

# Oxygen and potassium vacancies in KTP calculated from *first principles*

A Bocchini<sup>✉</sup>, S Neufeld, U Gerstmann and W G Schmidt

Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, Paderborn 330095, Germany

E-mail: [adrianab@mail.upb.de](mailto:adrianab@mail.upb.de)

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## Abstract

The atomic geometry and energetics of oxygen and potassium vacancies in potassium titanyl phosphate (KTP) as well as their electronic and optical properties are studied within density-functional theory in dependence of their charge state. Oxygen vacancies formed between Ti and P are characterized by a negative- $U$  behavior. Their neutral charge state is favored for Fermi levels near the conduction band and gives rise to a defect level in the band gap, which leads to an additional optical absorption peak. In contrast, the two-fold positive charge state, stable for low and intermediate values of the Fermi level, modifies the KTP optical response only slightly. Oxygen vacancies formed between two Ti atoms are two-fold positively charged, while potassium vacancies are negatively charged irrespective of the Fermi level position. In both these cases, the KTP optical response is essentially not affected.

Keywords: potassium titanyl phosphate,  $\text{KTiOPO}_4$ , KTP, point defects, formation energy, gray tracks

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

## 1. Introduction

Potassium titanyl phosphate (KTP,  $\text{KTiOPO}_4$ ) is a ferroelectric material with numerous applications in optical devices, e.g. for frequency doubling in solid-state lasers. Its high optical nonlinearity is attributed to distorted  $\text{TiO}_6$  octahedra [1] and  $\text{KO}_{8,9}$  conglomerates [2]. The transparency of KTP for wavelengths between 350 nm and 4500 nm allows for the fabrication of high-quality waveguides [3].

KTP crystallizes in an orthorhombic crystal lattice with the space group  $\text{Pna}2_1$ . The unit cell contains 64 atoms and consists of eight  $\text{KTiOPO}_4$  macromolecules that belong to two nonequivalent groups [5]. This results in two nonequivalent Ti, P and K sites and ten nonequivalent O sites, see figure 1. The O atoms can be classified according to their coordination: following the notation in [6], oxygen atoms bonded to Ti and P are denoted here  $\text{O}(1)\text{--O}(8)$ , while  $\text{O}(9)$  and  $\text{O}(10)$  are bonded to two Ti atoms.

The usage of KTP is affected by the so-called gray tracking, i.e. photochromic damage [5] caused by high-intensity laser irradiation [7], electric fields [8] or the exposition in a hydrogen atmosphere at high temperatures [6]. Microscopically, the reduction of Ti atoms has been suggested to cause gray tracking: electron paramagnetic resonance (EPR) signatures assigned to  $\text{Ti}^{3+}$  in intrinsic defect centers were detected in crystals affected by gray tracks [8]. The transformation of  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$  ions has been proposed to result from charge balance conservation after oxygen vacancy formation [6, 9]. Subsequent to optical excitation, the photoelectrons are assumed to be trapped by Ti atoms near an O vacancy [8], while photoholes may be captured by Ti–Ti bonded O atoms near a K vacancy [10].

The present study aims at determining the most favorable single O and K vacancy configurations in KTP. Oxygen vacancies between Ti and P, i.e.  $V_{\text{O}(1)\text{--O}(8)}$ , as well as the vacancies  $V_{\text{O}(9)}$  and  $V_{\text{O}(10)}$  between two Ti atoms and the two inequivalent potassium vacancies  $V_{\text{K}(1)}$  and  $V_{\text{K}(2)}$  (see figure 1) are considered. By including charging effects, we go beyond previous calculations [6]. Besides the defect formation energy, the impact of the defects on the KTP charge distribution and optical absorption is explored.



