



Field evaporation of oxides: A theoretical study

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ABSTRACT

To understand atom probe results on the field evaporation of oxides we use density functional theory on MgO clusters to follow the structural changes during field evaporation and to obtain potential energy curves, partial charges and desorption pathways. It is straightforward to understand that Mg evaporates doubly charged. We also show that MgO^+ , MgO_2^+ , MgO^{2+} and O^+ ions leave the surface. Two questions are however new for oxides. (1) Where do the electrons go? When the oxides are deposited on a metal tip it can be assumed that the electrons are used to complete the electrical circuit. However this leaves the second question unanswered, namely (2) what happens to the oxygen? We will argue that there are two channels for the oxygen, namely (a) To travel down the (metallic) surface of the tip and eventually to desorb either as atoms or molecules. (b) The oxygen can recombine within the oxide layer itself and desorbs as a neutral molecule accelerated in the inhomogeneous field due to its induced dipole.

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1. Introduction

The atom probe, developed by Müller et al. in 1968 [1], allows for the identification of the atomic composition of micro- and nano-specimens. It is based on the field ion microscope invented by Müller in 1951 [2]. In field ion microscopy, a sharp metal tip is produced through electropolishing and placed in an ultra high vacuum chamber, which is backfilled with an imaging gas such as helium or neon. The tip is then cooled to cryogenic temperatures and a positive voltage of 5–10 kV is applied to the tip. The imaging gas atoms adsorbed on the tip are ionized by the strong electric field in the vicinity of the tip becoming positively charged and repelled from the tip. The repelled ions are collected by a detector forming an image of the individual atoms on the tip surface. The atom probe is used to study the structure of the tip through field evaporation. This is where a field of the order of volts per angstroms leads to the field-induced evaporation of surface atoms by high voltage pulses as positively charged ions who are registered on a screen with atomic spatial resolution and whose charge to mass ratio is identified by employing time-of-flight techniques. The result is a 2-D layer-by-layer map of the atomic composition of the exposed surfaces of the specimen. The use of a position-sensitive detector deduces the lateral location of atoms allowing a 3-D reconstruction of the field emission tip to be generated. The method is now known as atom probe tomography or APT [3].

Although originally developed for metallic tips and used extensively for the study of the atomic composition of steels and other alloys it has also been adapted for the study of semiconductors and more recently for insulators through the assistance of ultrafast laser pulses. Before laser assisted APT, analysis of oxides was restricted to small geometries such as thin tunnel barrier layers of Al_2O_3 up to 2.5 nm thick [4] and 2 nm thick MgO layers in magnetic tunnel junctions [5]. Now with laser assisted APT the analysis of much thicker oxide layers is possible such as 15 nm thick NiO [6,7], 50 nm thick WO_3 [6], 4 and 32 nm thick MgO [8], and bulk MgO and ZnO [9]. The analysis of bulk insulating ceramics such as zirconia/spinel nano-composites has also proven successful [10].

A quantum-mechanical theory was developed in the 1980s and 1990s for field desorption of atoms and molecules on metal tips and also for the understanding of field-induced chemistry [11–14]. A similar first principles approach is largely lacking for semiconductors, and for oxides and other insulators, key materials in micro-electronics. As the authors of a recent laser assisted APT study of MgO state [8]: “although APT has provided a large number of results on a wide panel of materials, interpretation of 3-D images is sometimes difficult due to a lack in the understanding of the different evaporation mechanisms involved in semiconductors and oxides”. It is the objective of this paper to develop the lacking theoretical framework.

