Check for updates

RESEARCH ARTICLE

First-principles calculation of electron-phonon coupling in doped KTaO3

[version 1; peer review: 1 approved, 3 approved with reservations]

Tobias Esswein, Nicola A. Spaldin

Department of Materials, ETH Zurich, Zürich, Zurich, 8093, Switzerland

v1 **First published:** 17 Oct 2023, **3**:177
https://doi.org/10.12688/openreseurope.16312.1
Latest published: 17 Oct 2023, **3**:177
https://doi.org/10.12688/openreseurope.16312.1

Abstract

Background: Motivated by the recent experimental discovery of strongly surface-plane-dependent superconductivity at surfaces of KTaO3 single crystals, we calculate the electron-phonon coupling strength, λ, of doped KTaO3 along the reciprocal space high-symmetry directions.
Methods: Using the Wannier-function approach implemented in the EPW package, we calculate λ across the experimentally covered doping range and compare its mode-resolved distribution along the [001], [110] and [111] reciprocal-space directions.
Results: We find that the electron-phonon coupling is strongest in the optical modes around the Γ point, with some distribution to higher k values in the [001] direction. The electron-phonon coupling strength as a function of doping has a dome-like shape in all three directions and its integrated total is largest in the [001] direction and smallest in the [111] direction, in contrast to the experimentally measured trends in critical temperatures.
Conclusions: This disagreement points to a non-BCS character of the superconductivity. Instead, the strong localization of λ in the soft optical modes around Γ suggests an importance of ferroelectric soft-mode fluctuations, which is supported by our findings that the mode-resolved λ values are strongly enhanced in polar structures. The inclusion of spin-orbit coupling has negligible influence on our calculated mode-resolved λ values.

Keywords

KTaO3, electron-phonon coupling, polarization, spin-orbit coupling

This article is included in the European Research Council (ERC) gateway.

Open Peer Review

Approval Status ✓ ? ? ?

	1	2	3	4
version 1 17 Oct 2023	✓ view	? view	? view	? view

1. **Matthias Geilhufe**, Chalmers University of Technology, Chalmers, Sweden
2. **Xuetao Zhu**, Chinese Academy of Sciences, Beijing, China
University of Chinese Academy of Sciences, Beijing, China
3. **Zhen Tong**, Sun Yat-Sen University, Shenzhen, China
4. **Jon Lafuente-Bartolome**, University of the Basque Country (UPV/EHU), Bilbao, Spain

Any reports and responses or comments on the article can be found at the end of the article.

H2020 This article is included in the Horizon 2020 gateway.

Corresponding authors: Tobias Esswein (t.esswein@mailbox.org), Nicola A. Spaldin (nicola.spaldin@mat.ethz.ch)

Author roles: Esswein T: Conceptualization, Data Curation, Formal Analysis, Investigation, Methodology, Project Administration, Software, Validation, Visualization, Writing – Original Draft Preparation, Writing – Review & Editing; **Spaldin NA**: Conceptualization, Data Curation, Formal Analysis, Funding Acquisition, Investigation, Methodology, Project Administration, Resources, Supervision, Validation, Visualization, Writing – Original Draft Preparation, Writing – Review & Editing

Competing interests: No competing interests were disclosed.

Grant information: This work was funded by the European Research Council under the European Union's Horizon 2020 Research and Innovation Program, grant agreement no. 810451. Computational resources were provided by ETH Zurich and the Swiss National Supercomputing Center (CSCS) under project ID s1128.

Copyright: © 2023 Esswein T and Spaldin NA. This is an open access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

How to cite this article: Esswein T and Spaldin NA. **First-principles calculation of electron-phonon coupling in doped KTaO3 [version 1; peer review: 1 approved, 3 approved with reservations]** Open Research Europe 2023, **3**:177 https://doi.org/10.12688/openreseurope.16312.1

First published: 17 Oct 2023, **3**:177 https://doi.org/10.12688/openreseurope.16312.1

Check for updates

RESEARCH ARTICLE

First-principles calculation of electron-phonon coupling in doped KTaO3

Tobias Esswein, Nicola A. Spaldin

Department of Materials, ETH Zurich, Zürich, Zurich, 8093, Switzerland

v1 **First published:** N/A, **N/A**: N/A N/A
Latest published: N/A, **N/A**: N/A N/A

Abstract

Background: Motivated by the recent experimental discovery of strongly surface-plane-dependent superconductivity at surfaces of KTaO3 single crystals, we calculate the electron-phonon coupling strength, λ, of doped KTaO3 along the reciprocal space high-symmetry directions.
Methods: Using the Wannier-function approach implemented in the EPW package, we calculate λ across the experimentally covered doping range and compare its mode-resolved distribution along the [001], [110] and [111] reciprocal-space directions.
Results: We find that the electron-phonon coupling is strongest in the optical modes around the Γ point, with some distribution to higher k values in the [001] direction. The electron-phonon coupling strength as a function of doping has a dome-like shape in all three directions and its integrated total is largest in the [001] direction and smallest in the [111] direction, in contrast to the experimentally measured trends in critical temperatures.
Conclusions: This disagreement points to a non-BCS character of the superconductivity. Instead, the strong localization of λ in the soft optical modes around Γ suggests an importance of ferroelectric soft-mode fluctuations, which is supported by our findings that the mode-resolved λ values are strongly enhanced in polar structures. The inclusion of spin-orbit coupling has negligible influence on our calculated mode-resolved λ values.

Keywords

KTaO3, electron-phonon coupling, polarization, spin-orbit coupling

Open Peer Review

Approval Status *AWAITING PEER REVIEW*

Any reports and responses or comments on the article can be found at the end of the article.

Corresponding authors: Tobias Esswein (tobias.esswein@mat.ethz.ch), Nicola A. Spaldin (nicola.spaldin@mat.ethz.ch)

Author roles: Esswein T: Conceptualization, Data Curation, Formal Analysis, Investigation, Methodology, Project Administration, Software, Validation, Visualization, Writing – Original Draft Preparation, Writing – Review & Editing; **Spaldin NA**: Conceptualization, Data Curation, Formal Analysis, Funding Acquisition, Investigation, Methodology, Project Administration, Resources, Supervision, Validation, Visualization, Writing – Original Draft Preparation, Writing – Review & Editing

Competing interests: No competing interests were disclosed.

Grant information: This work was funded by the European Research Council under the European Union's Horizon 2020 Research and Innovation Program, grant agreement no. 810451. Computational resources were provided by ETH Zurich and the Swiss National Supercomputing Center (CSCS) under project ID s1128.

Copyright: © 2023 Esswein T and Spaldin NA. This is an open access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

How to cite this article: Esswein T and Spaldin NA. **First-principles calculation of electron-phonon coupling in doped KTaO3** Open Research Europe , : https://doi.org/

First published: N/A, **N/A**: N/A N/A

Introduction

Perovskite-structure potassium tantalate ($KTaO_3$, KTO) exhibits many interesting phenomena, resulting from its high dielectric constant[1], strong spin orbit coupling[2] and charged ionic layers[3]. The strong spin-orbit coupling (SOC), caused mainly by the heavy tantalum ion, leads to a band splitting of up to 400 meV[2,4] and possible applications in spintronic devices[5,6]. The high dielectric constant, associated with a quantum paraelectric state[7] similar to that of $SrTiO_3$ (STO)[8], indicates proximity to ferroelectricity, which is predicted to yield a large strain-dependent Rashba spin splitting[9,10]. The need to compensate the alternating charged ionic layers at the surfaces is predicted to induce lattice polarization in thin films[11], and leads to the accumulation of compensating charges at the surfaces of bulk samples[3]. The origin and nature of the compensating charge are still open questions, with reports of conducting two-dimensional electron gases (2DEGs)[12,13], charge-density waves with strongly-localized electron polarons[14], and terrace-like structures of alternating termination[15], depending on the annealing atmosphere and temperature.

