Hole-lattice Coupling and Photo-induced Insulator-Metal Transition in VO$_2$

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Photo-induced insulator-metal transition in VO$_2$ and the related transient and multi-timescale structural dynamics upon photoexcitation are explained within a unified framework. Holes created by photoexcitation weaken the V-V bonds and eventually break V-V dimers in the M$_1$ phase of VO$_2$ when the laser fluence reaches a critical value. The breaking of the V-V bonds in turn leads to an immediate electronic phase transition from an insulating to a metallic state while the crystal lattice remains monoclinic in shape. The coupling between excited electrons and the 6.0 THz phonon mode is found to be responsible for the observed zig-zag motion of V atoms upon photoexcitation and is consistent with coherent phonon experiments.

Despite decades of intensive research, the physics behind the metal-insulator transition in VO$_2$ at about 340 K[1] remains a subject of unabated debate. The electronic phase transition is accompanied by a seemingly “simultaneous” structural change from a low temperature monoclinic (M$_1$) to a high temperature rutile (R) structure. It is likely that the phase transition involves multiple intermediate states that occur at distinct timescales. Unfortunately, the delicate and transient interplay between the atomic and electronic degrees of freedom, which determines the dynamics and the kinetic pathway of the phase transition in VO$_2$, cannot be easily accessed within time averaged or equilibrium measurements. Therefore, recent advances in ultrafast spectroscopy have brought much excitement and inspired a new wave of investigations [2–12] with unprecedented time resolution and accuracy.

These new experiments reveal a great deal of details on the ultrafast dynamics and intermediate states associated with the phase transition, offering rare insights into the intriguing physics of VO$_2$. For example, an ultrafast (∼100 fs) photo-induced insulator-metal transition was observed [2–9]. The observed response cannot be explained by simply considering the effects of the excited carriers, and a structurally driven phase transition mechanism was proposed [4]. The structural change was ascribed to coherently generated optical phonons at ultrashort time scales. Indeed, a coherent phonon mode with frequencies at about 6.0 THz (∼200 cm$^{-1}$) is often observed [4, 5, 8, 11]. Other coherent phonons at about 4.5 THz (∼150 cm$^{-1}$) [11] and 6.75 THz (∼225 cm$^{-1}$) [4] have also been observed. However, the precise role these coherently generated phonons play and the mechanism of their generation upon photoexcitation are still not well understood.

More recently, a 4D visualization of the transitional structures of VO$_2$ after photoexcitation was carried out using a femtosecond electron diffraction technique [10]. A multi-timescale structural evolution ranging from subpicosecond to nanoseconds was uncovered. The first step of the structural change shortly after photoexcitation was identified as a rapid (subpicosecond) separation of the initially paired V atoms (i.e., V-V dimers) in the M$_1$ phase VO$_2$. It is natural to associate this subpicosecond displacements of V atoms with the observed ultrafast (∼100 fs) photo-induced insulator-metal transition. Unfortunately, there is no direct evidence that supports this connection.

In this letter, results from first-principles electronic structure calculations are used to establish a theory that is able to explain the ultrafast photo-induced insulator-metal transition and the the multi-timescale structural dynamics associated with photoexcitations. The strong coupling between the lattice and the excited holes is responsible for the observed rapid separation of V-V pairs after photoexcitation. The atomic motion is found to be primarily associated with a 339 cm$^{-1}$ (10.2 THz) phonon mode, instead of the much discussed 6.0 THz (∼200 cm$^{-1}$) mode. The separation of the V-V pair in-turn leads to an immediate electronic phase transition. Although the crystal lattice remains monoclinic in shape. The longer timescale (∼a few picoseconds) structural dynamics observed in experiment is associated with a phonon mode at 200 cm$^{-1}$ (∼6.0 THz) often observed in coherent phonon experiments [4, 5, 8, 11]. This phonon mode involves zig-zag movements of V atoms and is found to couple primarily with the excited electrons. However, the excitation of this phonon mode is not responsible for the subpicosecond photo-induced insulator-metal transition. Instead, it is just an important step toward the full structural phase transition from the monoclinic to the rutile phase.

