Ab-initio investigation of Er$^{3+}$ defects in tungsten disulfide

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We use density functional theory (DFT) to explore the physical properties of an Er$_W$ point defect in monolayer WS$_2$. Our calculations indicate that electrons localize at the dangling bonds associated with a tungsten vacancy (V$_W$) and at the Er$^{3+}$ ion site, even in the presence of a net negative charge in the supercell. The system features a set of intra-gap defect states, some of which are reminiscent of those present in isolated Er$^{3+}$ ions. In both instances, the level of hybridization is low, i.e., orbitals show either strong Er or W character. Through the calculation of the absorption spectrum as a function of wavelength, we identify a broad set of transitions, including one possibly consistent with the $^4I_{15/2} \rightarrow ^4I_{13/2}$ observed in other hosts. Combined with the low native concentration of spin-active nuclei as well as the two-dimensional nature of the host, these properties reveal Er:WS$_2$ as a potential platform for realizing spin qubits that can be subsequently integrated with other nanoscale optoelectronic devices.

KEYWORDS: rare-earth ions, point defects, tungsten disulfide, optoelectronic properties, density functional theory

I. INTRODUCTION

Single photon emitters in the form of rare-earth (RE) impurities in garnet minerals are being actively explored as solid-state spin-qubits, largely due to their electronically screened $4f$ states that result in hours-long coherence lifetimes$^3$ and, as in the case of Er$^{3+}$, homogeneous linewidths as narrow as 50 Hz in the telecom band.$^{2,3}$ In addition, these systems show promise for nanoscale sensing and as long-term quantum memories, with storage times exceeding a second.$^{4–7}$

Despite the intrinsic potential of RE ions, most host materials bring in unwanted interactions, particularly in the form of deleterious hyperfine couplings between the ion and surrounding spin-active nuclei and/or impurities.$^{8,9}$ Dynamic decoupling techniques have been adapted to mitigate this problem, though at the expense of an increased complexity in the control protocols.$^{1,8}$ Isotopic depletion of spin-active nuclei can arguably prove effective but this route is not viable for all atomic species (e.g., yttrium), and material growth tends to be costly, particularly if the host contains heavy elements.$^{10,11}$ Even in the case of materials where hyperfine couplings are less critical (such as Er$^{3+}$:YSO or Nd$^{3+}$:YVO$_4$)$^{3,8,12}$ the problem of interfacing RE spins with optoelectronic elements remains a challenge as these hosts are not necessarily compatible with present material processing methods. All in all, these obstacles impose serious constraints for quantum information processing applications, particularly if scalability and device-integration requirements are taken into account.

With these considerations in mind, this work investigates the point defect formed by a substitutional Er impurity in tungsten disulfide (WS$_2$). Guiding this selection is the notion of the RE ion as a ‘building block’, rather insensitive to the host material of choice.$^{13}$ The system also leverages the two-dimensional (2D) nature of WS$_2$, suitable for integration into heterostructures and optoelectronic devices.$^{14–16}$ From among other candidate materials, tungsten disulfide is especially attractive for three main reasons: (1) the lattice is sufficiently large to accommodate a substitutional Er (taking the place of a W site) without introducing much strain, (2) a sizable bandgap of $\sim$2.1 eV$^{16}$ makes it suitable for excitation and detection of photon emission in the near infrared, and (3) both S and W isotopes are mostly spin-less nuclei (their spin-active isotopes have natural abundances of only 0.7% and 14%, respectively) which results in an intrinsically low nuclear-spin material.

Recent years have seen various studies on rare-earth defects in solid-state systems using electronic structure methods. Defect systems require the explicit consideration of large system sizes (supercells) to accurately describe the host-defect interaction and limit defect-defect interactions. At the same time, the strongly correlated nature of the localized $4f$ states in

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Er$^{3+}$ limits the number of applicable electronic structure methods. While the many-body character of the Er$^{3+}$ could be described accurately by recent developments in so-called embedding techniques,\textsuperscript{17–20} such calculations are computationally very demanding if large supercells are required. Due to its much more favorable scaling properties, in the past regular density-functional theory (DFT) methods, in particular the DFT+$U$ approach\textsuperscript{21} has been used to characterize structural and optical properties of Er ions in GaN,\textsuperscript{22,23} AlN,\textsuperscript{24} and ZnO\textsuperscript{25,26} hosts as well as other rare-earth ions such as Eu ions in GaN\textsuperscript{27} with DFT+$U$ or hybrid-functional DFT.\textsuperscript{28}

Following these approaches, in this work we use the DFT+$U$ approach to characterize the electronic properties of Er ions in WS$_2$. Specifically, we determine the formation energies for this defect, and find it is most stable in two different charge states, namely, neutral, and negatively charged. In both instances, electrons localize at dangling bonds leaving behind an Er$^{3+}$ core. Our calculations indicate that the ground state of this system populates the highest energy levels in the WS$_2$ valence band; we also identify unoccupied intra-gap states reminiscent of the structure seen for the Er$^{3+}$ ion in other hosts. Solving the Casida equation and analyzing the resulting oscillator strengths, we conclude that a substitutional Er in WS$_2$ is potentially optically active near $\sim$0.8 eV (1550 nm). Adding to ongoing work targeting spin-active, optically addressable photon emitters in 2D materials,\textsuperscript{29–32} our results highlight the Er impurity in WS$_2$ as an intriguing material platform for applications in solid-state quantum technologies.

