these parameters are indicated in Table I.

We have calculated the lattice energy of the cubic structure because the shell parameter representing the effective number of polarizable electrons in each ion, the most important parameter and the most difficult term to

TABLE II. Comparison of parameters calculated using Born-Mayer constants in Table I with results in other literatures. (Top) potential energy, E_{PT} , of each ion and the lattice energy per formula unit of TiO₂ in which every energy except the repulsive interaction is referred to previous results (Refs. 10 and 23), where E_0 and E_{LE} represent the zero-point energy and the experimental lattice energy determined by Born-Haber cycle analysis (Refs. 10 and 23). ΔE_L is the discrepancy between E_L and E_{LE} . Units of eV are used. (Middle) force constants in the tetragonal structure of BaTiO₃ where values in columns of A , B , C , and D are results calculated by Havinga (Ref. 24), Fowler (Ref. 25), Pauling's procedure (Ref. 26), and obtained in this report, respectively. Units of 10³ dyn are used. (Bottom) experimental lattice constant a_E (Ref. 24) and calculated value a_T .

	E_M	E_R	E_{vdw}	E_{PT}	E_0	E_L	E_{LE}	ΔE_L (%)
Ti ⁴⁺	-179.00	22.89	-1.55	-157.66				
O ²⁻	-51.79	12.22	-1.39	-40.96				
TiO ₂					0.27	-119.52	-124.68	4.13
Ion pair	A	B	C	D				
Ti-O(1)	50.0	46.5	41.9	41.3				
Ti-O(2)	12.5	10.1	10.1	13.9				
				(Å)				
				$a_E = 4.007$				
				$a_T = 4.005$				

TABLE III. Electronic (Ref. 28), ionic (Ref. 28), and free-ion polarizabilities (Ref. 30) with average exciting energies in BaTiO₃ (Refs. 10 and 29).

	α^e (Å ³)	α^i (Å ³)	α^0 (Å ³)	E_{ex} (eV)
Ba ²⁺	1.955	0	1.562	14.40
Ti ⁴⁺	0.187	0.382	0.186	72.19
O ²⁻	2.405	0.378	3.880	19.90

evaluate in the shell model, is to be determined by using the experimental result on the energy required to form an oxygen vacancy in the cubic structure with the lattice constant,²⁴ $a = 4.007$ Å. The contributions of Madelung, repulsive and van der Waals energies to the potential energy of each ion, are tabulated in Table IV. The total of these contributions yield a calculated lattice energy of 157.49 eV per formula unit.

III. A POLARIZABLE POINT-ION SHELL MODEL

A brief description on the framework of the polarizable point-ion shell model, including our modifications, will be given in this section because full details were published elsewhere.⁶ When an imperfection such as a polaron or a lattice defect is formed in a perfect crystal, it has an effective charge Ze , the electric field from which acts over all of the ions in a crystal. Each ion is then displaced so as to minimize the energy of the crystal; that is, a relaxation takes place. The displacement of an ion results in a dipole moment on that ion. The total energy of the crystal containing an imperfection E_T is given by

$$E_T = E_L + E_{Relax}, \quad (4)$$

where E_{Relax} represents the relaxation energy which consists of the changes in Madelung, repulsive, and van der Waals energies, i.e., ΔE_M , ΔE_R , and ΔE_{vdw} and the polarization energy, E_P , consisting of three components,

TABLE IV. Potential energies of ions, zero-point energy, and the lattice energy in the cubic structure of BaTiO₃, where E_{PT} is the potential energy which is the sum of Madelung, repulsive, and van der Waals energies. Units of eV are used.

	E_M	E_R	E_{vdw}	E_{PT}	E_0	E_L
Ba ²⁺	-38.72	5.07	-1.64	-35.29		
Ti ⁴⁺	-177.92	19.70	-1.06	-159.28		
O ²⁻	-46.40	8.63	-2.51	-40.28		
BaTiO ₃					0.22	-157.49

i.e., the interaction between the dipole moment and the monopole field due to the imperfection (E_{P1}), the dipole-dipole interaction energy (E_{P2}), and the so-called dipole self-energy (E_{P3}). The last term E_{P3} includes the free-ion polarizabilities for which we have used the values obtained by Pauling³⁰ (see Table III). After the relaxation has taken place, the vector between ions, i and j , changes from \mathbf{r}_{ij} , the vector before the relaxation, to the effective vector \mathbf{r}'_{ij} which is given by