As field-induced chemistry is important for the problem at hand we add a few general comments [11–14]: electric field effects on matter can be classified, rather arbitrarily, into two categories: (i) In low fields, i.e. below roughly 10^{-1} V/Å, atoms, molecules and condensed matter only get polarized; we will call

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such effects physical. (ii) In larger fields chemical effects come into play because the electronic orbitals get distorted to such a degree that the chemical characteristics of an atom or molecule become altered, e.g. by establishing new bonding orbitals. As a simple example, applying an electric field F across a diatomic molecule adsorbed perpendicularly on a metal surface will change the electronic levels of the atom further down the field by an energy of the order of eFd relative to the first atom. This changes the character of the local molecular bonding orbital

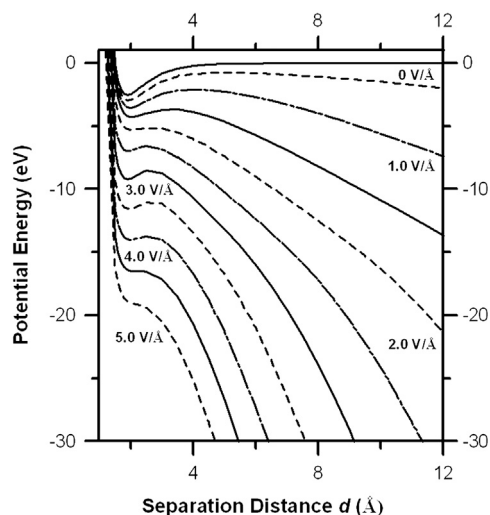


Fig. 1. Potential energy curves of MgO molecule in a field.

either weakening or strengthening it. This is the essence of field-induced chemistry. In this way, molecules, unstable in field-free situations, may be stabilized by a strong electric field. When we proceed to insulators or semiconductors the situation is of course more complicated as the field itself inside the material gets locally reduced to various degrees. That is why self-consistent calculations at the quantum mechanical level are needed as we will demonstrate in this paper.

Because field emitter tips have typical radii of curvature of 100 Å the field, produced by a voltage drop to a counter-electrode is huge, i.e. up to several V/Å, large enough to field-desorb surface atoms as ions. Also, because of the small curvature these fields decay within a few radii by several orders of magnitude so that the ions traverse an almost field-free region on their way to the detector. It should also be pointed out that there is a significant field enhancement at step sites and above individual metal atoms on flat facets of the field-emitter tip by as much as a factor of three [15,16].

Field evaporation of insulators, and oxides in particular, needs additional considerations. To establish the large fields necessary for field evaporation one needs a metallic field emitter tip. On this, layers of oxide or any other insulator are formed using various methods such as oxidation during or after ion beam sputtering, ozone assisted oxidation, thermal oxidation, and field-induced low temperature oxidation which produce layers thick enough to establish proper crystal structure and to allow sufficient ion yields. As a result the electric field penetrates the insulating layer and is further enhanced by its dielectric constant. What is observed in the laser assisted APT of MgO is mostly Mg^{2+} ions [8,9], and more recently also MgO_2^+ , MgO^+ , Mg^+ , O_2^+ and O^+ [9,17]. Our ab initio cluster calculations will reproduce these