II. COMPUTATIONAL METHODS

Our DFT calculations are performed within the projector-augmented wave (PAW) method using the Vienna \textit{ab initio} Simulation Package (VASP).\textsuperscript{33,34} All calculations are within the generalized-gradient approximation (GGA), using Perdew-Burke-Ernzerhof (PBE) functionals\textsuperscript{35} to account for the exchange-correlation interaction. The atomic supercells are composed of 7 by 7 unit-cells for both pristine and Er-doped WS$_2$ monolayers, with a vacuum region of 20 Å along the z-axis to avoid spurious interactions between adjacent layers. Given the large supercell, and because the introduced point defect should yield localized atomic-like electronic states, it is reasonable to sample the irreducible Brillouin zone (IBZ) by using the $\Gamma$-point only. A high 700-eV plane-wave kinetic energy cut-off is chosen for all calculations. Convergence criteria for the electronic and the ionic loops are set to $10^{-8}$ eV and $10^{-4}$ eV/Å, respectively, to ensure convergence to the ground-state structure. Additionally (whenever specified), we have performed non-collinear calculations to add spin-orbit coupling (SOC) self-consistently. We note that in such calculations it is usually safer to switch off all symmetries, which translates in assuming that all atomic configurations belong to the $C_1$ point-group.

For comparison, we have also employed calculations considering symmetry. In both cases, we find a lattice constant of 3.18 Å for unit-cell pristine WS$_2$, and direct bandgaps (at $K$) of 1.82 and 1.56 eV for collinear and SOC cases, respectively. These results agree well with previous calculations based on DFT within PBE\textsuperscript{36,37}

We characterize the overall electronic properties of Er-doped WS$_2$ monolayers by calculating the electronic density of states (DOS) using an 8 by 8 $k$-point grid, while the Kohn-Sham (KS) eigenvalues are calculated along high symmetry paths ($\Gamma$-M-K-$\Gamma$) to obtain the corresponding band structures. Additionally, the optical absorption coefficients are calculated using two different methods: (1) sum over all empty states within the independent particle approximation (IPA),\textsuperscript{38} and (2) the Casida equation (within the Tamm-Dancoff approximation (TDA))\textsuperscript{39–41} for several valence/conduction states, both at the $\Gamma$-point. We perform both sets of calculations at the DFT level, namely, using the PBE exchange-correlation functional.

III. RESULTS AND DISCUSSION

Figure 1(a) shows top and angle views of a substitutional Er impurity in a WS$_2$ monolayer for the negatively charged state. Relaxing the defect structure and comparing it to the bulk WS$_2$ lattice indicates that not much local strain is introduced by the substitution of a W atom in WS$_2$ with Er since the relative size of both species is quite similar. This is evident from the slight bond-length distortions near the Er impurity. For instance, in pristine WS$_2$, we find 2.42 and 3.18 Å for W–S and W–W bond lengths, respectively, while in the Er:WS$_2$ case (with $C_1$ symmetry), Er–S and Er–W are 2.60 and 3.28/3.29 Å. Keeping high symmetry, the atomic configuration of the Er-doped WS$_2$ monolayer remains in the $D_{3h}$ point group, with 2.61 and 3.29 Å for the Er–S and Er–W bond lengths, respectively. Overall, these local distortions remain relatively small (<8% bond-length) across all studied supercell charge states (+1 to -3) for both $C_1$ and $D_{3h}$ cases. We note, however that the lower symmetry structures are 100–300 meV more stable in energy than the high-symmetry structures.
In general, defect stabilities are characterized by calculating the formation energies with respect to the Fermi level. The difference between formation energies leads to the charge state transition energies, as shown for this system in Figure 1(b). In calculating the formation energies, we employ the correction scheme by Freysoldt et al. for charged defects suitable for 2D materials within the supercell approach. First, we find that a substitutional Er in monolayer WS$_2$ is most stable in its neutral ($\text{Er}^0_{\text{W}}$) and negatively charged ($\text{Er}^-_{\text{W}}$) states. Both charge states are stable across a wide (~0.7 eV) range of the bandgap, suggesting that $\text{Er}^0_{\text{W}}$ and $\text{Er}^-_{\text{W}}$ could coexist under photoexcitation conditions. We also find $\text{Er}^-_{\text{W}}^2$ to be stable along a narrow range, which suggests it may also be observed experimentally. Due to the high confinement and strong correlations found in heavy atoms (e.g., REs), Er($f$) states might not be well described by the standard PBE functional within DFT. To preempt this problem, we explore the use of the DFT+$U$ approach, that has been applied to other Er defect systems in the past. We calculate the charge state transition levels for different values of the Hubbard $U$ value in Fig. 1, with $J = 1$ eV in all calculations. We find that changes in formation energy show only a slight dependence on $U$ (up to 7 eV), typically of the order of $10^{-2}$ eV. To obtain the $U$ parameters self-consistently, methods based on constrained RPA or linear response could also be used.