Perhaps the most intriguing behavior of KTO is its recently discovered low-temperature superconductivity on electron doping[16]. Superconductivity was first achieved using ionic liquid gating on the (001) surfaces of KTO single crystals, for which critical temperatures (T_c) of up to 50 mK were found at 2D doping concentrations of between 2×10^{14} and 4×10^{14} cm^{-2}[16,17]. Note that these values correspond to 3D doping concentrations of approximately 4.1×10^{20} cm^{-3} to 1.2×10^{21} cm^{-3}, considerably higher than the ~1.4×10^{20} cm^{-3} possible using chemical doping with barium in bulk KTO[18]. (For the conversion between 2D and 3D carrier concentrations see Ref. 16 and Figure A1 in the appendix file in the data avaliability statement). A subsequent study of $LaAlO_3$-capped KTO (110) surfaces, with 2D doping concentrations of 7×10^{13} cm^{-2}, reached markedly higher critical temperatures up to 0.9 K[19]; (111)-oriented KTO interfaces with either EuO or $LaAlO_3$ showed even higher T_cs of up to 2.2 K at similar carrier concentrations[20]. Note that no superconductivity was found down to 25 mK at (001)-oriented KTO interfaces at these lower carrier concentrations[20]. More recently, in an ionic liquid gating setup similar to that of Ref. 16, but at lower 2D doping densities of around 5×10^{13} cm^{-2}, superconductivity was found at the (110) and (111) surfaces with T_c of around 1 K and 2 K respectively, and not at the (001) surface down to 0.4 K[21]. The reported critical temperatures from the literature are collected as a function of carrier concentration in Figure 1. The mechanism underlying the superconductivity, as well as its strong and unusual dependence on the orientation of the surface or interfacial plane, are not yet established. Indeed, even in the related quantum paraelectric STO, in which superconductivity was found more than half a century ago[22,23], the pairing mechanism remains a subject of heated debate (for a recent review see Ref. 24). While the persistence to low carrier concentrations[23] and the anomalous isotope effect[25] challenge conventional BCS (Bardeen–Cooper–Schrieffer) theories[26,27], it is likely that electron-phonon coupling in some form, as well as proximity to ferroelectricity[28–33] play a role. Spin-orbit coupling has also been implicated[34–37], and would be consistent with the observed higher critical temperatures in KTO, with its heavy tantalum ion, compared to STO[32,33,38]. The surface-plane dependence in KTO is captured by a model in which out-of-plane polar displacements of the Ta and O ions allow a linear coupling of the transverse optical (TO) phonon to the electrons in the t_{2g} (d_{xy}, d_{yx} and d_{zx}) orbitals; this coupling would otherwise go to zero as the phonon wavevector q approached Γ[39]. The strong dependence of the superconducting T_c on surface orientation is then explained by different inter-orbital hopping of electrons between adjacent tantalum sites via the oxygen orbitals, with the highest hopping at (111) surfaces, followed by (110) surfaces, and no hopping allowed by symmetry at (001) surfaces.

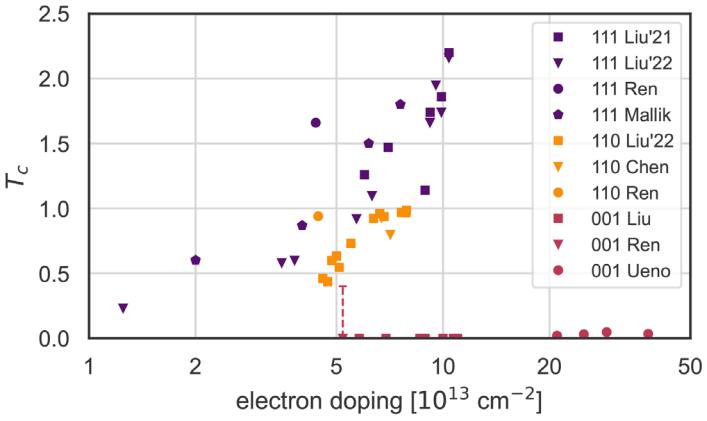

Figure 1. Superconducting critical temperatures, extracted from studies by Ueno *et al.*[16], Chen *et al.*[19], Liu *et al.*[20,39], Ren *et al.*[21], and Mallik *et al.*[40]. The (111) surface/interface reaches the highest T_c of up to 2 K (dark blue markers), followed by the (110) surface/interface reaching almost 1 K (bright yellow markers). The original paper by Ueno *et al.*[16] reported a T_c up to 0.05 K for the (001) surface at high doping, but more recent publications at lower doping found no (001) superconductivity down to 0.025 K[20] and 0.4 K[21] (red markers at bottom).

It is clear that a thorough picture of the electron-phonon coupling as a function of electron doping and throughout the Brillouin Zone in KTO is an essential step towards developing a complete theory of its superconductivity. While the electron-phonon coupling has been calculated from first principles for STO[41], to our knowledge it is lacking for KTO, and the goal of this work is to remedy this gap. Here we report the mode-resolved electron-phonon coupling strengths, λ, obtained using first-principles calculations based on density functional theory, for cubic $KTaO_3$ across the range of experimentally accessible electron doping values. We extract the mode-resolved total λ as a function of carrier density, and focus in particular on differences between the [001], [110] and [111] high-symmetry directions, which are reciprocal to the corresponding experimentally measured surface and interfacial planes. Additionally, for one doping value, we compare the behavior with and without spin-orbit coupling, and for polar and non-polar structures to determine the effect of both properties. Our main findings are that i) the calculated total electron-phonon coupling strengths do not follow the measured trends in superconducting T_c; ii) λ is concentrated in the optical modes around Γ and polar distortions increase λ by a factor of approximately five, suggesting a mechanism involving the polar soft mode; iii) spin-orbit coupling has negligible influence on the calculated electron-phonon coupling.

Methods

To calculate the forces and total energies we use density functional theory within the generalized gradient approximation (GGA) as implemented in the Quantum ESPRESSO 7.0 and 7.1 codes[42–44]. We describe the exchange and correlation using the PBEsol functional[45], and perform the core-valence separation with the ultrasoft GBRV[46,47] and pslibrary (to compare results with and without spin-orbit coupling) pseudopotentials[48]. We use a kinetic energy cutoff of 60 Ry (816 eV) for the wavefunctions, 600 Ry (8163 eV) for the charge density and a 24 × 24 × 24 k-point mesh including Γ for all unit cells. Doping is achieved in the range from 0.0001 to 0.1 electrons/formula unit (e/fu) using the background-charge method with Gaussian smearing of 1 meV width. Total energies are converged to 1 μeV (7.35×10^{-8} Ry) and forces to 0.1 meV/Å (3.89×10^{-6} Ry/bohr).