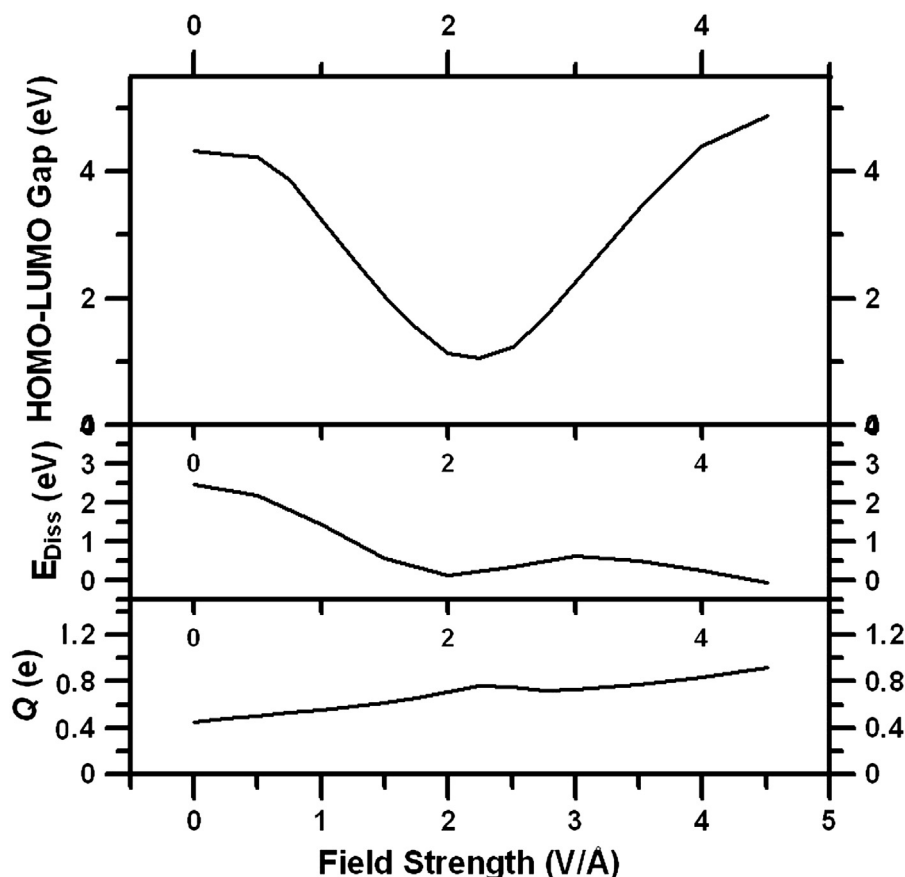


Fig. 2. MgO molecule in a field displaying the HOMO-LUMO gap, the energy barrier for field dissociation and the Mulliken charge.

findings, give explanations, and also answer questions like what happens to the oxygen? We will establish several pathways to remove oxygen: (a) O^- can migrate down the metallic shaft of the field emitter tip and eventually desorb as a molecule. (b) Oxygen can recombine on top of the oxide layer and desorb as a neutral species or even as O_2^+ . An excellent theoretical treatment of the laser assisted field evaporation of bulk MgO was done by Tsukada et al. [18]. They investigated the effects of holes on the sublimation energy of corner ions and potential energy surfaces of corner Mg ions without a field and in a field of 0.514 V/\AA . The result was that holes reduce the sublimation energy and activation barrier for desorption. However they did not look at the various ionic species produced during the field evaporation of MgO as we have done in our calculations.

As for the computational approach to field-induced chemistry it should be noted that relative changes in molecular energy levels are of the order of eV, so that field effects can be adequately described by the simplest methods such as the tight binding approach as has been shown in comparisons with density functional theory [19–21]. Nevertheless, because of the ready availability nowadays of sophisticated software packages we will base our calculations on density functional theory as implemented in the GAUSSIAN'09 software package [22]. In this paper we will only deal with small clusters of MgO. The underlying metallic tip enters the calculations as the source of a constant electric field across the cluster. For each cluster size and external field strength one starts from an initial geometry guess for which Gaussian calculates the electronic structure. This in turn is used to calculate internal forces on the atoms as a basis for the next geometry guess. The use of a cluster model in a (homogeneous) electric field has several advantages: (1) The internal field is automatically generated. (2) The crystal structure of the cluster adjusts to the electric field. (3) Edge effects can be studied. (4) Negative ion loss in the downward field can be avoided by fixing the bottom plane of atoms in the cluster.

The paper is structured as follows: In the next section we start with a single MgO molecule in a field to establish the minimal

wave function set needed for reliable results. Next we look at various cluster sizes from $3 \times 3 \times 3$ to $4 \times 3 \times 3$ to see how cluster size influences field disintegration of these clusters. In the concluding chapter we will summarize our findings and add some speculative ideas.