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## 2. Methodology

The present calculations are based on density-functional theory (DFT) as implemented in the VIENNA *ab initio* SIMULATION PACKAGE (VASP) [11]. The electron exchange and correlation (XC) is modeled within the generalized gradient approximation (GGA) using the PBEsol functional [12]. Projector augmented wave (PAW) pseudopotentials that contain Ti  $3d^3 4s^1$ , P  $3s^2 3p^3$ , K  $3p^6 4s^1$ , and O  $2s^2 2p^4$  states as valence electrons are used to model the electron-ion interaction. The electron wave functions are expanded in plane waves up to an energy cutoff of 600 eV. All calculations are performed in a periodically repeated 128 atom supercell that corresponds to the KTP unit cell doubled along the [010] direction. The Brillouin zone is sampled with a shifted  $3 \times 3 \times 3$  Monkhorst-Pack mesh [13]. The calculated equilibrium lattice parameters amount to  $a = 12.859$  Å,  $b = 6.432$  Å, and  $c = 10.599$  Å. These values agree within 0.4% with experimental data [3] and are used for all ideal bulk and defect calculations throughout this work. It is thus assumed that the defect concentration is sufficiently low not to alter the lattice constants.

The Slater–Janak transition state model [14–16] is used for the calculation of charge transition levels. This method circumvents the comparison of total energies of differently charged supercells and thus eliminates the need for additional correction schemes [17–19]. According to Janak’s theorem, the Kohn–Sham eigenvalues  $\varepsilon_i$  correspond to the derivative of the total energy  $E$  with respect to the occupation  $\eta_i$  of the corresponding Kohn–Sham orbital

$$\varepsilon_i = \frac{\partial E}{\partial \eta_i}. \quad (1)$$

Assuming that the Kohn–Sham eigenvalue of the highest occupied state  $\varepsilon_H$  varies linearly with its occupation number [20], the energy difference of the  $N + 1$  and  $N$  electron system is given as

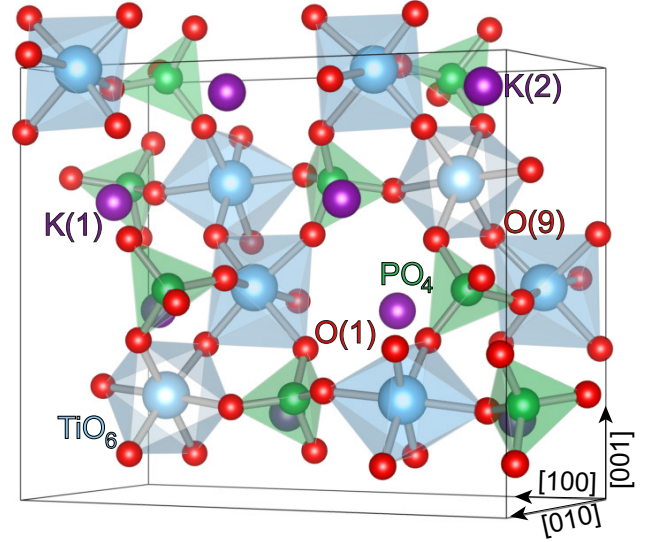
$$E^{N+1} - E^N = \int_0^1 \varepsilon_H(\eta) d\eta = \varepsilon_H\left(\frac{1}{2}\right). \quad (2)$$

The value  $\varepsilon_H\left(\frac{1}{2}\right)$  thus defines the transition state.

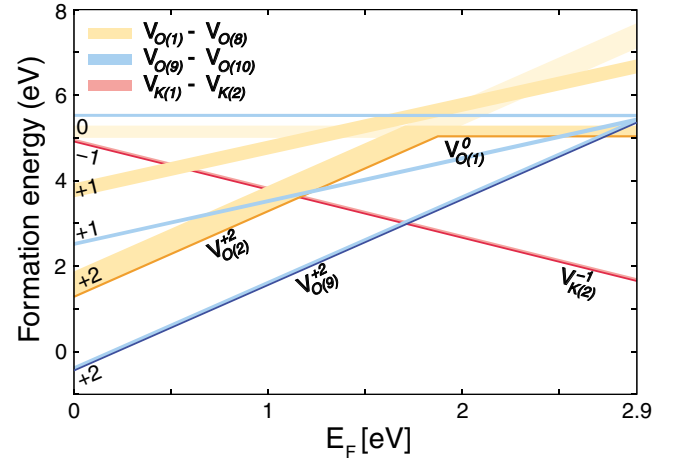
Due to size of the supercell used in the present work, the optical response calculations are restricted to the independent-particle approximation (IPA) level of theory. However, we expect them to provide meaningful trends, since the electron quasiparticle effects and the excitonic effects in KTP, albeit pronounced, tend to cancel each other [21–23]. Therefore, the line shape of the KTP optical response is well described within the IPA, even though the DFT-PBEsol band gap of 2.9 eV underestimates the measured onset of the optical absorption. A detailed discussion of the influence of many-body effects on the KTP optical response can be found in [23].

