

This is the accepted manuscript made available via CHORUS. The article has been published as:

Oxygen vacancy induced electronic structure modification of KTaO_3

Shashank Kumar Ojha, Sanat Kumar Gogoi, Prithwijit Mandal, S. D. Kaushik, J. W. Freeland, M. Jain, and S. Middey

Phys. Rev. B **103**, 085120 — Published 15 February 2021

DOI: [10.1103/PhysRevB.103.085120](https://doi.org/10.1103/PhysRevB.103.085120)

Oxygen vacancy induced electronic structure modification of KTaO_3

Shashank Kumar Ojha,^{1,*} Sanat Kumar Gogoi,^{1,*} Prithwijit Mandal,¹
S. D. Kaushik,² J. W. Freeland,³ M. Jain,^{1,†} and S. Middey^{1,‡}

¹Department of Physics, Indian Institute of Science, Bengaluru 560012, India

²UGC-DAE-Consortium for Scientific Research Mumbai Centre,

R5 Shed, Bhabha Atomic Research Centre, Mumbai 400085, India

³Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA

The observation of metallic interface between band insulators LaAlO_3 and SrTiO_3 has led to massive efforts to understand the origin of the phenomenon as well as to search for other systems hosting such two dimensional electron gases (2-DEG). However, the understanding of the origin of the 2-DEG is very often hindered as several possible mechanisms such as polar catastrophe, cationic intermixing and oxygen vacancy (OV) etc. can be operative simultaneously. The presence of a heavy element makes KTaO_3 (KTO) based 2-DEG a potential platform to investigate spin orbit coupling driven novel electronic and magnetic phenomena. In this work, we investigate the sole effect of OV in KTO, which makes KTO metallic. O K -edge X-ray absorption spectroscopy measurements find that OV dopes electron in Ta t_{2g}^* antibonding states. Photoluminescence measurements reveal the existence of highly localized deep mid-gap states in oxygen deficient KTO. Our detailed *ab initio* calculations demonstrate that such deep mid-gap state arises due to linear clustering of OVs around Ta. Our present work emphasizes that we must pay attention about the possible presence of OVs in interpreting emergent behavior of KTO based heterostructure

I. INTRODUCTION

SrTiO_3 -based oxide heterostructures are hosts of several emergent phenomena such as two-dimensional electron gas (2-DEG), ferromagnetism, superconductivity, etc.^{1–9}. The larger carrier density ($\geq 10^{13}$ - 10^{14} cm^{-2} vs. 10^{10} - 10^{12} cm^{-2}) and shorter confinement length (1-2 nm vs. 10 nm) of the carriers at the interface of these SrTiO_3 (STO) based 2-DEGs, compared to traditional semiconductor 2-DEGs makes these systems attractive for device applications^{3,10}. However, mobility of these STO-based heterostructures is significantly low compared to semiconductor 2-DEGs, prompting to search for non-STO based 2-DEG systems¹¹. Bulk KTO is a wide band gap insulator ($E_g \sim 3.5$ eV) and has a lot of similarities with STO such as cubic structure, quantum paraelectricity¹² etc. Similar to STO, electron doping makes KTO metallic and even superconducting at very low temperature^{13–15}. The presence of heavy element Ta further offers possibility of achieving new emergent phases due to strong spin orbit coupling (SOC), leading to many experimental works about KTO based heterostructures^{16–25}. Comparable values of SOC strength with other energy scales in KTO leads to significant reconstruction of orbital symmetries at the surface²⁶, which can further result non-trivial spin-orbital texturing of conduction electrons²⁷. Presence of such unconventional spin texturing of conduction electrons can be further utilized for engineering novel topological phenomena such as topological Hall effect²⁸, making KTO based 2DEG a unique platform for topological spintronics applications²⁹.

Similar to the controversial origin of the metallic behavior in $\text{LaAlO}_3/\text{SrTiO}_3$ interface^{30–37}, the origin of 2-DEG in KTO based heterostructures has been linked to electronic reconstruction due to polar catastrophe^{19,24}, as well as OV formation²¹. While a higher carrier density has been achieved in $\text{LaTiO}_3/\text{KTO}$ interface as predicted by the polar catastrophe model¹⁹, the presence of OVs within KTO substrate is also highly probable due to the use of high vacuum atmosphere

during the growth.

In order to understand the sole effect of OV without any involvement of polar catastrophe and cationic intermixing issues²⁰, we have deliberately introduced OV in KTO single crystal through thermal annealing in a reduced atmosphere. In contrast to the method of electron doping by Ar^+ bombardment, the present method does not damage crystallinity of the sample²⁸ and results metallic KTO. O K -edge X-ray absorption spectroscopy (XAS) measurements reveal electron doping in Ta t_{2g}^* bands. Interestingly, we detect presence of deep mid-gap states through photoluminescence (PL) measurements. Our detailed *ab initio* calculations with isolated OV finds that both the electrons, donated by each isolated OV, are doped into the conduction band, derived from Ta t_{2g}^* antibonding states, resulting metallic behavior. We further find that linear clustering of OVs is more favorable than the formation of isolated OVs. Most importantly, our calculations predict that such clustering would lead to the formation of deep narrow mid-gap state between the fully filled valence band and partially filled conduction band and explains the experimentally observed deep mid-gap states in oxygen deficient KTO.

II. METHODOLOGY

Commercially available (Princeton Scientific Corporation) KTO (0 0 1) single crystal (5 mm $\times$ 5 mm $\times$ 0.5 mm) was sealed with Ti metal wire in a quartz tube under a vacuum of 10^{-4} bar³⁸. This sealed tube was heated at 900°C for 24 hrs. Temperature dependent dielectric measurement was carried out using impedance analyzer from Keysight technology instruments (Model No- E49908). Resistance was measured with wire-bonded Al contact in a Van der Pauw geometry using a 9 Tesla Physical Property Measurement system (Quantum Design). XAS measurement on O K -edge at 300 K was carried out at 4-ID-C beamline of Advanced Photon Source,

Argonne National Laboratory. PL spectra was collected in Horiba LabRAM HR instrument under excitation with a 266 nm ultraviolet laser at room temperature.

