Fast Track Communication

Charge order at magnetite Fe₃O₄(0 0 1): surface and Verwey phase transitions

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Abstract
At ambient conditions, the Fe₃O₄(0 0 1) surface shows a (√2 × √2)R45° reconstruction that has been proposed as the surface analog of the bulk phase below the Verwey transition temperature, Tᵥ. The reconstruction disappears at a high temperature, Tₛ, through a second order transition. We calculate the temperature evolution of the surface electronic structure based on a reduced bulk unit cell of P2₁/m symmetry that contains the main features of the bulk charge distribution. We demonstrate that the insulating surface gap arises from the large demand of charge of the surface O, at difference with that of the bulk. Furthermore, it is coupled to a significant restructuration that inhibits the formation of trimerons at the surface. An alternative bipolaronic charge distribution emerges below Tₛ, introducing a competition between surface and bulk charge orders below Tᵥ.

Keywords: surface phase transitions, magnetite, Verwey transition

1. Introduction
Magnetite (Fe₃O₄) is the oldest known magnet and a fascinating material both for understanding the fundamental physics that emerge from electronic correlations, and for novel technologies related to oxide electronics [1–3]. At ambient conditions, it crystallizes in the inverse spinel structure with cubic Fd₃m symmetry. The O atoms form a fcc lattice, with Feₐ atoms in tetrahedral sites acting with a nominal +3 valence, and Feₐ⁺ cations with +2.5 valence in octahedral positions. The Feₐ and Feₐ⁺ sublattices are antiferromagnetically coupled, and the minority spin t₂g states of the Feₐ⁺ atoms cross the Fermi level, leading to a half-metallic ferrimagnet with high magnetic moment, 4µB per formula unit (f.u.). Half-metallicity was unambiguously predicted from early ab initio calculations [4], and though its experimental identification is difficult and controversial [5, 6], it seems to be confirmed from recent measurements based on different techniques [7].

At a critical temperature Tᵥ ~ 120 K, magnetite undergoes the first-order Verwey transition (VT), that manifests in a structural modification to a monoclinic symmetry accompanied by a drop of the conductivity of 2–3 orders of magnitude [8]. The decrease of the conductivity is due to a freezing of the electron hopping between different octahedral Fe sites, causing a charge disproportionation that results in two types of Feₐ⁺ atoms acting with a slightly enhanced (Fe₃⁺) or reduced (Fe²⁺) valence. The distribution of the different Feₐ⁺ atoms at the unit cell configures the charge order (CO), intimately linked to the orbital order [9, 10], and determines the full monoclinic Cc symmetry [11–15].

Decades of efforts have been devoted to the understanding of the VT [16, 17], and yet some puzzling fundamental aspects remain unanswered, such as the structural or electronic origin of the transition, or the extent of the short range order above Tᵥ. The present consensus is that the phase transition is governed by electron–phonon couplings in the presence of strong electronic correlations [18]. A local perturbation of the extended CO has been recently identified in the form of trimerons: linear chains of three adjacent Feₐ⁺ cations dominantly formed by a central Fe²⁺ and two Fe³⁺, with a significant reduction of the interatomic Fe–Fe distances and...
a polaronic distribution of shared charge [15]. Trimerons reveal as the essential short-range unit in the electronic phase transitions of magnetite [19]. Furthermore, laser pump-probe experiments have created a non-equilibrium version of the VT by introducing holes in the trimeron lattice [20]. This invokes the possibility of obtaining analogs of the VT under sizes much lower than those required by a full Cc cell, and in fact, as a first result of this work, we will demonstrate the ability of trimerons to emerge in a reduced unit cell of $P2/m$ symmetry.

