Quasiparticle self-consistent GW band structures and phase transitions of LiAlO$_2$ in tetrahedrally and octahedrally coordinated structures

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A first-principles computational study is presented of various phases of LiAlO$_2$. The relative total energies and equations of state of the $\alpha$, $\beta$ and $\gamma$ phases are determined after structural relaxation of each phase. The $\beta$ and $\gamma$ tetrahedral phases are found to be very close in energy and lattice volume with the $\gamma$ phase having the lowest energy. The octahedral $\alpha$ phase is a high-pressure phase and the transition pressure from the $\gamma$ and $\beta$ phases to $\alpha$ is determined to be about 1 GPa. The electronic band structures of each phase at their own equilibrium volume are determined using the quasiparticle self-consistent (QS) GW method as well as using the 0.8$\Sigma$ approach in which the QSGW self-energy is reduced by a factor 0.8 to correct for the underscreening of $W$ in QSGW. The effective masses of the band edges and the nature of the band gaps are presented. The lowest energy $\gamma$ phase is found to have a pseudodirect gap of 7.69 eV. The gap is direct at $\Gamma$ but corresponds to a dipole forbidden transition. The imaginary part of the dielectric function and the absorption coefficient are calculated in the long-wavelength limit and the random phase approximation, without local field or electron-hole interaction effects for each phase and their anisotropies are discussed. Si doping on the Al site is investigated as a possible $n$-type dopant in $\gamma$-LiAlO$_2$ using a 128 atom supercell corresponding to 3.125 $\%$ Si on the Al sublattice in the generalized gradient approximation and a smaller 16 atom cell with 25 $\%$ Si in the QSGW approximation. The Si is found to significantly perturb the conduction band and lower the gap but a clearly separated deep donor defect level is not found. However, the donor binding energy is still expected to be relatively deep, of order a few 0.1 eV in the hydrogenic effective mass approximation.

I. INTRODUCTION

LiAlO$_2$ is a ceramic material that is known to occur in at least five crystal structures: rhombohedral $\alpha$-LiAlO$_2$ (space group R$\overline{3}$m, #166) [1], orthorhombic $\beta$-LiAlO$_2$ (space group Pna$\overline{2}$1, #33) [2], tetragonal $\gamma$-LiAlO$_2$ (space group P$\overline{4}$1$2_12_1$ (#92)) [3], and tetragonal $\delta$-LiAlO$_2$ (space group I$\overline{4}$_1/amd, #141) [4, 5]. Among these, both $\beta$ and $\gamma$ forms are tetrahedrally coordinated while $\alpha$ and $\delta$ are octahedrally coordinated. The $\delta$ form is essentially a slightly disordered rocksalt type phase, in which the 4a Wyckoff positions are about 80 $\%$ occupied with Al, 20 $\%$ Li and with the roles of Al and Li reversed on the 4b positions. A fully disordered $\epsilon$ cubic phase has also been reported [6]. A 48 atom cell with spacegroup $P\overline{4}m2$ is listed in Materials Project and provides an approximate computational model for these disordered rocksalt type phases.

LiAlO$_2$ has been investigated for applications in tritium breeding in fusion reactors [8, 9], as a matrix in molten carbonate fuel cells [10], and as a substrate for GaN light-emitting diodes (LED) due to the small lattice mismatch between $\gamma$-LiAlO$_2$ and GaN [11]. Moreover, LiAlO$_2$ is closely related to LiGaO$_2$—another ceramic material that is also known to adopt $R\overline{3}$m and Pna$\overline{2}$1 structures and that has recently become of interest as a possible ultra-wide band gap (UWBG) semiconductor due to suggestions that LiGaO$_2$ could be $n$-type doped by silicon or germanium [12–16]. Various experimental works have found the band gap of LiGaO$_2$ in the range of 5.26-5.6 eV [17–20], and quasiparticle self-consistent GW (QSGW) [21] calculations predict a gap of 5.81 eV [22]. We expect LiAlO$_2$ to have an even larger band gap than LiGaO$_2$.

LiAlO$_2$ has recently also been considered in the context of Li-ion batteries. It was used as a coating to protect LiCoO$_2$ [23] but Li was also found to diffuse in LiAlO$_2$ itself at high temperatures [24] and solid solutions of LiAlO$_2$ with LiMO$_2$, where M is a transition metal, were proposed by Cedex et al. [25]. LiAlO$_2$ has also been used as an additive in composite electrolytes [27]. For a more complete literature overview of these recent applications, see Singh et al. [28]. The phase transitions of LiAlO$_2$ at high temperature are important in this context and were studied by Singh et al. [28], as well as the pressure induced transitions we consider here.

The electronic structure and phase transitions of LiAlO$_2$ have already been studied to some extent. The structure of $\gamma$-LiAlO$_2$ at ambient pressure and temperature was determined experimentally by Marezio via Cu $K\alpha$ and Mo $K\alpha$ radiation photographs [3]. The $\gamma$ to $\delta$ phase transition has been studied experimentally [11, 5], and Sailuam et al. [29] have carried out a first-principles computational study of the band structures and pressure-induced $\gamma$ to $\delta$ phase transition [29]. Ma et al. have done a first-principles study of $\alpha$-LiAlO$_2$ [1]. Singh et al. [25] did an extensive computational study of the temperature-pressure phase diagram and also reported electronic band structures of the various phases. However, there still remain open questions, especially on the electronic struc-
ture. With the exception of the study by Sailhuam [29], prior first-principles works have largely used density functional theory (DFT) methods with local or semilocal exchange correlation functionals, which are well-known to significantly underestimate band gaps. Sailhuam et al. [29] obtained a gap of 6.56 eV for $\gamma$-LiAlO$_2$ using the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional, much larger than previous DFT studies. We seek to further improve upon these estimates using the more accurate QS$\text{GW}$ method. Not only the band gap but other details of the band structure, such as the direct or indirect nature of the gap and the effective masses, are relevant to the potential semiconductor applications, which have not yet received attention. Thus, our paper is focused on the electronic structure and its properties relevant to potential but not yet explored applications of the material as an active semiconductor. Therefore we will also briefly consider the possibility of doping.