## 3. Results

The calculated oxygen vacancy formation energies in dependence on the Fermi level position are shown in figure 2.



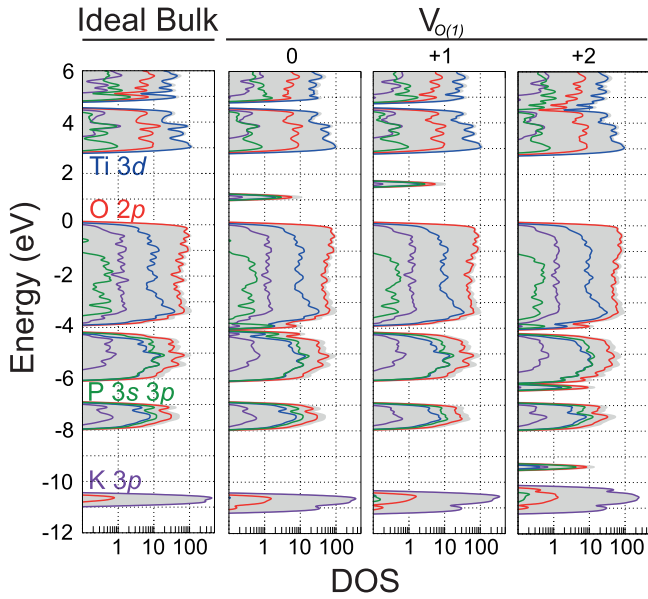
**Figure 1.** Schematic view of the KTP unit cell. Distorted  $\text{TiO}_6$  octahedra and  $\text{PO}_4$  tetrahedra connected via O atoms form chains along the [100] and the [010] direction. Examples for Ti–P and Ti–Ti bonded oxygen atoms are denoted O(1) and O(9), respectively. Two nonequivalent K atoms are marked [4].



**Figure 2.** Calculated oxygen and potassium vacancy formation energy in dependence on the Fermi level position.

Irrespective of the structural details, the formation energies increase with rising Fermi energy, i.e. the vacancies are electron donors. The two-fold positively charged Ti–Ti-bonded oxygen vacancy  $V_{O(9)}^{+2}$  is most stable for a wide range of the Fermi level, and energetically nearly degenerate with  $V_{O(10)}^{+2}$ . The charge transition levels of these Ti–Ti-bonded oxygen vacancies would be located at energies higher than the band gap, i.e. these vacancies are stable only in the +2 charge state.

According to the present calculations, the Ti–P bonded O vacancies (see figure 4) are stable only in a very narrow range of the Fermi level position, close to the conduction band minimum. These vacancies feature a pronounced negative- $U$  behavior, i.e. with rising Fermi level they switch directly from the two-fold positive to the neutral charge state. A defect has negative- $U$  properties if it can trap two electrons (or holes)