One of the handicaps for the exploitation of the VT in novel technologies is the low value of $T_V$, well below room temperature (RT). The measurement at the Fe$_3$O$_4$(0 0 1) surface of an insulating gap at RT [21] and the further prediction that its existence was accompanied by a subsurface CO similar to the bulk one [22], caused thus great excitement. Fe$_3$O$_4$(0 0 1) presents a $\sqrt{2} \times \sqrt{2} R45^\circ$ reconstruction which corresponds to a bulk truncation at an Fe$_2$–O plane [23–25]. Its origin was initially assigned to a Jahn–Teller distortion causing a wavelike displacement of the Fe$_2$ surface atoms along (1 1 0) directions [26, 27]. The existence of an insulating surface questions this interpretation, and has also consequences on the reduced spin polarization found at different magnetite samples [5, 28]. Seemingly, the RT reconstruction is not significantly altered across the VT [27, 29]. However, the evolution in the surface CO has not been investigated, setting forth interrogants about the formation of surface trimerons and the relation between the surface and bulk COs below $T_V$. A recent study proves that the bulk low temperature phase (LTP) manifests at the surface in distinct structural features than the reconstruction [29]. Furthermore, the $\sqrt{2} \times \sqrt{2} R45^\circ$ symmetry is lost in favor of a $(1 \times 1)$ structure at a temperature $T_S \sim 720$ K through a second-order transition involving loss of long-range CO [30]. These results suggest the existence of fundamental differences between the surface and bulk insulating phases.

In this work, we provide firm proof of this fact, calculating the evolution with temperature of the electronic structure of the Fe$_3$O$_4$(0 0 1) surface. Our results evidence that the surface insulating state originates from the combination of large O electron affinity and loss of O bonds, and remains unaltered across the bulk and surface transitions. This has an impact for the disappearance of trimerons close to the surface, replaced by bipolaronic structures below $T_V$. As a consequence, a competition between the local bulk and surface COs emerges below $T_V$, that manifests in modulations of the surface CO arising both from bulk trimerons and from the surface reconstruction.

### 2. Theoretical method

We have performed first principles calculations of both bulk magnetite and its (0 0 1) termination, based on the density functional theory including correlation effects. We employ a plane wave basis set [31] and the projector augmented waves (PAW) method to describe the core electrons [32], with an energy cutoff of 400 eV and a Monkhorst-Pack sampling of the Brillouin zone (BZ) of $(7 \times 7 \times 5)$ for the bulk and up to $(6 \times 6 \times 2)$ for the surface slabs, that guarantee convergence in the total energy better than 0.1 meV/f.u. We use the exchange-correlation functional parametrization of Perdew–Burke–Ernzenhof (PBE), adding an effective on-site Coulomb repulsion term $U = 4$ eV [33]. This choice of U is based on the recovery of an equilibrium value of the cubic lattice parameter $a = 8.4$ Å in excellent agreement with experiments, and the adequate description of the Verwey transition in terms of charge disproportionation (0.27 e) and electronic band gap (0.2 eV) when reducing the symmetry from the cubic $Fd\bar{3}m$.

Our description of bulk magnetite is based on a $P2/m$ unit cell formed by 28 atoms. We have determined the equilibrium structures above and below $T_V$ starting from the ideal cubic lattice and allowing relaxation of the lattice vectors and atomic positions, with no symmetry constraints for the low temperature phase (LTP). Even at the high temperature phase (HTP) there exists a noticeable distortion of the O sublattice, that introduces a slight tetragonal deformation of the unit cell with a small reduction of the total volume of 3 Å$^3$. At the LTP, relaxation of the lattice vectors leads to an orthorhombic symmetry, but again the distortion of the unit cell is small, with a similar reduction of the total volume.

To model the Fe$_3$O$_4$(0 0 1) surface, we have used slabs of different thicknesses, containing from 8 to 16 atomic planes, supported on a Au substrate and including a vacuum region of at least 12 Å that avoids interaction between opposite slab surfaces. The choice of the substrate has been performed to minimize interface effects and to confine them to the interface layer. In all cases, we have employed $(\sqrt{2} \times \sqrt{2}) R45^\circ$ two-dimensional unit cells, starting our calculations either from the $(1 \times 1)$ termination or from the Jahn–Teller induced wavelike pattern, and allowing to relax the atomic positions of the 3 outermost surface layers until the forces on all atoms are below 0.01 eV Å$^{-1}$. We have done this for slabs constructed both from the HTP and the LTP bulk structures. The slabs of 12 planes provide the minimum thickness to recover the bulk structure at the inner layers below $T_V$ including the distribution of trimerons, and all the results presented here correspond to