2. Results

2.1. Preliminary: MgO molecule in a field

As a preliminary exercise we study the effect of a large electric field on the structure and energetics of a MgO molecule, also with the aim to establish the minimum wave function basis set such that adding more wave functions does not alter the results by much. Because in field evaporation surface atoms leave their adsorption sites as partially charged entities and only acquire their final charge state, Mg^{2+} in our case, several angstroms above the surface, it is important to have sufficiently diffuse wave functions in the basis set. After many trials we found that the set B3LYP/6-311+G* is sufficient.

For MgO in a field we fix the position of the oxygen to avoid that the molecule as a whole drifts down the field. In Fig. 1 we show the potential energy curves $V(d) = -[E_{el}(MgO, d) - E_{el}(Mg) - E_{el}(O)]$. Here $E_{el}(MgO, d)$ is the total electronic energy of the molecule with its constituent atoms separated by a distance d , and $E_{el}(Mg)$ and $E_{el}(O)$ are the respective energies of the isolated atoms. In the absence of a field we find a bond length $d_0 = 1.9 \text{ \AA}$, a vibrational frequency $\nu = 1.8 \times 10^{13} \text{ s}^{-1}$, and a dissociation energy $E_{diss} = V(d_0) + \hbar\nu/2 = 2.5 \text{ eV}$ in reasonable agreement with experimental and recent theoretical values of 1.76 \AA and $2.56 \pm 0.22 \text{ eV}$ [23].

In a field, $F > 0$, the adiabatic potential energy curve goes through a maximum at which the Mg is sufficiently charged to get accelerated away from the oxygen. It is the position of this Schottky hump that requires an extended, diffuse basis set for its accurate determination. The energy difference between the

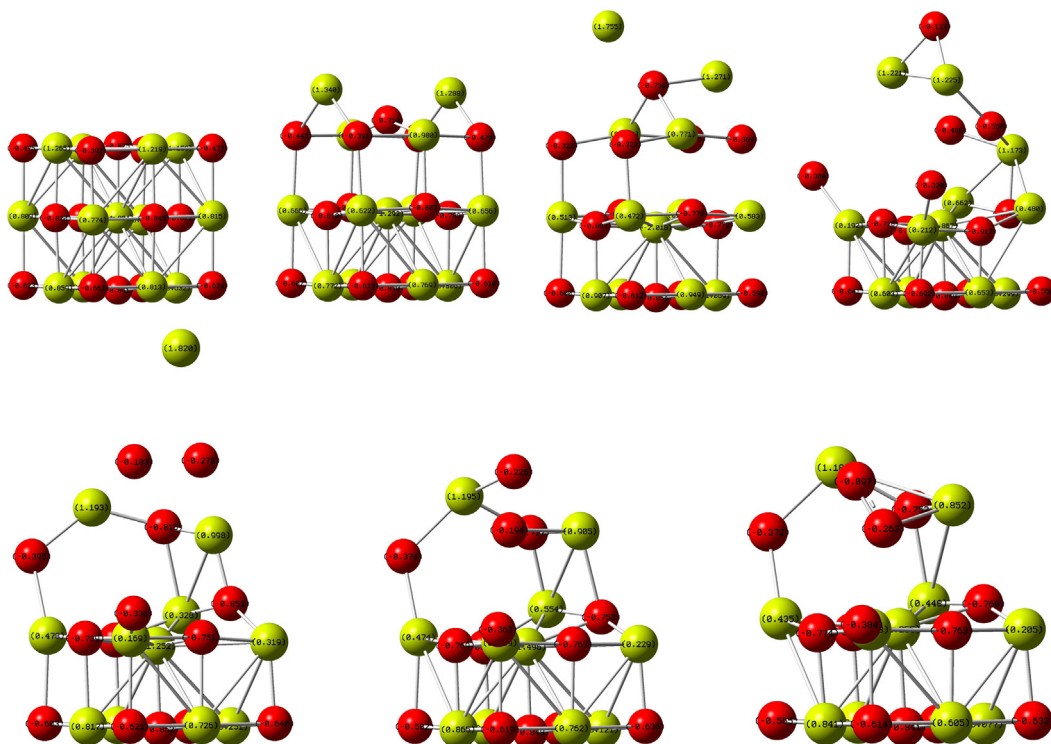


Fig. 3. A $3 \times 3 \times 3$ cluster of MgO in a field of 2.5 V/\AA . Shown are snapshots during the DFT iterations leading to the evaporation of Mg^{2+} and melting of the top row.