In relation to the band gap and opto-electronic properties, we point that Huang et al. [30] determined an optical absorption onset from transmission of VIS-UV to occur at 191 nm indicating a gap of $\sim$6.5 eV consistent with Zou et al. [31] who also measured a drop in transmission near 190 nm. More recently, Holston et al. [32, 33] measured optical defects in LiAlO$_2$ induced by radiation of doping with Cu. They also do not see any absorption in as-grown crystals above 200 nm wavelength. From these we can deduce that the optical gap appears to be near 6.5 eV at room temperature. Besides optical properties, they also report electron paramagnetic resonance (EPR) spectra of these defects.

The lowest-energy and most thermally stable form of LiAlO$_2$ is the $\gamma$ phase, but coexistence of the $\alpha$ and $\gamma$ phases is a common result of syntheses performed below 973 K [34], and surface contamination of bulk $\gamma$-LiAlO$_2$ with $\beta$-LiAlO$_2$ is known to occur as a result of matching between the $a$ and $b$ axes of the orthorhombic $\beta$ phase with the $a$ and $c$ axes of the tetragonal $\gamma$ phase [2]. Therefore, we consider each of the $\alpha$, $\beta$, and $\gamma$ phases. Additionally, the $R3m$ structure was found to be a high-pressure phase of LiGaO$_2$ [22], so it is also interesting to study $\alpha$-LiAlO$_2$ for the sake of comparing these two closely related materials. We omit here the $\delta$-phase because it is actually a disordered phase, which requires larger cells to model, and the octahedral coordination is already represented by the $\alpha$-phase. While other work in literature [28] has already studied phase transitions extensively, it is useful to compare our results to their work. The structures studied in this paper and their Brillouin zones are shown in Fig. 1.

II. COMPUTATIONAL METHODS

The structure relaxation calculations in this work are performed using the Quantum Espresso pseudopotential...
tial plane-wave implementation of density functional theory (DFT) \cite{35}. We use projector augmented-wave pseudopotentials for all Quantum Espresso calculations \cite{36}. The exchange-correlation energy was treated in the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) parametrization\cite{37}. For each of the $\alpha$, $\beta$, and $\gamma$ phases, we start with the lattice parameters provided by Materials Project \cite{38} where available. The unit cell is relaxed at a range of volumes around the equilibrium volume, and the cohesive energy per formula unit is calculated from the total energy at self-consistency and the reference energies of the free atoms (not including spin-polarization corrections of the atom). Bulk moduli and first derivatives of the bulk moduli w.r.t. pressure are then extracted for each phase by fitting the corresponding energy vs. volume points to the energy curve obtained from integrating the Birch-Murnaghan equation of state \cite{39} via nonlinear least squares. Transition pressures between different phases are then extracted from these fits via the common tangent method. The structural relaxation results for the internal coordinates were further checked with the all-electron full-potential linearized muffin-tin orbital method (FP-LMTO) as implemented in the QUESTAAL code\cite{40} while keeping the lattice constant ratios fixed. The obtained energy ordering of the phases was found to be consistent with QUANTUM ESPRESSO results provided the same muffin-tin radii were kept for all phases.

To overcome the limitations of semilocal DFT for band gaps, we use the many-body-perturbation theoretical GW method\cite{41}. The band structure calculations performed here use the quasiparticle self-consistent version of the GW method\cite{21} (QSGW) as implemented in the QUESTAAL code\cite{40}. The $G$ in GW represents the one-particle Green’s function, and the $W$ represents the screened Coulomb interaction. The QSGW approach is independent of the DFT starting point Hamiltonian $H_0$, because a non-local exchange-correlation potential is extracted from the GW self-energy, in the form of its matrix in the basis set of $H_0$ eigenstates $\Sigma_{nm} = \frac{1}{2} \text{Re} \left[ \Sigma_{nm}(\epsilon_n) + \Sigma_{nm}(\epsilon_m) \right]$ where $\text{Re}$ indicates taking the hermitian part, and is used to update $H_0$ and iterated to convergence. At each iteration $\Sigma(\omega) = iG^0(\omega) \otimes W(\omega)$ with $\otimes$ standing for convolution. At convergence, the quasiparticle energies of GW become equal to the Kohn-Sham eigenvalues of the updated $H_0$. This approach is known to give much more accurate band gaps than semilocal DFT but is known to systematically underestimate the band gaps slightly because the screening of $W$ is calculated in the random phase approximation and thereby underestimates screening by not including electron-hole interaction effects. This shortcoming can be overcome by including ladder diagrams\cite{42,43} but this is still a rather expensive approach and it was found that reducing the self-energy correction $\Sigma - \Sigma_{\text{DF}}$ by a universal factor 0.8, which we call $0.8\Sigma$ provides an practical alternative \cite{44,45}.

The main factors that determine the accuracy and convergence of the FP-LMTO implementation of the QSGW method\cite{21} include the basis-set choice and the k-point mesh on which the self-energy is calculated. In the FP-LMTO method we use augmented spherical waves with smoothed Hankel functions as radial functions outside the spheres and typically use a basis set with two sets of Hankel function energies and smoothing radii. Here we use an $spdfsdp$ basis set on each of the atoms, which means one set of smoothed Hankel functions includes orbitals up to $f$ and the second up to $d$ spherical harmonics. The smoothing radii and energies are chosen in a standard way by fitting these radial wave functions to the tail of the free atom eigenstates. The basis functions are expanded to $l_{\text{max}} = 4$ within each augmentation sphere. To further test the convergence, we added high-energy $s$ and $p$ local orbitals but found them to affect the band gap negligibly. The two-point quantities, such as the bare and screened Coulomb interaction $W$ are represented in a separate basis set of Bloch functions which include products of partial waves inside the spheres and plane waves projected on the interstitial region. This basis set is far more efficient than a plane wave basis set at representing the screening within the Hilbert space of the bands of interest and thereby also reduces the need to include high-lying empty states in calculating the polarization propagator $P$ used in $W = v + vPW$ with the bare Coulomb interaction and in the calculation of $\Sigma$. The mixed product basis set and interstitial plane wave basis functions in the QSGW scheme are expanded to $G_{\text{max}}$ of 2.7 Ry$^{1/2}$ and 3.3 Ry$^{1/2}$, which are standard values.