### Table 1. Mean Fe–O bond-lengths ($d$(Fe–O)) and values of the interatomic distances between first Fe$_B$ neighbors ($d^{FF}$) at the HTP and LTP of bulk Fe$_3$O$_4$. Units are Å.

|          | Fe$^{2+}$–O | Fe$^{3+}$–O | Fe$_4$–O |
|----------|-------------|-------------|----------|
| HTP      | 2.06        | —           | 1.89     |
| LTP      | 2.03        | 2.08        | 1.89     |
| $d^{FF}$ | Fe$^{2+}$–Fe$^{2+}$ | Fe$^{2+}$–Fe$^{3+}$ | Fe$^{3+}$–Fe$^{3+}$ |
| HTP      | 2.96        | —           | —        |
| LTP      | 2.95        | 2.89/3.03   | 2.95     |
of states (DOS), the Bader charges \((QB)\) and inequivalent \(Fe\) values correspond to majority (minority) spin projections. This configuration. We have also modelled thicker unsupported symmetric slabs of 16 planes to check the independence of our conclusions on the slab configuration, particularly concerning the penetration of surface effects.

3. Bulk Fe\(_3\)O\(_4\)

Figure 1 and table 1 summarize our results for the density of states (DOS), the Bader charges \((QB)\) and the interatomic distances at both the HTP and the LTP of bulk magnetite. The energy barrier between both phases is 170 meV/f.u. The higher symmetry of the HTP reflects in the existence of only one type of \(O\) and \(Fe\) sites with a bond length of 2.06 Å, and in the uniform value of the \(Fe_B\)–\(Fe_B\) interatomic distance \((d_{FF} = 2.96\) Å). Below \(T_V\), while \(Fe_A\) remains essentially unaffected by the transition, a charge disproportionation of 0.27 e appears in the \(Fe_B\) sublattice, opening a band gap of 0.2 eV. Within our reduced \(P2/m\) cell, the \(Fe^{3+}\) and \(Fe^{2+}\) ions alternate along the \([001]\) direction, as evidenced in figure 2. Different values of the \(d_{FF}\) can be found depending on the \(Fe\) valence. This is accompanied by a noticeable dispersion of the \(Fe_B\)–\(O\) bond lengths, with larger average values for \(Fe^{2+}\) (2.08 Å) than for \(Fe^{3+}\) (2.03 Å). The result is a non-uniform distribution of charge and magnetic moments that leads to slightly different \(O\) atoms at the \(Fe^{3+}\) \((O_1)\) and \(Fe^{2+}\) \((O_2)\) planes, as reflected in the dispersion of the \(QB\) values. However, the same net magnetization of 4 \(\mu_B/f.u.\) is obtained above and below \(T_V\).

The inhomogeneities in the \(d_{FF}\) at the LTP have important consequences for the emergence of trimerons. Regarding figure 2, every \(Fe^{3+}\) is surrounded by 4 \(Fe^{3+}\) placed at the adjacent upper and lower \((001)\) layers. Two of them are at 2.89 Å (solid colored lines) and the other two are at 3.03 Å (dotted lines), while the interatomic distance between coplanar \(Fe_B\) atoms is 2.95 Å, as shown in table 1. This defines linear \(Fe^{3+}\)–\(Fe^{2+}\)–\(Fe^{3+}\) chains of shortened lengths, with a charge accumulation over 0.027 e Å\(^{-3}\) at the middle of each \(Fe^{3+}\)–\(Fe^{2+}\) segment, in analogy with the experimental features assigned to trimerons [15]. The orbital character of the electronic states confirms the polaronic charge distribution, with the occupied \(Fe^{2+}\) minority spin states lying along the central axis of the chain and inducing a small contribution of the same orbital character at the closer \(Fe^{3+}\).

