Competing electronic states in high temperature phase of NaTiO$_2$

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Abstract
First principle density functional theory calculations on the high temperature phase of layered triangular lattice system NaTiO$_2$ have revealed that a collective electronic state exists energetically close to the ground state but with competing transport properties: the latter is metallic with partially occupied doubly degenerate $e'_{\text{g}}$ orbitals, whereas the former is insulating with $a_{1g}$ orbital fully occupied. Significant occupation of this excited state is possible at non zero temperature either thermally or thanks to very soft (large amplitude) oxygen vibrations. Possible explanations of the experimental low conductivity based on competing orbital transport and of the specific heat jump at a structural transition based on orbital entropy are discussed.

Keywords: density functional theory, metal-insulator transition, triangular lattice

(Some figures may appear in colour only in the online journal)
2. Methodology

We have taken the experimental structure of NaTiO$_2$ in its high temperature phase from Clarke et al [6]. We have performed a detailed electronic structure calculation for the rhombohedral phase of NaTiO$_2$ using the standard full potential linearized augmented plane wave method implemented in WIEN2k code [12]. For the experimental structure, the muffin tin sphere radii were chosen to be 2.23, 2.07 and 1.83 a.u. for Na, Ti and O respectively. Plane wave cutoff parameter $R_{\text{mt}}K_{\text{max}}$ was chosen as 7.00 and approximately 120 k-points were used over the irreducible first Brillouin zone. Convergence has been achieved to energy values less than 1 meV per formula unit with respect to the variation of number of k-points and the parameter $R_{\text{Kmax}}$.

As NaTiO$_2$ contains a transition metal ion having one d electron in the outermost shell, Coulomb correlations are expected to be significant in this system. Therefore, we have performed calculations within the local spin density approximation (LSDA) and the LSDA+$U$ approximation (which includes orbital Coulomb correlation). More than one implementation is available for the latter method, generating different double-counting corrections for the underlying LSDA functional. For moderately correlated (or metallic) systems a mean field approximation to the d-orbital part of the LSDA functional is considered to be appropriate. This is described in detail as the around mean field (AMF) function in [13]. As NaTiO$_2$ is observed to be a bad metal in both high and low temperature phases experimentally [6], we have chosen the AMF method in our LSDA+$U$ calculations reported below. In this work we consider a range of $U$ values (3.3–4 eV) with emphasis on two in particular: 3.6 eV and 4.0 eV. The former is obtained theoretically via constrained LDA calculations by the authors of [14], specifically for this compound. This value is very close to that used ($U = 3.3$ eV) for compounds like TiOCl [15], NaTiSi$_2$O$_6$ and (La,Y)TiO$_3$ which gives good agreement with experimental data such as magnetic susceptibility [16], spin gap [17] and optical measurements [18], respectively. Therefore we take it as a physically reasonable value. The latter is considered merely for theoretical purposes.

3. Results and discussion

3.1. Experimental structure: ground state

We first study the electronic ground state of the experimental crystal structure within the LSDA and LSDA+$U$ functionals. Figure 2 shows the electronic band structure within LSDA. The ground state is found to be metallic with Ti d states present at the Fermi level in both spin directions. One also observes that after the octahedral crystal field splitting only $t_{2g}$ states lie at the Fermi level. These are then further split due to the trigonal crystal field of oxygens into two sub-manifolds: $e'_g$ and $a'_g$, the former being doubly degenerate in the $xy$ plane: the two pointing towards the oxygen (direction $z = \sqrt{2}$) vanish and the two pointing in between the other two oxygens are conserved.

From band structure analysis we see that the bands cutting the Fermi level have predominantly $e'_g$ character. In particular the $yz$ component lies in the lowest band and the $xy$ and $x^2−y^2$ components in the next one. The highest band of the $t_{2g}$ group has mainly $a'_{1g}$ character.

In table 1 we present electron population analysis within LSDA, i.e. the occupation numbers of the $t_{2g}$ bands up to the Fermi level (excluding the valence band contributions due to double-counting).

![Figure 1. Crystal structure of NaTiO$_2$ showing the layered triangular lattice formed by Ti ions.](image-url)

$$a_{1g} : 3z^2−r^2$$

$$e'_g : 11/\sqrt{3} [yz + \sqrt{2}xy] = 1/\sqrt{3} [zx − \sqrt{2} (x^2−y^2)].$$

The $a_{1g}$ orbital has the typical $d_{z^2}$ shape along the trigonal axis and is perpendicular to the Ti plane (see figure 3); as a result the $a_{1g}$-$a_{1g}$ direct overlap of $\sigma$ type is very small. Direct overlap is mainly of $\pi$ type, generating a small bandwidth (~ 0.6 eV), as evident from figure 2. The electron density in real space with $a_{1g}$ orbital occupied at all Ti sites is shown in figure 3. The negligible $a_{1g}$-$a_{1g}$ direct overlap of $\sigma$ type is clearly evident from figure 3.