Both unit-cell size and shape, as well as internal coordinates, are fully relaxed, resulting in a non-polar cubic perovskite structure with a lattice constant of 3.988 Å, which is very close to the experimental one of 3.989 Å[49]. Phonons are calculated on a 4×4×4 q-point mesh, with convergence tests on 6×6×6 and 8×8×8 q-point meshes showing only minor quantitative differences (see Figure A2 in the appendix). The resulting phonon dispersion for very low doping, using the PBEsol-relaxed unit cell, corresponds well with the room-temperature phonon dispersion calculated recently using Quantum Self-Consistent Ab Initio Lattice Dynamics (QSCAILD), which is based on DFT and a self-consistent sampling method to capture both thermal and quantum fluctuations[50]. Note that, since our study is for doped KTO, we neglect the LO-TO splitting, assuming that it will be screened by the metallicity. To our knowledge, the evolution of the LO-TO splitting from the insulating to the metallic state as a function of doping in transition-metal oxides has not been determined, and this would be an important topic for future work.

The electron-phonon coupling properties are calculated using the EPW 5.4.1 and 5.5 codes[51,52], which are included in the Quantum ESPRESSO package, and notation follows those references. The relevant electronic bands in $KTaO_3$ are the three Ta-5*d* t_{2g} bands, which are reproduced using maximally localized Wannier functions as implemented in the Wannier90 code[53], used internally by EPW. The electron-phonon matrix elements are first calculated on coarse 24 × 24 × 24 k-point and 4 × 4 × 4 q-point meshes and then interpolated onto fine grids using maximally localized Wannier functions. We use a random fine mesh with 1′000′000 k points to calculate the mode-resolved electron-phonon coupling strengths, λ_{qv}, along a path between cubic high-symmetry points with 200 q points between each point. Convergence test results can be found in the appendix file in the data availability statement. Estimates of the total electron-phonon coupling strength and bulk T_c are not provided, as they would require full sampling of both k- and q-space, which we did not perform due to the excessive computational cost.

Results and discussion

Our calculated mode-resolved electron-phonon coupling strengths λ at seven different doping levels, covering the experimental range, are shown in Figure 2, along the high symmetry directions of the Brillouin zone, with λ integrated at each q point shown in the top part of each subplot, and λ integrated over frequency (decomposed into 100 frequency steps) shown on the right of each subplot. There are several points to note. First, there are no imaginary frequencies, as the structural relaxation of KTO using the PBEsol functional results in a cubic unit cell with no structural instabilities. The frequency of the polar soft mode at Γ, which can be imaginary using the PBE functional, is 2.7 THz for the lowest doping value of 0.0001 e/fu, and hardens to 5.0 THz at the highest doping value of 0.1 e/fu. It has the strongest electron-phonon coupling strength λ throughout the whole doping range. Additionally, contributions to λ can be seen in the higher-energy optical modes around Γ. The strong coupling of the electrons to the polar modes at the Γ point suggests that the ferroelectric fluctuations associated with quantum paraelectricity could play a key role in the superconductivity in KTO, as already suggested for quantum paraelectric STO[24,28,31].

In the [110] (Γ to M) and [111] (Γ to R) directions, the electron-phonon coupling occurs only close to the Γ point; here the optical phonons correspond to long-wavelength ferroelectric displacements. In the [001] Γ-X direction, in contrast, the coupling, while strongest close to Γ, remains present along the entire high-symmetry line, also at higher doping. This results also in a larger total contribution along the [001] direction than along [110] and [111]. We note that the form of λ in reciprocal space closely follows that of the Fermi surface, which at these doping levels is close to spherical except for elongations

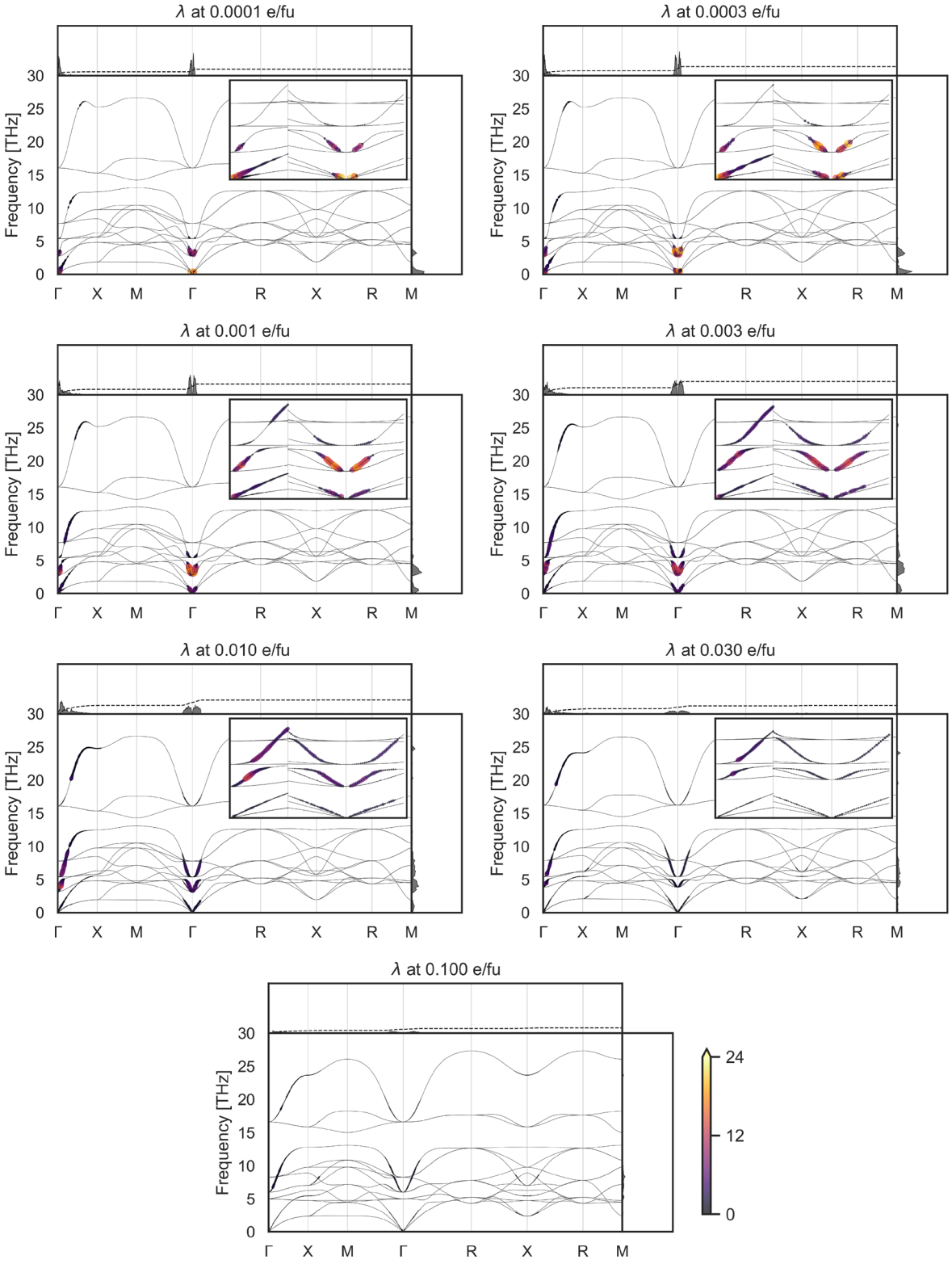

Figure 2. Phonon-mode-resolved electron-phonon coupling strength λ at different doping values ranging from 0.0001 e/fu to 0.1 e/fu, which correspond to 1.6 × 10^{18} e/cm^3 to 1.6 × 10^{21} e/cm^3 or roughly 6.2 × 10^{12} e/cm^2 to 4.7 × 10^{14} e/cm^2, plotted on top of phonon frequencies (narrow black lines). All plots are on the same scale and share the same colorbar for the dimensionless λ, shown at the bottom. The insets in the top right corners of each subplot show a zoomed-in part of the area around Γ towards the X, M and R points, ranging from from 0 THz to 10 THz. Integrated λ values along vertical and horizontal directions are shown in the top and right subpanels, respectively.