Trimerons are uniquely characterized by the coexistence of all these features—short \(d_{FF}\) (\(<2.93\) Å), enhanced charge accumulation (\(>0.027\) e Å\(^{-3}\)) and orbital directionality, as confirmed by exploring alternative solutions without CO along the \((001)\) direction where trimerons do not form. Moreover, the existence of these solutions points to the complex link between the long- and short-range COs [19]. We have observed that already under a cubic lattice, the reduced \(P2/m\) unit cell is enough for the Verwey metal-insulator transition to emerge, merely by relaxing the symmetry constraints of the HTP in the presence of electronic correlations \((U > 2\) eV) [9]. The additional full relaxation of the lattice vectors and atomic positions introduces a slight orthorhombic distortion at the LTP, and is accompanied by the formation of the local trimeron structures. This links the metal-insulator transition to the extended CO, and separates it from the short-range correlations, in good agreement with recent evidence [19]. Though the intricate relation between the different COs can only be ultimately integrated under the full \(Cc\) symmetry, the results presented in this section prove that our reduced unit cell contains the main features of the charge distribution at the LTP: a dominant CO along the \([001]\) axis [34], and the existence of trimerons as short-range features that are distinct to the low temperature CO but intimately connected to it. This supports the use of the \(P2/m\) cell as a basis to explore the surface properties below \(T_V\).

4. The Fe\(_3\)O\(_4\)(0 0 1) surface above \(T_V\)

We will first focus on the unreconstructed surface of the HTP above \(T_S\). A sketch of the structure corresponding to our
A large distortion of the O sublattice, the opposite occurs for the FeB at the two outermost layers, L1 and L3. Each FeB along the surface [1 1 0] and subsurface [1 1 0] rows approaches one of their adjacent Fe neighbors at the cost of moving further from the opposite. As shown in figure 3(b), the movement is more pronounced at the subsurface.

The result of this restructuring in the electronic properties can be seen in figure 4, that provides the atomic-resolved DOS and the corresponding $Q_B$ at the outermost FeB–O planes, where all surface effects are contained. Although the O charges show significant dispersion, the differences are not apparent in the DOS, and their $Q_B$ are close to bulk values throughout the structure. The FeB atoms at L1 behave as Fe$^{3+}$, opening an insulating gap. However, the emergence of the gap is not accompanied by any charge disproportionation at the FeB sublattice. A gradual recovery of bulk-like behavior starts at L3, and is almost restored at L5. As our slabs are not completely free from confinement effects, we cannot discard that it could be restored even at L3, as inferred from STM observations of the structure of antiphase boundaries (APB) [30, 35]. It is also important to remark that although uncompensated and slightly enhanced magnetic moments emerge at the surface plane ($4.16 \mu_B$ for Fe, $0.4 \mu_B$ for O), the antiferromagnetic coupling between the FeA and FeB sublattices remains unaltered. This preserves the bulk-like high magnetic moment of Fe$_3$O$_4$ also at the high temperature surface, validating it as a promising material for spintronics applications.

When the temperature is lowered below $T_S$, the ($\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction sets in. This surface has already been studied in detail, but there are yet controversies about the origin of the reconstruction and its dependence on electronic correlations [22, 26]. Our results indicate that all effects described for the unreconstructed surface are still present below $T_S$, with only minor modifications of $d_{33}$ and $d_{34}$ of less than 0.04 Å, and slightly more asymmetric Fe–O coordination units. This is also in agreement with previous quantitative low energy electron diffraction (LEED) experiments, where similar oscillatory relaxations of the interlayer distances and large corrugations of the atomic positions were found [27]. Figure 5 shows a sketch of the structure and figure 6 the corresponding DOS and $Q_B$ at the 3 outermost FeB–O planes. The most relevant feature introduced by the reconstruction is the emergence of a charge disproportionation of $\sim 0.10$ e between Fe sites at L3, that defines a CO pattern within the (0 0 1) plane reducing the dispersion of O charges. This subsurface CO was already proposed on the basis of purely electronic effects [22]. However, we obtain that the atomic wavelike displacement at the surface Fe rows lowers the energy by 28 meV/f.u. with respect to the (1 × 1) surface also in the presence of electronic correlations. Reminiscence of this CO persists at L5, though
half-metallicity is recovered. In fact, we cannot discard some penetration of the surface effects at deeper layers in real samples, where the existence of defects or APB may contribute to alterations of the CO, as the energy barrier between different charge distributions is of only a few meV [35].