The $e'_g$ orbitals are doubly degenerate and have four different contributions from the canonical d orbitals. The $xy$ and $x^2−y^2$ components have maximum amplitude within the $xy$ plane ($z = 0$) and generate an almost circularly symmetric density, providing distributed overlap over all six coordinating Ti atoms. Their direct overlap is of $\sigma$ type (therefore much stronger than the $a_{1g}$-$a_{1g}$ overlap) and produces an efficiently delocalising wave function. This is reflected in figure 2 by the bandwidth of the $e'_g$ bands of almost 2 eV. The $yz$ component has all four lobes $\pi$-bonding along the $y$ axis, where the Ti–Ti distance is shortest. The $xz$ component has only two lobes remaining from its linear combination with $x^2−y^2$ within the $xz$ plane: the two pointing towards the oxygen (direction $z = \sqrt{2}$) vanish and the two pointing in between the other two oxygens are conserved.
As mentioned above, we note that the occupied bands (labelled $e'_g$ in figure 2) have a non negligible character of type $a_1g$. This is due to the significant trigonal distortion of the oxygen octahedron which causes the mixing of the two $t_{2g}$ subgroups. The LSDA functional, however, predicts a slight predominance of $e'_g$ over $a_1g$ occupation (for comparison the former should be divided by two because of its degeneracy). This is explained by the fact that $e'_g$ states allow the hopping of electrons over a dense 2d triangular network of Ti atoms (high coordination number and effective orbital overlap, in contrast to analogous compound such as f.i. TiOCl \[15\]), thus generating a significant energy gain due to electron delocalization. Since they are doubly degenerate and not fully occupied (one electron per Ti atom) the electronic structure is metallic.

For transition metal atoms like Titanium the effect of local electron correlation $U$ is analysed via the LSDA+$U$ functional. Figure 4 shows the band structure in both majority and minority spin channels for a physically reasonable value of $U = 3.6$ eV for Titanium \[14\]. The effect here consists merely of a complete spin polarization of the bands. Due to the degeneracy of the $e'_g$ states at the Fermi level, no further orbital polarization could be induced by the orbital Coulomb correlation $U$ within LSDA+$U$ approximation. Therefore, the two majority spin bands remain half filled and the system behaves as a metal.

From table 1 we note that the occupation number of the $a_{1g}$ orbital is smaller but rather close to the $e'_g$ one (divided by two because of its degeneracy). This suggests that the electronic excitation with $a_{1g}$ orbital occupied is low energy. In order to estimate the magnitude of this excitation energy, we took the approach of orbital locking. In this approach, the occupation of a chosen orbital is kept fixed till convergence and then relaxed within a second convergence run. The orbital occupation is fixed by manually setting the initial density matrices (see appendix for details). We call the electronic configuration with $a_{1g}$ orbital occupied predominantly an ES1 state and that with $e'_g$ orbital occupied predominantly an ES2 state, hereafter. Note that for $U = 3.6$ eV ES2 is the ground state. By forcing the single Ti d-electron to occupy the $a_{1g}$ orbital and then allowing it to relax (ES1) we obtain a stable

| Table 1. LSDA orbital occupation numbers of the trigonal projections within $t_{2g}$ manifold. |
|---------------------------------------------------------------|
| $a_{1g}$ | $e'_g$  |
| spin up | 0.17 | 0.40 |
| spin dn | 0.05 | 0.08 |

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solution with a total energy of about 5 meV (per formula unit) higher than that of the ground state (figure 5), using \( U = 3.6 \) eV. This state represents a collective excited state and its electronic structure is illustrated in figure 5(a). It shows the feature of an almost zero gap semiconductor, therefore having extremely limited conductivity.

Increasing \( U \) to a theoretical value of 4 eV, the ES1 state becomes the ground state whereas ES2 is now an excited state by a tiny energy difference (see next discussion on dependence on \( U \)). Figure 5(b) shows the ES1 state with a single \( a_{1g} \) band below the Fermi level and the opening of a gap in the majority spin channel due to a stronger \( U \) value. In comparison to previous \( U \) values, here conductivity is totally absent.

Based on this result and given the proximity in energies of the ES1 and ES2 states, we study their stability as DFT solutions with varying \( U \) values. This is obtained using the approach of orbital locking, as mentioned earlier. The plot of the resulting total energy difference of the two solutions is presented in figure 6. We see that for \( U \) values in the region considered physically reasonable for Titanium (around 3.6 eV) the ES2 state is the ground state but lower in energy than the ES1 state by only about 5 meV or less (this is well above the error bar mentioned in the methodology section). As \( U \) crosses the value 3.7 eV, ES1 becomes the ground state, with the gradual opening of a gap. For \( U = 4 \) eV the gap magnitude in the majority spin channel amounts to about 0.4 eV (see figure 5(b)).