We now focus on the electronic properties of $\text{Er}^-_{\text{W}}$, starting with the electronic band structure and DOS, shown in Figure 2(a) in the absence of spin-orbit coupling (SOC). For reference, we first note that Er$^{3+}$ has eleven electrons in the 4$f$ manifold. Following Hund’s rule, eight of these electrons are paired, leaving three unpaired electrons that give rise to a local magnetic moment. Figure 2(a) shows a similar electronic configuration for substitutional Er in WS$_2$, namely, we find three unoccupied Er($f$) states within the bandgap. On the other hand, the highest Er($f$) occupied states lie on the same (minority) spin channel and just below the valence band maximum (VBM), which we have set to zero in all band structures and DOS plots. A high spin unbalance, resulting from the partial 4$f$ occupation in Er causes the occupied Er($f$) states in the other (majority) spin channel to lie deep within the valence band (VB).

We emphasize the distinction of the total charge state of the supercell and the local charge state of the Er ion. In fact, we find that when changing the overall charge state of the defect, the Er ion remains in its +3-charge state, while the occupancies of localized dangling bonds of W and S atoms are changed instead. As discussed later, these dangling bonds lead to localized defect states reminiscent of a plain W-vacancy ($V_W$), which correlates well with previous studies in TMDs.

We warn that the relative energy alignment of these states — here alternating with the Er$^{3+}$ levels — must be regarded as tentative given the limitations derived from the exchange-correlation treatment in DFT calculations. On the other hand, we find that the dangling bond states have a strong W($d$) character while the empty states of the Er ion stay nearly intact (see DOS plots in Figure 2(a)). These low levels of hybridization suggest the electronic properties of Er$^{3+}$ remain mostly unchanged relative to those found in other host crystals (e.g., YSO).
Because highly aspherical electronic orbitals are present in heavy atoms, SOC is expected to play an important role both for W and Er. The results in Figure 2(b), however, confirm this view only partly: most band features remain unchanged in the presence of SOC, except for a slight reordering of the occupied defect states and a minor decrease in the DOS of Er. On the other hand, inclusion of SOC introduces significant changes in the total energies (of order \(-0.06\) eV/atom), making the overall system more stable. For this reason, we focus our discussion below on results that do include SOC (unless otherwise stated).

Recalculating this band structure at the DFT+\(U\) level, we find that even small \(U\) values (2 eV in Figure 2c) lead to a substantial increase of the gap between occupied and unoccupied states, pushing occupied states well within the VB as indicated by the blue arrow in Figure 2(c). The experimental value for the \(1\i_{5/2} - 4\i_{13/2}\) transition in Er\(^{3+}\) (being an Er\(^{3+}\) HOMO-LUMO transition in our picture) has been determined to be \(-0.80\) eV and almost independent of the host crystal for a wide range of materials.\(^{3,15,52,53}\) From our calculated KS energies in the \(U = 0\) case, we deduce an energy difference (‘transition energy’) of 0.91 eV, which surprisingly only slightly overestimates the experimental value. This transition energy, however, grows as the value of \(U\) is increased, reaching 3.88 eV for \(U = 3\) eV. This finding highlights the limitations of ground-state DFT to study excited state properties for these systems and shows the need for more accurate methods beyond ground state DFT, such as \(\Delta\)SCF,\(^{54,55}\) time-dependent DFT (TDDFT),\(^{39}\) GW/BSE\(^{56}\) or correlated embedding methods.

In the following, we turn our focus to the optoelectronic features of the Er\(_W\) point defect. Typical transition rates in RE ions are comparatively slow, with absorption/emission features that may be surprisingly narrow, but weak in intensity. Thus, we anticipate any absorptive feature in Er\(_W\) coming from Er\(^{3+}\) to be relatively weak. Turning back to the band structure in Figure 2(a) for \(U = 0\), we calculate the projected partial charge densities of the relevant states (Figure 3(b)) to visually inspect the atomic nature of each of these, along with potential hybridization. We see that the Er\(_f\) HOMO state (close to the VBM) is localized without any appreciable hybridization. Further, what we identify as the defect’s HOMO state, appears localized on the Er ion in Figure 3(b) but has mostly a W\(_d\) character, which is the reason why we characterize it as a defect state (def.).

