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LETTER TO THE EDITOR

On the average charge of the oxygen vacancy in perovskites necessary for kinetics calculations

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Abstract

An analytical result has been obtained for the value of the dynamical charge necessary for calculations of oxygen vacancy kinetics in dielectric perovskite-type crystals. It is shown, by using the Berry phase analysis, that this charge equals the nominal charge of the vacancy: for example, for the doubly charged state (no electrons associated with the vacancy), it is $2e$ where e is the electron charge; a neutral vacancy (two electrons in the vacancy) has zero average charge.

Oxygen vacancies in oxides of the perovskite family can be easily created or removed by thermal treatment in a reducing or oxidizing atmosphere respectively [1]. The vacancies are always present in single crystals and even more so in ceramics and thin films. This nonstoichiometry has a great impact on some properties of perovskite-type oxides: dielectric permittivity can have a noticeable [2–4] and sometimes even large [5] contribution from electrons connected with the oxygen vacancies; second-harmonic generation and luminescence experiments revealed a large effect of oxygen vacancies on the intensities [6, 7]; the electroconductivity of the samples is strongly dependent on the oxygen vacancy concentration and, hence, on the thermal treatment [8].

Sometimes the presence of oxygen vacancies helps to improve properties of materials; for instance, it is possible to obtain extremely high dielectric permittivity over a wide temperature interval due to Maxwell–Wagner relaxation [5]. However, it happens to be the case that these unavoidable point defects spoil some properties; for example, in ferroelectric memory applications the presence of oxygen vacancies is thought to be crucially important, resulting in the phenomenon called ‘fatigue’ [9, 10]: ferroelectric thin films degrade after a large number of polarization switching events due to the movement of the oxygen vacancies, leading to the creation of large frozen internal fields preventing the switching process.

In order to study the last effect, one can use kinetic equations describing charge transport in a bias field [11]. Charged oxygen vacancies are thought to be moved in this field [9, 10]. For quantitative estimations, one needs to know the oxygen vacancy charge Z and the field E_a acting on the vacancy. In the review [12] this problem was discussed in detail—there have

been several attempts to describe these quantities, regarding which there are two very different proposals: one of them suggests using Lorentz's expression for the local field, $E_a = (\varepsilon+2)E/3$; the other assumes that each of the vacancies can be surrounded by a sphere and that the field inside this sphere is described by an Onsager expression: $E_a = 3\varepsilon/(2\varepsilon + 1)E$ where ε is the dielectric permittivity and E the bias macroscopic field. Scott and Dawber [12] criticized the first approach as giving an unrealistic diverging value of the local field at large ε inherent to ferroelectrics, and they suggested using the Onsager expression which produces a much better match to experimental data.

In this letter I will show that the problem of choosing the local field and charge of the vacancy can be solved analytically with the help of a Berry phase analysis [13–16]. This approach rigorously considers not only the local field effect but also the covalent effect connected with the covalent binding of the ions. In the Berry phase analysis, polarization is treated quantum mechanically by averaging momentum over the Brillouin zone.

Instead of dealing with local fields it is easier to consider an average, macroscopic, field. In this case the charge of the vacancy must be replaced by the dynamical charge

$$Z_{i\alpha,\beta}^* = \frac{\partial P_\alpha}{\partial r_{i\beta}} \quad (1)$$

where P_α is α th component of the polarization, and $r_{j\beta}$ is the displacement of the i th ion in the β th direction. As the average field is uniform, only the dynamical charge should be averaged over the path of the oxygen vacancy:

$$Z = \frac{1}{l} \int Z_{V_{Oz}}^*(\mathbf{r}) d\mathbf{r} \quad (2)$$

where l is the length of this path; for the sake of simplicity, we directed the field along the z -axis. By substituting definition (1) into the integral in (2), one obtains

$$Z = \frac{1}{l} \int \frac{\partial P_z}{\partial r_{V_{Oz}}} d\mathbf{r} = \frac{\Delta P_z}{l_z} \quad (3)$$

where ΔP is the finite difference in the polarization after performing the run over the path, and l_z the z -component of the displacement.