The final (i.e. after checking convergence) k-meshes and energy cutoffs for $\Sigma$ used in the QSGW calculations for each phase are given in Table I. In the QSGW iterations the $\Sigma$ is replaced by an average value between $E^\text{max}_{\Sigma}$ and $E^\text{max}_{\Sigma} - 0.5$ Ry. The atom-centered LMTO basis set provides a natural interpolation scheme for the self-energy matrix to a finer k-point mesh used in the charge-potential self-consistency iterations and for obtaining the bands along the symmetry lines. It thus provides accurate band dispersions and also effective masses. For details about the QSGW implementation we refer the reader to the method description papers \cite{21,40}.

| Phase | k-Mesh | $E^\text{max}_{\Sigma}$ (Ry) |
|-------|--------|-------------------------------|
| $\alpha$ | $6 \times 6 \times 6$ | 3.9 |
| $\beta$ | $3 \times 3 \times 3$ | 3.5 |
| $\gamma$ | $3 \times 3 \times 3$ | 3.4 |
First, we discuss the fitted energy vs. volume curves for α, β, and γ-LiAlO₂, along with common tangents corresponding to the β → α (green dashed) and γ → α (blue dashed) and γ → β (black dotted) high-pressure phase transitions.

TABLE II. Fitting parameters corresponding to Fig. 2, $B_0$, bulk module at equilibrium, $B'_0$, pressure derivative of the bulk modulus at equilibrium volume, $p_t$ is the transition pressure.

| Phase | $B_0$ (GPa) | $B'_0$ | $p_t$ (GPa) |
|-------|-------------|--------|-------------|
| α     | 136         | 3.64   |             |
| β     | 70.5        | 6.01   | 1.4         |
| γ     | 90.2        | 3.14   | 0.98        |

These results agree well with those of Singh et al. [28] who also found the β and γ phases to have very close energy minima and establish a γ → α transition at ~1.3 GPa. They obtain this by calculating the energy and enthalpy directly as function of pressure, by explicitly imposing the pressure as a stress tensor as independent variable in their calculation, whereas we start from the energy-volume curves and use the common tangent construction, but in principle, these procedures should give equivalent results. They also mention that in the range 0 − 1.2 GPa the β-structure already has lower enthalpy. We calculate a transition pressure of 0.22 GPa for γ → β based on the fitted equations of state.

The study by Singh et al. [28] is more complete than ours in terms of the phase diagrams by their inclusion of temperature and entropy effects and by also considering the higher pressure transitions to the δ-phase but for low temperatures our results agrees well with theirs. Previously, Sailuam [29] studied the γ → δ transition and found a transition pressure of about 2-3 GPa depending on which functional was used. This agrees qualitatively with Singh et al. [28]. They did not consider the α-phase but did evaluate energy barriers between the phases as function of pressure. We preferred here to focus on the basic tetrahedral to octahedral phase transition by considering the simpler α phase. After all, the δ-phase which is a disordered cubic phase with tetragonal distortion is not as well established structurally or can only approximately be described by a small unit cell because of the fractional occupations of lattice sites.

For reference, we give the equilibrium lattice constants of each phase in Table III as obtained from the Quantum Espresso minimization. These are used later for the electronic structure on which we focus. For the
α-phase, we here use the primitive rhombohedral cell parameters \( a \) and the opening angle between the three equal size lattice vectors. To compare with the hexagonal conventional cell, used in the work by Singh et al., \[ \alpha_h = \sqrt{2}a_c \sqrt{1 - \cos \alpha}, \quad c_h = 3a_c \sqrt{1 + 2 \cos \alpha/\sqrt{3}}. \] This gives \( a_h = 2.82 A, \quad c_h = 14.36 A, \) in good agreement with the values by Singh et al. \[28\].

It is also interesting to study how the lattice parameters themselves change as functions of unit cell volume. For the rhombohedral α-structure the volume of the unit cell is given by \( V = a^3 \sqrt{3/4} - 3 \cos \alpha + 2 \cos^3 \alpha \). Part (a) of Fig. 3 shows that the opening angle \( \alpha \) between each pair of lattice vectors, decreases with increasing volume. For the \( β \)-structure we can see in panel (b) that \( b/a \) and \( c/a \) stay more or less constant as the volume is decreased until the volume approaches the region where the phase transition to the α-phase occurs. The sudden change in these ratios indicates the incipient instability of the \( β \)-structure and is possibly related to the transition path between wurtzite and rocksalt suggested in Ref. 46. Likewise in the γ-structure, the \( c/a \) ratio is seen to increase when approaching the transition volume but otherwise stays constant and \( b/a \) stays equal to 1 as required by symmetry. We have checked that during the relaxation procedure, the symmetries required by each lattice were maintained.

### B. Band structures

For our final band structure calculations, we use the lattice parameters corresponding to the lowest-energy point on each of the equation of state fits of Fig. 3 i.e. those given in Table 111.

The QSGW 0.8Σ approximation band structure of α-LiAlO\(_2\) is shown over a wide energy range in Fig. 3 with corresponding plots of the partial densities of states (resolved by \( ℓ \)) in both the valence and conduction bands shown in Fig. 5. We find that the \( α \) phase has an indirect gap of 9.30 eV, with the conduction band minimum occurring at the \( Γ \)-point. The indirect nature is already present also in the GGA-band structure. From the partial densities of states, we can discern that the deep-lying bands spanning \( ~20 \) to \( ~17.5 \) eV are those derived primarily from the oxygen-2s orbitals. The higher-lying valence states from \( ~5 \) to \( 0 \) eV are primarily due to the oxygen-2p-derived bands, though there are contributions from both aluminum-3s and 3p as well because these are bonding states with the cation atomic orbitals. The lowest-lying (around 10 eV) conduction states consist of a mixture of lithium-2s, (antibonding) oxygen-2s and 2p, and aluminum-3s orbitals. At higher energy, there are peaks corresponding to significant lithium-2s, oxygen-2p, and aluminum-3p contributions. This confirms the ionic picture in which Li donates its electrons to the oxygen.