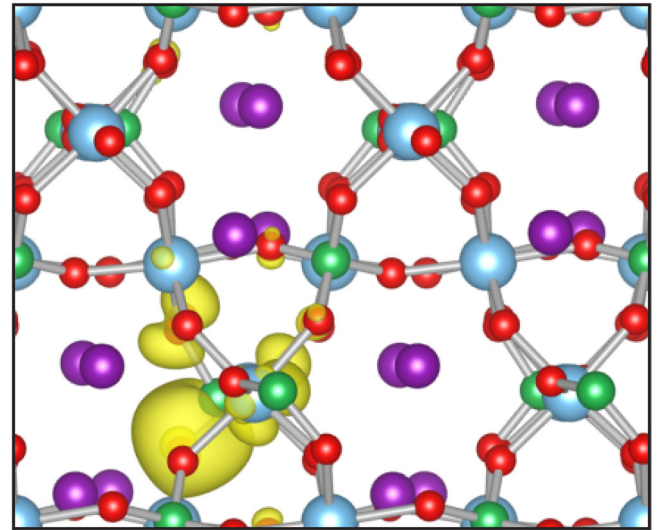
**Figure 3.** Calculated electron density of states (DOS) of ideal bulk KTP and supercells that contain  $V_{O(1)}$  in different charge states.

with the second bond more strongly than the first, see, e.g. [24]. We mention that the formation of negative- $U$  centers by defects or interstitials in the range close to the bottom of the conduction band is of high interest in doped perovskites where defects or interstitials [25, 26] have been proposed to create negative- $U$  centers playing a key role in high temperature superconductivity [27–29]. In the present case, as will be explained below in detail, the negative- $U$  behaviour is related to a strong coupling between the vacancy charge and the vacancy geometry.

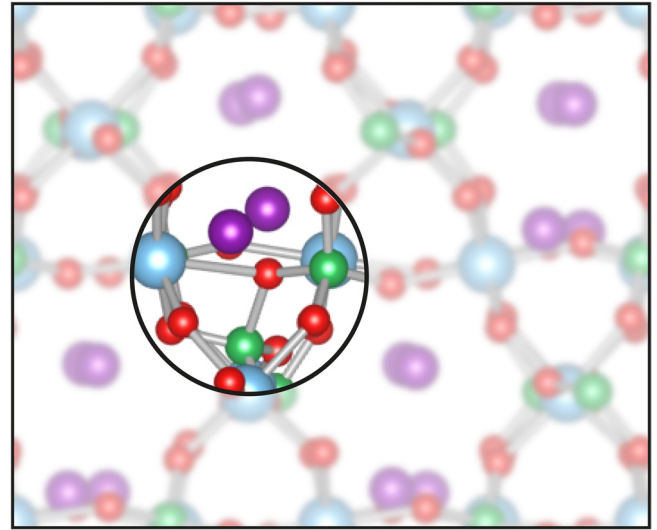
While the stability range of  $V_{O(9)}^{+2}$  extends over the majority of the band gap,  $V_{O(1)}^0$  is most favored for Fermi levels close to the conduction band minimum (CBM). In the following, we therefore mainly discuss the properties of these two defects, which serve as representative examples for vacancies between two Ti atoms and between Ti and P, respectively.

As shown in figure 3, the bulk KTP electron density of states (DOS) partitions into blocks: K 3p states at an energy of about  $-10.5$  eV, P 3s3p states between  $-8$  eV and  $-4$  eV, O 2p states (together with Ti) in the upper valence bands as well as the energy region of the P 3s3p and Ti 3d states (together with O) at the conduction band edge. The  $V_{O(1)}^0$  vacancy formation gives rise to a distinct defect level in the KTP band gap. The defect level moves up in energy if depopulated.

As mentioned above, the negative- $U$  behavior of  $V_{O(1)}$  is related to its structural response to charging effects and can be understood in terms of Coulomb interactions. The electrons occupying the midgap  $V_{O(1)}^0$  defect level screen the electrostatic repulsion between the both positively charged Ti and P atoms, see charge density plot in figure 4. Emptying the defect level quenches the screening, and the Ti–P repulsion causes a strong structural relaxation. Compared to the ideal bulk, the Ti–P distance decreases by  $0.11$  Å in the neutral charge state and increases by  $0.19$  Å and  $1.17$  Å in the +1 and +2 charge states, respectively. As shown in figure 5,



