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ORIGINAL REPORT



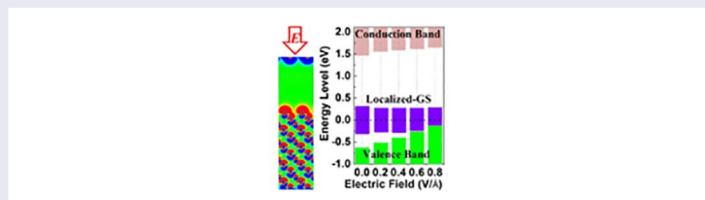
Reversible formation-dissociation of polaron in rutile driven by electric field

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ABSTRACT

Density functional theory with Hubbard U correction is employed to study the polaron in rutile under external electric fields. It is found that electric-field-induced displacements of the ions enhance the sampling of the polaron configurations, which is helpful to find the most stable structure among local minima. More importantly, we demonstrate that with increasing electric field, the polaron may vanish, i.e. the excess electron can dissociate from the bounded Ti^{3+} , and this process is reversible with the opposite electric field. The present findings shed light on more complex mechanisms for the polaron-related conductivity in oxides and corresponding devices.



IMPACT STATEMENT

The first *ab initio* demonstration of the polaron dynamics under electric fields provides a complete picture of the polaron in rutile, deepening the understanding of the conductivity in the oxides.

ARTICLE HISTORY

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KEYWORDS

Polaron; electric field; rutile; density functional theory

Introduction

Point defects in transition metal oxides and the induced charge carriers play a vital role in virtually all the applications of the oxides [1]. As one typical point defect, a neutral oxygen vacancy in these oxides can result in two excess electrons in the system which is normally localized and coupled with the lattice distortions, forming a so-called polaron [2]. The behavior of the polaron can determine the physical and chemical properties of the material. For instance, hopping of the polaron is found accounting for the conductivity of the filament in the oxide-based resistance random access memory (RRAM) [3,4].

Among the various transition metal oxides, TiO_2 has been extensively studied owing to its wide applications such as in photocatalysis [5,6], solar cells [7], anodes in battery [8] and RRAM [9–11]. As an intrinsic defect in TiO_2 , oxygen vacancy (Vo) induced polaron has

been demonstrated theoretically [12,13] and experimentally [14–17]. So far it has been agreed that the polaron configurations can be diverse, i.e. the excess electrons can localize on different Ti ions, and the energy difference between various configurations is quite small, meaning that the potential energy surface for the polaron configuration is rather flat. And this explains the controversial results about the localization site of the excess electrons when different calculation methods are used [18]. Moreover, the polaron hopping which accounts for the electron conductivity in rutile has an adiabatic activation energy of about 0.09 eV according to the density functional theory calculation [13], close to the 0.07 eV measured in the experiment [19], when no field is applied. In essence, a variety of the polaron configurations can be traced to different displacements of the neighboring atoms. When the temperature is added as in *ab initio* molecular dynamic (AIMD) studies [15], the sampling of the

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atomic displacements is enhanced and the ‘multi-states’ nature of the polarons is thus directly demonstrated. In fact, for many practical applications of TiO_2 , external electric field exists [10,20,21]. As the electric field can motivate the displacements of the ions in the oxide, it should affect the polaron configurations. Thus, the study on the influence of the electric field on the polaron is both fundamentally and applicationally important. Yet, as far as we know, the response of the polaron to the electric field from a first-principles perspective is still lacking.

Calculation details

In the present work, by using the rutile as the example, the polaron in the oxides under the electric field is studied. Here, the surface structure is employed, which can provide different coordination environments for the oxygen ions/vacancies, enabling sufficient sampling to study the configuration and evolution of the polarons under electric fields. The stable rutile (100) surface [22] is used instead of the extensively studied (110) surface [14,15] in the literature, which is helpful to make general conclusions for polaron behavior in TiO_2 and even other transition metal oxides. Vienna Ab initio Simulation Package [23] is used to perform the first-principles calculations. As the electronic structure and the defect states are affected by the choice of the exchange–correlation function [24] or the U value in Hubbard U [25] model, here $U = 4.5$ eV is chosen for the d orbital of Ti, which has been proved to well describe the energy level of the defect states [26] and polaron dynamics at zero field [15]. The electric field is included by placing an artificial dipole sheet in the middle of the vacuum, as proposed by Feibelman [27]. More calculation details can be found in the supplemental materials. The surface model used here can be seen in Figure 1, and the applied electric field is perpendicular to the surface, with the direction set to push the electrons out of the surface we are interested in, as shown in Figure 1.