We now turn to a magnified view of the valence states near the Fermi level, shown in Fig. 6. This show that two almost equal energy valence band maxima (VBM) occur between \( Γ \) and \( L \) and \( Γ \) and \( S_0 \). The nomenclature for the high-symmetry points follows the convention of the Bilbao crystallographic server website (https://www.crysalis.crystallography) and is also given in Fig. 4. The conduction band minimum (CBM) meanwhile is at \( Γ \) and the material thus has an indirect band gap. At \( Γ \) the VBM is doubly degenerate and has \( E_u \) symmetry of the \( D_{3d} \) point group, which is \( (x, y) \)-like while the state below it is non-degenerate with \( A_{1u} \) symmetry, which is \( z \)-like. This indicates that direct vertical transitions from the VBM at \( Γ \) to the conduction band which has \( A_{1g} \) symmetry (\( s \)-like) are dipole-allowed for polarization perpendicular to the three-fold symmetry axis, while the transitions from the crystal field split-off state will occur for polarization along the symmetry axis. This is confirmed by the optical absorption calculations discussed below. However, the indirect gap is about 0.1 eV lower than the direct gap. One may notice some avoided band crossings just below the VBM along \( Γ - T \), \( Γ - L \) and \( Γ - S_0 \). These were checked by using a fine spacing of the \( k \)-points along the lines and indicate that these bands belong to the same irreducible representation of the group of \( k \) along these lines and can therefore not cross.

The band structure of the \( β \)-structure is shown in Figs. 7\[9\] and 10. The \( ℓ \)-resolved partial densities of states are shown in Fig. 8. The overall orbital character of the bands is the same as in the \( α \)-structure. The zoom in near the VBM shows again an indirect band gap, and which is also already present in the GGA. The VBM occurs near the point \( T \), which is \( (0, 0.5, 0.5) \) in units of the reciprocal lattice vectors. An even closer zoom shown in Fig. 10 right near the \( T \) point in the directions \( T - Z \) and \( T - R \) shows that \( T \) is a saddle point with a minimum in the \( T - Z \) direction and a maximum along \( T - R \). The line along \( T - Z \) contains two maxima close in energy to one another. It also is at a maximum in the \( T - Y \) direction. Thus, great care is required to determine the effective mass tensor at the actual VBM. The VBM at \( Γ \) lies \( ~0.24 \) eV below it. The valence bands at \( Γ \) from the highest one and down have irreducible symmetries, \( a_2 \), \( a_1 \), \( b_1 \), \( b_2 \) which are respectively forbidden, allowed for \( z, x, y \) polarization for transitions the the \( a_1 \) symmetry CBM at \( Γ \). These symmetry labels were determined by inspection of the eigenvectors.

Finally for the \( γ \) structure, the band structure is shown in Figs. 11\[12\] and 13 with the \( ℓ \)-resolved partial densities of states in Fig. 12. The overall orbital character of the bands is similar to the \( α \) and \( β \) phases. The zoom up show that this phase has a direct band gap. The CBM has \( A_1 \) symmetry but the VBM has \( B_1 \) symmetry in the point group \( D_4 \). This implies that the gap is pseudodirect. In other words it is direct but dipole forbidden. The next lower VBM at \( Γ \) is double degenerate and therefore has \( E \) symmetry but lies about \( 0.63 \) eV lower. However, along \( Γ - X \) the group of \( k \) is \( C_2 \) and contains the \( C_{2z} \) symmetry axis under which \( B_1 \) is even. This means direct vertical
and 6.2 eV respectively. Qualitatively, the differences in conduction band become allowed for transitions from the valence band along $\Gamma B$ direction, under which $\alpha$ eV for $z$ the direct gap at $\Gamma$ but also very close to it transitions for states along the $\Gamma X$ direction become allowed. We will see that thus both $\alpha$- and $\beta$-polarization should be allowed for energies slightly above the VBM. In other words, the VBM has irreducible representation $C_2$ because the CBM is still even under that $\gamma$-operation. This implies that vertical transitions from the valence band along $\Gamma M$ to the conduction band become allowed for $x$ or $y$ polarization because the CBM is still even under that $C_2$-operation. In other words, the VBM has irreducible representation $B$ while the CBM has irreducible representation $A$ and transitions are allowed for $x$ or $y$ because these belong to the $B$ irrep. Along $\Gamma Z$ the group of $k$ is $C_4$ and the top VB belongs to the $B$ irreducible representation and thus the transitions are still forbidden. We will see that thus both $x$ and $y$ polarization should be allowed for energies slightly above the direct gap at $\Gamma$ but also very close to it transitions for $z$ polarization.

The band gaps of all three phases are summarized in Table IV. Our GGA band gaps of 4.48 eV for $\gamma$ and 6.18 eV for $\alpha$ agree reasonably with Singh et al.’s 4.7 eV and 6.2 eV respectively. Qualitatively, the differences in gap between the different structures agree well with prior work in the sense that the $\beta$ structure has only slightly higher gap than $\gamma$ but the octahedral phases have a significantly larger gap. The QSGW gaps of course are significantly larger and are more reliable. In terms of details of the band structure, prior work missed the indirect nature of the gap in the $\alpha$ and $\beta$ structures. For the $\alpha$-structure, they used the conventional hexagonal cell and hence show the bands in the corresponding hexagonal Brillouin zone. They may thus have missed the points where the actual VBM occurs. Secondly, for all three phases, they only show a band structure on large energy scale, were the top valence bands are very flat and therefore it is difficult to ascertain where the actual VBM occurs.

### C. Effective masses

The curvature of the bands near the band edges provide the effective masses, which are important for transport properties. They are summarized in Table V.

As expected from the symmetries of the $\alpha$ and $\gamma$...
FIG. 4. QS\textsuperscript{GW} 0.8Σ band structure of \(\alpha\)-LiAlO\textsubscript{2} spanning a wide range of valence and conduction states.