$$\mathbf{r}'_{ij} = \mathbf{r}_{ij} + \frac{\boldsymbol{\mu}_i}{Q_i} - \frac{\boldsymbol{\mu}_j}{Q_j}, \quad (5)$$

where $\boldsymbol{\mu}_i$ and Q_i are the dipole moment and the shell parameter of the i th ion. In this scheme, the total energy E_T is a function of dipole moments. The equilibrium dipole moments are obtained by minimizing the total energy with respect to the components of individual dipole moments as follows:⁶

$$\frac{\partial E_T}{\partial \mu_{ik}} = 0, \quad k = x, y, \text{ or } z, \quad (6)$$

where μ_{ik} is the k component of the i th dipole moment. From Eq. (6), we have the following expression along the x direction which includes our modifications:

$$\begin{aligned} \mu_{ix} & \left[\frac{1}{\alpha_i^0} + \sum_j \frac{(e_{ij})_x^2 B_{ij}^2 A_{ij} \exp(-B_{ij} r_{ij})}{Q_i^2} \right] + \mu_{iy} \left[\sum_j \frac{(e_{ij})_x (e_{ij})_y B_{ij}^2 A_{ij} \exp(-B_{ij} r_{ij})}{Q_i^2} \right] \\ & + \mu_{iz} \left[\sum_j \frac{(e_{ij})_x (e_{ij})_z B_{ij}^2 A_{ij} \exp(-B_{ij} r_{ij})}{Q_i^2} \right] = \epsilon_{ix} \left[1 - \frac{q_i e}{Q_i} \right] + \sum_j \frac{(e_{ij})_x B_{ij} A_{ij} \exp(-B_{ij} r_{ij})}{Q_j} \\ & + \sum_j \frac{(e_{ij})_x B_{ij}^2 A_{ij} (\boldsymbol{\mu}_j \cdot \mathbf{e}_{ij}) \exp(-B_{ij} r_{ij})}{Q_i Q_j} - \sum_j \frac{6C_{ij} (e_{ij})_x}{Q_i r_{ij}^7} \\ & + \sum_j \frac{3(\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij})(e_{ij})_x - r_{ij} \mu_{jx}}{r_{ij}^4}, \end{aligned} \quad (7)$$

where $\mathbf{e}_{ij} = \mathbf{r}_{ij}/r_{ij} = (e_{ij})_x \mathbf{i} + (e_{ij})_y \mathbf{j} + (e_{ij})_z \mathbf{k}$, \mathbf{i} , \mathbf{j} , and \mathbf{k} being the unit vectors along the x , y , and z axes, e is the electronic charge, ϵ_i is the electric field acting on the i th ion, which is the sum of the monopole field ϵ_{im} and the electric field from the imperfection with the effective charge Ze . Compared with the original shell model constructed by Dienes *et al.*,⁶ we have taken into account

the contributions of the Coulombic interaction between the imperfection and the i th ion, i.e., $-\epsilon_{ix} q_i e / Q_i$, van der Waals interactions [the fourth term in the right-hand side in Eq. (7)], and the dipole-dipole interactions (the last term). Along other directions, we have the similar relations.

By solving the system of linear equilibrium equations,

typified by Eq. (7), by the matrix techniques, each component of the dipole moments can be obtained. Since it is impractical to solve the equilibrium equations for all ions in the crystal, the dipole moments in a spherical region of diameter $\sim 3.2a$ around an imperfection have been determined in this fashion, a being the lattice constant. In the shell of diameter $\sim 12a$ outside of the spherical region, the dipole moments have been evaluated by the approximate method of Mott and Littleton³¹ which involves the static dielectric constant of BaTiO₃, i.e., 5000 (Ref. 32), besides ionic and electronic polarizabilities of individual ions. Every ion in the remainder of the crystal is fixed. In the sphere, there are about 100 ions, while we have taken into account about 4500 ions in the outer shell. By using the shell parameters, which are to be determined in the next section, with the dipole moments obtained in this way, the effective vectors, \mathbf{r}'_{ij} , were evaluated and then each energy term in Eq. (4) has been calculated.