Results and discussions

For each of the vacancy created in Figure 1, structure relaxations are performed, and the energetic data are shown in Figure 2, in which the energy of the vacancy L1/L2 contained structure is set as the reference. Here, for a thorough sampling, the structures with the ions displaced (relaxed) by the applied electric field are used again as the input for the searching of the ground states under no field. With this strategy, different minima are found, and in Figure 2 only the most stable structures are shown. It is worth mentioning that for

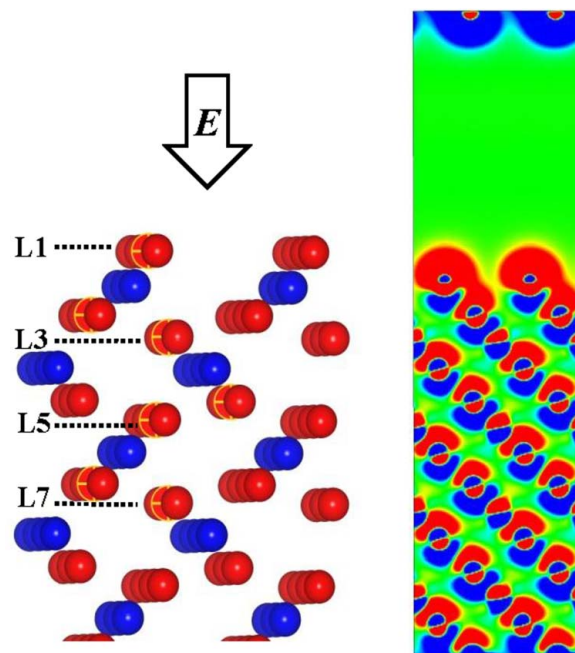


Figure 1. Rutile (100) surface structure used in the calculations, only the upper part of the supercell is shown for clarity. The positions of oxygen vacancies under investigation are marked with ‘+’. Vacancies in different oxygen layers are labeled (L1, L3, etc, and vacancies in other layers are labeled in the same way, such as L2 the following context). The right panel is the two-dimensional view of the charge density variation for the ion-fixed perfect cell induced by the electric field of $0.1 \text{ V/\AA}$. Red and blue mean charge accumulation and depletion, respectively. Blue and red balls represent the Ti and oxygen, respectively.

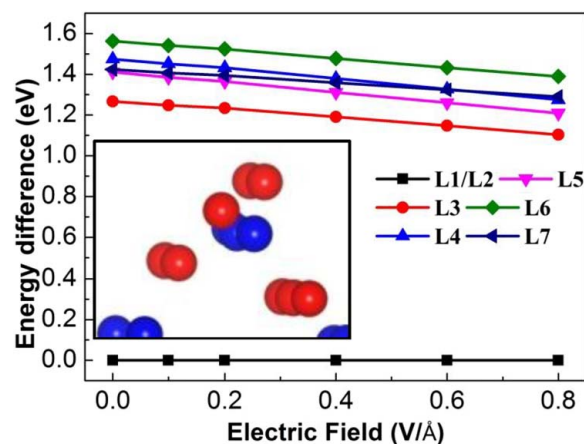


Figure 2. Total energy variation of various vacancies contained supercell relative to that with surface vacancy (L1/L2) under different fields. The inset shows part of the relaxed structures in case of L1 and L2, which is identical for the two vacancies. Blue and red balls represent the Ti and oxygen, respectively.

vacancy L1/L2, the final relaxed structures are exactly the same (inset of Figure 2), due to the significant displacement of oxygen occupying position L2/L1; in the relaxed structure oxygen ions form a triangle configuration with