TABLE IV. Band gaps of \(\alpha\), \(\beta\), and \(\gamma\)-LiAlO\textsubscript{2} from various approximations, of which QS\textsuperscript{GW} 0.8Σ is expected to be the most accurate.

| Phase | GGA  | QSGW | QS\textsuperscript{GW} 0.8Σ |
|-------|------|------|-----------------------------|
| \(\alpha\) | 6.18 eV  | 10.1 eV  | 9.30 eV  |
| \(\beta\)  | 4.93 eV  | 8.94 eV  | 8.16 eV  |
| \(\gamma\) | 4.48 eV  | 8.47 eV  | 7.69 eV  |

phases, the Γ-point CBM of the \(\alpha\) phase and CBM and VBM of the \(\gamma\) phase have effectively one transverse and one longitudinal effective mass. The valence band masses are significantly higher than the conduction band masses as is evident from the flat top valence band. For the \(\beta\)-phase they were determined by zooming in very closely to the actual VBM along \(T-Z\), as shown in Fig. 10. Note that we here give electron masses, so the negative signs for the VBM indicate positive hole-masses.

D. Optical absorption

The imaginary part of the dielectric function \(\varepsilon_2(\omega)\), which is proportional to the optical absorption coefficient was calculated in the long-wavelength independent particle approximation, ignoring local field and excitonic effects, according to

\[
\varepsilon_2(\omega) = \frac{8\pi^2e^2}{\Omega\omega^2} \sum_v \sum_c \sum_{\mathbf{k}\in BZ} f_{v\mathbf{k}} (1 - f_{c\mathbf{k}}) 
\left| \langle \psi_{v\mathbf{k}} | [H, \mathbf{r}] | \psi_{c\mathbf{k}} \rangle \right|^2 \delta(\omega - \varepsilon_{c\mathbf{k}} + \varepsilon_{v\mathbf{k}})\quad (2)
\]

where the commutator \([H, \mathbf{r}]\) gives the band velocity and includes the contributions from the non-local self-energy, \(\varepsilon_{v\mathbf{k}}\) and \(\varepsilon_{c\mathbf{k}}\) are the valence and conduction band states at \(\mathbf{k}\) obtained in the QSGW method. The \(f_{v\mathbf{k}}\) are the band occupation numbers (Fermi functions at zero temperature) and are 1 for \(n = v\) and 0 for \(n = c\). \(\Omega\) is he volume of the unit cell.

These functions are shown in Figs. 14, 15, and 16 for the \(\alpha\), \(\beta\), and \(\gamma\)-LiAlO\textsubscript{2}, respectively, along with the real parts of the dielectric function \(\varepsilon_1(\omega)\) and the absorption coefficients \(\alpha(\omega)\). The real parts are obtained from the imaginary parts via a Kramers-Kronig transformation, and the optical absorption from the relation \(\alpha(\omega) = 2\varepsilon_2(\omega)/n(\omega)\), where \(n(\omega)\) is the real part of the index of refraction \(n(\omega) = \sqrt{\varepsilon_1(\omega) + 2\varepsilon_2(\omega)}\). The onsets of absorption and their respective polarizations are consis-

TABLE V. Effective electron masses at the VBMs and CBMs of \(\alpha\), \(\beta\), and \(\gamma\)-LiAlO\textsubscript{2}, extracted from the band curvatures near the extremal points.

| Phase/Extreme Point | \(m_{xx}\) (\(m_e\)) | \(m_{yy}\) (\(m_e\)) | \(m_{zz}\) (\(m_e\)) |
|---------------------|---------------------|---------------------|---------------------|
| \(\alpha\) (VBM)    | -6.6                | -0.69               | -2.8                |
| \(\alpha\) (CBM)    | 0.47                | 0.47                | 0.58                |
| \(\beta\) (VBM)     | -1.3                | -0.57               | -0.94               |
| \(\beta\) (CBM)     | 0.43                | 0.39                | 0.36                |
| \(\gamma\) (VBM)    | -1.7                | -1.7                | -2.9                |
| \(\gamma\) (CBM)    | 0.41                | 0.41                | 0.44                |

\(^a\) Principal values of the mass tensor. The masses labeled \(x\) and \(z\) actually correspond to principal axes 15° from the crystal axes.

FIG. 5. \(\ell\)-resolved partial densities of states in \(\alpha\)-LiAlO\textsubscript{2} in the (top) valence and (bottom) conduction bands.
FIG. 6. Magnified view of the high-lying valence states of the QSGW 0.8Σ band structure of α-LiAlO₂.

FIG. 7. QSGW 0.8Σ band structure of β-LiAlO₂ spanning a wide range of valence and conduction states.

FIG. 8. ℓ-resolved partial densities of states in β-LiAlO₂ in the (top) valence and (bottom) conduction bands. A Gaussian broadening with a width of 0.1 eV was applied to these spectra to better distinguish some of the features.

From Γ either along Γ – X or Γ – M the onset of optical transitions would not follow the usual √(E – E₀) behavior for direct allowed transitions but rather a ((E – E₀)³/2) behavior, where E₀ is the onset of transitions. On the other hand, even for the direct allowed transitions in the β case, the expected √(E – E₀) behavior is only seen very close to the onset. This is because the conduction band at somewhat higher energies above the CBM becomes linear in k, in which case, the ϵ₂(ω) will turn over to become proportional to ω². In the γ-phase we have a combination of linearly increasing matrix elements and a conduction band that turns from parabolic to linear behavior but in any case, it is clear from the figures that the absorption coefficient turns on slower for the γ than for the β case.

At present, no experimental data on the optical absorption or dielectric function over the range we have calculated, are available. This is not surprising giving the difficulty to obtain adequate light sources in this deep UV range, which is only available at synchrotrons. As mentioned already in the introduction, there were two prior experimental studies [30, 31] which showed a decrease in transmission at about 190 nm or 6.5 eV for the γ-phase. No data are available for the high-pressure phases. These onsets of absorption are significantly lower than the here
FIG. 9. Magnified view of the high-lying valence states of the QSGW 0.8Σ band structure of β-LiAlO$_2$.