along the cartesian reciprocal axes reflecting the flat electronic bands along Γ to X (see e.g. fig 3.3 of Ref. 54). As expected, at low doping, the electron-phonon coupling is limited largely to the lowest phonon frequencies, then extends to higher frequencies as the doping is increased and higher energy electronic bands are populated.

The calculated integrated λ values along the three high-symmetry directions, which we use as proxies for the total electron-phonon coupling strength in each reciprocal direction, are shown as a function of doping concentration in Figure 3. In all directions in reciprocal space there is a dome-like structure in the calculated λ, with a smooth maximum between 1×10^{19} e/cm^{-3} to 1×10^{20} e/cm^{-3} (2.0×10^{13} e/cm^{-2} to 8.3×10^{13} e/cm^{-2}) for the [110] and [111] directions. The more pronounced peak around 1×10^{20} e/cm^{-3} in the [001] direction coincides with the electron doping reaching the X point of the band structure, as can also be seen in the third row of Figure 2.

If KTO were a conventional BCS-theory superconductor, we would expect the critical temperatures of Figure 1 to follow roughly the electron-phonon coupling strength of Figure 3. Comparing those two figures, it is clear that there is no obvious correlation. First, the experimental data do not show such a dome-like trend, with the (111) surfaces/interfaces in particular showing a linear increase of T_c with increasing doping. Second, while experimentally the highest T_c is observed for the (111) surfaces/ interfaces, and the T_c for the (001) surfaces/interfaces is very low, the electron-phonon coupling is strongest for the [001] direction, and weakest for the [111] direction. Note that we do not consider explicitly the role of Coulomb interactions, which could also influence the anisotropy and T_cs[24], for technical reasons, but this could be a focus of future work.

Influence of spin-orbit coupling and polar symmetry

Finally, to determine the influence of spin-orbit coupling and polar structural distortions, we present in Figure 4 our calculated mode-resolved λ for both non-polar and [111]-polarized KTO with and without spin-orbit coupling (SOC). (The influence of SOC on the electronic bands is shown in Figure A4 in the appendix.) The polar structure is obtained by increasing the cubic lattice constant to 4.010 Å and relaxing the internal coordinates; the soft mode frequency is then close to that of the original cubic structure (~3.0 THz).

First we compare the results with and without SOC in the cubic structures (top row)[1] and see that the differences are negligible. In contrast, the differences between the non-polar and polar structures (down the columns) are substantial. First, the integrated values of λ in the polar structures are larger by a factor of around five than the non-polar values. Second, the lowest energy branches of the soft TO modes around Γ, which had negligible electron-phonon coupling in the cubic structures, are now among the main contributors to λ. Third, coupling along the Γ-X direction is enhanced by the polar distortion, especially in the polar case without SOC. Note that in the polar case, spin-orbit coupling slightly reduces the λ values.

The fact that the polar symmetry breaking has such a large calculated effect on λ is consistent with recent reports of polar symmetry breaking coexisting with superconductivity in STO[55,56] and theories of coupling to polar modes in KTO[57]. Note that the tendency of KTO to become polar is strongest along the [111] direction, and weakest along the [001] direction, as shown in Figure 5. This trend is consistent with that of the measured T_c, again pointing to a possible relevance of the ferroelectric soft mode.

[1]Note the small difference between the 'no SOC/non-polar' panel of Figure 4 and the corresponding 'λ at 0.010 e/fu' panel of Figure 2. The difference arises from the fact that for Figure 4 we calculated everything using scalar-relativistic pslibrary pseudopotentials to make it directly comparable to the SOC results which we obtained using fully-relativistic pslibrary pseudopotentials.

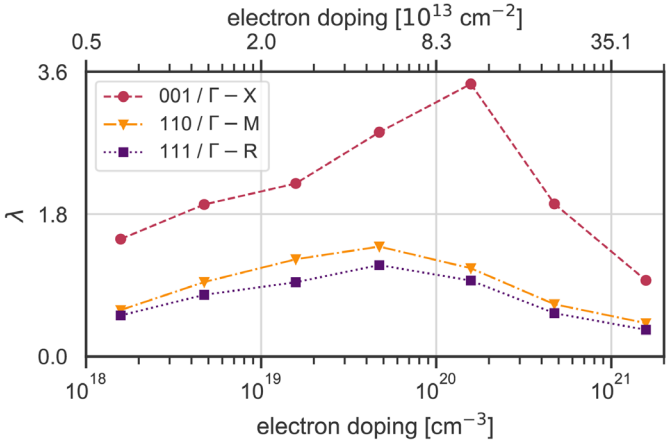

Figure 3. Total electron-phonon coupling strength λ integrated along each high-symmetry direction at different doping values, covering a range from low concentration to the maximum achieved by ionic liquid gating[16]. The numbers on the left axis correspond to the mean lambda value of each point along each high-symmetry direction. The 2D doping values on top are estimated from the 3D values on the bottom axis using the conversion method described in section A in the appendix file. The strongest electron-phonon coupling is along the [001] direction, while the [110] and [111] directions have almost the same magnitude and evolution with doping.