IV. RESULTS AND DISCUSSION

A. Shell parameters

Shell parameters are, in general, determined empirically by using experimental results such as formation energies of point defects.⁶ As a useful starting point, we have employed the following theoretical relation proposed by Dick and Overhauser:³³

$$\alpha^0 = \frac{(Q_f e)^2}{k_f}, \quad (8)$$

where Q_f and k_f represent the shell charge (the effective number of polarizable electrons corresponding to the shell parameter of a free ion) and the spring constant coupling the shell and core in the free state. Based upon the theory of Dick and Overhauser, Shanker *et al.*^{34,35} obtained theoretically a correlation between the shell charge in the free state and the atomic number, from which we can estimate the shell charges, Q_f , of Ti⁴⁺, Ba²⁺ and O²⁻. Then, Eq. (8) and the free-ion polarizabilities in Table III enable us to deduce the spring constants of free ions. In a crystal, there is also a similar relation,

$$\alpha^e = \frac{(Q_0 e)^2}{k}, \quad (9)$$

where Q_0 and k abbreviate the shell parameter and the spring constant in the lattice. Substituting the spring constants in free states for k in Eq. (9), the electronic polarizabilities in Table III yield the shell parameters in BaTiO₃, Q_0 . The parameters (Q_f and Q_0) are tabulated in

Table V together with spring constants in free states.

Using the polarizable point-ion shell model with the shell parameters Q_0 , we have calculated the formation energy of a doubly charged oxygen vacancy ($Z = +2$) in the cubic structure because the experimental value on the formation energy of this point defect confirmed by two different groups,³⁶⁻³⁸ 5.70–5.79 eV, is the most reliable and the most reproducible one in the experiments on point defects in BaTiO₃. In the cubic structure, the monopole field acting on each ion is essentially zero because of the high point symmetry. The contributions to the energy of relaxation and polarization and the consequent energy of formation of a doubly charged oxygen vacancy in the relaxed, polarized lattice of cubic BaTiO₃, calculated with these shell parameters, are collected in Table VI together with the energy of formation in the rigid, unpolarized lattice, $(E_F)_0$.

Then, we find a deviation of the calculated formation energy from the experimental value. Such a deviation must be due to the substitution of spring constants in free states for k in Eq. (9). The effective spring constants in the lattice must be different virtually from those in free states. In order to compensate for this deviation, we have changed the shell parameters, as did Dienes *et al.*⁶ Every shell parameter has been changed in the same ratio, step by step, and we have obtained the final parameters, Q , which yield the best agreement of the theoretical formation energy with the experimental one. These shell parameters and the spring constants in the lattice are indicated in Table V as well. The resulting energies for relaxation, polarization, and formation are shown in Table VI.

As described before, we have taken into account about 100 ions in a spherical region around the vacancy and about 4500 ions in the outer shell. We have changed the numbers of these ions within $\pm 30\%$. The formation energy of an oxygen vacancy is nearly independent of the numbers of ion employed. This fact indicates the legitimacy of the shell model used. In addition, the final shell parameters, Q , are very close in values to the theoretical parameters, Q_0 , evaluated by the procedure of Shanker *et al.*,^{34,35} i.e., $Q/Q_0 \approx 0.9$. This is indicative of the appropriateness of their theoretical treatments in assignments of shell charges.

B. Combination of Anderson's attractive potential and shell model

Our experiments⁷ provide the dielectric relaxations due to hopping motions of small polarons with an activation

TABLE V. Shell parameters and spring constants in free states, Q_f and k_f , shell parameters in BaTiO₃ obtained by using spring constants in free states and electronic polarizabilities, Q_0 , and shell parameters which yield the best agreement with the experimental result on the energy required to form a doubly charged oxygen vacancy in the cubic structure and spring constants in the lattice, Q and k .

	$Q_f(e)$	k_f (eV/Å ²)	$Q_0(e)$	$Q(e)$	k (eV/Å ²)
Ba ²⁺	5.650	294.29	6.321	5.688	238.30
Ti ⁴⁺	4.350	1464.95	4.362	3.924	1185.70
O ²⁻	2.400	21.38	1.890	1.701	17.32

TABLE VI. Contributions to the formation energy, E_F , of doubly charged oxygen vacancy in units of eV with shell parameters Q_0 and Q , where $(E_F)_0$ represents the energy of formation in the rigid, unpolarized lattice.