All calculations are carried out using the projector augmented wave method [14] implemented in VASP [15], and the Perdew-Burke-Ernzerhof (PBE) functional is used. It is worth mentioning that although the PBE functional
is not able to produce an insulating ground state for the M\textsubscript{1} phase VO\textsubscript{2} if the experimental structure is used, upon structural relaxation, a small band gap ($\sim \) 0.13 eV) actually develops, as shown in Fig 1. The use of the theoretically relaxed structure also gives a satisfactory description of the lattice dynamics of the M\textsubscript{1} phase VO\textsubscript{2}. Table I compares the calculated zone-center phonon frequencies with experiment. The agreement between theory and experiment is very good.

Photoexcitations naturally introduce hot electrons and holes into the system. However, as mentioned earlier, the observed optical response upon photoexcitation cannot be explained by simply considering the effects of these excited electrons/holes [4], and the transient lattice dynamics must be taken into account. In order to separate the effects of the excited electrons and holes on the transient lattice dynamics of the system, in particular, the observed rapid separation of V-V pairs, we introduce electrons and hole into the system in our calculation separately. Our calculations start with a fully relaxed M\textsubscript{1} structure. Additional electrons or holes are then introduced into the system, and the structures are fully relaxed for a given electron (or hole) “doping” level while keeping the monoclinic lattice vectors.

Figure 2 illustrates the drastically different effects of electrons and holes on the calculated V-V separation:

Whereas the V-V separation is nearly unchanged upon electron doping, hole doping results in a gradual elongation of the V-V bond length below a critical level of $\sim$ 0.15 holes per VO\textsubscript{2} formula unit, above which a sudden jump in V-V separation is observed. The existence of a critical hole level and the sudden jump in V-V separation may be related to the required critical excitation fluence in experiments [5, 10]. Therefore, we conclude that the observed rapid V-V separation upon photoexcitation is a result of a strong lattice-hole coupling in this system.

In order to relate our results to the observed mult timescale atomic motion after photoexcitations [10], we compare the experimentally observed atomic displacements [Figs. 3(a) and 3(b)] at two distinct timescales and the directions of the calculated initial forces [Figs. 3(c) and 3(d)] on atoms with electron or hole doping with a “doping” level (carrier density) of 0.15 per VO\textsubscript{2} formula unit. The calculation starts with the relaxed M\textsubscript{1} structure before introducing carriers into the system. Carriers are then introduced, the forces on atoms are then calculated. Upon hole doping, the calculated forces on V atoms are directed primarily along the direction of V-V pairs [the two V atoms in the middle Fig. 3(c)] and they tend to elongate the V-V bonds. This result coincides nicely with the observed [10] subpicosecond displacement of V atoms upon photoexcitation of VO\textsubscript{2} as shown in Fig. 3(a). Electron doping, on the other hand, results in forces on V atoms that are nearly parallel to the lattice direction and zig-zag along the lattice $c$ direction, as shown in Fig. 3(d). This result compares well with the observed subnanosecond atomic displacements as shown in Fig. 3(b). Therefore, our results clearly illustrate that the subpicosecond V-V separation comes from the coupling between lattice and holes, whereas the subnanosecond structural dynamics should be attributed to the electron-lattice coupling and is related to the zig-zag motion of the V atoms.

This disparate structural responses to electrons and holes into the system.

![Graph](image1.png)

FIG. 1: (Color online) Calculated band structure of the M\textsubscript{1} phase VO\textsubscript{2} using theoretically relaxed crystal structure.

![Graph](image2.png)

FIG. 2: (Color online) Relaxed V-V dimer distance after introducing holes or electrons to the system.

| $A_g$ | $B_g$ | $A_u$ | $B_u$ |
|-------|-------|-------|-------|
| Cal. | Exp. | Cal. | Exp. | Cal. | Exp. | Cal. | Exp. |
| 152  | 149  | 0.54  | 212  | ...  | ...  | ...  | ...  |
| 197  | 199  | 2.72  | 231  | 259  | 187  | 189  | ...  |
| 224  | 225  | 0.96  | 247  | 265  | 265  | 270  | 253  | 227  |
| 331  | 313  | 0.59  | 374  | 395  | 304  | 310  | 295  | 285  |
| 339  | 339  | 1.58  | 432  | 444  | 333  | 340  | 324  | 324  |
| 389  | 392  | 0.82  | 447  | 453  | 415  | 392  | 374  | 355  |
| 508  | 503  | 0.79  | 495  | 489  | 508  | 505  | 490  | 478  |
| 605  | 618  | 0.26  | 593  | 595  | 560  | 600  | 572  | 530  |
| 675  | 670  | 0.11  | 758  | 830  | 721  | 710  | 721  | 700  |