ΔP is the sum of the contributions to the polarization stemming from the displacement of independent ions, ΔP_i , and electrons which are treated quantum mechanically, ΔP_e :

$$\Delta P_z = \Delta P_i + \Delta P_e. \quad (4)$$

In order to determine the ionic contribution, we will consider an ionic model in which the electronic contribution is absent due to the absence of covalent bonding; the nominal ionic charges of the ions will be employed: for example, the Ti charge is 4+, the oxygen charge is -2 . The use of the dynamical charge concept allows one to exclude local field effects. In this case, a shift of the crystal by the lattice parameter would not produce polarization if there was no charged point defect. In the ionic approximation, the vacancy has the nominal charge: $m_i = +2$. The resulting polarization is

$$\Delta P_i = nm_i e \Delta z \quad (5)$$

where n is the oxygen vacancy concentration, e the electron's charge, a the lattice parameter, and Δz the oxygen vacancy shift. Then we will consider the contribution to the polarization stemming from the electron's flow.

The computation of the electronic (covalent) contribution can be carried out with the help of Berry phase analysis [13–16]:

$$\Delta P_e = -n \frac{ea \Delta \varphi}{\pi} \quad (6)$$

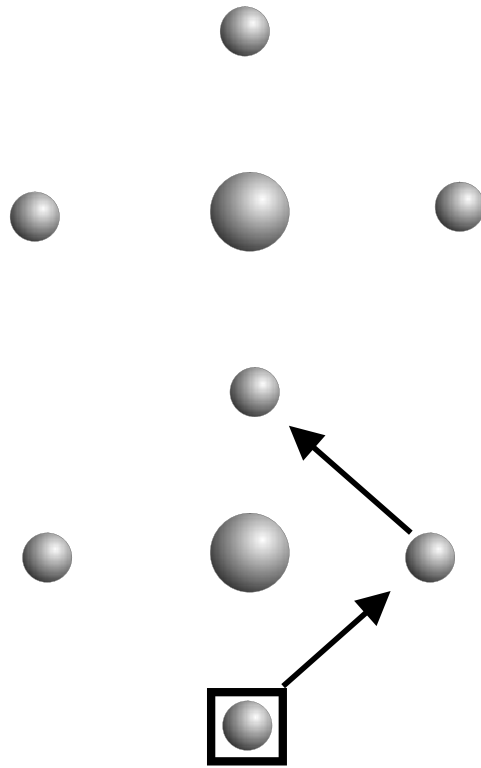


Figure 1. A path taken by an oxygen vacancy between equal points in the perovskite-type lattice. Large circles correspond to B ions in the ABO_3 perovskite structure, small ones to oxygens, and the square indicates the oxygen vacancy.

where $\varphi(z)$ is the Berry phase averaged over the electronic bands. The Berry phase changes strongly inside the crystal unit cell and it is a periodic function with respect to the displacement with the period coinciding with the lattice parameter.

Consider the path shown in figure 1: in this path the vacancy is simply shifted in the z -direction by one lattice parameter. The initial and final states in this path have the same symmetry and, consequently, the Berry phases at the beginning and end of the path can differ only by an integer number, m_e , multiplied by π : $\varphi(a) - \varphi(0) = m_e\pi$. As a result, the total polarization arising upon the shift of the vacancy by the lattice parameter is

$$\Delta P_z = nmea \quad (7)$$

where $m = m_i - m_e$. The meaning of the integer number m_e is the number of electrons transferred with the vacancy. Hence m is the oxygen vacancy nominal charge which is always an integer: for the doubly charged vacancy (no electrons) it is 2; for the singly charged vacancy (one electron) it equals 1; and, finally, for the neutral vacancy (two electrons) this charge is zero. Indeed, when the vacancy is displaced by a macroscopic distance, only the displacement of macroscopic charges is important, and this limiting case allows us to define m as the ionic nominal charge. Another argument in favour of this meaning of m is the fact that m does not depend on the scheme of computation of the electronic wavefunctions, and, consequently, the ionic approximation can be employed, which corresponds to using the oxygen vacancy nominal charge.

It follows from the analyses performed that the Lorentz expression for the local field provides the wrong result for the kinetics of oxygen vacancies in oxides. This expression gives a very large value which, in fact, reflects the fact of the strong local field in a centrosymmetric position in the simple cubic lattice made of polarizable ions. If one averages this field over the unit cell, as was in fact suggested in [12], then the difference between the local field and the average one completely vanishes. Notice that we have shown that it is enough just to average the dynamical charge over any of the paths connecting two points in the lattice with equal symmetry. The charge averaged over such a path equals the charge averaged over the unit-cell volume. A close result can be obtained if one uses the Onsager expression at high ϵ : this result is only $3/2$ times larger than that obtained with the correct expression which employs the average over the path dynamical charge.

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