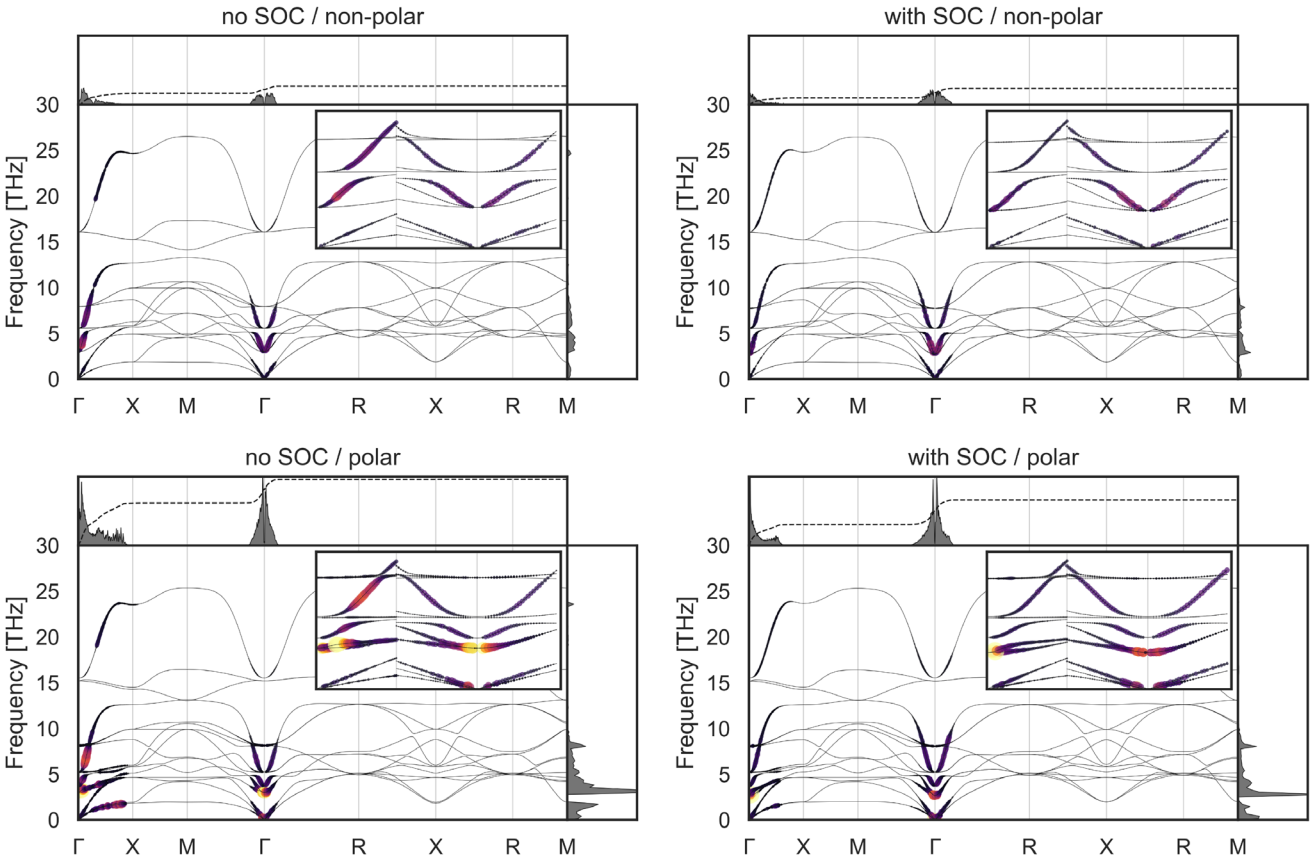

Figure 4. Calculated phonon-mode-resolved electron-phonon coupling strength λ at a doping value of 0.01 e/fu for non-polar (top) and polar (bottom) KTO without (left) and with (right) spin-orbit coupling (SOC). All plots share the same colorbar, shown at the bottom of Figure 2, for the dimensionless λ.

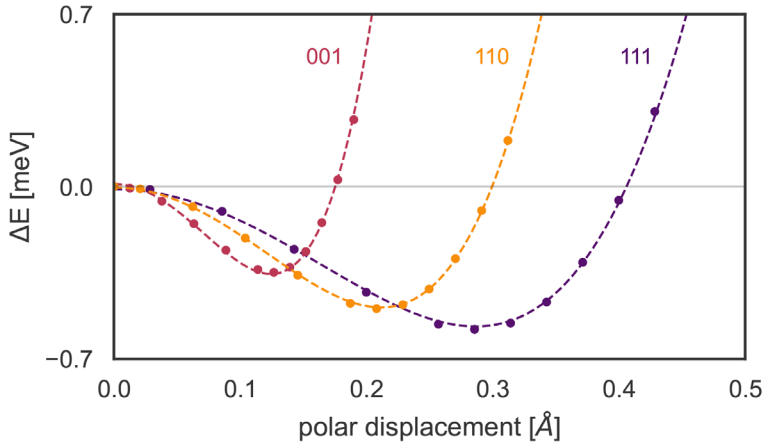

Figure 5. Calculated energy as a function of polar distortion along the high-symmetry directions in the doped (0.01 e/fu) KTO unit cell, as used in the bottom left of Figure 4 ('no SOC/polar'). The horizontal axis shows the summed displacement of all atoms in a unit cell relative to their non-polar positions. A polarization along the [111] direction has both the largest energy gain and the largest displacement.

Summary

In summary, we have calculated the electron-phonon coupling in $KTaO_3$ for electron dopings between 1.6×10^{18} e/cm^3 and 1.6×10^{21} e/cm^3 and analyzed the results in light of the recently reported superconductivity and its surface dependence. Our calculations indicate that the measured trends in superconducting T_c are not reflected in the calculated electron-phonon coupling strengths λ along the corresponding reciprocal directions, confirming earlier suggestions that the superconductivity is not bulk BCS-like in nature[7,17,20,58]. In this context, recent angle-resolved photoemission spectroscopy measurements implicating coupling of bulk-like electrons to Fuchs-Kliewer *surface* phonons are highly relevant[59]. The concentration of λ in the lowest frequency optical modes close to Γ hints towards a mechanism in which the polar soft mode plays a role. A comparison of the mode-resolved λ values between non-polar and polar structures shows clearly that polarization strongly enhances the electron-phonon coupling. In contrast, a comparison of mode-resolved λ values between calculations without and with spin-orbit coupling shows negligible difference.

Data availability

Underlying data

Materials cloud. "First-principles calculation of electron-phonon coupling in doped KTaO3".

DOI: 10.24435/materialscloud:3t-k3.

This project contains the following underlying data:

- README.txt
- materialscloud_KTO_EPW.zip (zip file containing all input files)
- Appendix.pdf (Additional computational and convergence details)

Creative Commons Attribution 4.0 International license (CC-BY 4.0).

Acknowledgements

The authors acknowledge helpful discussions with Jose Lorenzana, Manuel Bibes and Michael Fechner. A preprint version of this manuscript can be found on the arXiv at https://doi.org/10.48550/arXiv.2210.14113.