**Figure 4.** Orbital character of the  $V_{O(1)}$  midgap defect level for the neutral charge state.

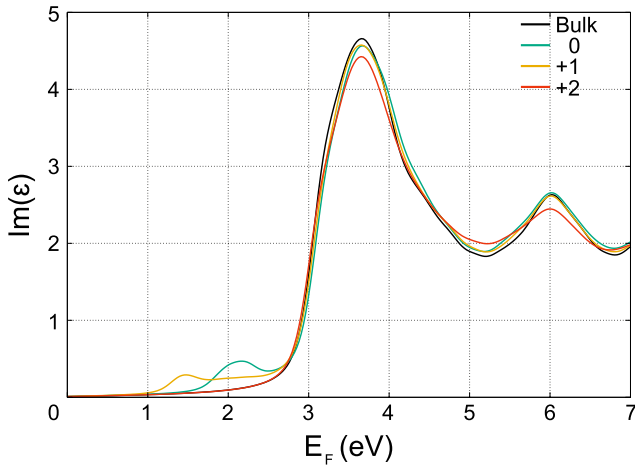


**Figure 5.** Crystal structure of the supercell containing  $V_{O(1)}^{+2}$ . The three-fold coordinated O atom is highlighted.

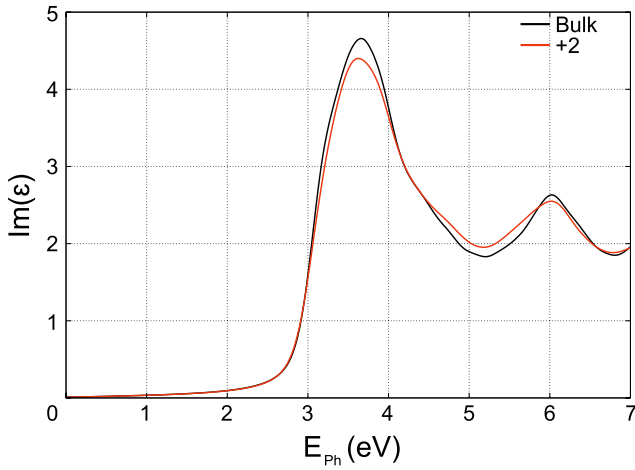
the P atom which is pushed away from the Ti atom binds to an oxygen in the vicinity. The modified coordination leads to variety of new defect levels in the valence bands, i.e. at about  $-4$ ,  $-6$  and  $-9.5$  eV, see figure 3. In addition, the K 3p state below  $-10.5$  eV broadens. The charge transition state between the +1 and the +2 charge state is at least  $0.8$  eV higher in energy than the neutral charge state, resulting in the above mentioned negative- $U$  effect.

In order to quantify the impact of oxygen vacancy formation on the KTP charge density, a Bader analysis [30] is performed. For ideal bulk, Bader charges of 2.016, 1.322, 6.131, 7.390, and 6.969 e are determined for Ti, P, K, Ti–P bonded O, and Ti–Ti bonded O atoms, respectively. As expected, there is an electron transfer from Ti, P and K towards O. The atoms O(1)–O(8) hold a slightly higher negative charge than the atoms O(9) and O(10). The  $V_{O(1)}$  vacancy formation reduces both the neighboring Ti and P atoms. We find





**Figure 6.** Imaginary part of the calculated dielectric function of ideal bulk KTP and KTP with  $V_{O(1)}$  vacancies in different charge states. The spectra of  $V_{O(2)}$ - $V_{O(8)}$  look very similar.



**Figure 7.** Imaginary part of the calculated dielectric function of ideal bulk KTP and KTP with  $V_{O(9)}^{+2}$  vacancies. The spectrum of  $V_{O(10)}$  looks very similar.

a partial reduction of the Ti(1) atom by about 0.06 electrons nearly irrespective of the charge state of the vacancy. Does this reduction correspond to a transformation of  $Ti^{4+}$  to  $Ti^{3+}$ ? In order to answer this question, a Bader analysis has been performed for bulk  $Ti_3O_5$  known to host Ti atoms in both the +3 and +4 oxidation states [31]. We calculate the charge difference of the two inequivalent  $Ti^{3+}$  ions to  $Ti^{4+}$  to amount to 0.08 and 0.1 e, respectively. This is of the same order of magnitude as the Ti reduction calculated here to result from the  $V_{O(1)}$  vacancy formation. Our calculations thus support the scenario that oxygen vacancies reduce titanium and may be related to the gray tracking of KTP. We also note a reduction of P(1) upon  $V_{O(1)}$  formation, which amounts to 1.4, 0.9, and 0.05 electrons for the neutral, +1, and +2 vacancy. In addition, a slight oxidation of the O atoms belonging to the same  $PO_4$  tetrahedron is observed.