From these results it is clear that the surface transition arises from the interplay between CO and electron-lattice couplings, as already proposed on the basis of thermodynamic models [30]. But although an insulating and charge-ordered state exists below $T_S$, the surface introduces significant differences with the bulk LTP. At L3, the Fe charge and DOS width are influenced by the demand of charge from surface O, and show reduced values with respect to the bulk $Fe^{3+}$ and $Fe^{2+}$. More important, as we will prove now, neither the surface structure nor the orbital character of the surface $t_{2g}$ states support the definition of trimerons.

Regarding figure 5, the wavelike Fe$_B$ surface displacements define narrow and wide regions occupied respectively by $Fe^{2+}$ and $Fe^{3+}$. As a result, along each subsurface [1 1 0] row, pairs of $Fe^{2+}$ and $Fe^{3+}$ alternate, inhibiting the formation of linear $Fe^{3+}$–$Fe^{2+}$–$Fe^{3+}$ chains within the (0 0 1) plane. Even though the longitudinal movement of the surface Fe$_B$ along (1 1 0) rows (not shown in the figure) is similar to that above $T_S$, at the subsurface the displacement of $Fe^{3+}$ is suppressed, originating shortened $d^{FF} = 2.70$ Å between $Fe^{2+}$–$Fe^{2+}$ and large $d^{FF} = 3.09$ Å between $Fe^{3+}$–$Fe^{3+}$. This leads to in-plane charge sharing between $Fe^{2+}$ sites, forming a kind of localized bipolarons [22, 24] with a large charge accumulation of 0.035 e Å$^{-3}$, but opposes to the structure of bulk trimerons. This tendency persists with respect to the adjacent planes: as shown in figure 5(a), the $d^{FF}$ to the Fe$_B$ neighbors at L1 is similar for $Fe^{3+}$ and $Fe^{2+}$, and much larger than 2.70 Å. Similarly, the Fe$_B$ closer to subsurface $Fe^{3+}$ ($Fe^{2+}$) at L5 are those of $Fe^{3+}$ ($Fe^{2+}$) type, and are also farther than 2.70 Å. In conclusion, neither the interatomic distances nor the charge distribution arising from the surface reconstruction support the formation of bulk-like trimerons.

5. The Fe$_3$O$_4$(0 0 1) surface below $T_V$

The different nature of the low temperature surface and bulk phases discards that the $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction acts as the first stage for the development of the VT. However, it suggests the possibility of a competition between surface and bulk COs below $T_V$. In order to explore this, we have modelled the Fe$_3$O$_4$(0 0 1) surface of the LTP departing from our $P2/m$
bulk unit cell. Although this cell contains limited information of the actual long-range CO, we will show that yet important insights about the mutual influence of the bulk and surface short-range correlations become evident.

The surface can be constructed exposing either Fe$^{3+}$ or Fe$^{2+}$ planes, which has implications for the continuity of bulk trimerons close to the surface, as shown in figures 7 and 9. The most stable situation by $\sim 70$ meV/f.u. corresponds to the Fe$^{2+}$-ended case in figure 7, that at difference with the Fe$^{3+}$ termination, preserves the bulk CO up to the subsurface. This energy difference is much larger than that between the $(\sqrt{2} \times \sqrt{2})R45^\circ$ and $(1 \times 1)$ surfaces at high temperatures, evidencing the high impact of the bulk CO on the surface properties. We have estimated that the loss of the bulk CO at the subsurface lowers the work function by 0.30 eV, a variation close to that induced by the adsorption of water [36].