Next level up, we have a slightly delocalized (defect) state that is identified as the LUMO. Clearly, the overlap between the Er\(_f\) HOMO state and this LUMO is minimal. Thus, we focus on the empty states that are above this LUMO level, which we find to be localized almost entirely on the Er ion (\(f\) states). Here we show only two of them as examples, namely the lowest (LUMO+1) and the highest (LUMO+3) in energy among the three, noting that the energy difference between them is rather small (<90 meV). Again, we see negligible hybridization of these Er\(_f\) states. Overlap between the Er\(_f\) HOMO state and these highest empty states within the bandgap should be appreciable, which would correspond to an Er\(_f\)\(\rightarrow\)\(_f\) transition within monolayer WS\(_2\).

To understand the optical features arising from transitions between these electronic states, we turn our focus to the absorption coefficients, as calculated from the imaginary and real components of the dielectric tensor. We expect to see most contributions

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**Figure 2.** Electronic band structure and partial DOS of Er\(_W\) in monolayer WS\(_2\). We calculate the band structures within DFT, (a) without the inclusion of SOC and (b) with SOC. We also calculate the band structures within DFT+\(U\) (\(U = 2\) eV, \(J = 1\) eV shown as an example) including SOC, as shown in (c). DOS labels represent majority and minority spin channels, while pink, blue and gray fills represent partial W\(_d\), Er\(_f\) and total DOS contributions, respectively. Red/orange colors distinguish band structure results without/with SOC. For the DFT+\(U\) case, the Er\(_f\) occupied states go deep within the VB (indicated by the blue arrow in (c)).
from the relevant localized defect states in the vicinity (±1 eV) of the Fermi level, so we focus on the low-energy region of the optical spectrum in all plots. For $V_{W}^{−}$, a few transitions are observed within this spectral region at the independent particle approximation (IPA) level (lower panel in Figure 3(c)), with the lowest (in-plane) ones centered at 0.39, 0.60 and 0.96 eV. At this level, it is not possible to determine the state origins of each excitation within DFT, but we note that these depend on the energy gap between the KS states. Correlating the energy gaps with each absorption maximum, we conclude that the peaks at ~0.96 eV originate from $f(x−f)$ transitions. This value is slightly greater than that observed experimentally (~0.60 eV) though this type of overestimation is typical.38,57 Using the Casida equation, one can expect to obtain more accurate excitation energies, since it is based on linear response TDDFT, which is defined rigorously for electronic excitations.39,58 The corresponding spectrum within this formalism at the Tamm-Dancoff approximation (TDA) level for $V_{W}^{−}$ is shown in the upper panel of Figure 3(c). We now find one main (lowest) transition in the vicinity of 0.9–1.0 eV, with the lower-energy peaks previously observed at the IPA level being absent, and a stronger peak arising at ~1.5 eV.

To better understand the origin of these peaks, we first inspect more closely the optoelectronic signatures of a bare W-vacancy defect states, as well as the possible changes introduced to these states upon doping. To this end, we perform the same set of optoelectronic calculations for $V_{W}^{−}$ (Figure 3(d)). Interestingly, we find similar features in both cases, with some slight changes to the relative intensity and shape of the overall spectrum. In principle, the overall differences observed between the optical signatures of the $V_{W}^{−}$ and $V_{W}^{+}$ centers should be attributed to $V_{W}^{+}$, but to do this rigorously, it is important to disentangle $V_{W}^{−}$ and $V_{W}^{+}$ contributions to the peaks identified in Figure 3(c). To do so, we consider the oscillator strengths $f$, wavefunctions overlap, and transition dipole moments (TDM) for three main cases: (i) the isolated $V_{W}^{+}$ ion, (ii) the $V_{W}^{−}$ defect, and (iii) the $V_{W}^{−}$ center. Comparison between these results allows for an efficient deconvolution of the absorption features into contributions from various excitations, while helping understand the overall optoelectronic properties expected for a $V_{W}^{−}$ center in WS$_2$.

Figure 4(a) zeroes in on the case of bare $V_{W}^{+}$: the top panel shows $f$ as calculated from the Casida equation at the TDA level. We focus only on transitions between the HOMO and the three empty $f$ states (shown in red), as well as those originating from the level right below the HOMO (HOMO-1) and the same three empty $f$ states (shown in black). In the bottom panel, we plot $f$ as calculated from DFT (based on standard overlap of the wavefunctions). As in Figure 3, the results from TDA are slightly blue shifted as compared to those from IPA. Further, TDA level calculation yields a slightly broader transition, which comes from the inclusion of many more states in the construction of the Casida equation, as well as

**Figure 3.** Optoelectronic properties of the $V_{W}^{−}$ center in monolayer WS$_2$. (a) Electronic band structure of $V_{W}^{−}$ (same as Figure 2(b)). (b) Partial charge density plots for few relevant states across the vicinity of the Fermi level. ‘HOMO (def.)’ and ‘LUMO (def.)’ represent what we identify as defect states inside the bandgap, while ‘HOMO (Er $f$)’ and ‘LUMO+x (Er $f$)’, $x = 1, 3$ are levels defined only with respect to Er$^{3+}$ occupancies. Optical absorption coefficients for (c) $V_{W}^{−}$ and (d) $V_{W}^{+}$ within two levels of approximation, IPA and TDA. Blue solid and orange dashed lines represent in-plane components, while green solid lines represent the out-of-plane components.
coupled transitions that are considered independent at the DFT level.