The *ab initio* calculations were carried out using the QUANTUM ESPRESSO package³⁹. Perdew, Burke and Ernzerhof generalized gradient approximation (PBE-GGA) was used for the exchange correlation functional⁴⁰. We have also performed calculations using the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE)⁴¹. Optimized norm conserving pseudopotentials^{42–44} were used in all the calculations. The Brillouin zone was sampled with $8 \times 8 \times 8$ k -points for the unit cell and the wave functions were expanded in plane waves with an energy up to 90 Ry. We have performed noncollinear density functional theory (DFT) calculations with fully relativistic pseudopotentials for the Ta atom to capture the effect of the strong SOC. Upon including an additional onsite Coulomb potential of 1.35 eV⁴⁵ on the Ta d -orbitals, the qualitative conclusions remain unchanged. The structural relaxations were performed until the force on each atom reduced to 0.07 eV/Å.

III. RESULTS AND DISCUSSION

Stoichiometric KTO with Ta⁵⁺ ions in d^0 configuration is a band insulator. Owing to its incipient ferroelectric nature, it is characterized by a large dielectric constant at low temperature. This is evident from Fig. 1(a), where we plot temperature dependent dielectric constant (ϵ) and dielectric loss ($\tan \delta$) of as received pristine KTO single crystal. The values of ϵ and $\tan \delta$ and their temperature dependencies are very similar to earlier works^{46,47}. KTO, annealed in presence of Ti wire becomes metal as evident from the temperature dependent sheet resistance (R_S) from 2 K to 300 K (Fig. 1(b)). Upon reheating this sample in oxygen atmosphere, we found that it becomes insulating, establishing that the origin of metallic behavior is related to the presence of OV. The R_S of oxygen deficient KTO at 300 K is about two order of magnitude smaller compared to that of 2-DEG behavior of LaTiO₃/KTaO₃¹⁹, EuO/KTaO₃²¹, LaVO₃/KTaO₃²⁴ heterostructures. Similar to the cases of thin films grown on KTO substrates^{19,21,24}, R_S becomes temperature independent at low

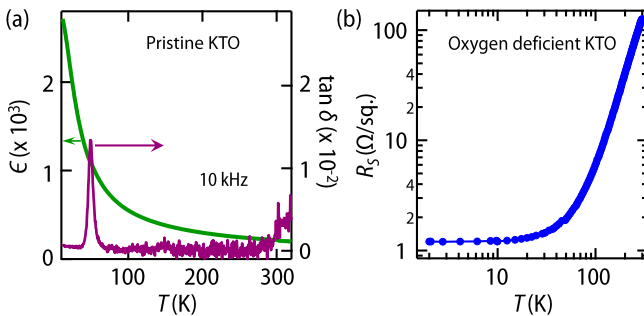


FIG. 1. (Color online) (a) Temperature dependence of dielectric constant (ϵ) and dielectric loss ($\tan \delta$) of pristine KTO. (b) Temperature dependence of sheet resistance for oxygen deficient KTO.

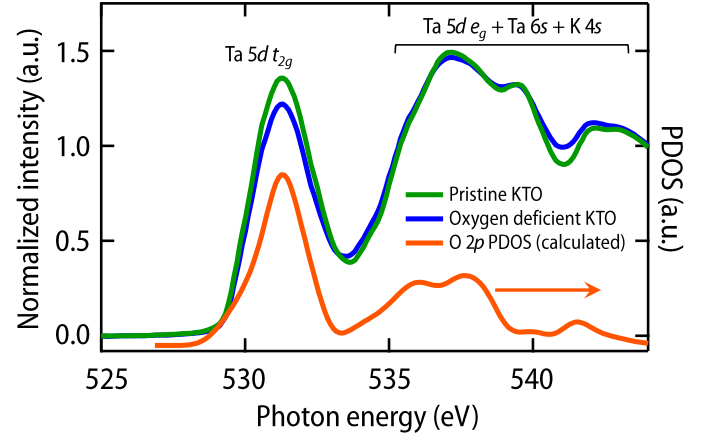


FIG. 2. (Color online) O K -edge XAS spectra for pristine and oxygen deficient KTO along with calculated O $2p$ PDOS for pristine KTO.

temperature due to the dominant contribution of electron scattering from defects^{11,48}. Assuming single band transport, we found carrier density $n_S \sim 2 \times 10^{15} \text{ cm}^{-2}$ and electron mobility $\mu_e \sim 20 \text{ cm}^2/\text{V-s}$ at room temperature from Hall effect measurement (not shown).

We have investigated the effect of OV on electronic structure of KTO by O K -edge XAS, where one core electron from O $1s$ state is excited to O $2p$ states⁴⁹. In an ionic picture, such O $1s \rightarrow$ O $2p$ transition is not allowed as $2p$ orbitals are completely occupied for the O²⁻ ion. However, the strong hybridization between oxygen and other elements in a real material gives rise to a finite spectral weight of oxygen $2p$ character in the unoccupied density of states, which can be approximately described by O K -edge XAS⁵⁰. Normalized XAS spectra, recorded in bulk sensitive total fluorescence yield (TFY) mode have been compared in Fig. 2. To understand the origin of various features of these XAS spectra, convoluted density of states of O $2p$ states, obtained from density functional theory (discussed later in the manuscript), has been also plotted (for details see section A of supplemental information (SI)⁵¹. The first peak around 531.3 eV is due to transition to the states just above Fermi level and primarily consists of Ta $5d t_{2g}$ orbital, hybridized with O $2p$ orbitals⁵². The lower intensity of this peak in oxygen deficient sample, compared to the pristine KTO implies that some of the doped electrons have occupied Ta t_{2g}^* anti bonding states, which is also concluded by our calculations shown later. The features from 534 eV to 544 eV are related to the transitions to the Ta $5d e_g$, Ta $6s$, K $4s$ states hybridized with O $2p$.