References

1. Barrett JH: **Dielectric Constant in Perovskite Type Crystals.** *Phys Rev.* 1952; **86**(1): 118–120.
Publisher Full Text
2. Uwe H, Oka K, Unoki H, *et al.*: **Raman Scattering from Conduction Electrons in KTaO3.** *J Phys Soc Jpn.* 1980; **49**(Suppl. A): 577–580.
3. Stengel M: **Electrostatic stability of insulating surfaces: Theory and applications.** *Phys Rev B.* 2011; **84**(20): 205432.
Publisher Full Text
4. Mattheiss LF: **Energy Bands for $KNiF_3$, $SrTiO_3$, $KMoO_3$, and $KTaO_3$.** *Phys Rev B.* 1972; **6**(12): 4718–4740.
Publisher Full Text
5. Nakamura H, Kimura T: **Electric field tuning of spin-orbit coupling in $ktao_3$ field-effect transistors.** *Phys Rev B.* 2009; **80**(12): 121308.
Publisher Full Text
6. Gupta A, Silotia H, Kumari A, *et al.*: **$KTaO_3$—The New Kid on the Spintronics Block.** *Adv Mater.* 2022; **34**(9): e2106481.
PubMed Abstract | Publisher Full Text
7. Rowley SE, Spalek LJ, Smith RP, *et al.*: **Ferroelectric quantum criticality.** *Nat Phys.* 2014; **10**(5): 367–372.
Reference Source
8. Müller KA, Burkard H: **$SrTiO_3$: An Intrinsic Quantum Paraelectric below 4 K.** *Phys Rev B.* 1979; **19**(7): 3593–3602.
Publisher Full Text
9. Tao LL, Wang J: **Strain-tunable ferroelectricity and its control of Rashba effect in $KTaO_3$.** *J Appl Phys.* 2016; **120**(23): 234101.
Publisher Full Text
10. Gastiasoro MN, Temperini ME, Barone P, *et al.*: **Generalized Rashba Electron-Phonon Coupling and Superconductivity in Strontium Titanate.** *Phys Rev Res.* 2022; **5**: 023177.
Publisher Full Text
11. Gattinoni C, Spaldin NA: **Prediction of a strong polarizing field in thin film paraelectrics.** *Phys Rev Res.* 2022; **4**(3): L032020.
Publisher Full Text
12. King PDC, He RH, Eknapakul T, *et al.*: **Subband structure of a two-dimensional electron gas formed at the polar surface of the strong spin-orbit perovskite $ktao_3$.** *Phys Rev Lett.* 2012; **108**(11): 117602.
PubMed Abstract | Publisher Full Text
13. Santander-Syro AF, Bareille C, Fortuna F, *et al.*: **Orbital symmetry re-construction and strong mass renormalization in the two-dimensional electron gas at the surface of $ktao_3$.** *Phys Rev B.* 2012; **86**(12): 121107(R).
Publisher Full Text
14. Reticcioli M, Wang Z, Schmid M, *et al.*: **Competing electronic states emerging on polar surfaces.** *Nat Commun.* 2022; **13**(1): 4311.
PubMed Abstract | Publisher Full Text | Free Full Text
15. Setvin M, Reticcioli M, Poelzleitner F, *et al.*: **Polarity compensation mechanisms on the perovskite surface $KTaO_3$ (001).** *Science.* 2018; **359**(6375): 572–575.
PubMed Abstract | Publisher Full Text
16. Ueno K, Nakamura S, Shimotani H, *et al.*: **Discovery of superconductivity in $KTaO_3$ by electrostatic carrier doping.** *Nat Nanotechnol.* 2011; **6**(7): 408–412.
PubMed Abstract | Publisher Full Text
17. Ueno K, Shimotani H, Yuan H, *et al.*: **Field-Induced Superconductivity in Electric Double Layer Transistors.** *J Phys Soc Jpn.* 2014; **83**(3): 032001.
Publisher Full Text
18. Sakai A, Kanno T, Yotsuhashi S, *et al.*: **Thermoelectric Properties of Electron-Doped $KTaO_3$.** *Jpn J Appl Phys.* 2009; **48**(9R): 097002.
Publisher Full Text
19. Chen Z, Liu Z, Sun Y, *et al.*: **Two-dimensional superconductivity at the $laalo_3$/$ktao_3$(110) heterointerface its control of Rashba effect in $KTaO_3$.** *Phys Rev Lett.* 2021; **126**(2): 026802.
Publisher Full Text
20. Liu C, Yan X, Jin D, *et al.*: **Two-dimensional superconductivity and anisotropic transport at $KTaO_3$ (111) interfaces.** *Science.* 2021; **371**(6530): 716–721.
PubMed Abstract | Publisher Full Text
21. Ren T, Li M, Sun X, *et al.*: **Two-dimensional superconductivity at the surfaces of $KTaO_3$ gated with ionic liquid.** *ArXiv220100990 Cond-Mat.* 2022.
Reference Source
22. Schooley JF, Hosler WR, Cohen ML: **Superconductivity in Semiconducting $SrTiO_3$.** *Phys Rev Lett.* 1964; **12**(17): 474–475.
Publisher Full Text
23. Schooley JF, Hosler WR, Ambler E, *et al.*: **Dependence of the superconducting transition temperature on carrier concentration in semiconducting $srtio_3$.** *Phys Rev Lett.* 1965; **14**(9): 305–307.
Publisher Full Text
24. Gastiasoro MN, Ruhman J, Fernandes RM: **Superconductivity in dilute $SrTiO_3$: A review.** *Ann Phys (N Y).* 2020; **417**: 168107.
Publisher Full Text

25. Stucky A, Scheerer GW, Ren Z, *et al.*: **Isotope effect in superconducting n-doped srtio$_3$.** *Sci Rep.* 2016; **6**: 37582.
PubMed Abstract | Publisher Full Text | Free Full Text

26. Bardeen J, Cooper LN, Schrieffer JR: **Microscopic Theory of Superconductivity.** *Phys Rev.* 1957; **106**(1): 162–164.
Publisher Full Text

27. Bardeen J, Cooper LN, Schrieffer JR: **Theory of Superconductivity.** *Phys Rev.* 1957; **108**(5): 1175–1204.
Publisher Full Text

28. Edge JM, Kedem Y, Aschauer U, *et al.*: **Quantum Critical Origin of the Superconducting Dome in SrTiO$_3$.** *Phys Rev Lett.* 2015; **115**(24): 247002.
Publisher Full Text

29. Ruhman J, Lee PA: **Superconductivity at very low density: The case of strontium titanate.** *Phys Rev B.* 2016; **94**(22): 224515.
Publisher Full Text

30. Coak MJ, Haines CRS, Liu C, *et al.*: **Pressure dependence of ferroelectric quantum critical fluctuations.** *Phys Rev B.* 2019; **100**(21): 214111.
Publisher Full Text

31. van der Marel D, Barantani F, Rischau CW: **Possible mechanism for superconductivity in doped SrTiO$_3$.** *Phys Rev Research.* 2019; **1**(1): 013003.
Publisher Full Text

32. Gastiasoro MN, Trevisan TV, Fernandes M: **Anisotropic superconductivity mediated by ferroelectric fluctuations in cubic systems with spin-orbit coupling.** *Phys Rev B.* 2020; **101**(17): 174501.
Publisher Full Text

33. Gastiasoro MN, Temperini ME, Barone P, *et al.*: **Theory of superconductivity mediated by Rashba coupling in incipient ferroelectrics.** *Phys Rev B.* 2022; **105**(22): 224503.
Publisher Full Text

34. Kozii V, Fu L: **Odd-Parity Superconductivity in the Vicinity of Inversion Symmetry Breaking in Spin-Orbit-Coupled Systems.** *Phys Rev Lett.* 2015; **115**(20): 207002.
Publisher Full Text

35. Kanasugi S, Yanase Y: **Spin-orbit-coupled ferroelectric superconductivity.** *Phys Rev B.* 2018; **98**(2): 024521.
Publisher Full Text

36. Kanasugi S, Yanase Y: **Multiorbital ferroelectric superconductivity in doped SrTiO$_3$.** *Phys Rev B.* 2019; **100**(9): 094504.
Publisher Full Text

37. Kozii V, Bi Z, Ruhman J: **Super-conductivity near a Ferroelectric Quantum Critical Point in Ultralow-Density Dirac Materials.** *Phys Rev X.* 2019; **9**(3): 031046.
Publisher Full Text

38. Yu Y, Hwang HY, Raghu S, *et al.*: **Theory of superconductivity in doped quantum paraelectrics.** *npj Quantum Mater.* 2022; **7**(1): 63.
Publisher Full Text

39. Liu C, Zhou X, Hong D, *et al.*: **Tunable superconductivity at the oxide-insulator/KTaO$_3$ interface and its origin**. 2022.
Publisher Full Text