Schottky hump and the potential minimum is the activation energy for dissociation. It enters the rate constant of dissociation which in a simplified Arrhenius parametrization reads $r_{\text{diss}} = \nu \exp[-E_{\text{diss}}/k_B T]$. Thus to keep the molecule intact for 1 min after applying a field at room temperature we need $E_{\text{diss}} > 0.1$ eV. This is reached at a field of the order of 1 V/Å, i.e. at considerably lower fields than the field strength of spontaneous disintegration, $F=2$ V/Å.

An unexpected feature of the field dependence is the fact that for fields larger than 2 V/Å a Schottky hump develops again to disappear at a much higher field of 4.5 V/Å. This could be reached by increasing the field rapidly so that dissociation does not happen at 2 V/Å. To shed some light onto this phenomenon we have plotted in Fig. 2 the HOMO-LUMO gap which shows a marked minimum around 2 V/Å to rise again after that. Curiously the bond length changes by less than 0.1 Å over the full field

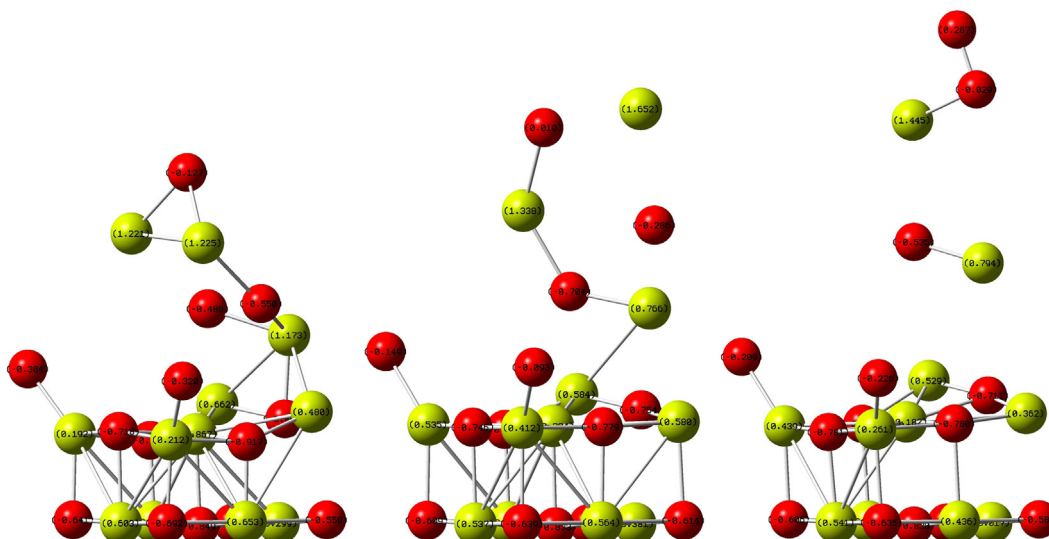


Fig. 4. Further iterations beginning with the last structure in the top row of Fig. 3 with two electrons removed to make it neutral.