In contrast to the carrier doping by elemental substitution at A or B site in ABO_3 perovskite, OV creation not only dopes electrons to the system but can also lead to the formation of non dispersible mid-gap states⁵³. Resultantly, some of the electrons are trapped in such mid-gap states and are localized around the vacancy in the real space. In order to check the presence of such mid-gap state, we did PL measurement as this technique has been found to be very successful in locating the exact position of such defect states in oxygen de-

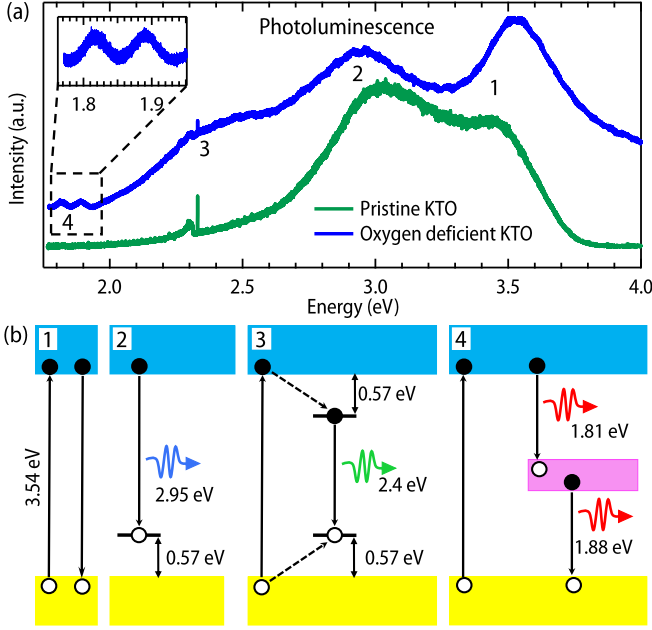


FIG. 3. (Color online) (a) PL spectra of pristine and oxygen deficient KTO. The inset shows the zoomed in view of mid-gap states around 1.8 eV. (b) The first panel corresponds to the near band edge emission. The second panel shows the recombination process between the excited electrons and the self-trapped excited holes. The third panel demonstrates the recombination process of excited holes and electrons in a self-trapped excited state. The fourth panel highlights the recombination process via defect band resulting in the peak around 1.8 eV in PL. Filled circle denotes electrons and open circle denotes holes.

ficient STO^{53–57}. Fig. 3(a) shows the room-temperature PL spectra for the pristine and oxygen deficient KTO. The corresponding mechanism for the peaks marked by 1, 2, 3, and 4 have been shown in Fig. 3(b). The peak at 3.5 eV for the pristine sample corresponds to the near band edge emission. Position of this peak directly corresponds to the band gap of KTO and matches very well with the reported band gap from UV-visible spectroscopy⁵⁸. Since, this transition occurs from bottom of conduction band to top of valence band, this peak is also observed for oxygen deficient KTO. KTO is an incipient ferroelectric¹² and has strong electron-phonon coupling⁵⁹. In presence of electron-phonon coupling, photo generated electron and hole pairs are quickly trapped by phonons to form more stable self-trapped electron/hole states^{60–62}. Recombination between these self-trapped electron and hole centres (3rd panel of 3(b)) leads to the ‘green’ luminescence around 2.4 eV, which has been reported extensively in various perovskite oxides⁶³ including KTO⁵⁹. This feature is strongly enhanced in present case upon introduction of OV, as reported earlier for STO⁶⁴. The peak at 2.95 eV can be attributed to the recombination of excited and conduction electrons with the self-trapped holes (2nd panel of the Fig. 3(b)).

Apart from these broad features, two new peaks have been observed at 1.81 eV and 1.88 eV (also see inset of Fig. 3(a)) in oxygen deficient KTO. The origin of these peaks can be

understood by considering a defect band, which would be at 1.8 eV below the minima of conduction band (4th panel of Fig. 3(b)). This mid-gap state is separated equally from the valence and conduction band. Microscopic origin behind the existence of such mid-gap states in our samples will be discussed later in the paper.

To understand OVs’ role in transforming the electronic properties of KTO, we have performed first principle electronic structure calculations. The optimized lattice parameter of pristine cubic KTO was found to be 4.02 Å from PBE-GGA approximated DFT calculations. This is very close to the experimentally reported value (3.989 Å⁵⁸). The band structure of pristine KTO (for a $2 \times 2 \times 2$ supercell) is shown in Fig. 4 (a). In this calculation, we found a band gap of 2.05 eV, which is also in good agreement with previous PBE-GGA approximated DFT results^{65–68}. Upon inclusion of an onsite Coulomb potential $U_{eff}=1.35$ eV⁴⁵, band gap increases to 2.1 eV (see section C of SI⁵¹). We have also found a split of the conduction bands at $\Gamma(0, 0, 0)$ point by 400 meV, as reported before^{16,17}. As a remedy to the underestimated band gap, we have further performed HSE calculations, which yields a band gap of 3.6 eV (for details see section E of SI⁵¹), agreeing well with the experimentally reported band gap.

To examine OV’s effect, we first considered isolated OV, as found by scanning probe microscopy study on vacuum annealed KTO⁶⁹. For the calculations with an isolated OV within PBE-GGA, we considered a $2 \times 2 \times 2$ supercell of KTO where one oxygen atom has been removed ($\text{K}_8\text{Ta}_8\text{O}_{24} \rightarrow \text{K}_8\text{Ta}_8\text{O}_{23}$). This corresponds to an OV concentration of 4.2%. As evident from the band structure plot shown in Fig. 4(b), the Fermi level is shifted to the conduction band, describing the experimentally observed metallic phase of oxygen-deficient KTO (density of states have been shown in section B of SI⁵¹). Our calculations find that one isolated OV donates two electrons to the conduction band. Among the 24 t_{2g} bands (3 t_{2g} bands for each Ta) in the conduction band manifold, six bands are partially filled by the two electrons. No localized defect state is found in the gap. This conclusion remains unaffected upon increasing the supercell size to $3 \times 3 \times 3$ (see section D of SI⁵¹).