The above results show the interplay between two standard and competing mechanisms (energy scales) in transition metal compounds: the localization (\( U \)) favouring \( a_{1g} \)
occupation and the delocalization (kinetic energy) favouring \( e'_g \). This holds for a wide range of temperatures up to room temperature, but for very low temperature (<5 mev ≈ 50 K) the excited state cannot be thermally reached and only the \( e'_g \) state is populated.

For the physical value of \( U = 3.6 \text{ eV} \) our results are in line with experimental results by Clarke [6], where a bad metal with low but non zero conductivity is found. The bad metallic behaviour is ascribed to the existence of an almost metallic with low but non zero conductivity is found. The bad metallic state (ES1, a\(_1\)g) very close in energy (5 mev) to a conducting ground state (ES2, e\(_g\)). Previous calculations on the high temperature phase of this system were reported in [14] where the authors found an insulating behaviour within the LSDA+U \( (U = 3.6 \text{ eV}) \) approximation with a spin-polarized a\(_1\)g band being fully occupied and a gap of about 1 eV.

Though we observe the insulating ES1 state as ground state for higher \( U \) values \( (U > 3.7 \text{ eV}) \), for \( U = 3.6 \text{ eV} \) we clearly see that ES2 state is the ground state. More importantly, we observe that these two electronic states (ES1 and ES2) are very close in terms of energy over a reasonably large range of \( U \) values (see figure 6). We would also like to mention that in the calculation reported in [14], already within LSDA the a\(_{1g}\) occupation obtained was higher than that of e\(_g\), which is opposite to what we observe here (see table 1). We believe that this discrepancy is due to the adoption of the linear muffin tin orbital (LMTO) basis set in the previous calculations against the linearized augmented plane wave (LAPW) basis used here. In comparison to the LAPW method, LMTO is known to be deficient in describing the interstitial region in between atomic (muffin tin) spheres (see section 3 of [18] as an example). The appropriate description of this region is to take into account electron delocalization effects via a realistic overlap of the orbitals of e\(_g\) symmetry. Finally [14] finds the compound to be insulating, in contrast to experimental results [6]. Hence the findings presented in this work better describe the experimental situation.

3.2. Lattice effects: optimization of oxygen position

Following an ab initio approach we investigate the equilibrium structure within the high temperature phase symmetry that allows only for oxygen displacements along the z-axis (figure 1). Given the low dimensionality of the problem, we choose to optimize the oxygen positions using the total energy minimization method, which is based on drawing the energy curve as a function of the oxygen coordinate \((z, z, z)\) [15]. Lattice parameters are kept at their experimental values. This has the advantage of simulating the effect of van der Waal’s forces between layers given that they are not taken into account within DFT. As learnt in the previous section, the system presents two almost degenerate ground states for relevant \( U \) values: ES2 (ground state) and ES1 (low-lying excited state). Therefore we study the stability of both states as a function of the oxygen coordinate, applying the orbital locking method as in previous section.

In figure 7 we present the results for two values of \( U \). The full curve represents the total energy of the ES1 state and the dashed one is that of the ES2 state. For the theoretical \( U \) \( (=4 \text{ eV}) \) (figure 7(b)) the ES1 state is much lower in energy than the ES2 state and represents the ground state for all oxygen positions. (Note that the ES2 state is not stable for all oxygen positions, as indicated by the dashed curve having no value below the experimental \( z \) (=0.2348). This is probably due to the crystal field of oxygen atoms preventing electron delocalization within the ES2 state.) However, for the physical \( U \) \( (3.6 \text{ eV}) \) (figure 7(a)) the energies of ES1 and ES2 become comparable for several oxygen positions. As a consequence there exists a range of oxygen positions (0.233, 0.235) for which the total energy is almost constant. As a result oxygen thermal vibrations would be characterized by large amplitudes and generate pronounced orbital fluctuations between a\(_{1g}\) and e\(_g\) states.

The overall energy landscape for three values of \( U \) is shown in figure 8. Within the LSDA functional \( (U = 0) \), the experimental structure is found to be the equilibrium one. By contrast, for the physical \( U \) \( (3.6 \text{ eV}) \), the energy landscape is clearly flat as it is for \( U = 4 \text{ eV} \) but to a lesser degree. In the inset, a zoom-in of the energy curve for \( U = 3.6 \text{ eV} \) is given, showing quantitatively the flatness of the energy curve: its variation remains below 20 meV in a wide range of \( z \) values (0.231, 0.236). At room temperature this landscape gives rise to soft oxygen vibrational modes with quite large oscillation amplitudes which enhance orbital fluctuations significantly.