FIG. 10. Close zoom-ins on the saddle point at $T$ and the actual VBM along $T - Z$ in the valence bands of β-LiAlO$_2$. The left panel shows the top-most bands along $R - T - Z$ and the right panel shows the top-most bands along $Y - T - S$.

calculated quasiparticle band gaps. There are two possible reasons for this discrepancy: finite temperature effects and zero-point motion of the band gap and secondly, excitonic effects. In a very ionic material, as we have here, excitonic effects can be expected to be large and could substantially reduce the optical absorption onset from the band-to-band onset. An initial estimate can be made within the hydrogenic Wannier exciton model. Using a reduced mass of 0.33 and a dielectric constant of about 3.5, the binding energy would be 0.36 eV. On the other hand, electron-phonon coupling band gap renormalization effects could also be substantial leading to a zero point motion correction and even larger reductions at room temperature. A full calculation of these effects is beyond the scope of the present paper. However, comparing to other ionic oxides like MgO suggest the finite temperature effects could yield be of order 0.5 eV. Combining this with the estimated exciton binding energy a reduction by about 0.9-1.0 eV would bring the absorption onset down to 6.7 eV in reasonable agreement with experiment. Finally, we should point out that the optical measurements carried out thus far had a cut-off at about 190 nm in the UV and only a start of the reduction of transmission was measured at this wave length. The nature of the absorption onset, which we here predict to be forbidden direct is therefore still unclear but is challenging to measure with standard available light sources in the UV. Furthermore, defect related absorption band tails can often lead to an underestimate of the band gap.

E. Silicon Doping of γ-LiAlO$_2$

With band gaps larger than 7 eV, the utility of LiAlO$_2$ in ultra-wide band gap (UWBG) semiconductor applications will depend heavily on whether it can successfully be doped. Otherwise, it is just another insulator. The electrical conductivity is also of importance in the context of Li-diffusion and the opportunities for LiAlO$_2$ as electrodes in Li batteries. For successful $n$-type doping one must find a dopant which leads to shallow donor levels in the gap and can be readily introduced in the material. For example, Si is used as $n$-type dopant in GaN but in Al$_x$Ga$_{1-x}$N alloys of high Al content $x > 0.8$ leads to a deep donor due to a distortion of the defect structure away from the simple substitutional cation site.[17] which is called a DX type defect. Donor binding energies larger than a few 0.1 eV are usually considered ineffective for doping. Inspired by prior work on LiGaO$_2$ [10] we were consider Si doping in LiAlO$_2$.

In this section we present the results of a band structure calculation for γ-LiAlO$_2$ doped with silicon as a candidate $n$-type dopant. First, we simply replaced one Al in the 16 atom unit cell by Si, which corresponds to 25% doping. While this is an unrealistically high doping level, the advantage is that we can readily perform the calculation at the QSGW level. Next, we studied a 128 atom $2 \times 2 \times 2$ supercell, with a single Si$_{Al}$ corresponding
FIG. 12. ℓ-resolved partial densities of states in γ-LiAlO₂ in the (top) valence and (bottom) conduction bands. A Gaussian broadening with a width of 0.1 eV was applied to these spectra to better distinguish some of the features.

We first calculate it at the GGA level. Finally, we use a recently developed cut-and-paste approach [48] to obtain approximately the QSGW band structure in the 128 atom cell with a single Si, from the real-space self-energy of the perfect crystal and the self-energy matrix of the Si atom and its neighbors from the 16 atom QSGW calculation. In this approach we use a cut-off of the real space self-energy matrices of 6.27 Å. Fig. 17 shows the results of the 16 atom cell. The Fermi level now lies about 2 eV above the CBM indicating that no new levels occur in the gap and the additional electron just starts to fill the conduction band. However, the bottom of the conduction band is clearly strongly Si dominated and the QSGW gap at 5.33 eV is significantly lower than that of pure γ-LiAlO₂. This might at first sight indicate that the Si may actually introduce a deep donor level, which is here broadened into an impurity band because of the high Si concentration and merging with the conduction band. We need a larger cell to refute this possibility.

The results for the 128 atom cell are shown in Fig. 18. We here show only two directions of the Brillouin zone. The faint red-color of the lowest three conduction bands indicates their small Si contribution. The back ground color for the bands without any Si-s was chosen a light grey because otherwise it would obscure the red color. The lowest three conduction bands both have some Si-s contribution but it is less pronounced because the Si concentration is lower and the Fermi level now lies only 0.67 eV above the CBM. These bands essentially are the folded version of the conduction band of the 16 atom cell in the Brillouin zone of the supercell, which has half the size in each direction, although at the new Brillouin zone edge, a gap opens. The band gap between the O-2p like
VBM and the Si-like CBM is about 7.28 eV and is close that of the corresponding perfect crystal gap of 7.43 eV. It is here a little bit lower than the converged value of Table [V] because of the real-space cut-off of the self-energy. Thus the Si still pushes the CBM slightly down but less so than in the 16 atom cell and there is no evidence of a deep donor level. Compared to the corresponding GGA results, the CBM is simply pushed up along with its Si contribution. These results did not include relaxation of the structure. However, relaxation of the nearest neighbor O atoms around the Si, show an inward relaxation of the Si-O bonds by about 6%. They do not indicate a strong distortion or DX center formation. Indeed, it did not lead to any notable difference in the band structure in the GGA, which still does not show a defect level to emerge in the gap.

These results indicate n-type doping should be possible. However, the hydrogenic donor model would predict $E_B = m^* R / \varepsilon^2$, which, with $R$ the Rydberg unit (13.6057 eV), $m^* \approx 0.4$ and $\varepsilon \approx 3.5$, gives $E_B \approx 0.4$ eV. This estimate includes only electronic screening. Estimating the phonon contributions to the screening requires the calculation of LO-phonons, which we have not yet done. However, comparison with LiGaO$_2$ indicates a static dielectric constant of about 6.5 is expected. This would reduce the donor binding energy to about 0.1 eV. This shows that even if Si doping does not produce a well separated defect band in the gap in a first-principles calculation in the cell size we can here accommodate, it will likely act as a relatively deep donor with of order 100 meV binding energy. This is similar to LiGaO$_2$ for which experimental confirmation of n-type doping also is still to be accomplished but promising enough to warrant experimental attempts to dope these materials with Si. While these estimates indicate efficient n-type doping may be challenging for both LiGaO$_2$ and LiAlO$_2$, they would significantly extend the gap range of UWBG semiconductors. Some compromise between efficiency of
doping and larger band gaps may be necessary. For comparison, in $\beta$-Ga$_2$O$_3$, the conduction band effective mass is about 0.3 and the dielectric constant about 10, giving a binding energy of order 40 meV. The expected donor binding energy in LiGaO$_2$ and LiAlO$_2$ are thus relatively high, but on the other hand, still smaller than typical acceptor binding energies related to $p$-type doping in for example GaN.