Apart from the existence of isolated OV, perovskite compounds like STO also show a strong tendency for OV clustering^{70–73}. To examine such clustering, we have considered a $2 \times 2 \times 4$ supercell containing two OVs with 4 different arrangements of OV (see Fig. 5 for the relative position of two OVs). To check the stability of such defect configurations, we have calculated the defect formation energy $E_f[\text{O}_v]$, defined as⁷⁴

$$E_f[m\text{O}_v] = E_{tot}[m\text{O}_v] + \frac{1}{2}m\mu_{\text{O}_2} - E_{tot}[0\text{O}_v] + q(E_{vbm}^{pristine} + \epsilon_F) \quad (1)$$

where $E_{tot}[m\text{O}_v]$ is the total energy of the system with m number of OV, $E_{tot}[0\text{O}_v]$ is the total energy of the pristine cell, μ_{O_2} is the chemical potential of oxygen molecule, $E_{vbm}^{pristine}$ is the valance band maxima (VBM) for the pristine cell, ϵ_F is the Fermi Energy and q is the charge of the system. Formation energies for isolated OV as well as oxygen divacancy in different configurations in the neutral state ($q = 0$)

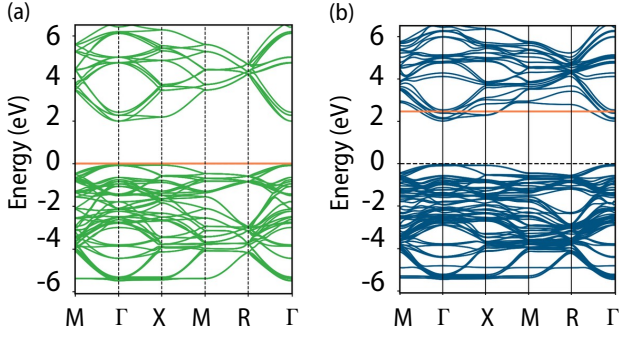


FIG. 4. (Color online) (a) Band structure of pristine KTO for a $2 \times 2 \times 2$ supercell. The Fermi level is marked with a solid orange line. (b) Band structure of oxygen-deficient KTO ($\text{KTaO}_{2.875}$) for a $2 \times 2 \times 2$ supercell with single isolated oxygen vacancy. The Fermi level is marked with a solid orange line.

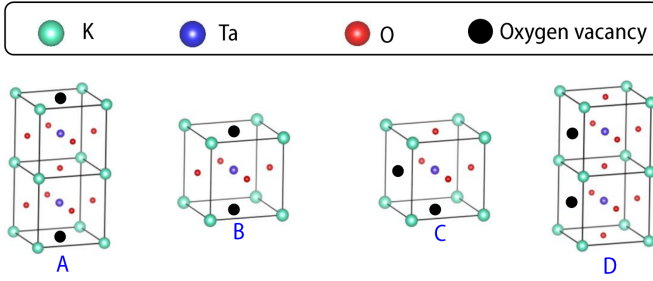


FIG. 5. (Color online) Various relative configurations for oxygen divacancy in KTO.

are listed in the TABLE I. The oxygen defect formation energies are in the same range that have been reported for other perovskite oxides^{75,76} (also see section F of SI⁵¹). Moreover, we found that the linear oxygen divacancy around a Ta atom (configuration B) has the lowest formation energy which suggests that in a real system the formation of a linear oxygen divacancy has a higher probability than two isolated vacancies.

TABLE I. Table of formation energy (E_f) per OV and interaction energy (E_{int}) for different oxygen divacancy configurations in KTO calculated using supercell $2 \times 2 \times 4$ and $4 \times 4 \times 4$ within PBE-GGA.

Configuration	E_f (eV)		E_{int} (eV)	
	$2 \times 2 \times 4$	$4 \times 4 \times 4$	$2 \times 2 \times 4$	$4 \times 4 \times 4$
A	6.64	6.81	0.91	1.06
B	5.95	6.08	-0.49	-0.39
C	6.41	6.38	0.44	0.21
D	6.69	6.51	0.99	0.46
single OV	6.84	—	—	—

Owing to the fact that the divacancies have lower formation energy compared to two isolated OVs, we also calculated the interaction energy E_{int} between the vacancies, which is

defined as⁷¹

$$E_{int} = E_{tot}[2O_v] + E_{tot}[0O_v] - 2E_{tot}[1O_v] \quad (2)$$

The negative (positive) sign of E_{int} specifies whether the interaction is attractive (repulsive). The interaction energies for different divacancy configurations are listed in the TABLE I. As can be seen, configuration B, also known as apical divacancy (OV-Ta-OV), has the most attractive interaction, implying that it is the most favorable configuration among all divacancy configurations. Our calculations demonstrate that the linear vacancy clustering is favorable around Ta. It should be noted that even though configurations B and D have the same separation between the two vacancies, the E_{int} is very different. This implies that the location of the vacancies is important and not just the relative distance.

The left panel of Fig. 6(a) shows the band structure plot of configuration B and projected density of states (PDOS) right next to it with the same energy scale used in the band structure plot. Interestingly, apart from the partially filled conduction bands, we find a highly localized defect band (marked in red color), which is almost equidistant from conduction and valence band edges. This explains the experimentally observed mid-gap state (which is almost equally separated from band edges) through PL measurement. Our conclusions remain unaffected upon inclusion of onsite coulomb potential (see section C of SI⁵¹).

The PDOS plot shows that the Ta $5d$ states mainly contribute to the defect band. The isosurface plot of the squared wave function of the defect band (Fig. 6(c)) is localized around the Ta atom in between the two OVs. Such electron localization around the vacancy site would lead to reduction of free carrier density. The $d_{3z^2-r^2}$ symmetry of this occupied defect band is related to the fact that the particular Ta atom with oxygen divacancy has a square planar environment locally, and the $d_{3z^2-r^2}$ is the lowest orbital for square planar crystal field⁷⁷. A highly localized defect band has also been obtained in band structure calculation for the configurations A and C (shown in section G of SI⁵¹).

We have also performed the calculations for a bigger supercell of size $4 \times 4 \times 4$ for all the divacancy configurations A, B, C, and D. As evident from TABLE I, the formation energies do not change much upon increasing the supercell size. The formation energy for configuration B again turns out to be the lowest among all the configurations, similar to the case of $2 \times 2 \times 4$ supercell. Further, the position of defect state for the most stable divacancy configuration B remains unaffected upon increasing the supercell size to $4 \times 4 \times 4$ (see section D of SI⁵¹).