SP	$(E_F)_0$	ΔE_M	ΔE_R	ΔE_{vdw}	E_P	E_F
Q_0	20.14	-11.86	7.04	-1.34	-10.71	3.26
Q	20.14	-10.03	7.69	-1.64	-10.42	5.74

energy of 0.068 eV, which was also obtained in the conduction measurements, in the rhombohedral structure at temperatures below 100 K as stated before, while Ridpath and Wright³⁹ also obtained a value of 0.074 eV for the hopping energy of small polarons in the cubic structure at high temperatures (~ 500 K). Then, we can assign ~ 0.07 eV to the hopping energy of the small polaron which looks insensitive to temperatures, being nearly independent of phase transitions. Therefore, estimates of the electron-phonon interaction have been made, first, in the cubic structure.

The total energy in the relaxed, polarized lattice of BaTiO₃ containing a Ti ion trapping an electron, which is just localized on a Ti ion and does not interact with phonons of neighboring ions, is given as follows:

$$(E_T)_a = E_L(\text{Ti}^{3+}) + (E_{\text{Relax}})_a, \quad (10)$$

where $E_L(\text{Ti}^{3+})$ is the lattice energy of the rigid, unpolarized crystal containing a Ti^{3+} ion and the subscript "a" represents the energy without electron-phonon interactions. The Born-Mayer parameters of the ion pairs containing Ti^{3+} are determined by the scaling procedure based upon ionic radii^{40,41} because Wedepohl¹⁵⁻¹⁷ treats spherical symmetric negative charge distributions of electrons such as s^2p^6 . The relaxation term $(E_{\text{relax}})_a$ is induced by the electric field from a Ti^{3+} ion ($Z = -1$). The dipole moments on individual ions are to be determined by the conditions similar to Eq. (6) and then the values for $(\mathbf{r}'_{ij})_a$ are obtained. We have employed a value of $(3.924 + 1.000)e$ for the shell parameter of Ti^{3+} because a trapped electron can polarize very easily compared with the electrons in inner shells.

In a material containing small polarons, Anderson² proposed an attractive potential like Eq. (1). Denote the Ti^{3+} ion as the i th ion and the another ion, the phonon of which interacts with the localized electron, as the j th ion, then the electron-phonon interaction energy $E_{e\text{-ph}}$ [the second term in Eq. (1)] is represented precisely in the following form:

$$\begin{aligned} E_{e\text{-ph}} &= - \sum_j \lambda_{ij} x_{ij} \\ &= - \sum_j \lambda_{ij} [|(\mathbf{r}'_{ij})_b| - |(\mathbf{r}'_{ij})_a|], \end{aligned} \quad (11)$$

where λ_{ij} and x_{ij} represent the electron-phonon-coupling constant and the change in the spacing between ions i and j . The vector between these ions changes from $(\mathbf{r}'_{ij})_a$ to $(\mathbf{r}'_{ij})_b$, i.e., the vector in the crystal where the electron-phonon interactions are included in the relaxation. As we convert the ionic spacings obtained above to $|(\mathbf{r}'_{ij})_a|$, we can treat these terms as constants.

Then, the total energy of the crystal containing a single

polaron ($Z = -1$) is given as follows:

$$(E_T)_b = E_L(\text{Ti}^{3+}) + (E_{\text{Relax}})_b + E_{e\text{-ph}}, \quad (12)$$

where the subscript "b" indicates the energies after the electron-phonon interactions are taken into consideration. In such a crystal, the effective vector between ions i and j can be expressed in the similar way as before,

$$(\mathbf{r}'_{ij})_b = \mathbf{r}_{ij} + \frac{(\boldsymbol{\mu}_i)_b}{Q_i} - \frac{(\boldsymbol{\mu}_j)_b}{Q_j}. \quad (13)$$

Then, $|(\mathbf{r}'_{ij})_b|$ is approximated reasonably as follows:

$$\begin{aligned} |(\mathbf{r}'_{ij})_b| &= |(\mathbf{r}'_{ij})_b(\mathbf{r}'_{ij})_b|^{1/2} \\ &\simeq |\mathbf{r}_{ij}| + \left[\frac{\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|} \right] \cdot \left[\frac{(\boldsymbol{\mu}_i)_b}{Q_i} - \frac{(\boldsymbol{\mu}_j)_b}{Q_j} \right]. \end{aligned} \quad (14)$$

From the conditions, $\partial(E_T)_b / \partial(\boldsymbol{\mu}_i)_{bk} = 0$ ($k = x, y, \text{ or } z$), we can determine $(\mathbf{r}'_{ij})_b$ if λ_{ij} is known.