40. Mallik S, Ménard GC, Saïz G, *et al.*: **Superfluid stiffness of a KTaO$_3$-based two-dimensional electron gas.** *Nat Commun.* 2022; **13**(1): 4625.
Publisher Full Text

41. Zhou JJ, Hellman O, Bernardi M: **Electron-phonon scattering in the presence of soft modes and electron mobility in SrTiO$_3$ perovskite from first principles.** *Phys Rev Lett.* 2018; **121**(22): 226603.
Publisher Full Text

42. Giannozzi P, Baroni S, Bonini N, *et al.*: **QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials.** *J Phys Condens Matter.* 2009; **21**(39): 395502.
Publisher Full Text

43. Giannozzi P, Andreussi O, Brumme T, *et al.*: **Advanced capabilities for materials modelling with Quantum ESPRESSO.** *J Phys Condens Matter.* 2017; **29**(46): 465901.
Publisher Full Text

44. Giannozzi P, Baseggio O, Bonfà P, *et al.*: **Quantum ESPRESSO toward the exascale.** *J Chem Phys.* 2020; **152**(15): 154105.
Publisher Full Text

45. Perdew JP, Ruzsinszky A, Csonka GI, *et al.*: **Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces.** *Phys Rev Lett.* 2008; **100**(13): 136406.
PubMed Abstract | Publisher Full Text

46. Garrity KF, Bennett JW, Rabe KM, *et al.*: **Pseudopotentials for high-throughput DFT calculations.** *Comput Mater Sci.* 2014; **81**: 446–452.
Publisher Full Text

47. Garrity KF, Bennett JW, Rabe KM, *et al.*: **GBRV pseudopotentials**. 2019.
Reference Source

48. Dal Corso A: **Pseudopotentials periodic table: From H to Pu.** *Computational Materials Science.* 2014; **95**: 337–350.
Publisher Full Text

49. Wemple SH: **Some transport properties of oxygen-deficient single-crystal potassium tantalate (KTaO$_3$).** *Phys Rev.* 1965; **137**(5A): A1575–A1582.
Publisher Full Text

50. Meier QN, Mingo N, van Roekeghem A: **Finite temperature dielectric properties of KTaO$_3$ from first principles and machine learning: Phonon spectra, barrett law, strain engineering and electrostriction**. 2022.
Publisher Full Text

51. Giustino F, Cohen ML, Louie SG: **Electron-phonon interaction using Wannier functions.** *Phys Rev B.* 2007; **76**(16): 165108.
Publisher Full Text

52. Poncé S, Margine ER, Verdi C, *et al.*: **EPW: Electron–phonon coupling, transport and superconducting properties using maximally localized Wannier functions.** *Comput Phys Commun.* 2016; **209**: 116–133.
Publisher Full Text

53. Pizzi G, Vitale V, Arita R, *et al.*: **Wannier90 as a community code: New features and applications.** *J Phys Condens Matter.* 2020; **32**(16): 165902.
Publisher Full Text

54. Esswein T: **Exploring Ferroelectric Quantum Criticality and Superconductivity in KTaO3**. Master Thesis. 2018.
Publisher Full Text

55. Salmani-Rezaie S, Ahadi K, Stemmer S: **Polar Nanodomains in a Ferroelectric Superconductor.** *Nano Lett.* 2020; **20**(9): 6542–6547.
Publisher Full Text

56. Salmani-Rezaie S, Jeong H, Russell R, *et al.*: **Role of locally polar regions in the superconductivity of SrTiO$_3$.** *Phys Rev Materials.* 2021; **5**(10): 104801.
Publisher Full Text

57. Venditti G, Temperini ME, Barone P, *et al.*: **Anisotropic Rashba coupling to polar modes in KTaO$_3$.** 2022.
Publisher Full Text

58. Klein A, Kozii V, Ruhman J, *et al.*: **A theory of criticality for quantum ferroelectric metals**. 2022.

59. Chen X, Yu T, Liu Y, *et al.*: **Orientation-dependent electron-phonon coupling in interfacial superconductors LaAlO3/KTaO3**. 2023.
Publisher Full Text

Open Peer Review

Current Peer Review Status: ✔ ? ? ?

Version 1

Reviewer Report 21 December 2023

https://doi.org/10.21956/openreseurope.17609.r36500

© **2023 Lafuente-Bartolome J.** This is an open access peer review report distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

?

Jon Lafuente-Bartolome
University of the Basque Country (UPV/EHU), Bilbao, Spain

The authors present an ab initio analysis of electron-phonon interactions as a function of doping in the quantum paraelectric KTaO3. This material has attracted increased interest recently, as it has been found experimentally that it shows a strong surface-orientation dependent interfacial superconductivity upon doping.

The manuscript introduces the topic with a comprehensive and clear introduction to the recent literature in this field, and in general I found that the article is well written and accessible for a broader audience. The ab initio calculations presented here constitute an important first step towards a better theoretical understanding of superconductivity in this material, and might serve as a very useful reference for future works in this direction.

However, I believe that there are some technical aspects that should be clarified by the authors so that this manuscript can serve as a solid reference:

- The authors use ultrasoft pseudopotentials from the pslibrary and GBRV libraries. Although the results might be correct, currently only norm-conserving pseudopotentials are officially supported by EPW (see npj Comput Mater 9, 156 (2023) section “Computational workflow and basic capabilities”). I would suggest testing the presented results, at least for one doping level, against calculations using norm-conserving pseudopotentials.

- In Fig. 5, the authors show the energy surface as a function of polar displacements. They find a clear double-well structure, showing that distortions along any of the three directions minimize the total energy towards a polar structure. In this case, how are the frequencies of the corresponding TO modes not imaginary? I would assume that including anharmonic effects would be needed to obtain a dynamically stable structure and well-defined phonons (see e.g. Adv Quantum Technol. 6, 2200131 (2023)).

- From the convergence tests shown in the Appendix, it seems that the calculations are not converged with respect to the coarse-q mesh. The authors mention that “actual \lambda values

are about twice as large in the q6 and q8 cases compared to the q4 case". I believe that at least 6x6x6 coarse-q grids should be used for the calculations presented in the manuscript.

- The integrated \lambda values shown in Fig. 3 are quite large. They would result in relatively high Tc estimates following e.g. the McMillan-Allen-Dynes formula, and as far as I understand, no bulk superconductivity has been measured in bulk KTaO3. Could the authors comment on this?

- In the top and right subpanels of Figs. 2 and 4, the axes have no labels, and the shaded areas are invisible in some cases. What is the dashed line in the top subpanel? It might be more useful to define the Eliashberg function in the right panel, from which the integrated coupling strength might be obtained and visualized as a function of frequency (see e.g. Eq. (205)-(206) of Rev. Mod. Phys. 89, 015003). Moreover, I would suggest labeling the mode and momentum dependent electron-phonon interaction strength as \lambda_{q\nu} throughout the text and figures, to discern it from the total integrated coupling strength \lambda.

Is the work clearly and accurately presented and does it cite the current literature?
Yes

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Yes

If applicable, is the statistical analysis and its interpretation appropriate?
Not applicable

Are all the source data underlying the results available to ensure full reproducibility?
Yes

Are the conclusions drawn adequately supported by the results?
No

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Computational Condensed Matter Physics; Electron-phonon interactions; Polarons;

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Reviewer Report 18 December 2023

https://doi.org/10.21956/openreseurope.17609.r36498

© 2023 Tong Z. This is an open access peer review report distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. The author(s) is/are employees of the US Government and therefore domestic copyright protection in USA does not apply to this work. The work may be protected under the copyright laws of other jurisdictions when used in those jurisdictions.