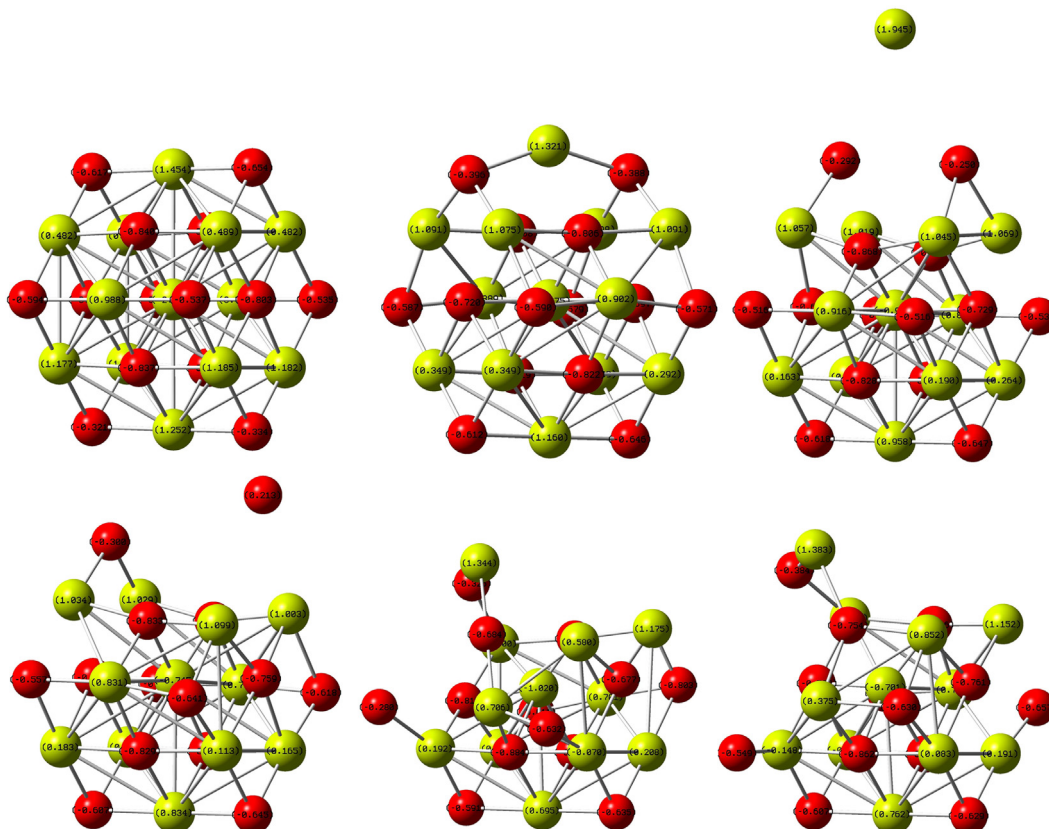


Fig. 5. A $3 \times 3 \times 3$ cluster of MgO tilted into a field of 3 V/Å. Shown are snapshots during the DFT iterations leading to the evaporation of Mg^{2+} and melting of the top row. In addition to the evaporation of Mg^{2+} also O^+ evaporates at a later stage, and a O^- migrates down the cluster.

range whereas the partial (Mulliken) charge increases from 0.4 e to 1.0 e. Also plotted, in the central panel, is the dissociation barrier for completeness.

2.2. MgO clusters

On our quest to understand field evaporation of solid MgO we start with a small cluster of $3 \times 3 \times 3$ atoms in zero field obtaining the proper crystal structure with a bond length of 1.9 Å. Keeping the lowest layer of the cluster fixed we apply a field and find that up to a field of about 2 V/Å little happens to the cluster apart from a small upward move of the Mg atoms. Things change drastically beyond 2.5 V/Å when a Mg has been removed as Mg^{2+} and the top two layers “melt” without reaching a stable equilibrium except when only the lowest fixed layer remains. Typical snapshots during the iterative procedure are shown at 2.5 V/Å in Fig. 3. The first picture in the top row is the starting configuration at field zero with the second image showing the upward buckling of the Mg atoms in the top layer. A few iterations later, image three, the first Mg leaves the cluster as Mg^{2+} . This is followed in the last image of the top row with a situation where the top layer has more or less disintegrated leading to the evaporation of a second Mg^{2+} in the first image of the bottom row, and further re-arrangements in the

following two pictures. It is crucial to note that the negative charge left on the cluster after the Mg^{2+} evaporations resides in the centre of the leftover cluster, and no oxygen has left the cluster at this stage. Of course in the APT experiment an MgO layer is deposited on a metal tip. This allows the negative charge to flow into the tip. In addition, negative O^- can also migrate down the metal shaft. To see what happens if the leftover negative charges were removed from the cluster we do this manually and take the last (now neutral) structure in the top row of Fig. 3 as the starting point for further iterations, see Fig. 4.