On the other hand, surface effects are similar to those at the HTP under both terminations: an insulating Fe$^{3+}$ surface layer, shortened surface O–Fe$_B$ bonds, and a similar pattern of outermost interlayer distances and longitudinal atomic displacements within the Fe$_B$ rows. This helps to attain bulk values of the O charge, though the surface causes an additional dispersion in $Q_B$, as shown in figures 8 and 10 for the Fe$^{2+}$- and Fe$^{3+}$-ended cases, respectively. Surprisingly, at the Fe$^{3+}$ termination the same electronic structure corresponds to the $(1 \times 1)$ and $(\sqrt{2} \times \sqrt{2})R45^\circ$ surfaces, separated by less than 7 meV/f.u. This is because the LTP bulk structure introduces an additional charge modulation within (0 0 1) planes, that obscures that induced by the reconstruction: regarding figure 7, half of the Fe$^{3+}$ sites at L3 would develop trimerons with the upper Fe$_B$, but these have changed their valence inhibiting the polaronic charge distribution. As the other half participates in trimerons with the layers below, two types of Fe$_B$ sites exist at the subsurface, with similar DOS but slightly different $Q_B$ and interatomic distances to the surface Fe$_B$. Again this proves the influence of the bulk CO on the surface properties below $T_V$.

In turn, the robust insulating surface layer, which seems to be a universal feature of magnetite even under metastable terminations [21, 22], has an important local effect on the bulk CO. This better manifests at the Fe$^{3+}$ termination in figures 9 and 10, where the lack of continuity of the trimerons at the subsurface allows for the emergence of localized bipolarons, indicating the possible coexistence of local surface and bulk COs. But figure 7 evidences that also at the Fe$^{2+}$ termination those trimerons closer to the surface are slightly affected by it: the Fe$^{3+}$–Fe$^{2+}$ distances between L3 and L5 are moderately enlarged, which introduces an asymmetry in the Fe chain weakening the charge sharing in its upper branch. In summary, though preservation of the bulk CO seems to have a dominant effect on the surface stability, it is conditioned by the insulating Fe$^{3+}$ surface layer, and there is a mutual influence of the bulk and surface properties that extends several layers below the surface plane.

![Figure 8](image8.png)

**Figure 8.** Layer and spin-resolved DOS of the Fe$^{3+}$ (blue), Fe$^{2+}$ (red) and O (black) atoms of the structure in figure 7, providing the corresponding $Q_B$.

![Figure 9](image9.png)

**Figure 9.** Same as figure 7 for the Fe$^{3+}$-ended surface of the LTP.

![Figure 10](image10.png)

**Figure 10.** Same as figure 8 for the structure in figure 9.
6. Summary and conclusions

Our results prove that the Fe₃O₄(001) surface shows a robust insulating state that persists across the surface and bulk phase transitions. It is originated by the large demand of charge from surface O arising from bond breaking, and causes a significant restructuration at the outermost planes that inhibits the formation of trimerons. Below Tₛ, a surface CO distinct from that of the bulk LTP emerges. Its distinct nature manifests in a lower charge disproportionation as compared to the bulk LTP, and in the preferential bipolaronic CO within (001) planes. When the temperature is lowered below Tₛ, this surface CO competes with the dominant bulk one. This competition is conditioned by the insulating Fe³⁺ character of the surface, which weakens the trimeron structures.

Aside its intrinsic interest, the relation between CO and dimensionality has implications for the multifunctional properties of magnetite, since the emergence of ferroelectric and dimensionality has implications for the multifunctional properties of magnetite, since the emergence of ferroelectric