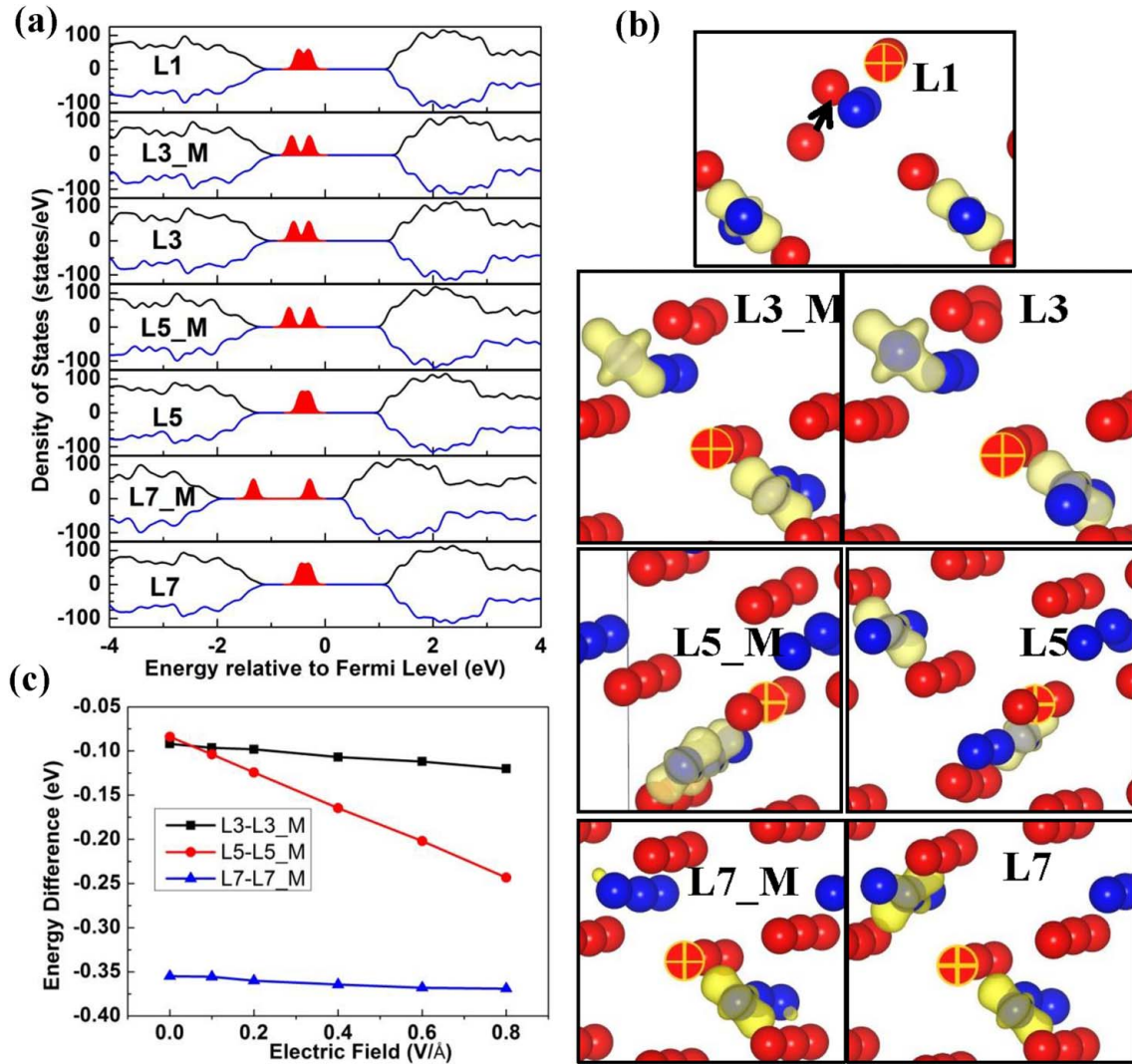


Figure 3. (a) DOS and (b) polaron configurations (yellow region, isosurface: $0.03 \text{ eV}/\text{\AA}^3$) for various vacancy contained structures. In (a), the gap states filled in red composing of two electrons are scaled by 10 for visibility. L3_M corresponds to the vacancy in the third oxygen layer while is metastable compared to L3, so is the situation for L5_M and L7_M. (c) The energy differences between these stable and metastable structures in the presence of electric field. For the atomic structure in (b), blue and red balls represent the Ti and oxygen, respectively; position of the vacancy is marked, and the arrow shows the direction of the displacement of the neighboring O ion.

high symmetry surrounding the surface Ti. As shown in Figure 2, vacancy L1/L2 contained supercell is much more stable than other structures, i.e. the vacancies tend to segregate onto the (100) surface. With increasing field, the energy difference between the surface vacancy (L1/L2) and others is decreasing, with a gradient of about $0.2 \text{ eV}/\text{V}/\text{\AA}$. Recent experimental [28] and theoretical studies [29] have shown similar electric-field-induced energetic change between surface and subsurface Vo in anatase, another form of TiO_2 . The various vacancy contained structures provide sufficient samples for the following polaron study in rutile, ensuring the universal conclusions.