We have also monitored the position of defect state using the HSE functional for divacancy configuration B. We found the mid-gap to be localised around 1.5 eV from VBM, shown in Fig. 6(b), close to the results we observed from PL measurement.

Till now we have investigated the formation energies for a neutral system with isolated OV and divacancies with different defect configurations. Since, formation energy (E_f) is dependent on the charge state (q) of the system and position of the Fermi level (ϵ_F) (Eqn. 1), we have also computed E_f

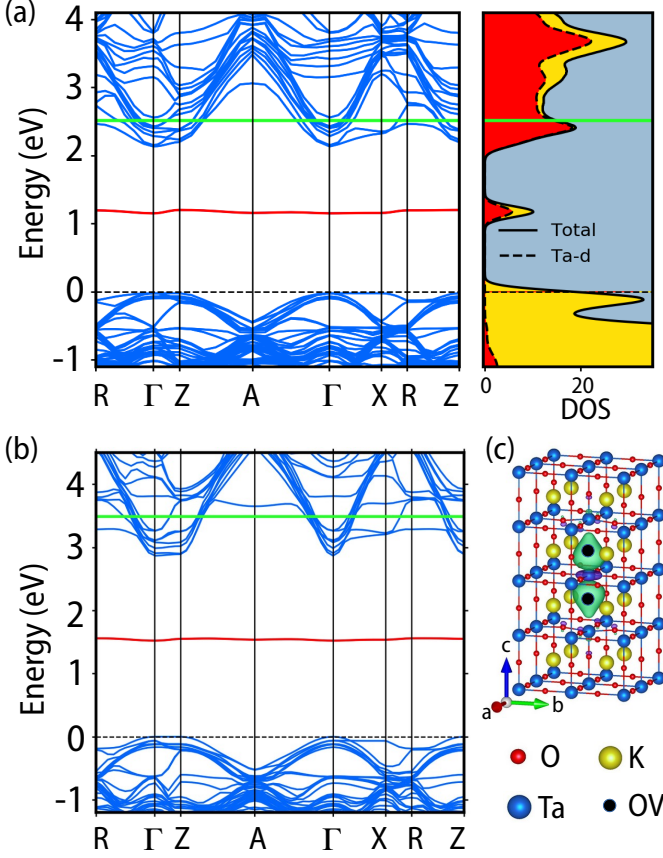


FIG. 6. (Color online) (a) The PBE-GGA band structure of apical divacancy (configuration B) situated along z direction for a $2 \times 2 \times 4$ supercell is shown in the left panel. The defect band is marked with the color red. The right panel shows the projected density of states (PDOS) for Ta 5d orbitals in red and the total density of states in yellow color. The Fermi level is shown in color green. (b) The band structure calculated using HSE for a $2 \times 2 \times 4$ supercell with apical divacancy situated along z direction. The defect band (≈ 1.5 eV from VBM) is shown in red and the Fermi level is marked with a straight line in green. (c) The isosurface of the squared wave function for the defect band which shows Ta $d_{3z^2-r^2}$ characteristics marked by the green bubbles, calculated using $2 \times 2 \times 4$ supercell within PBE-GGA having defect configuration B. The two black spots are the position of the two oxygen vacancies.

per vacancy as a function of Fermi level position in different charge states (q) for the most favourable divacancy configuration B.

It is well known that^{78–84} calculations of charged defect system using periodic supercells can introduce some unphysical contributions into the defect formation energy calculations. From the calculations on the neutral divacancy system, one can see that 2 electrons are localized in the defect band discussed above, while other 2 electrons are in the conduction band (see Fig. 6). Considering apical oxygen divacancy with +1 (+2) charge state in KTO, we remove 1 electron (2 electrons) from the conduction band manifold, which is smeared inside the whole cell. Thus, even though we are performing charged defect calculations, owing to the background charge

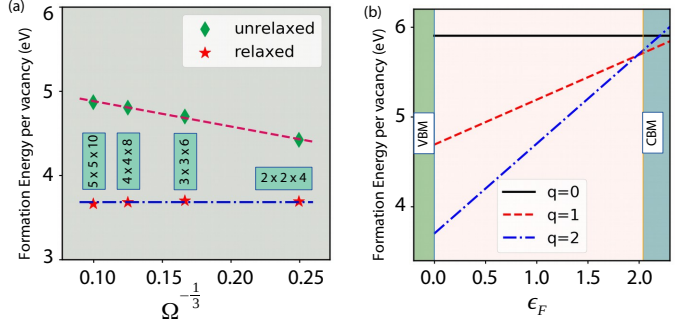


FIG. 7. (Color online) (a) Formation energy per vacancy of an apical divacancy system as a function of system size (Ω) in the charge state $q = +2$. The considered supercell sizes are $5 \times 5 \times 10$, $4 \times 4 \times 8$, $3 \times 3 \times 6$ and $2 \times 2 \times 4$. (b) Formation energy diagram for different charge states of an apical divacancy in a $2 \times 2 \times 4$ supercell.

compensation in periodic supercell calculations, we expect our calculated formation energies to behave close to the neutral system and to have a small electrostatic correction. To check the validity of the same, we have calculated the formation energies as a function of system size for the supercell of sizes $2 \times 2 \times 4$, $3 \times 3 \times 6$, $4 \times 4 \times 8$ and $5 \times 5 \times 10$ for the most stable divacancy configuration B (within PBE-GGA) shown in Fig. 7(a). The unrelaxed data has been fitted with a straight line, which goes as $\frac{1}{L}$ (where L is the measure of system length). However, once we allow the system to relax after creating the vacancies, the computed formation energies are invariant over system size variation, denoted by the red stars in Fig. 7(a). Moreover, the large dielectric constant of KTO is also responsible for the fact that the charged oxygen defects are screened from each other, which allow us to use comparatively small supercells in our calculations. Thus, we conclude that $2 \times 2 \times 4$ supercell is sufficient to calculate the formation energies in this system. It shows that the correction needed in our formation energy calculations is negligible. The +1 charge state is metallic, and there is only one electron in the conduction band manifold. However, the +2 charge state is insulating in nature (see section H and section I of SI⁵¹).