From the overlap of the DFT wavefunctions, we have access to the transition dipole moments (lower panel in Figure 4(a)). Not surprisingly, these TDMs are vanishing, which may be the main reason for the absence of any low-energy absorption features for Er\(^{3+}\) at the TDA level within VASP (dielectric tensor components \(\varepsilon_{ii}\) lying below the non-zero threshold of \(10^{-4}\)). A relevant observation in these calculations is the overestimation of the energies corresponding to the \(f-f\) transitions within Er\(^{3+}\) noting that, in principle, any crystal field effect should be only on the order of \(10^2\) cm\(^{-1}\) for Er\(^{3+}\) \(f\) states.\(^{19}\) It is thus natural to expect the transitions to be overestimated for the case of Er\(^{3+}\) in WS\(_2\), which in fact correlates with what we have calculated.

Let us now turn to the case of the V\(_W\) center in WS\(_2\). For simplicity, we consider only transitions from the defect's HOMO state to all empty defect states within the bandgap. From the top panel of Figure 4(b) we already see relatively good agreement between the most prominent oscillator strengths and the absorption spectrum suggesting the latter arises mainly (though not fully) from contributions associated to the considered transitions. As compared to the bottom panel of Figure 4(b), we again obtain (as expected) what seems to be a blue shift of the transitions at the IPA level. There are two prominent transitions that lie at 0.62 and 1.3 eV, with larger TDMs as compared to the transition for the bare Er\(^{3+}\). Importantly, these features correspond to the bare vacancy, and they should change as the Er ion is incorporated owing to, for example, electrostatic interactions introduced by the ion.

In Figure 4(c), the picture is more complex due to mixed excitations to/from defect states and Er(\(f\)) states that need to be taken into account. The color coding in Figure 4(c) captures transitions between Er\(^{3+}\) states and slightly hybridized states (‘Er-hyb’), between Er\(^{3+}\)(\(f\)) states (‘Er-Er’), between Er\(^{3+}\) and the defect’s LUMO state (‘Er-W’), and between defect states (‘Def-Def’). Note that the bright transitions prominent in Figure 4(b) have now shifted towards lower energies (shown in purple in Figure 4(c)) and become substantially less bright. The latter is likely a consequence of changes in the extension and shape of the occupied and unoccupied V\(_W\) states, impacted differently by the inclusion of Er.

We finally focus on the region around 1.0 eV of the spectrum, where we have obtained a transition with TDA peaks centered at 0.89 and 1.05 eV. We indeed find that most of the excitation character for these optical features comes from Er-Er transitions at both the DFT level and within the Casida approach. Despite the overestimation of optical transitions within DFT, both results suggest that a substitutional Er impurity in monolayer WS\(_2\) should be optically active within the telecom band, a response reminiscent of the \(^4l_{15/2} \leftrightarrow^4l_{13/2}\) transition in Er\(^{3+}\).

**IV. CONCLUSIONS**

DFT calculations indicate that an Er impurity occupying a W site in a WS\(_2\) monolayer forms a stable point defect. The Er impurity introduces only a minor distortion in the WS\(_2\) lattice, a manifestation of the
close match between the Er and W atomic radii. Formation energies favor the neutral and negatively charged states, but other charge states (e.g., $\text{Er}^{2+}$) may be experimentally observable. Valence electrons from the Er atom (along with any excess electrons in the super-cell) localize at the dangling bonds from nearby sites, hence leaving behind an $\text{Er}^{3+}$ ion core. The system’s ground state energy lies slightly below the valence band maximum, and there is some spatial overlap between the defect and the $\text{Er}^{3+}$ ground state orbitals although the level of hybridization is low. The latter also applies to the set of excited states some of which remain confined to the Er site (and can be associated to the excited $\text{Er}^{3+}$ orbitals) while the rest delocalize (and can be loosely seen as $V_W$ states).

We built on the strong differences between these two classes of states to characterize the optical response of the defect, which we determined through optical absorption and oscillator strength calculations. In particular, we found Er (f-f) absorption near 0.9 eV, hence suggesting the $^4_{15/2}\rightarrow^4_{13/2}$ transition in $\text{Er}^{3+}$ remains active in the 2D host. We also want to emphasize the possible limitations of DFT to describe strongly correlated systems such as the Er ion and systems of multi-reference character. While the DFT+U approach can overcome some of those shortcomings in particular for ground state calculations, more accurate methods, such as correlated embedding methods$^{17-20}$ are necessary to predict accurate excitation energies. For such methods, our calculations can serve as the starting point. Future work will include comparison of our findings with these methods as well as the study of the role of phonons in these optical transitions.