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References

[1] Orozco A et al 1999 Phys. Rev. Lett. 83 1680
[2] Wu H C, Myrasov O N, Abid M, Radican K and Shvets I V 2013 Sci. Rep. 3 1830
[3] Liu M, Hoffman J, Wang J, Zhang J, Nelson-Cheeseman B and Bhattacharya A 2013 Sci. Rep. 3 1876
[4] Zhang Z and Satpathy S 1991 Phys. Rev. B 44 13319
[5] Tobin J G, Morton S A, Yu S W, Waddill G D, Schuller I K and Chambers S A 2007 J. Phys.: Condens. Matter 19 315218
[6] Fonin M, Dedkov Y S, Pentcheva R, Rüdiger U and Güntherodt G 2008 J. Phys.: Condens. Matter 20 142201
[7] Kobayashi H, Nago T, Itoh M, Todo S, Barbiellini B, Mijnarends P E, Bansil A and Sakai N 2009 Phys. Rev. B 80 104423
[8] Müller G M et al 2009 Nat. Mater. 8 56
[9] Wang W et al 2013 Phys. Rev. B 87 085118
[10] Verwey E J W 1939 Nature 144 327
[11] Leonov I, Varesko A N, Antonov V N, Korotin M A and Anisimov V I 2004 Phys. Rev. Lett. 93 146404
[12] Huang D J et al 2006 Phys. Rev. Lett. 96 096401
[13] Iizumi M, Koetzel T F, Shirane G, Chikazumi S, Matsui M and Todo S 1982 Acta Crystallogr. B 38 2121
[14] Blasco J, García J and Subías G 2011 Phys. Rev. B 83 104105
[15] Senn M S, Wright J P and Attfield J P 2012 Nature 481 173
[16] Walz F 2002 J. Phys.: Condens. Matter 14 R285
[17] García J and Subías G 2004 J. Phys.: Condens. Matter 16 R145
[18] Hoesch M, Piekarz P, Bosak A, Le Tacón M, Krisch M, Kozłowski A, Ole A M and Parlinski K 2013 Phys. Rev. Lett. 110 207204
[19] Bosak A, Chernyshov D, Hoesch M, Piekarz P, Le Tacón M, Krisch M, Kozłowski A, Ole A M and Parlinski K 2014 Phys. Rev. X 4 011040
[20] de Jong S et al 2013 Nat. Mater. 12 882
[21] Jordan K, Cazacu A, Manai G, Ceballos S F, Murphy S and Shvets I V 2006 Phys. Rev. B 74 085416
[22] Lodziana Z 2007 Phys. Rev. Lett. 99 206402
[23] Stanka B, Hebenstreit W, Diebold U and Chambers S A 2000 Surf. Sci. 448 49
[24] Shvets I V, Mariotto G G, Jordan K, Berdunov N, Kantor R and Murphy S 2004 Phys. Rev. B 70 155406
[25] Novotny Z, Mulakaluri N, Edes Z, Schmid M, Pentcheva R, Diebold U and Parkinson G S 2013 Phys. Rev. B 87 195410
[26] Pentcheva R, Wendler F, Meyerheim H L, Moritz W, Jedrecy N and Scheller M 2005 Phys. Rev. Lett. 94 126101
[27] Pentcheva R, Moritz W, Rupprecht J, Frank S, Schupp D and Scheller M 2008 Surf. Sci. 602 1299
[28] Fonin M, Dedkov Y S, Pentcheva R, Rüdiger U and Güntherodt G 2007 J. Phys.: Condens. Matter 19 315217
[29] de la Figuera J et al 2013 Phys. Rev. B 88 161410
[30] Bartelt N C, Nie S, Starodub E, Bernal-Villamil I, Gallego S, Vergara L, McCary K F and de la Figuera J 2013 Phys. Rev. B 88 235436
[31] Kresse G and Hafner J 1993 Phys. Rev. B 47 558
[32] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[33] Blochl P E 1994 Phys. Rev. B 50 17953
[34] Kresse G and Joubert J 1999 Phys. Rev. B 59 1758
[35] Dudarev S L, Botton G A, Savrasov S Y, Humphreys C J and Sutton A P 1998 Phys. Rev. B 57 1505
[36] Wright J P, Radaelli P G and Attfield J P 2001 Phys. Rev. Lett. 87 266401
[37] Wright J P, Attfield J P and Radaelli P G 2002 Phys. Rev. B 66 214422
[38] Parkinson G S, Manz T A, Novotny Z, Sprunger P T, Kurtz R L, Schmid M, Sholl D S and Diebold U 2012 Phys. Rev. B 85 195405
[39] Kendelevicz T, Kaya S, Newberg J T, Bluhm H, Mulakaluri N, Moritz W, Scheller M, Nilsson A, Pentcheva R and Brown G E R 2013 J. Phys. Chem. C 117 2719
[40] Skomurski F N, Keres K and Rosso K M 2010 Geochim. Cosmochim. Acta 74 4234
[41] Parkinson G S, Novotny Z, Argentero G, Schmid M, Pavelec J, Kosak R, Blaha P and Diebold U 2013 Nat. Mater. 12 724