IV. CONCLUSIONS

The main conclusions of this paper are as follows. First, in terms of structures, the $\gamma$-phase has the lowest energy but is very close to the $\beta$-phase, which may already be stabilized at slight pressures of about 0.2 GPA. A phase transition from these tetrahedrally bonded phases to the octahedrally bonded $\alpha$-phase is predicted to occur near 1GPa. The band structures of the three phases were obtained in the QSGW method and yield band gaps larger than 7 eV with a pseudodirect gap of 7.69 eV in the $\gamma$-phase, indirect gap of 8.16 eV in the $\beta$-phase, and indirect gap of 9.30 eV in the $\alpha$-phase. The calculated onset of absorption in the $\gamma$-phase, slightly above the pseudodirect gap of 7.7 eV and stemming from direct transitions along $\Gamma - M$ and $\Gamma - X$ is significantly higher than the until now reported optical absorption onset of about 6.5 eV. We suggested this can be explained by a combination of finite temperature renormalization effects on the gap due to electron-phonon coupling and strong excitonic effects in this ionic material. A fuller investigation of these effects will require additional work in the future. For future use, we have provided details of the band structure near the band edges, including the effective masses. We have also briefly discussed the possibility of silicon as a donor for $\gamma$-LiAlO$_2$, which indicates that $n$-type doping should be possible although efficient doping will be challenging due to the relatively high donor binding energy.

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[1] S.-G. Ma, T. Gao, S.-C. Li, X.-J. Ma, Y.-H. Shen, and T.-C. Lu, Theoretical investigations on the alpha-LiAlO$_2$ properties via first-principles calculation, Fusion Engineering and Design 113, 324 (2016).
[2] R. R. Vanfleet, J. A. Simmons, D. W. Hill, M. M. C. Chou, and B. H. Chai, Antiphase ordering and surface phases in lithium aluminate, Journal of Applied Physics 104, 093530 (2008).
[3] M. Marezio, The crystal structure and anomalous dispersion of $\gamma$-LiAlO$_2$, Acta Crystallographica 19, 396 (1965).
[4] X. Li, T. Kobayashi, F. Zhang, and K. Kimoto, A new high-pressure phase of LiAlO$_2$, Journal of Solid State Chemistry - J SOLID STATE CHEM 177, 1939 (2004).
[5] L. Lei, D. He, Y. Zou, W. Zhang, Z. Wang, M. Jiang, and M. Du, Phase transitions of LiAlO$_2$ at high pressure and high temperature, Journal of Solid State Chemistry 181, 1810 (2008).
[6] https://jp-minerals.org/vesta/en/.
[7] https://www.questaal.org/docs/.
[8] J. Charpin, F. Botter, M. Briec, B. Rasneur, E. Roth, N. Roux, and J. Sannier, Investigation of $\gamma$ lithium aluminates as tritium breeding material for a fusion reactor blanket, Fusion Engineering and Design 8, 407 (1989).
[9] R. B. Khomane, A. Agrawal, and B. D. Kulkarni, Synthesis and characterization of lithium aluminate nanoparticles, Materials Letters 61, 4540 (2007).
[10] V. Batra, S. Maudgal, S. Bali, and P. Tewari, Development of alpha lithium aluminate matrix for molten carbonate fuel cell, Journal of Power Sources 112, 322 (2002).
[11] X. Ke, X. Jun, D. Peizhen, Z. Yongzong, Z. Guoqing, Q. Rongsheng, and F. Zujie, $\gamma$-LiAlO$_2$ single crystal: a novel substrate for GaN epitaxy, Journal of Crystal Growth 198, 127 (1998).
[12] A. Boonchun and W. R. L. Lambrecht, Electronic structure, doping, and lattice dynamics of LiGaO$_2$, in [Oxide-based Materials and Devices II] Vol. 7940, edited by F. H. Teherani, D. C. Look, and D. J. Rogers, International Society for Optics and Photonics (SPIE, 2011) pp. 129–134.
[13] A. Boonchun, K. Dabsamut, and W. R. L. Lambrecht, First-principles study of point defects in LiGaO$_2$, Journal...
of Applied Physics 126, 155703 (2019).

[14] C. A. Lenyk, M. S. Holston, B. E. Kananen, L. E. Halliburton, and N. C. Giles, Lithium and gallium vacancies in LiGaO2 crystals, Journal of Applied Physics 124, 135702 (2018).

[15] D. Slachkov, W. R. L. Lambrecht, K. Dabsamut, and A. Boonchun, Computational study of electron paramagnetic resonance spectra for li and ga vacancies in LiGaO2, Journal of Physics D: Applied Physics 53, 17LT01 (2020).

[16] K. Dabsamut, A. Boonchun, and W. R. L. Lambrecht, First-principles study of n- and p-type doping opportunities in LiGaO2, Journal of Physics D: Applied Physics 53, 274002 (2020).

[17] I. Ohkubo, C. Hirose, K. TAMURA, J. Nishii, H. Saito, H. KONINMA, P. AHMET, T. ChIKYOW, T. Ishii, S. Miyazawa, Y. Segawa, T. FUKUMURA, and M. Kawasaki, Heteroepitaxial growth of β-LiGaO2 thin films on ZnO, Journal of Applied Physics 92, 5587 (2002).

[18] J. T. Wolan and G. B. Hoflund, Chemical alteration of the native oxide layer on LiGaO2(001) by exposure to hyperthermal atomic hydrogen, Journal of Vacuum Science & Technology A 16, 3414 (1998).

[19] C. Chen, C.-A. Li, S.-H. Yu, and M. M. Chou, Growth and characterization of β-LiGaO2 single crystal, Journal of Crystal Growth 402, 325 (2014).

[20] N. W. Johnson, J. A. McLeod, and A. Moewes, The electronic structure of lithium metagallate, Journal of Physics: Condensed Matter 23, 445501 (2011).