In the following part, the electronic structures of the vacancy contained surface supercells are studied,

including the density of states (DOS) and the polaron configurations. As we mentioned earlier, different local minima are found for the same vacancy. To distinguish the minima, a suffix ‘_M’ is added to represent the metastable structures, as can be seen for the representative systems in Figure 3. The electronic states of the two excess electrons are highlighted in Figure 3(a). Clearly, the two electrons may form two separated states or one single merged state, even for one specific vacancy position as in L3_M/L3, L5_M/L5, L7_M/L7. Combining the energy data in Figure 3(c), the merged electronic states are more stable than the case of two separated states, especially for L7_M and L7. This correlation between the stability and the electronic state is consistent with the findings of the AIMD simulations [15]. The configurations of

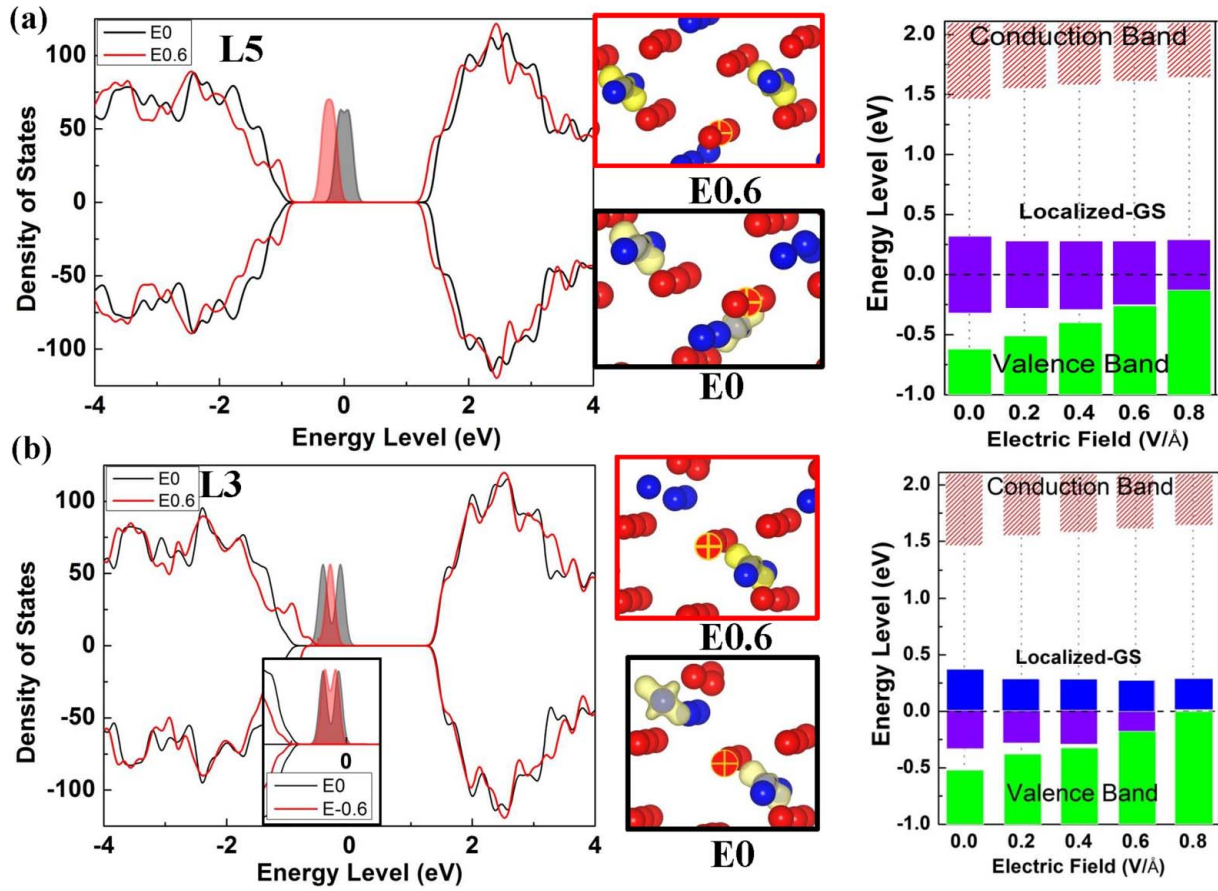


Figure 4. DOS and the configurations of the polaron under field of zero and 0.6 V/Å. For the left panel, the Fermi levels are near 0 energy level; the gap states are scaled by 10 for visibility. In the middle panel, configurations of the polaron in the lattice are shown, which correspond to the shaded gap states in the left panel; the isosurface value for the partial charge contour is 0.03 eV/Å³. The right panel is the schematic view of the DOS profiles under different fields, and the energy is aligned considering the center of the gap states. (a) is for the oxygen vacancy L5 and (b) for L3. The inset in DOS figure of (b) shows the DOS near the Fermi level when the opposite field of 0.6 eV/Å is applied, in comparison with the case without external field.

the polaron formed by the excess electrons are shown in Figure 3(b). In general, we find that the excess electrons localize on the Ti ions in neighboring layers, which will turn the Ti⁴⁺ to Ti³⁺, and the Ti³⁺ ions are not necessarily the first or second nearest neighbors of the vacancy. Moreover, the two excess electrons tend to occupy two Ti ions, and the energy will go quite high when they stay on the same Ti ions (Ti²⁺), as in the case of L7_M. As can be seen from Figure 3(c), when the electric field is turned on, the energy difference between the metastable and stable states becomes larger, especially in the case of L5_M and L5, meaning that the field makes the potential energy surface for the polaron configurations less flat.