?

Zhen Tong
Sun Yat-Sen University, Shenzhen, China

In this manuscript, the authors studied the electron-phonon coupling strength of doped $KTaO_3$ along the reciprocal space high symmetry directions. They discovered that in contrast to the experimentally measured trends in critical temperatures, the electron-phonon coupling strength as a function of doping has a dome-like shape in all three directions, which points to a non-BCS character of the superconductivity. This work is very interesting and meaningful. It should address the following improvements before the publication.

(1) It is recommended to add a schematic diagram of the KTO crystal structure to the appendix so that even readers unfamiliar with perovskites can understand it.

(2) The authors discussed the calculated total electron-phonon coupling strengths do not follow the measured trends in superconducting T_c because KTO is not a conventional BCS-theory superconductor. Could the authors explain this in more detail? Which other theory do the authors think is more reasonable to explain the superconductivity of KTO?

(3) In Fig. 4, the effect of SOC on the non-polar structure is negligible, but the effect of SOC on the polar structure is obvious. Perhaps the authors could add new curves (*Calculated energy as a function of polar distortion along the high-symmetry directions in the doped KTO unit cell, 'SOC/polar'*) to Figure 5 to illustrate how SOC affects the polar structure.

(4) In the Title and Abstract, it should be "$KTaO_3$", not "KTaO3".

Is the work clearly and accurately presented and does it cite the current literature?
Yes

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Partly

If applicable, is the statistical analysis and its interpretation appropriate?
Partly

Are all the source data underlying the results available to ensure full reproducibility?
Partly

Are the conclusions drawn adequately supported by the results?

Partly

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: electron-phonon coupling transport

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Reviewer Report 15 December 2023

https://doi.org/10.21956/openreseurope.17609.r36513

© 2023 Zhu X. This is an open access peer review report distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

?

Xuetao Zhu
[1] Institute of Physics,, Chinese Academy of Sciences, Beijing, China
[2] School of Physical Sciences, University of Chinese Academy of Sciences, Beijing, China

The superconductivity discovered in doped $KTaO_3$ has attracted a lot of attention. Especially, the unique orientation-dependent T_C provides an interesting perspective to view the mechanism of superconductivity.

The paper entitled “First-principles calculation of electron-phonon coupling in doped $KTaO_3$” by Tobias Esswein and Nicola A. Spaldin, reports a detailed study by first-principles calculation of the electron-phonon coupling (EPC) strength along different directions in doped $KTaO_3$. The authors discovered that the EPC in the [001] direction is stronger than that in the [110] and [111] directions, which is not consistent with the experimentally measured orientation-dependent trend of T_C. Based on this contrast, the authors claim that the superconducting mechanism of doped $KTaO_3$ is not a conventional BCS-like picture. In this work, the calculations are carefully performed and the study of the EPC in doped $KTaO_3$ will provide useful information for the understanding of the superconducting mechanism. After carefully reading the manuscript, I am still puzzled by the following aspects. I hope the authors can give more explanations.

1. Since I am not an expert on first-principles calculations, I cannot evaluate the accuracy of the EPC constants obtained by the authors. However, it seems the EPC constants obtained in Figure 3, especially the ones in the [001] direction (with the highest value up to ~3.5), are much larger than commonly reported EPC constants of any material, at least according to my knowledge. If this is true, such strong EPC must have some nonnegligent effect on the properties of $KTaO_3$. But I don’t notice any reports of the interesting properties related to such strong EPC in $KTaO_3$.
2. It seems all the EPC calculations are performed in the framework of the Eliashberg picture, which is usually applicable for metals with the Fermi energy (E_F) much larger than the phonon energy ($\hbar\omega$), i.e., $E_F >> \hbar\omega$, in an adiabatic EPC limit. However, for the doped $KTaO_3$,

the E_F should be much lower than conventional metals. For example, in Ref.[39] (Nature Communications, 14, 951 (2023)), the E_F of the doped $KTaO_3$ was estimated to lie in the range of 10—80 meV, in the same energy range as the phonon energies of $KTaO_3$. In this case (E_F comparable with $\hbar\omega$), the EPC should be in the nonadiabatic limit. I am not sure if the nonadiabatic effect was included in the calculations of the current work.

By the way, there are several format errors in the References:

1. Lots of chemical formulas are not capitalized. For example, Refs. [5] [13] [19] and [25].
2. The paper title in Ref. [19] is not correct.
3. The journal information of several references is missing, e.g., Refs. [39] [50] [57] [58].

Please carefully check all the references.

Is the work clearly and accurately presented and does it cite the current literature?
Yes

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Yes

If applicable, is the statistical analysis and its interpretation appropriate?
Not applicable

Are all the source data underlying the results available to ensure full reproducibility?
No source data required

Are the conclusions drawn adequately supported by the results?
Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Surface Phonon; Plasmon; Electron-Phonon Coupling; High-Resolution Electron Energy Loss Spectroscopy; Helium Atom Scattering

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Reviewer Report 15 December 2023

https://doi.org/10.21956/openreseurope.17609.r35727

© 2023 Geilhufe M. This is an open access peer review report distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Matthias Geilhufe
Chalmers University of Technology, Chalmers, Sweden

"The manuscript titled 'First-Principles Calculation of Electron-Phonon Coupling in Doped KTaO3' authored by Esswein and Spaldin presents state-of-the-art ab initio calculations regarding the strength of electron-phonon coupling in $KTaO_3$ (KTO). In its pristine state, KTO behaves as a quantum paraelectric, exhibiting no observable ferroelectric phase transition at temperatures below liquid helium. However, it can transition into a ferroelectric state when adequately doped. Esswein and Spaldin link their computational findings to recently observed superconductivity on KTO surfaces, particularly highlighting its dependence on the surface orientation.

The manuscript suggests that the electron-phonon interaction alone is insufficient to explain the surface-dependence observed in the superconducting transition temperature. This implies the presence of an unconventional mechanism, potentially mediated by polar soft modes.
The article begins with a comprehensive summary of recent superconductivity measurements, effectively contextualizing the new computational results. While the methods used are adequately described, the manuscript primarily focuses on the physical implications of the results, making it accessible to a broad readership.

One aspect that could benefit from further elaboration is the projection scheme used to relate bulk electron-phonon coupling to the surface. The authors employ the correspondence (001):Gamma-X; (011):Gamma-M; (111):Gamma-R, associating these high-symmetry lines with the wave-vector mediating a phonon pointing out of the respective surface area. However, it might be worth exploring the potential contribution of other phonon modes to the surface normal direction.

Furthermore, the manuscript raises intriguing questions about the notably stronger electron-phonon direction along (001), according to Figure 3, despite the apparent suppression of superconductivity in this direction. This finding poses an interesting avenue for further investigation.

Is the work clearly and accurately presented and does it cite the current literature?
Yes

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Yes

If applicable, is the statistical analysis and its interpretation appropriate?
Yes

Are all the source data underlying the results available to ensure full reproducibility?
Yes

Are the conclusions drawn adequately supported by the results?

Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Condensed matter and materials theory; ab initio materials modelling;

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.