TABLE I: Calculated zone-center phonon modes of the M\textsubscript{1} phase VO\textsubscript{2}. Zone-center phonons are grouped into Raman active ($A_g$ or $B_g$) and infrared active ($A_u$ or $B_u$) modes. Experimental results are taken from Ref.[16] (Raman) and Ref.[17] (infrared). The projections $\eta$ of the $A_g$ modes are discussed in the text.
holes can be understood by investigating the bonding character of the valence band maximum (VBM) and the conduction band minimum (CBM) states as shown in Fig. 4. The VBM states are primarily of V-V bonding character [Fig. 4(a)]. Therefore, removing electrons from the VBM states (adding holes) results in a weakening of V-V bonds. When this weakening reaches a critical point, the V-V dimerization is no longer intact. This explains the sudden jump in the V-V separation when hole level reaches a critical value of about 0.15 holes per VO$_2$ formula unit as shown in Fig. 2. This critical hole density may also be related to the critical lase fluence in experiment. The CBM states, on the other hand, involve an antibonding character of the shortest V-O bonds, as shown in Fig. 4(b). These short V-O bonds are related to the zig-zag arrangement of the V atoms along the lattice a direction as shown in Fig. 3. Therefore, adding electrons to the antibonding V-O states tends to alleviate the zig-zag arrangement of the V atoms. These results are consistent with the force analysis shown in Figs. 3(c) and 3(d); they also agree with the measured atomic displacement as shown in Figs. 3(a) and 3(d).

Although the transient structural dynamics involved in the photo-induced insulator-metal transition of VO$_2$ is very different from the conventional description of lattice dynamics in terms of phonons, it is still instructive to map the structural change onto polarization vectors of relevant phonon modes. Here we define a displacement vector from the M$_1$ to the R phase:

\[ \Delta \mathbf{R} \equiv \{ \mathbf{R}_i^R - \mathbf{R}_i^{M_1} \}; \ i = 1, 2, ..., N, \]  

(1)

where \( \mathbf{R}_i \) is the position of the \( i \)th atom in the unit cell and \( N \) is total number of atoms. We double the size of the unit cell of the R phase so that there is one-to-one correspondence between atoms in both phases. As it was suggested experimentally [10], changes in internal structure after photoexcitations happen much faster than the change in the shape of the lattice. Therefore, in order to analyze the initial structural evolution, we use the lattice vectors of the M$_1$ phase. Symmetry requires that the displacement vector \( \Delta \mathbf{R} \) has the A$_g$ symmetry. Therefore, this displacement vector can only be projected onto

FIG. 3: (Color online) Atomic displacements upon photoexcitation: comparison between theory and experiment. Left panels: the observed subpicosecond (a) and subnanosecond (b) movement of V atoms in the M$_1$ phase VO$_2$ upon photoexcitation [10]. Middle panels: calculated initial forces on V atoms with additional holes (c) and electrons (d). Right panels: atomic displacement (schematic) of the 339 cm$^{-1}$ (e) and the 197 cm$^{-1}$ phonon modes (f). The directions of the displacements of V atoms are shown for comparison. The V and O atoms are shown with large (dark blue) and small (red) balls, respectively. Atoms after displacement are shown with light colors.

FIG. 4: (Color online) Charge density of the VBM (a) and the CBM (b) states on the (-110) plane of the M$_1$ phase. The shortest V-O and V-V bonds are approximately on the (-110) plane and are shown with dashed lines.
Raman active $A_g$ phonons. The overlap between a Raman active phonon $i$ and the displacement vector $\Delta \mathbf{R}$ is calculated via

$$\eta_i = \sum_j \frac{1}{m_j} \mathbf{e}_{ij} \cdot \Delta \mathbf{R},$$

(2)

where $m_j$ is the mass of the $j$th atom, $\mathbf{e}_{ij}$ is $j$th atomic component of the polarization vector of the $i$th phonon mode. The result of this projection of the atomic displacement is shown in Table I.