After several iterations another Mg^{+2} ion is removed and the stretched structure left over breaks up further with singly charged MgO_2^+ and MgO^+ leaving.

Next we look at the same cluster but this time tilted so that an apex shows in the field direction to mimic a protrusion or an edge showing again evaporation events while iterations proceed, this time in a field of 3 V/Å, see Fig. 5. Similarly to the previous cluster we see in the top row the upward buckling of the center Mg atom and its evaporation as Mg^{2+} . After that, new phenomena appear. In the iteration represented by the first image in the second row we note an O atom moving up as a positively charged ion! It would be interesting to see whether this is manifested in APT mass spectra. Another spectacular effect takes place after that,

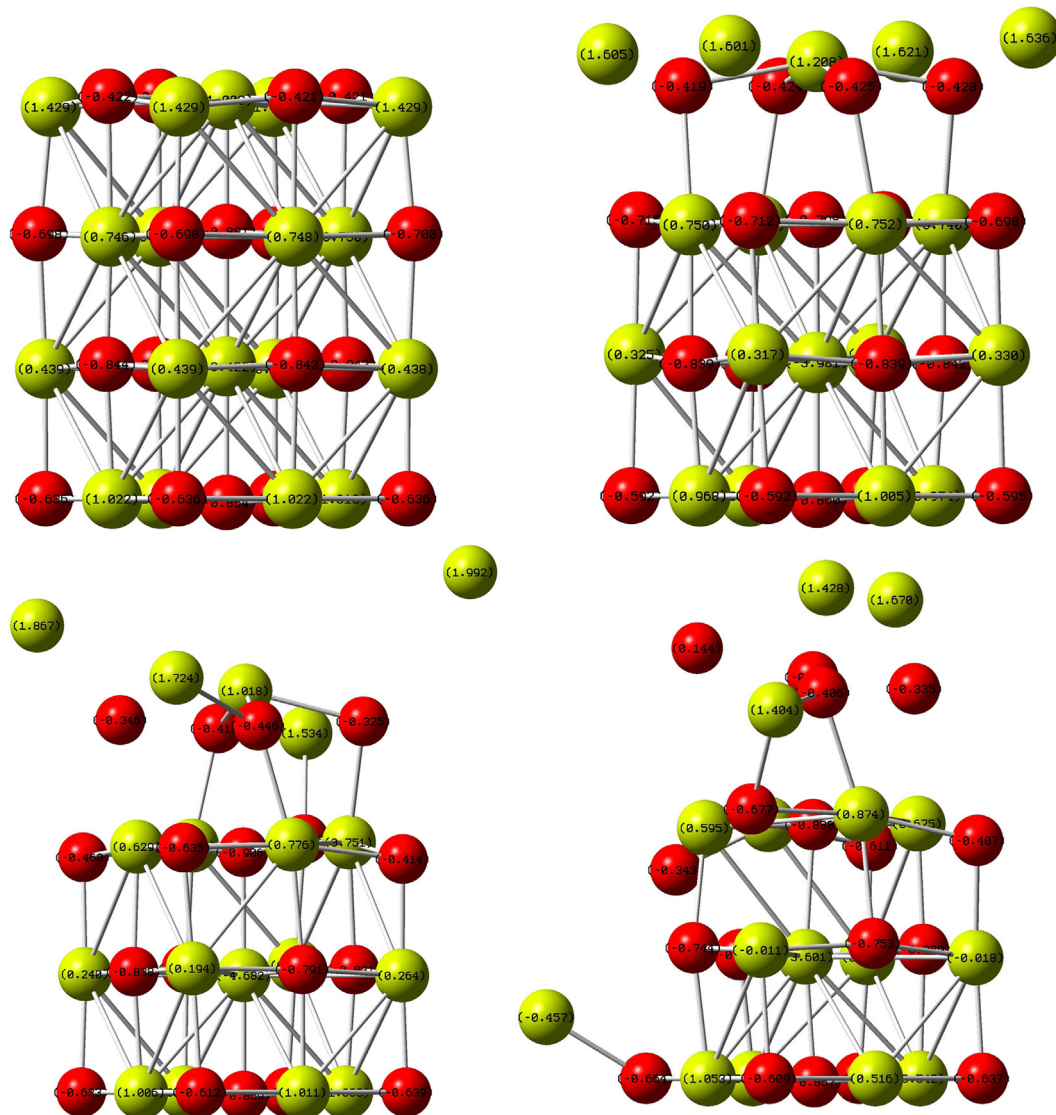


Fig. 6. A $4 \times 3 \times 3$ cluster of MgO in a field of 4 V/Å. Shown are snapshots during the DFT iterations leading to the evaporation of Mg^{2+} and melting of the top row.

namely that an O atom moves downward on the side of the cluster to begin its journey down the shaft.

Lastly, we look at a larger cluster of four 3×3 layers in a field of 4 V/Å, see Fig. 6. Buckling of Mg in the top layer is again the initiation of field evaporation. Soon two corner Mg atoms get loose and evaporate as Mg^{2+} . Shortly thereafter, a positively charged O^+ moves towards the detector. This ion should be looked for in the APT experiment. In addition, a negatively charged Mg^- migrates down the cluster. Unfortunately, the size of this cluster prevented further iterations in a reasonable time. Similarly, one should examine the effects to charging and decharging the cluster.

3. Discussion and outlook

The crucial difference in field evaporation of metals and insulators is the basic fact that metals expel electrostatic fields and insulators allow them full penetration with semiconductors somewhat in between. This has a direct consequence for the operation of the Atom Probe. (a) Metals: the fields penetrate less than the first atomic surface layer and are enhanced by up to a factor of 3 at protrusions, corners and