Different polaron configurations and energetic for one specific vacancy are related to the local distortion of the lattice [15]. Here, it is found that for the stable configurations, the displacements of the neighboring Ti ions are more significant compared to the metastable cases. The displacement data are shown in Table S1, with

the atomic structures shown in Figure S1 in the supplemental material. Consequently, different local minima obtained by first-principles calculations can be explained: starting from the perfect structure with one newly created vacancy, the displacement of neighboring atoms occur; when one local minimum is reached and the relaxation terminates, i.e. searching of the more stable states by further displacing the ions are inhibited. While in our situation, the application of the electric field can displace the cations and anions in opposite directions, making the optimization de-trap the local minimum and leads to more stable structures.

Next, the polaron dynamics under the electric field is investigated. In Figure 4, two systems with vacancy L5 and L3, respectively, are shown: one with the totally merged gap states including two electrons, and the other with partially merged states exhibiting two peaks in the DOS profile, when no external field exists, as can be seen from Figure 3(a). As the electric field is applied, the

electrons in the valance bands are ‘excited’ to a higher energy level, as shown in Figure 4 at a field of 0.6 V/Å. Interestingly, the positions of the gap states move towards the valance band. For L3 under a field of 0.6 V/Å, one of the localized states has merged with the valance band, i.e. one of the two excess electrons delocalizes on extensive ions instead of one, and correspondingly the two-polaron configuration becomes a one-polaron state. As summarized in the schematic picture in Figure 4, the applied electric field will induce the merge of the localized gap states with the valance bands, leading to the ‘dissociation’ of the polaron, namely de-bounding the excess electron with its bounded Ti^{3+} . In this case, the concentration of the polaron in the system should be decreased. Moreover, as shown in the inset of the DOS figure in Figure 4(b), when the directions of the applied field are reversed, the gap states move away from the valance band, indicating that the polaron dissociation under electric field is reversible. Unfortunately, so far we have not seen any experimental study on the polaron concentration under high electric field; while a relevant report from Zhao et al [30] shows that the external electric field can induce the reversible modulation of the effective ‘magnetic’ polaron (the local moment bound to carriers) in Co-doped anatase TiO_2 , which is induced by the changes in the local exchange energy and the global geometry of the percolation network under electric field. By analogy, the electric-field-induced displacements of anion and cations in the opposite direction should account for the reversible behavior of the electric polaron found here. As for the practical materials/devices, our theoretical calculations show that the polaron hopping which is believed to dominate the conduction in some oxide-based RRAM [3,31] might be weakened at a high electric field with certain direction, given the reduced polaron concentration due to its electric-driven dissociation. Ideally, when the polaron in the system is annihilated by the electric field, the conduction mechanism might change from polaron hopping to free-carrier generation which is typical for a semiconductor. The reversible behavior of polaron as the direction of the external electric field changes indicates a different role of the polaron for conductance under a polar electric field. Overall, a further experimental study based on high-quality samples with high breakdown voltage is desirable in order to explore the role of the polaron on the conductivity of the oxides, especially under a high electric field.

Conclusions

In summary, GGA + U calculations are performed to study the polaron in rutile in the presence of external electric fields. Firstly, oxygen vacancy tends to segregate

on the (100) surface and electric fields show effects on the segregation tendency. Then it is found that the excess electrons may localize on different Ti ions with different electronic features in the DOS profile, resulting in a variety of polaron configurations. The electric fields can be used to tune the energy difference between different polaron configurations. More importantly, we find that the electric field can induce the merger of the localized gap states with the valance band, i.e. the ‘dissociation’ of the polaron. And the process is found reversible under the opposite electric field. The present findings demonstrate the quite significant effects of the electric field on the behavior of the polaron, which deepens the understanding of the polarons that commonly exist in transition metal oxides and provide an alternative way to the understanding of the conductivity in the materials as well as the corresponding electronic devices. Finally, to study the electric-field-induced dissociation behavior of the polarons under finite temperature, AIMD simulations with the electric field turned on which can take into account the ion displacements induced by both of the electric field and temperature, should be performed. We think this is an interesting topic that is worth studying in the future.

Disclosure statement

No potential conflict of interest was reported by the authors.

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