Interestingly, two phonon modes with wave numbers $197 \text{ cm}^{-1}$ ($\sim 6.0 \text{ THz}$) and $339 \text{ cm}^{-1}$ ($\sim 10.2 \text{ THz}$) show the greatest projection amplitudes. Polarization vectors of these two phonon modes are also shown in Figs. 3(e) and 3(f), and the vibration patterns of these two phonon modes also match nicely with the observed first two stages of the structural evolution after photoexcitation [10].

Combining this result with the analysis of forces exerted on individual atoms upon “optical doping” of electrons and holes, we have clearly identified the active phonon modes involved in the photo-induced insulator-metal transition of VO$_2$. In addition, our result indicates that the strong coupling between the $339 \text{ cm}^{-1}$ (10.2 THz) phonon and hole states is responsible for the rapid V-V separation upon photoexcitation, whereas the coupling between the $197 \text{ cm}^{-1}$ ($\sim 6.0 \text{ THz}$) phonon and electrons explains the zag-zig motion of V atoms at a longer timescale. The 6.0 THz phonon mode is often observed in coherent phonon experiment. However, the V-V separation happens at a much faster timescale [10] so that the corresponding phonon mode (10.2 THz) cannot be observed in coherent phonon experiment. In addition to these two phonon modes, there are several other modes that have large projection amplitudes. In particular, the $224 \text{ cm}^{-1}$ ($\sim 6.72 \text{ THz}$) phonon mode may be related to the 6.75 THz phonon modes observed in coherent phonon experiments [4].

There are still puzzles that need to be resolved before we can fully untangle the experimental findings. As mentioned above, it is very likely that the ultrafast ($\sim 100 \text{ fs}$) photo-induced insulator-metal transition and the rapid V-V separation upon photoexcitation are closely related, and uncovering their cause-effect relationship is the last step toward a full understanding of the physics of the phase transition in VO$_2$. So far our results are consistent with experiments, but we have not addressed the issue regarding the possible connection between the observed rapid V-V separation and the ultrafast photo-induced insulator-metal transition.

To this end, we have carried out two additional calculations. In the first calculation, the ideal M$_1$ crystal structure is displaced according to the projection of the displacement vector $\Delta \mathbf{R}$ in Eq. (1) onto the $339 \text{ cm}^{-1}$ (10.2 THz) phonon mode. This procedure naturally results in a separation of V-V dimers. A band structure calculation is then carried out using the distorted structure. In the second calculation, we introduce 0.15 holes per VO$_2$ formula unit into the system. The internal coordinates are then relaxed while the lattice vectors are fixed. A band structure calculation is then carried out using the relaxed structure with the presence of holes. Since photo-induced ultrafast insulator-metal transition occurs long before a full conversion of the lattice geometry from monoclinic to rutile, our calculations are carried out using the lattice vectors of the M$_1$ phase. The resulting band structures are shown in Fig. 5. Both band structures clearly show a metallic behavior beyond what is expected for a simple semiconductor with small structural distortions: There is a massive reorganization of the electronic states are the V-V bonds break. These results clearly illustrate the much discussed strong coupling between the lattice and electronic degrees of freedom in this system. However, not all lattice degrees of freedom are coupled equally with electrons. It is the phonon mode involving the separation of V-V dimer that has the most important impact on the underlying electronic structure. It is the rapid separation of V-V pairs (i.e., breaking of the V-V dimers), which itself is a direct result of a strong phonon-hole coupling, that is responsible for the observed ultrafast photo-induced insulator-metal transition.

The process of ultrafast photo-induced insulator-metal transition in VO$_2$ can now be summarized as follows: photoexcitation results in a depletion of electrons in the bonding states which are critical for V-V dimerization and the insulating behavior of the M$_1$ phase. When this weakening of the V-V bonds reaches a critical point (under critical laser fluence), the V-V bond breaks. This bond breaking (V-V separation) is a result of a strong lattice-hole coupling in this system. The breaking of the
V-V bonds in turn leads to an instantaneous electronic phase transition from the insulating to a metallic state. Note that at this stage, the lattice remains monoclinic in shape. Electron-lattice coupling and thermalization eventually eliminate the zig-zag arrangement of the V atoms and fully convert both the internal structure and the shape of the crystal from the M1 to the R phase. The corresponding subnanosecond lattice dynamics is associated with the 6.0 THz phonon often observed in coherent phonon experiment.

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