Fig. 7(b) shows the different charge states for the apical divacancy case calculated using a $2 \times 2 \times 4$ supercell. We have found that the +2 charge state is more stable than the neutral one when the Fermi level resides inside the gap. We have also noticed a charge transition level at ≈ 1.9 eV (from the top of the valance band) from +2 to +1 charge state. In the experimental observations, we have found the system to be metallic. The *ab-initio* calculations affirm that the Fermi level lies inside the conduction band. Thus, we expect the metallic states (+1 or neutral) to be more favourable. For the isolated oxygen vacancies also, it is found that the neutral state is more favourable⁸⁵. Thus we conclude that despite the type of oxygen vacancies, the metallic system is more stable.

IV. CONCLUSION

To conclude, we have successfully demonstrated the sole effect of oxygen vacancy on the electronic structure of KTO. Pristine insulating KTO undergoes insulator to metal transition (IMT) upon oxygen vacancy creation. DFT calculations show that IMT can be explained by just considering isolated oxygen vacancies. Further, our DFT calculations combined with photoluminescence measurements reveal that linear clustering of oxygen vacancies around Ta atom leads to the formation of a very localized state within the band gap, which can result in fascinating magnetotransport phenomena in KTO⁸⁶.

V. ACKNOWLEDGEMENT

SKO and SM thank Professor D. D. Sarma for giving access to several experimental facilities for this work. We

acknowledge Sayak Mondal, Ashutosh Mohanty, Subhadip Das and Dr. D. V. S. Muthu for help with the experiments. SKG and MJ acknowledge Professor H. R. Krishnamurthy, Dr. Tathagata Biswas and Sudipta Kundu for fruitful discussions. SM is funded by a DST Nanomission grant (DST/NM/NS/2018/246), and a SERB Early Career Research Award (ECR/2018/001512). SM also acknowledges support from Infosys Foundation, Bangalore. The authors are grateful to Supercomputer Education and Research Centre, IISc for providing computational facility SAHASRAT. MJ acknowledges Department of Science and Technology - Science and Engineering Research Board, India (file number: EMR/2016/007984) for financial support. SKG acknowledges DST-Inspire fellowship (IF170557). This research used resources of the Advanced Photon Source, a U.S. Department of Energy Office of Science User Facility operated by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

* These authors contributed equally

† mjain@iisc.ac.in

‡ smiddey@iisc.ac.in

- ¹ A. Ohtomo and H. Hwang, *Nature* **427**, 423 (2004).
- ² N. Reyren, S. Thiel, A. Caviglia, L. F. Kourkoutis, G. Hammerl, C. Richter, C. Schneider, T. Kopp, A.-S. Rüetschi, D. Jaccard, *et al.*, *Science* **317**, 1196 (2007).
- ³ J. Mannhart, D. H. Blank, H. Hwang, A. Millis, and J.-M. Triscone, *MRS bulletin* **33**, 1027 (2008).
- ⁴ J.-S. Lee, Y. Xie, H. Sato, C. Bell, Y. Hikita, H. Hwang, and C.-C. Kao, *Nature materials* **12**, 703 (2013).
- ⁵ A. Brinkman, M. Huijben, M. Van Zalk, J. Huijben, U. Zeitler, J. Maan, W. G. van der Wiel, G. Rijnders, D. H. Blank, and H. Hilgenkamp, *Nature materials* **6**, 493 (2007).
- ⁶ P. Zubko, S. Gariglio, M. Gabay, P. Ghosez, and J.-M. Triscone, *Annu. Rev. Condens. Matter Phys.* **2**, 141 (2011).
- ⁷ H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa, and Y. Tokura, *Nature materials* **11**, 103 (2012).
- ⁸ S. Stemmer and S. James Allen, *Annual Review of Materials Research* **44**, 151 (2014).
- ⁹ Y.-Y. Pai, A. Tylan-Tyler, P. Irvin, and J. Levy, *Reports on Progress in Physics* **81**, 036503 (2018).
- ¹⁰ J. Chakhalian, J. W. Freeland, A. J. Millis, C. Panagopoulos, and J. M. Rondinelli, *Reviews of Modern Physics* **86**, 1189 (2014).
- ¹¹ F. Trier, D. V. Christensen, and N. Pryds, *Journal of Physics D: Applied Physics* **51**, 293002 (2018).
- ¹² G. Samara and B. Morosin, *Physical Review B* **8**, 1256 (1973).
- ¹³ S. Harashima, C. Bell, M. Kim, T. Yajima, Y. Hikita, and H. Hwang, *Physical Review B* **88**, 085102 (2013).
- ¹⁴ K. Ueno, S. Nakamura, H. Shimotani, H. Yuan, N. Kimura, T. Nojima, H. Aoki, Y. Iwasa, and M. Kawasaki, *Nature nanotechnology* **6**, 408 (2011).
- ¹⁵ C. Liu, X. Yan, D. Jin, Y. Ma, H.-W. Hsiao, Y. Lin, T. M. Bretz-Sullivan, X. Zhou, J. Pearson, B. Fisher, *et al.*, *arXiv preprint arXiv:2004.07416* (2020).
- ¹⁶ H. Nakamura and T. Kimura, *Physical Review B* **80**, 121308 (2009).
- ¹⁷ P. King, R. He, T. Eknapakul, P. Buaphet, S.-K. Mo, Y. Kaneko, S. Harashima, Y. Hikita, M. Bahramy, C. Bell, *et al.*, *Physical review letters* **108**, 117602 (2012).
- ¹⁸ K. V. Shanavas and S. Satpathy, *Phys. Rev. Lett.* **112**, 086802 (2014).
- ¹⁹ K. Zou, S. Ismail-Beigi, K. Kisslinger, X. Shen, D. Su, F. Walker, and C. Ahn, *APL materials* **3**, 036104 (2015).
- ²⁰ J. Thompson, J. Hwang, J. Nichols, J. G. Connell, S. Stemmer, and S. S. A. Seo, *Applied Physics Letters* **105**, 102901 (2014).
- ²¹ H. Zhang, Y. Yun, X. Zhang, H. Zhang, Y. Ma, X. Yan, F. Wang, G. Li, R. Li, T. Khan, *et al.*, *Physical review letters* **121**, 116803 (2018).
- ²² H. Zhang, X. Yan, X. Zhang, S. Wang, C. Xiong, H. Zhang, S. Qi, J. Zhang, F. Han, N. Wu, *et al.*, *ACS nano* **13**, 609 (2019).
- ²³ H. Zhang, Y. Ma, H. Zhang, X. Chen, S. Wang, G. Li, Y. Yun, X. Yan, Y. Chen, F. Hu, *et al.*, *Nano letters* **19**, 1605 (2019).
- ²⁴ N. Wadehra, R. Tomar, R. Gopal, Y. Singh, S. Dattagupta, and S. Chakraverty, *arXiv preprint arXiv:1908.06636* (2019).
- ²⁵ N. Kumar, N. Wadehra, R. Tomar, S. Dattagupta, S. Kumar, and S. Chakraverty, *arXiv preprint arXiv:1908.04977* (2019).
- ²⁶ A. Santander-Syro, C. Bareille, F. Fortuna, O. Copie, M. Gabay, F. Bertran, A. Taleb-Ibrahimi, P. Le Fèvre, G. Herranz, N. Reyren, *et al.*, *Physical Review B* **86**, 121107 (2012).
- ²⁷ F. Y. Bruno, S. McKeown Walker, S. Riccò, A. De La Torre, Z. Wang, A. Tamai, T. K. Kim, M. Hoesch, M. S. Bahramy, and F. Baumberger, *Advanced Electronic Materials* **5**, 1800860 (2019).
- ²⁸ S. K. Ojha, S. K. Gogoi, M. M. Patidar, R. K. Patel, P. Mandal, S. Kumar, R. Venkatesh, V. Ganesan, M. Jain, and S. Middey, *Advanced Quantum Technologies* **3**, 2000021 (2020).
- ²⁹ A. Fert, N. Reyren, and V. Cros, *Nature Reviews Materials* **2**, 1 (2017).
- ³⁰ N. Nakagawa, H. Y. Hwang, and D. A. Muller, *Nature materials* **5**, 204 (2006).
- ³¹ M. Sing, G. Berner, K. Goß, A. Müller, A. Ruff, A. Wetscherek, S. Thiel, J. Mannhart, S. Pauli, C. Schneider, *et al.*, *Physical review letters* **102**, 176805 (2009).
- ³² G. Herranz, M. Basletić, M. Bibes, C. Carrétéro, E. Taffra, E. Jacquet, K. Bouzehouane, C. Deranlot, A. Hamzić, J.-M. Broto, *et al.*, *Physical review letters* **98**, 216803 (2007).