The difference between $(E_T)_a$ and $(E_T)_b$ is an increase of the total energy which is required to form a single polaron, corresponding to the binding energy of the polaron, W_P , i.e.,

$$\begin{aligned} W_P &= (E_T)_a - (E_T)_b \\ &= [(E_{\text{Relax}})_a - (E_{\text{Relax}})_b] - E_{e\text{-ph}} \\ &= -E_D - E_{e\text{-ph}}, \end{aligned} \quad (15)$$

where $E_D = [(E_{\text{Relax}})_b - (E_{\text{Relax}})_a]$ represents an increase of the lattice energy due to the local distortion associated with formation of a single polaron. We can replace the first term of the right-hand side in Eq. (1) with E_D .

C. Electron-phonon-coupling constants of a nonadiabatic small polaron in cubic structure

The experimental result, $E_D \simeq 0.12$ eV, and the theoretical approximation, $W_P \simeq 2W_H$, which holds in the case of nonadiabatic small polarons,⁴² i.e., $W_P \simeq 0.14$ eV, allow us to estimate electron-phonon-coupling constants. As is well known,¹ the electron localized on the cation site is stabilized by the electron-phonon interactions which draw the cations to the electron and the anions away from it. Then, the spacing between Ti^{3+} and a neighboring cation decreases, i.e., $[|(\mathbf{r}'_{ij})_b| - |(\mathbf{r}'_{ij})_a|] < 0$, and the electron-phonon-coupling constant between them must be negative so that $E_{e\text{-ph}}$ may be negative, while the coupling constant between Ti^{3+} and a neighboring anion must be positive for a similar reason.

Since there are no experimental results indicating

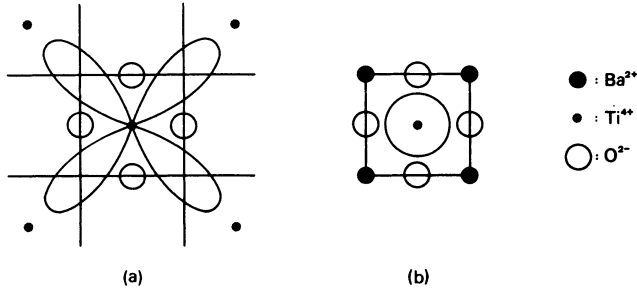


FIG. 1. Schematic illustrations of orbitals of (a) the 3d electron and (b) the s -like electron at the Ti^{3+} site in BaTiO_3 . The ions which interact with Ti^{3+} through the electron-phonon interactions are indicated.

direct evidence on the characteristics of the electron localized on a Ti ion, two possibilities are taken into account. One is that this electron has the nature of 3d electrons and another one is that the electron is loosely bonded to a Ti ion and, consequently, it behaves like an s -like electron. First, we have considered the case of 3d electrons. The lowest orbital of the electron is one of three singlets— $d\epsilon$ wave functions which point directly toward the nearest Ti^{4+} ions in $\langle 110 \rangle$. Then, we can expect the electron-phonon interactions of the Ti^{3+} ion with four neighboring Ti^{4+} ions in $\langle 110 \rangle$ and also four nearest-neighbor O^{2-} ions in $\langle 100 \rangle$ as illustrated in Fig. 1(a). Therefore, j in Eq. (11) refers to these ions. Since the maximum directions of the $d\epsilon$ wave function do not extend directly toward O^{2-} ions, the electron-phonon interaction between Ti^{3+} and O^{2-} must be rather weak compared with that between Ti^{3+} and Ti^{4+} .

We have changed the electron-phonon-coupling constant between Ti^{3+} and Ti^{4+} and also that between Ti^{3+} and O^{2-} in the range of 0.00 to ± 5.00 eV/Å. The method yields $\lambda(\text{Ti}^{4+}) \simeq -3.60$ eV/Å and $\lambda(\text{O}^{2-}) \simeq 0.82$ eV/Å, adjusted to fit the data, where $\lambda(\text{Ti}^{4+})$ and $\lambda(\text{O}^{2-})$ denote the electron-phonon-coupling constant between Ti^{3+} and Ti^{4+} and that between Ti^{3+} and O^{2-} . In Table VII, we have summarized the difference in the relaxation energies before and after the electron-phonon interactions are included, the electron-phonon interaction energy, $E_{e\text{-ph}}$, and the deformation energy, E_D , which were calculated with the coupling constants, $\lambda(\text{Ti}^{4+}) = -3.600$ eV/Å and $\lambda(\text{O}^{2-}) = 0.815$ eV/Å.