All in all, these findings point to Er:WS$_2$ as a potentially promising material platform for applications that rely on single photon emitters integrated to photonic structures. Whether or not the $\text{Er}^{3+}$ retains the useful spin and magneto-optical properties observed in other crystal hosts$^{59}$ is a most intriguing question, whose answer will require, nonetheless, additional computational and experimental work.

After initial submission of this manuscript, we became aware that electronic structure calculations for the electronic and optical properties of Er:WS$_2$ using molecular orbital theory within the SIESTA software package have been published.$^{60}$ Besides differences between these two studies in terms of methods for excited-state properties (molecular orbital theory/IPA and Casida equation) and software packages (SIESTA/VASP) we find qualitative agreement on the main findings.

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REFERENCES

1 Zhong, M.; Hedges, M. P.; Ahlefeldt, R. L.; Bartholomew, J. G.; Beavan, S. E.; Wittig, S. M.; Longdell, J. J.; Sellars, M. J., “Optically addressable nuclear spins in a solid with a six-hour coherence time”. Nature 2015 517, 177.
2 Sun, Y.; Thiel, C. W.; Cone, R. L.; Equall, R. W.; Hutcheson, R. L., “Recent progress in developing new rare earth materials for hole burning and coherent transient applications”. J. Lumin. 2002 98, 281.
3 Dibos, A. M.; Raha, M.; Phenicie, C. M.; Thompson, J. D., “Atomic source of single photons in the telecom band”. Phys. Rev. Lett. 2018 120 (24), 243601.
4 Alexander, A. L.; Longdell, J. J.; Sellars, M. J.; Manson, N. B., “Photon echoes produced by switching electric fields”. Phys. Rev. Lett. 2006, 96 (4), 043602.
5 Tittel, W.; Afzelius, M.; Chaneil, T.; Cone, R. L.; Kröll, S.; Moiseev, S. A.; Sellars, M. J., “Photon-echo quantum memory in solid state systems”. Laser Photonics Rev. 2010 4, 244.
6 Thomas Kornher, T.; Xiao, D.; Xia, K.; Sardi, F.; Zhao, N.; Kolesov, R.; Wrachtrup, J., “Sensing individual nuclear spins with a single rare-earth electron spin”. Phys. Rev. Lett. 2020 124, 170402.

7 Rančić, M.; Hedges, M. P.; Ahlefeldt, R. L.; Sellars, M. J., “Coherence time of over a second in a telecom-compatible quantum memory storage material”. Nat. Phys. 2018 14, 50.
8 Siyushev, P.; Xia, K.; Reuter, R.; Jamali, M.; Zhao, N.; Yang, N.; Duan, C.; Kukharroych, N.; Wieck, A. D.; Kolesov, R.; Wrachtrup, J., “Coherent properties of single rare-earth spin qubits”. Nat. Commun. 2014 5, 3895.
9 Böttger, T.; Thiel, C. W.; Sun, Y.; Cone, R. L., “Optical decoherence and spectral diffusion at 1.5 μm in Er$^{3+}$:Y$_2$SiO$_5$ versus magnetic field, temperature, and Er$^{3+}$ concentration”. Phys. Rev. B 2006 73, 075101.
10 Ahlefeldt, R. L.; Hush, M. R.; Sellars, M. J., “Ultranarrow optical inhomogeneous linewidth in a stoichiometric rare-earth crystal”. Phys. Rev. Lett. 2016 117, 250504.
11 Sigillito, A. J.; Jock, R. M.; Tvrysthkin, A. M.; Beeman, J. W.; Haller, E. E.; Itoh, K. M.; Lyon, S. A., “Electron spin coherence of shallow donors in natural and isotopically enriched germanium”. Phys. Rev. Lett. 2015 115, 247601.
12 Zhong, T.; Kindem, J. M.; Bartholomew, J. G.; Rochman, J.; Craiciu, I.; Verma, V.; Woo Nam, S.; Marsili, F.; Shaw, M. D.; Beyer, A. D.; Farao, A., “Optically addressing single rare-earth ions in a nanophotonic cavity”. Phys. Rev. Lett. 2018 121, 183603.
13 Reid, M. F., “Theory of rare-earth electronic structure and spectroscopy”. Handbook on the Physics and Chemistry of Rare Earths 2016 50 (284), 47.

14 Chen, F.; Wang, L.; Ji, X.; Zhang, Q., "Temperature-dependent two-dimensional transition metal dichalcogenide heterostructures: Controlled synthesis and their properties". ACS Appl. Mater. Interfaces 2017 9 (36), 3082.

15 Tian, H.; Chin, M. L.; Najmaei, S.; Guo, Q.; Xia, F.; Wang, H.; Dubey, M., "Optoelectronic devices based on two-dimensional transition metal dichalcogenides". Nano Research 2016 9, 1543.