- ³³ A. Kalabukhov, R. Gunnarsson, J. Börjesson, E. Olsson, T. Claesson, and D. Winkler, *Phys. Rev. B* **75**, 121404 (2007).
- ³⁴ J. Park, B.-G. Cho, K. Kim, J. Koo, H. Jang, K.-T. Ko, J.-H. Park, K.-B. Lee, J.-Y. Kim, D. Lee, *et al.*, *Physical review letters* **110**, 017401 (2013).
- ³⁵ M. von Soosten, D. V. Christensen, C.-B. Eom, T. S. Jespersen, Y. Chen, and N. Pryds, *Scientific Reports* **9**, 1 (2019).
- ³⁶ M. Salluzzo, S. Gariglio, X. Torrelles, Z. Ristic, R. Di Capua, J. Drnec, M. M. Sala, G. Ghiringhelli, R. Felici, and N. Brookes, *Advanced Materials* **25**, 2333 (2013).
- ³⁷ E. Breckenfeld, N. Bronn, J. Karthik, A. R. Damodaran, S. Lee, N. Mason, and L. W. Martin, *Phys. Rev. Lett.* **110**, 196804 (2013).
- ³⁸ S. Middey, C. Meneghini, and S. Ray, *Applied Physics Letters* **101**, 042406 (2012).
- ³⁹ P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. D. Corso, S. de Gironcoli, P. Delugas, R. A. D. Jr, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E. Kkbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A. O. de-la Roza, L. Paulatto, S. Ponc, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, and S. Baroni, *Journal of Physics: Condensed Matter* **29**, 465901 (2017).
- ⁴⁰ J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ⁴¹ J. Heyd, G. E. Scuseria, and M. Ernzerhof, *The Journal of Chemical Physics* **124**, 219906 (2006), <https://doi.org/10.1063/1.2204597>.
- ⁴² D. R. Hamann, *Phys. Rev. B* **88**, 085117 (2013).
- ⁴³ M. Schlipf and F. Gygi, *Computer Physics Communications* **196**, 36 (2015).
- ⁴⁴ P. Scherpelz, M. Govoni, I. Hamada, and G. Galli, *Journal of Chemical Theory and Computation* **12**, 3523 (2016).
- ⁴⁵ M. V. Ivanov, T. V. Perevalov, V. S. Aliev, V. A. Gritsenko, and V. V. Kaichev, *Journal of Applied Physics* **110**, 024115 (2011), <https://doi.org/10.1063/1.3606416>.
- ⁴⁶ C. Ang, A. S. Bhalla, and L. E. Cross, *Phys. Rev. B* **64**, 184104 (2001).
- ⁴⁷ O. Aktas, S. Crossley, M. A. Carpenter, and E. K. H. Salje, *Phys. Rev. B* **90**, 165309 (2014).
- ⁴⁸ A. Verma, A. P. Kajdos, T. A. Cain, S. Stemmer, and D. Jena, *Phys. Rev. Lett.* **112**, 216601 (2014).
- ⁴⁹ J. Suntivich, W. T. Hong, Y.-L. Lee, J. M. Rondinelli, W. Yang, J. B. Goodenough, B. Dabrowski, J. W. Freeland, and Y. Shao-Horn, *The Journal of Physical Chemistry C* **118**, 1856 (2014).
- ⁵⁰ D. D. Sarma, N. Shanthi, and P. Mahadevan, *Phys. Rev. B* **54**, 1622 (1996).
- ⁵¹ Supporting Information.
- ⁵² K. Kuepper, A. V. Postnikov, A. Moewes, B. Schneider, M. Matteucci, H. Hesse, and M. Neumann, *Phys. Rev. Lett.* **16**, 8213 (2004).
- ⁵³ D. Kan, T. Terashima, R. Kanda, A. Masuno, K. Tanaka, S. Chu, H. Kan, A. Ishizumi, Y. Kanemitsu, Y. Shimakawa, *et al.*, *Nature Materials* **4**, 816 (2005).
- ⁵⁴ M. L. Crespillo, J. T. Graham, F. Agulló-López, Y. Zhang, and W. J. Weber, *Journal of Physics D: Applied Physics* **50**, 155303 (2017).
- ⁵⁵ W. Xu, J. Yang, W. Bai, K. Tang, Y. Zhang, and X. Tang, *Journal of Applied Physics* **114**, 154106 (2013), <https://doi.org/10.1063/1.4825257>.
- ⁵⁶ J. Ravichandran, W. Siemons, M. L. Scullin, S. Mukerjee, M. Huijben, J. E. Moore, A. Majumdar, and R. Ramesh, *Phys. Rev. B* **83**, 035101 (2011).