[21] M. van Schilfgaarde, T. Kotani, and S. Faleev, Quasiparticle Self-Consistent GW Theory, Phys. Rev. Lett. 96, 226402 (2006).

[22] S. K. Radha, A. Ratnaparkhe, and W. R. L. Lambrecht, Quasiparticle self-consistent GW band structures and high-pressure phase transitions of LiGaO2 and NaGaO2, Phys. Rev. B 103, 045201 (2021).

[23] H. Cao, B. Xia, Y. Zhang, and N. Xu, LiAlO2-coated LiCoO2 as cathode material for lithium ion batteries, Solid State Ionics 176, 911 (2005).

[24] D. Wiedemann, S. Nakhal, J. Rahm, E. Witt, M. M. Islam, S. Zander, P. Heitjans, H. Schmidt, T. Breddow, M. Wilkening, and M. Lërch, Unravelling Ultraslow Lithium-Ion Diffusion in γ-LiAlO2: Experiments with Tracers, Neutrons, and Charge Carriers, Chemistry of Materials 28, 915 (2016).

[25] D. Wiedemann, S. Indris, M. Meven, B. Pedersen, H. Boysen, R. Uecker, P. Heitjans, and M. Lërch, Single-crystal neutron diffraction on γ-LiAlO2: structure determination and estimation of lithium diffusion pathway, Zeitschrift für Kristallographie - Crystalline Materials 231, 189 (2016).

[26] G. Ceder, Y.-M. Chiang, D. R. Sadoway, M. K. Aydinol, Y.-I. Jang, and B. Huang, Identification of cathode materials for lithium batteries guided by first-principles calculations, Nature 392, 694 (1998).

[27] M. A. K. Lakshman Dissanayake, Nano-composite solid polymer electrolytes for solid state ionic devices, Ionics 10, 221 (2004).

[28] B. Singh, M. K. Gupta, R. Mittal, and S. L. Chaplot, Phonons, phase transitions and thermal expansion in LiAlO2: an ab initio density functional study, Phys. Chem. Chem. Phys. 20, 12248 (2018).

[29] W. Salam, K. Sarasamak, and S. Limpijumnong, High Pressure Phase of LiAlO2: A First Principles Study, Integrated Ferroelectrics 156, 15 (2014).

[30] T. Huang, S. Zhou, H. Teng, H. Lin, J. Zou, J. Zhou, and J. Wang, Growth and Characterization of High-quality LiAlO2 Single Crystal, J. Mater. Sci. Technol. 24, 145 (2008).

[31] J. Zou, S. Zhou, J. Xu, L. Zhang, Z. Xie, P. Han, and R. Zhang, Influence of vapor transport equilibration on the crystal quality and thermal-expansion coefficients of γ-LiAlO2, Journal of Applied Physics 98, 084909 (2005).

[32] M. Holston, J. McClory, N. Giles, and L. Halliburton, Radiation-induced defects in LiAlO2 crystals: Holes trapped by lithium vacancies and their role in thermoluminescence, Journal of Luminescence 160, 43 (2015).

[33] M. Holston, I. Ferguson, N. Giles, J. McClory, and L. Halliburton, Identification of defects responsible for optically stimulated luminescence (OSL) from copper-diffused LiAlO2 crystals, Journal of Luminescence 164, 105 (2015).

[34] J. Jimenez-Becerril and I. García-Sosa, Synthesis of lithium aluminate by thermal decomposition of a lithium dawsonite-type precursor, Journal of Ceramic Processing Research 12, 52 (2011).

[35] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Scalzi, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, Journal of Physics: Condensed Matter 21, 395502 (2009).

[36] P. E. Blöchl, Projector augmented-wave method, Phys. Rev. B 50, 17953 (1994).

[37] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77, 3865 (1996).

[38] http://www.materialsproject.org/.

[39] F. Birch, Finite Elastic Strain of Cubic Crystals, Phys. Rev. 71, 809 (1947).

[40] D. Pushov, S. Acharya, W. R. Lambrecht, J. Jackson, K. D. Belaschenko, A. Chantis, F. Jamet, and M. van Schilfgaarde, Questaal: A package of electronic structure methods based on the linear muffin-tin orbital technique, Computer Physics Communications 249, 107065 (2020).

[41] L. Hedin, New Method for Calculating the One-Particle Green’s Function with Application to the Electron-Gas Problem, Phys. Rev. 139, A796 (1965).

[42] B. Cunningham, M. Grüning, P. Azarhoosh, D. Pushov, and M. van Schilfgaarde, Effect of ladder diagrams on optical absorption spectra in a quasiparticle self-consistent GW framework, Phys. Rev. Materials 2, 034603 (2018).

[43] B. Cunningham, M. Grüning, D. Pushov, and M. van Schilfgaarde, QSW: Quasiparticle Self consistent GW with ladder diagrams in W (2021), arXiv:2106.05759 [cond-mat.mtrl-sci].

[44] D. Deguchi, K. Sato, H. Kino, and T. Kotani, Accurate energy bands calculated by the hybrid quasiparticle self-consistent GW method implemented in the ecal package, Jap. J. Appl. Phys. 55, 051201 (2016).
[45] C. Bhandari, M. van Schilfgaarde, T. Kotani, and W. R. L. Lambrecht, All-electron quasiparticle self-consistent $GW$ band structures for SrTiO$_3$ including lattice polarization corrections in different phases, Phys. Rev. Materials 2, 013807 (2018).

[46] S. Limpijumnong and W. R. L. Lambrecht, Homogeneous Strain Deformation Path for the Wurtzite to Rocksalt High-Pressure Phase Transition in GaN, Phys. Rev. Lett. 86, 91 (2001).

[47] F. Mehnke, T. Wernicke, H. Pingel, C. Kuhn, C. Reich, V. Kueller, A. Knauer, M. Lapeyrade, M. Weyers, and M. Kneissl, Highly conductive n-Al$_x$Ga$_{1-x}$N layers with aluminum mole fractions above 80%, Applied Physics Letters 103, 212109 (2013).

[48] O. Dernek, D. Skachkov, W. R. L. Lambrecht, and M. van Schilfgaarde, Real space representation of the quasiparticle self-consistent $GW$ self-energy and its application to defect calculations (2022), arXiv:2202.09396.