There is only one group of the combinations of the coupling constants centered around $\lambda(\text{Ti}^{4+}) = -3.600$ eV/Å and $\lambda(\text{O}^{2-}) = 0.815$ eV/Å, which fit rather well to the experimental results. In the case of s -like electrons, six O^{2-} ions and eight Ba^{2+} ions around the Ti^{3+} ion are taken into consideration as indicated in Fig. 1(b). The calculations yield $\lambda(\text{Ba}^{2+}) \simeq -1.29$ eV/Å and $\lambda(\text{O}^{2-}) \simeq 0.60$ eV/Å, where $\lambda(\text{O}^{2-})$ and $\lambda(\text{Ba}^{2+})$ have the similar meanings. The energies relevant to this polaron calculated with $\lambda(\text{Ba}^{2+}) = -1.287$ eV/Å and $\lambda(\text{O}^{2-}) = 0.600$ eV/Å are summarized in Table VII as well. In both cases the coupling constant between Ti^{3+} and a cation has a negative value and that between Ti^{3+} and an anion a positive value, as predicted.

Table VIII demonstrates the interionic spacings between Ti^{3+} and other ions before and after the electron-phonon interactions are taken into account, $(r_{ij})_a$ and $(r_{ij})_b$, together with the changes in the spacings induced by these interactions, x_{ij} . The ions interacting directly with Ti^{3+} are found to displace in the ways as expected, i.e., cations (Ti^{4+} or Ba^{2+}) displace toward Ti^{3+} , while O^{2-} ions away from Ti^{3+} . The ions interacting with the Ti^{3+} ion knock on others but their displacements are found extremely small. The results in Tables VII and VIII reveal that the changes in the lattice energy and the interionic spacings due to formation of a polaron are very slight as expected in the Introduction, but every value obtained here suggests that small polarons are stabilized in the cubic structure.

Though no information can be obtained in our calculations regarding the nature of the electron localized on a Ti ion, the electron transfer integral between neighboring Ti ions in $\langle 110 \rangle$ estimated in the experiments^{7,43,44} suggests an interaction between Ti^{3+} and Ti^{4+} . This fact leads to a conclusion that the 3d electron is more plausible. In this case, the electron-phonon interaction energy of the Ti^{3+} - Ti^{4+} pair has a value of ~ -0.040 eV, while that of the Ti^{3+} - O^{2-} pair is ~ -0.025 eV. This agrees with the prediction mentioned above.

Our previous report⁴⁵ investigated the stability of Ti_4O_7 crystal in which a spatial ordering of highly packed bipolaron states on crystallographic shear planes is found at low temperatures. The electron-phonon-coupling constants of a bipolaron were also estimated in this material. It is of use, therefore, to compare the coupling constants in BaTiO_3 with those in Ti_4O_7 , although the polaron den-

TABLE VII. Difference in relaxation energies before and after electron-phonon interactions are included in calculations, deformation energies, E_D , electron-phonon interaction energies, $E_{e\text{-ph}}$ and binding energies, W_P , in units of eV. (Top) results in cubic and rhombohedral structures for 3d electrons, and (bottom) those in the case of s -like electrons.

Structure	$(\Delta E_M)_{a-b}$	$(\Delta E_R)_{a-b}$	$(\Delta E_{\text{vdw}})_{a-b}$	$(E_P)_{a-b}$	E_D	$E_{e\text{-ph}}$	W_P
3d electron							
Cubic	1.00	-1.18	0.13	-0.08	0.13	-0.26	0.13
Rhombohedral	0.14	0.28	-0.03	-0.51	0.12	-0.26	0.14
s -like electron							
Cubic	1.39	-1.49	0.16	-0.18	0.12	-0.26	0.14
Rhombohedral	0.75	0.02	0.02	-0.91	0.12	-0.25	0.13