Next, we study the impact of O vacancies in Ti–O–P bonds on the KTP optical absorption, see figure 6. The neutral  $V_{O(1)}$  vacancy, stable for Fermi level positions close to the CBM, gives rise to a pronounced shoulder below the onset of the

bulk optical absorption. This shoulder is due to transitions between the defect state shown in figure 3 and the conduction band. The shoulder broadens for the +1 charge state, because now transitions from the valence band in the half occupied defect state are possible. Due to the quenching of the defect state for the +2 charge state the absorption below the onset of the bulk optical absorption vanishes for this charge state.

In contrast to oxygen vacancies formed in Ti–O–P bonds, no defect levels within the band gap arise upon formation of Ti–Ti bonded O vacancies. The defect level occurs just below the bulk CBM of KTP. Once the defect level is emptied, i.e. for the energetically relevant  $V_{O(9)}^{+2}$  vacancy, the KTP optical absorption closely resembles that of the ideal bulk, see figure 7. Similar to oxygen vacancies in Ti–O–P bonds, also the vacancy formation between two Ti atom leads to their partial reduction:  $V_{O(9)}^{+2}$  formation leads to an electron transfer of 0.03/0.05 to Ti(1)/Ti(2), slightly lower than the reduction caused by  $V_{O(1)}$ . In addition, the O atoms near the defect oxidize by about 0.13 e.

Finally, we discuss the formation of potassium vacancies. There are two inequivalent vacancy positions, K(1) and K(2), respectively, see figure 1. After the removal of either K atom, the CBM is half filled. The neutral defect state is energetically unstable and  $V_K$  occurs thus only in the  $-1$  charge state, where the defect level is completely filled. This means that K vacancies are acceptors and their formation energy decreases with the Fermi energy, see figure 2.  $V_{K(1)}^{-1}$  and  $V_{K(2)}^{-1}$  are energetically nearly degenerate ( $\Delta E \approx 60$  meV), and give rise to a defect state close to the bulk VBM. The K vacancy does not introduce additional spectral signatures in the KTP optical response. Its formation only leads to a very minor charge redistribution in KTP. We calculate a slight oxidation of the O atoms that scales with the distance to the vacancy and amounts up to 0.05 e for  $V_K^{-1}$ .

#### 4. Conclusion

Single potassium and oxygen vacancies in KTP were studied within density-functional theory. It is found that O vacancies are donors, while K vacancies are acceptors.

Potassium vacancies are stable in the  $-1$  charge state irrespective of the Fermi energy, slightly oxidize the neighboring atoms and do not give rise to optical absorption in the band gap.

The formation of  $V_O^{+2}$  vacancies, most stable when located between two Ti atoms, leads to the reduction of the neighboring Ti atoms and does not introduce additional optical absorption peaks. For Fermi level positions close to the conduction band minimum,  $V_O^0$  vacancies between Ti and P are energetically favored. These vacancies feature a negative- $U$  effect that is caused by a strong geometry relaxation between the +1 and the +2 charge state. Also these vacancies reduce the Ti, but even more the neighboring P atom and give rise to optical absorption in the band gap.

The Ti reduction due to oxygen vacancy formation amount to 0.03–0.06 e, depending on the charge state and geometry.

This is of the same magnitude as the charge difference between  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$  in  $\text{Ti}_3\text{O}_5$ . The present calculations thus support the picture that O vacancies in KTP give rise to  $\text{Ti}^{3+}$  ions, suggested to be instrumental for the formation of gray tracks, responsible for the observed photochromic damage if the material is exposed to typical electro-optical environment [5–8].