edges. Thus atoms at these exposed sites are removed first, exposing atoms in the layer below and thus achieving layer-by-layer compositional analysis in atom probe tomography of metals and alloys. (b) Insulators: electrostatic fields penetrate insulators whether they are isolated species or grown on a metal substrate. The immediate consequence is that the field attacks the complete crystal simultaneously with perhaps some more action on the surfaces with fewer bonds and mobility out of the surface. However if large fields are used the whole crystal structure will change much akin to melting so that site specificity could be lost. On the other hand we have demonstrated in this and previous papers that the HOMO-LUMO gap closes with two consequences: if it goes to zero the tip becomes metallic. This is beneficial for at least two reasons: (i) charge accumulation inside the cluster is avoided and (ii) the field is actually expelled, at least partially, from the cluster. Both effects will aid APT. If the gap does not close completely we still get a narrow gap semiconductor instead of an insulator with the effects just discussed for a metallic tip at least partially invoked. Of course, using laser irradiation either resonantly or thermally, will aid the evaporation process as well and is possibly the reason why fields used in the experiment are smaller than the ones used in our calculations. A recent attempt at elucidating the mechanisms involved is due to Tsukada et al. [18].

Our cluster calculations also suggest that in addition to Mg^{2+} one should also see MgO^+ , MgO_2^+ , MgO^{2+} and O^+ ions in the mass spectrometer in fields of more than 2 V/Å. These ions have recently been observed in APT mass spectra by Chen et al. [9] and Larson et al. [17]. Our theoretical calculations show that MgO^{2+} is created by post-ionization of MgO^{2+} in the field.

In this paper we have only addressed static questions but did not address the kinetics of field evaporation. This can and will be

done using the framework worked out 20 years ago for field evaporation of metals [24,25].

Acknowledgments

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