It is worth mentioning that the optimization of lattice parameters does not alter the conclusions drawn above qualitatively. For example, optimization within LDA leads to reduction in both \( a \) and \( c \) parameters by about 2%. The reduction of \( a \) causes a greater overlap of e\(_g\) orbitals, thus making ES2 more stable, while the shrinking of \( c \) favours ES1 (a\(_{1g}\)) due to the crystal field of oxygen being closer to e\(_g\) orbitals.

We note that the above scenario suggests a possible explanation for the anomalous value of the specific heat jump at the structural transition: this is in fact found to be bigger than the one for pure spin system by Takeda et al [20]. Clarke et al [6] have extracted from Takeda's measurements a value of the
entropy change of 7 J K$^{-1}$ mol$^{-1}$. In the case of long range antiferromagnetic ordering of S=1/2 spins, the entropy change should be $R \ln(2S + 1) = R \ln 2 = 5.8$ J K$^{-1}$ mol$^{-1}$ [6]. No magnetic long range order is found in this system and short range antiferromagnetic correlations could only give rise to an entropy change lower than $R \ln(2S + 1)$. This would be even further away from the experimental value of 7 J K$^{-1}$ mol$^{-1}$.

In this work we have shown at length the relevance and interplay of orbital degrees of freedom. As there are both experimental and theoretical predictions [7, 10] for long range orbital order (with partial orbital polarization at each site) at low temperatures, the entropy change is expected to be lower but indicatively closer to $R \ln(2|\Omega| + 1)$ where the quantum number $|\Omega| = 1$ represents the three orbitals: a$_{1g}$ and e$'$$_{g}$. This upper bound amounts to 9.1 J K$^{-1}$ mol$^{-1}$, which would make the entropy change due to orbital order with partial orbital polarization close to the experimental 7 J K$^{-1}$ mol$^{-1}$.

4. Conclusions

We have performed a detailed electronic structure calculation for the high temperature rhombohedral phase of NaTiO$_2$. We first study the electronic properties of the (non optimized) experimental structure. The ground state is found to be conducting with e$'$$_{g}$ orbital symmetry. At an energy slightly greater than the ground state we find an excited state with a$_{1g}$ orbital symmetry and almost fully insulating. By thermal excitation the latter is populated comparably to the ground state, giving rise to an overall low conductivity. This is in line with the findings of Clarke et al [6] in their experiments. Secondly, we study the variation of the above properties with respect to lattice via static distortions of oxygen positions along the trigonal axis. Depending on the oxygen proximity to the Ti plane, the a$_{1g}$ (oxygens close to the Ti plane) or e$'$$_{g}$ (oxygens distant from the Ti plane) orbitals will be alternately populated. Moreover we find the energy landscape to be rather flat, which gives rise to a large vibrational amplitude. This implies that at room temperature the population of a$_{1g}$ or e$'$$_{g}$ orbitals will oscillate significantly. The specific heat jump at 250 K detected by Takeda et al [20] could, therefore, be tentatively accounted for by an entropy contribution coming from orbital degree of freedom rather than spin.

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Appendix

The initial density matrices (5 $\times$ 5) supplied for the ES1 and ES2 electronic states within the orbital lock approach are in the basis ($l = -2, -1, 0, 1, 2$) as described below. For the ES1 state the diagonal elements of the spin up density matrix are set to (0.0, 0.0, 1.0, 0.0, 0.0) and the remaining matrix elements to zero. Therefore only the d$z^2$ ($l = 0$) or a$_{1g}$ orbital is populated. The spin down density matrix is identically zero. For the ES2

Figure 7. Total energy as a function of oxygen coordinate for ES1 (full curve and squares) and ES2 (dashed curve and empty squares) states for (a) $U = 3.6$ eV and (b) 4 eV.

Figure 8. Total energy versus oxygen positions within LSDA and LSDA+$U$. Oxygen position $z$ is given in fractional coordinates. $z_{\text{exp}} = 0.2348$ corresponds to the experimental structure. Smaller values of $z$ represent shorter Ti–O bond length. Inset shows a closer view of the energy landscape near the equilibrium point for $U = 3.6$ eV; empty symbols represent the ES2 state and solid symbols the ES1 state.
state we have set the diagonal elements of the spin up density matrix to (0.25, 0.25, 0.0, 0.25, 0.25) and the remaining matrix elements to zero. Here we considered the simplest occupation spectrum with the $a_{1g}$ orbital empty: this consists in populating uniformly all the remaining harmonics ($l = -2, -1, 1, 2$) and therefore both the $e_g$ and $e_g'$ orbitals, counting on the fact that once the orbital lock is removed self consistency will surely depopulate the $e_g$ orbitals due to their energetics.

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