16 Gusakov, J.; Wang, X.; Shiau, L. L.; Krivosheeva, A.; Shaposhnikov, V.; Borisenko, V.; Gusakov, V.; Tay, B. K., “Electronic properties of bulk and monolayer TMDs: Theoretical study within DFT framework (GJV-2e Method)”. Phys. Stat. Sol. A 2017 214, 1700218.

17 Muechler, L.; Badrtdinov, D. I.; Hampel, A.; Cano, J.; Rössner, M.; Dreyer C. E., “Quantum embedding methods for correlated excited states of point defects: Case studies and challenges”. arXiv:2105.08705, 2021.

18 Lau, B. T. G.; Knizia, G.; Berkelbach, T. C., “Regional embedding enables high-level quantum chemistry for surface science”. J. Phys. Chem. Lett. 2021, 12, 1104.

19 Ma, H.; Sheng, N.; Govoni, M.; Galli, G., “Quantum embedding theory for strongly correlated states in materials”. J. Chem. Theory Comput. 2021, 17, 2116.

20 Yu, K.; Libisch, F.; Carter, E. A., “Implementation of density functional embedding theory within the projector-augmented-wave method and applications to semiconductor defect states”. J. Chem. Phys. 2015, 143, 102806.

21 Liechtenstein, A. I.; Anisimov, V. I.; Zaanen, J., “Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators”. Phys. Rev. B 1995 52, R5467(R).

22 Sanna, S.; Hourahine, B.; Gerstmann, U.; Frauenheim, T., “Efficient tight-binding approach for the study of strongly correlated systems”. Phys. Rev. B 2007 76, 155128.

23 Sanna, S.; Schmidt, W. G.; Frauenheim, T.; Gerstmann, U., “Rare-earth defect pairs in GaN: LDA+U calculations”. Phys. Rev. B 2009 80, 104210.

24 Wang, S.; Wang, X.; Li, J.; Jia, Y.; Wei, F., “Electronic and optical properties of Er doped in AlN”. Mod. Phys. Lett. B 2015 29, 1550114.

25 Wang, S.; Xia, X.; Lia, J., “Ferromagnetism properties of Er-doped ZnO: a GGA + U study”. RSC Adv. 2016 6, 107865.

26 Alkahtani, E. A.; Merad, A. E.; Boufatah, M. R.; Benosman, A., “DFT investigation of structural, electronic and optical properties of pure and Er-doped ZnO”. Optik 2017 128, 274.

27 Larson, P.; Lambrecht, W. R. L.; Chantis, A.; van Schilfgaarde, M., “Electronic structure of rare-earth nitrides using the LSDA+U approach: Importance of allowing 4f orbitals to break the cubic crystal symmetry”. Phys. Rev. B 2007 75, 045114.

28 Hoang, K., “Tuning the valence and concentration of europium and luminescence centers in GaN through co-doping and defect association”. Phys. Rev. Mat. 2021 5, 034601.

29 Gottscholl, A.; Diez, M.; Soltaov, V.; Kasper, C.; Sperlich, A.; Kianinia, M.; Bradac, C.; Aharonovich, I.; Dyakonov, V., “Room temperature coherent control of spin defects in hexagonal boron nitride”. Sci. Adv. 2021 7, eabf3630.

30 Stern, H. L.; Jarman, J.; Gu, Q.; Eizaguirre Barker, S.; Mendelson, N.; Chugh, D.; Schott, S.; Tan, H. H.; Sirringhaus, H.; Aharonovich, I.; Attürè, M., “Room-temperature optically detected magnetic resonance of single defects in hexagonal boron nitride”. arXiv:2103.16494 2021.

31 Exarhos, A. L.; Hopper, D. A.; Patel, R. N.; Doherty, M. W.; Bassett, L. C., “Magnetic-field-dependent quantum emission in hexagonal boron nitride at room temperature”. Nat. Commun. 2019 10, 2392.

32 Gotscholl, A.; Kianinia, M.; Soltaov, V.; Orlishkii, S.; Mamin, G.; Bradac, C.; Kasper, C.; Krambrock, K.; Sperlich, A.; Toth, M.; Aharonovich, I.; Dyakonov, V., “Initialization and read-out of intrinsic spin defects in a van der Waals crystal at room temperature”. Nat. Mater. 2020 19, 540.

33 Böchi, P. E., “Projector augmented-wave method”. Phys. Rev. B 1994 50 (24), 17953.

34 Kresse, G.; Furthmüller, J., “Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set”. Phys. Rev. B 1996 54 (16), 11169.

35 Perdew, J. P.; Ernzerhof, M.; Burke, K., “Rationale for mixing exact exchange with density functional approximations”. The Journal of Chemical Physics 1996 105 (22), 9982.