- ⁵⁷ J. Ravichandran, W. Siemons, H. Heijmerikx, M. Huijben, A. Majumdar, and R. Ramesh, *Chemistry of Materials* **22**, 3983 (2010), <https://doi.org/10.1021/cm1005604>.
- ⁵⁸ S. Wemple, *Physical Review* **137**, A1575 (1965).
- ⁵⁹ I. Katayama and K. Tanaka, *Journal of the Physical Society of Japan* **75**, 064713 (2006).
- ⁶⁰ S. Li, J. Luo, J. Liu, and J. Tang, *The Journal of Physical Chemistry Letters* **10**, 1999 (2019), <https://doi.org/10.1021/acs.jpclett.8b03604>.
- ⁶¹ D. Menzel, *Applied Physics A* **51**, 163 (1990).
- ⁶² R. Scholz, A. Y. Kobitski, D. R. T. Zahn, and M. Schreiber, *Phys. Rev. B* **72**, 245208 (2005).
- ⁶³ R. Eglitis, E. Kotomin, G. Borstel, S. Kapphan, and V. Vukobratovic, *Computational materials science* **27**, 81 (2003).
- ⁶⁴ S. Mochizuki, F. Fujishiro, and S. Minami, *Phys. Rev. B* **71**, 040401 (2005).
- ⁶⁵ J. Xi, H. Xu, Y. Zhang, and W. J. Weber, *Phys. Chem. Chem. Phys.* **19**, 6264 (2017).
- ⁶⁶ I. I. Tupitsyn, A. Deineka, V. A. Trepakov, L. Jastrabik, and S. E. Kapphan, *Phys. Rev. B* **64**, 195111 (2001).
- ⁶⁷ D. J. Singh, *Phys. Rev. B* **53**, 176 (1996).
- ⁶⁸ F. X. Zhang, J. Xi, Y. Zhang, Y. Tong, H. Xue, R. Huang, C. Trautmann, and W. J. Weber, *Journal of Physics: Condensed Matter* **30**, 145401 (2018).
- ⁶⁹ M. Setvin, M. Reticioli, F. Poelzleitner, J. Hulva, M. Schmid, L. A. Boatner, C. Franchini, and U. Diebold, *Science* **359**, 572 (2018), <https://science.sciencemag.org/content/359/6375/572.full.pdf>.
- ⁷⁰ D. A. Muller, N. Nakagawa, A. Ohtomo, J. L. Grazul, and H. Y. Hwang, *Nature* **430**, 657 (2004).
- ⁷¹ D. D. Cuong, B. Lee, K. M. Choi, H.-S. Ahn, S. Han, and J. Lee, *Phys. Rev. Lett.* **98**, 115503 (2007).
- ⁷² N. Shanthi and D. D. Sarma, *Phys. Rev. B* **57**, 2153 (1998).
- ⁷³ K. Eom, E. Choi, M. Choi, S. Han, H. Zhou, and J. Lee, *The Journal of Physical Chemistry Letters* **8**, 3500 (2017).
- ⁷⁴ C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti, and C. G. Van de Walle, *Rev. Mod. Phys.* **86**, 253 (2014).
- ⁷⁵ R. Astala and P. D. Bristowe, *Modelling and Simulation in Materials Science and Engineering* **9**, 415 (2001).
- ⁷⁶ R. Eglitis and S. Piskunov, *Computational Condensed Matter* **7**, 1 (2016).
- ⁷⁷ M. Moretti Sala, V. Bisogni, C. Aruta, G. Balestrino, H. Berger, N. B. Brookes, G. M. d. Luca, D. Di Castro, M. Grioni, M. Guarise, P. G. Medaglia, F. Miletto Granozio, M. Minola, P. Perna, M. Radovic, M. Salluzzo, T. Schmitt, K. J. Zhou, L. Braicovich, and G. Ghiringhelli, *Phys. Rev. B* **83**, 040401 (2011).
- ⁷⁸ G. Makov and M. C. Payne, *Phys. Rev. B* **51**, 4014 (1995).
- ⁷⁹ C. Freysoldt, J. Neugebauer, and C. G. Van de Walle, *Phys. Rev. Lett.* **102**, 016402 (2009).
- ⁸⁰ H.-P. Komsa, T. T. Rantala, and A. Pasquarello, *Phys. Rev. B* **86**, 045112 (2012).
- ⁸¹ M. Jain, J. R. Chelikowsky, and S. G. Louie, *Phys. Rev. Lett.* **107**, 216803 (2011).
- ⁸² A. Malashevich, M. Jain, and S. G. Louie, *Phys. Rev. B* **89**, 075205 (2014).
- ⁸³ T. Biswas and M. Jain, *Phys. Rev. B* **99**, 144102 (2019).
- ⁸⁴ S. Kundu, M. H. Naik, and M. Jain, *Phys. Rev. Materials* **4**, 054004 (2020).
- ⁸⁵ M. Choi, F. Oba, and I. Tanaka, *Phys. Rev. B* **83**, 214107 (2011).
- ⁸⁶ A. Lopez-Bezanilla, P. Ganesh, and P. B. Littlewood, *Phys. Rev. B* **92**, 115112 (2015).