sity in BaTiO₃ is very small compared with that in Ti₄O₇. Since the calculations on Ti₄O₇ were based upon 3*d* electrons, we employ the coupling constants of 3*d* electrons in BaTiO₃ for comparison. The values obtained in Ti₄O₇ are $\lambda(\text{Ti}^{4+}) = -10.7 \text{ eV/\AA}$ and $\lambda(\text{O}^{2-}) = 1.40 \text{ eV/\AA}$, $-\lambda(\text{Ti}^{4+})$ being larger than $\lambda(\text{O}^{2-})$ as well as BaTiO₃. The coupling constants in BaTiO₃ are, however, somewhat smaller than those in Ti₄O₇, but the differences are not so unreasonable for the following reasons. In BaTiO₃, a small polaron is treated as an isolated one because of the low density of polarons, while Ti₄O₇ is a "polaron crystal" and bipolarons in this material have strong polaron-polaron interactions.⁴⁶⁻⁴⁸ In addition, the difference between a single polaron and a bipolaron must be also one of the reasons responsible for such differences.

D. Electron-phonon-coupling constants in rhombohedral structure

Since our experiments⁷ observe the hopping motions of nonadiabatic small polarons directly in the rhombohedral structure, estimations of electron-phonon-coupling constants are also required in this structure. Ion positions in the rhombohedral structure with the lattice parameters, $a = 4.001 \text{ \AA}$ and $\alpha = 89.868^\circ$ (Ref. 49), are indicated in

Table IX. As is well known, this structure is in a ferroelectric state and every ion is spontaneously polarized. In such a crystal with a low point symmetry, a monopole field acts on each ion. The monopole field on the *i*th ion, ϵ_{im} , is given by

$$\epsilon_{im} = -\text{grad}\phi_i(0). \quad (16)$$

Table X collects the monopole field acting on each ion. As Dienes *et al.* suggest,⁶ the monopole fields allow ions in a perfect crystal to relax their positions in an identical fashion to the defect calculation and, consequently, Ti⁴⁺ ions as well as others in the perfect rhombohedral structure have a relaxation energy, $\Delta E(\text{Ti}^{4+})$, which is called the spurious "perfect-crystal relaxation energy." Then we have to correct Eqs. (10) and (12) in the following way:

$$(E_T)_a = E_L(\text{Ti}^{3+}) - \Delta E(\text{Ti}^{4+}) + (E_{\text{Relax}})_a, \quad (17)$$

$$(E_T)_b = E_L(\text{Ti}^{3+}) - \Delta E(\text{Ti}^{4+}) + (E_{\text{Relax}})_b + E_{e\text{-ph}}. \quad (18)$$

However, the final representation for the binding energy of the polaron, Eq. (15), does not change.

If the electron localized on a Ti ion has the nature of

TABLE VIII. Interionic distances between Ti³⁺ and a neighboring ion the phonon of which interacts with Ti³⁺, $(r_{ij})_a$ and $(r_{ij})_b$, and differences in spacings, x_{ij} , due to formation of a small polaron in both of cubic and rhombohedral structures.

Structure	Ion	$(r_{ij})_a$ (Å)	$(r_{ij})_b$ (Å)	x_{ij} (Å)
3 <i>d</i> electron				
Cubic	O ²⁻	2.151	2.182	0.031
	Ti ⁴⁺	5.666	5.655	-0.011
Rhombohedral	O ²⁻ ($\frac{1}{2}, 0, 0$)	1.884	1.887	0.003
	($0, \frac{1}{2}, 0$)	1.883	1.886	0.003
	($0, -\frac{1}{2}, 0$)	2.177	2.180	0.003
	($-\frac{1}{2}, 0, 0$)	2.177	2.180	0.003
	Ti ⁴⁺ (1, 1, 0)	5.654	5.640	-0.014
	(1, -1, 0)	5.651	5.637	-0.014
	(-1, 1, 0)	5.651	5.637	-0.014
	(-1, -1, 0)	5.675	5.661	-0.014
s-like electron				
Cubic	O ²⁻	2.151	2.176	0.025
	Ba ²⁺	3.469	3.453	-0.016
Rhombohedral	O ²⁻ ($\frac{1}{2}, 0, 0$)	1.884	1.894	0.010
	($0, \frac{1}{2}, 0$)	1.883	1.893	0.010
	($0, 0, \frac{1}{2}$)	1.908	1.918	0.010
	($0, 0, -\frac{1}{2}$)	2.152	2.164	0.012
	($0, -\frac{1}{2}, 0$)	2.177	2.189	0.012
	($-\frac{1}{2}, 0, 0$)	2.177	2.189	0.012
	Ba ²⁺ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)	3.411	3.391	-0.020
	($-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)	3.442	3.423	-0.019
	($\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}$)	3.441	3.422	-0.019
	($\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}$)	3.438	3.419	-0.019
	($-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}$)	3.484	3.465	-0.019
	($-\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}$)	3.478	3.459	-0.019
	($\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}$)	3.479	3.460	-0.019
	($-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}$)	3.527	3.508	-0.019