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## ORCID iDs

A Bocchini  <https://orcid.org/0000-0002-2134-3075>

## References

- [1] Zumsteg F C, Bierlein J D and Gier T E 1976 *J. Appl. Phys.* **47** 4980
- [2] Xue D and Zhang S 1997 *Appl. Phys. Lett.* **70** 943
- [3] Bierlein J D and Vanherzeele H 1989 *J. Opt. Soc. Am. B* **6** 622
- [4] Momma K and Izumi F 2011 *J. Appl. Crystallogr.* **44** 1272
- [5] Zhang Q, Feng G, Han J, Li B, Zhu Q and Xie X 2011 *Optik* **122** 1313
- [6] Zhang Y, Leng Y, Liu J, Ji N, Duan X, Li J, Zhao X, Wang J and Jiang H 2015 *CrystEngComm* **17** 3793
- [7] Boulanger B, Rousseau I, Feve J P, Maglione M, Menaert B and Marnier G 1999 *IEEE J. Quantum Electron.* **35** 281
- [8] Roelofs M G 1989 *J. Appl. Phys.* **65** 4976
- [9] Scripsick M P, Edwards G J, Halliburton L E, Belt R F and Loiacono G M 1994 *J. Appl. Phys.* **76** 773
- [10] Edwards G J, Scripsick M P, Halliburton L E and Belt R F 1993 *Phys. Rev. B* **48** 6884
- [11] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
- [12] Perdew J P, Ruzsinszky A, Csonka G I, Vydrov O A, Scuseria G E, Constantin L A, Zhou X and Burke K 2008 *Phys. Rev. Lett.* **100** 136406
- [13] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [14] Janak J F 1978 *Phys. Rev. B* **18** 7165
- [15] Sanna S, Frauenheim T and Gerstmann U 2008 *Phys. Rev. B* **78** 085201
- [16] Li Y, Sanna S and Schmidt W G 2014 *J. Chem. Phys.* **140** 234113
- [17] Makov G and Payne M C 1995 *Phys. Rev. B* **51** 4014
- [18] Schultz P A 2000 *Phys. Rev. Lett.* **84** 1942
- [19] Van de Walle C G and Neugebauer J 2004 *J. Appl. Phys.* **95** 3851
- [20] Göransson C, Olovsson W and Abrikosov I A 2005 *Phys. Rev. B* **72** 134203
- [21] Reshak A H, Kityk I V and Auluck S 2010 *J. Phys. Chem. B* **114** 16705
- [22] Ghoohestani M, Arab A, Hashemifar S J and Sadeghi H 2018 *J. Appl. Phys.* **123** 015702
- [23] Neufeld S, Bocchini A, Gerstmann U, Schindlmayr A and Schmidt W G 2019 *J. Phys. Mater.* submitted (<https://doi.org/10.1088/2515-7639/ab29ba>)
- [24] Watkins G D 1984 *Advances in Solid State Physics* (Berlin: Springer) pp 163–89
- [25] Jarlborg T, Bianconi A, Barbiellini B, Markiewicz R S and Bansil A 2013 *J. Supercond. Novel Magn.* **26** 2597
- [26] Jarlborg T and Bianconi A 2019 *Condens. Matter* **4** 15
- [27] Yu Kagan M 2013 *Phase Diagrams and the Physics of the Pseudogap in Superconductors with Attractive Interaction* (Dordrecht: Springer) pp 263–88
- [28] Geballe T H 2006 *J. Supercond. Novel Magn.* **19** 261
- [29] Bianconi A and Poccia N 2012 *J. Supercond. Novel Magn.* **25** 1403
- [30] Henkelman G, Arnaldsson A and Jónsson H 2006 *Comput. Mater. Sci.* **36** 354
- [31] Schlenker C, Buder R, Schlenker M, Houlihan J F and Mulay L N 1972 *Phys. Status Solidi B* **54** 247