TABLE IX. Ion positions in the rhombohedral structure translated to Cartesian coordinates in units of the lattice constant, $a = 4.001 \text{ \AA}$. O(1), O(2), and O(3) are O^{2-} ions in the x - y , y - z , and z - x planes. $\delta = 1.443 \times 10^{-4}$.

Ion	x	y	z
Ba ²⁺	δ	δ	δ
Ti ⁴⁺	0.5131	0.5131	0.5131
O(1)	0.4846	0.4846	-0.0084
O(2)	0.4869	-0.0131	0.4869
O(3)	-0.0131	0.4869	0.4869

$3d$ electrons, we have to consider three distributions of the electron orbitals which are not equivalent because of the distorted structure, i.e., the $3d$ electron lying on the x - y , y - z , or z - x plane, but the electron-phonon-coupling constants are found to be nearly independent of the plane. The calculations yield $\lambda(\text{Ti}^{4+}) \simeq -4.5 \text{ eV/\AA}$ and $\lambda(\text{O}^{2-}) \simeq 0.09 \text{ eV/\AA}$ for $3d$ electrons and $\lambda(\text{Ba}^{2+}) \simeq -1.6 \text{ eV/\AA}$ and $\lambda(\text{O}^{2-}) \simeq 0.17 \text{ eV/\AA}$ for s -like electrons. In Table VII, we have tabulated the difference in the relaxation energies before and after the electron-phonon interactions are included in calculations, the electron-phonon interaction energy $E_{e\text{-ph}}$ and the deformation energy E_D obtained with $\lambda(\text{Ti}^{4+}) = -4.501 \text{ eV/\AA}$ and $\lambda(\text{O}^{2-}) = 0.084 \text{ eV/\AA}$ for $3d$ electrons on the x - y plane and $\lambda(\text{Ba}^{2+}) = -1.580 \text{ eV/\AA}$ and $\lambda(\text{O}^{2-}) = 0.170 \text{ eV/\AA}$ for s -like electrons. Table VIII demonstrates the interionic spacings $(r_{ij})_a$ and $(r_{ij})_b$ and the changes in the spacings x_{ij} . In comparison with the electron-phonon-coupling constants in the cubic structure, the magnitudes of the coupling constants of cations $-\lambda(\text{Ti}^{4+})$ and $-\lambda(\text{Ba}^{2+})$ are large, while those of O^{2-} ions are considerably small. This fact suggests that the electron on a Ti ion interacts with phonons of cations more directly in the

TABLE X. Components of monopole fields acting on ions along the x , y , and z axes in the rhombohedral structure in units of e/eV .

Ion	x	y	z
Ba ²⁺	0.1387	0.1390	0.1388
Ti ⁴⁺	0.1175	0.1178	0.5125
O(1)	-0.2306	-0.2357	0.7089
O(2)	0.8193	-0.2238	-0.2415
O(3)	-0.2303	0.8211	-0.2415

rhombohedral structure. In fact, the interaction energy between the electron on the Ti ion and the phonon of a cation, i.e., $\sim -0.063 \text{ eV}$ for $3d$ electrons or $\sim -0.030 \text{ eV}$ for s -like electrons, is larger than that relevant to an O^{2-} ion, i.e., $\sim -0.0003 \text{ eV}$ for $3d$ electrons or $\sim -0.0017 \text{ eV}$ for s -like electrons.

Our calculations indicate that small polarons are stabilized not only in the cubic but also rhombohedral structures. This conclusion confirms, from the theoretical point of view, the polaronic conduction in n -type BaTiO₃. Moreover, it should be emphasized that values obtained theoretically in this paper are quite difficult, at this moment, to obtain experimentally.

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