36 Ding, Y.; Wang, Y.; Ni, J.; Shi, L.; Shi, S.; Tang, W., “First principles study of structural, vibrational and electronic properties of graphene-like MX2 (M=Mo, Nb, W; Ta=Si, S, Te) monolayers”. Physica B 2011 406, 2254.

37 Haastrop, S.; Strange, M.; Pandey, M.; Deilmann, T.; Schmidt, P. S.; Hinsche, N. F.; Gjerding, M. N.; Torelli, D.; Larsen, P. M.; Riis-Jensen, A. C.; Gath, J.; Jacobsen, K. W.; Jørgen Mortensen, J.; Olsen, T.; Thysgesen, K. S., “The computational 2D materials database: High-throughput modeling and discovery of atomically thin crystals”. 2D Mater. 2018 5, 042002.

38 Gajdoš, M.; Hummer, K.; Kresse G.; Furthmüller, J.; Bechstedt, F., “Linear optical properties in the projector-augmented wave methodology”. Phys. Rev. B 2006 73 (16), 045112.

39 Casida, M. E., “Recent developments and applications of modern density functional theory”. Theoretical and Computational Chemistry 1996 4, 391.

40 Tamm, I., “Selected Papers” (Springer, Berlin Heidelberg, 1991), 157.

41 Dancoff, S. M., “Non-adiabatic meson theory of nuclear forces”. Phys. Rev. 1950 78, 382.

42 Freysoild, C.; Grabowski, B.; Hick, T.; Neugebauer, J.; Kresse, G.; Janotti, A.; Van de Walle, C. G., “First-principles calculations for point defects in solids”. Rev. Mod. Phys. 2014 86, 253.

43 Lyons, J. L.; Van de Walle, C. G., “Computationally predicted energies and properties of defects in GaN”. npj Computational Materials 2017 3 (12).

44 Freysoild, C.; Neugebauer, J.; Van de Walle, C. G., “Fully ab initio finite-size corrections for charged-defect supercell calculations”. Phys. Rev. Lett. 2009 102, 016402.

45 Freysoild C.; Neugebauer, J., “First-principles calculations for charged defects at surfaces, interfaces, and two-dimensional materials in the presence of electric fields”. Phys. Rev. B 2018 97, 205425.

46 Larson, P.; Lambrecht, W. R. L.; Chantis, A.; van Schilfgaarde, M., “Electronic structure of rare-earth nitrides using the LSDA+U approach: Importance of allowing 4f orbitals to break the cubic crystal symmetry”. Phys. Rev. B 2007 75, 045114.

47 Hampsch, A.; Liu, P.; Franchini, C.; Ederer, C., “Energetics of the coupled electronic–structural transition in the rare-earth nickelates”. npj Quantum Materials 2019 4 (5).

48 Cococcioni, M.; De Gironcoli, S., “Linear response approach to the calculation of the effective interaction parameters in the LDA+U method”. Phys. Rev. B 2005 71, 035105.
Khan, M. A.; Erementchouk, M.; Hendrickson, J.; Leuenberger, M. N., "Electronic and optical properties of vacancy defects in single-layer transition metal dichalcogenides". Phys. Rev. B 2017 95, 245435.

Erementchouk, M.; Khan, M. A.; Leuenberger, M. N., "Optical signatures of states bound to vacancy defects in monolayer MoS2". Phys. Rev. B 2015 92, 121401(R).

Körner, W.; Urban, D. F.; Muñoz Ramo, D.; Bristowe, P. D.; Elsässer, C., "Prediction of subgap states in Zn- and Sn-based oxides using various exchange-correlation functionals". Phys. Rev. B 2014 90, 195142.

Gongxun Bai, G.; Yuan, S.; Zhao, Y.; Yang, Z.; Choi, S. Y.; Chai, Y.; Yu, S. F.; Lau, S. P.; Hao, J., "2D layered materials of rare-earth Er-doped MoS2 with NIR-to-NIR down- and up-conversion photoluminescence". Adv. Mater. 2016 28, 7472.

Cajzl, J.; Nekvindová, P.; Macková, A.; Malinský, P.; Sedmidubský, D.; Hušák, M.; Remeš, Z.; Varga, M.; Kromka, A; Böttgerf, R.; Oswald, J., "Erbium ion implantation into diamond – measurement and modelling of the crystal structure". Phys. Chem. Chem. Phys. 2017 19, 6233.

Thiering, G.; Gali A., "Ab initio magneto-optical spectrum of group-IV vacancy color centers in diamond". Phys. Rev. X 2020 10, 039901.

Ciccarino, C. J.; Flick, J.; Harris, I. B.; Trusheim, M. E.; Englund, D. R.; Narang, P., "Strong spin–orbit quenching via the product Jahn–Teller effect in neutral group IV qubits in diamond". npj Quantum Materials 2020 5, 75.

Onida, G.; Reining, L.; Rubio, A., "Electronic excitations: density-functional versus many-body Green’s-function approaches". Rev. Mod. Phys. 2002 74, 601.

Marini, A.; Del Sole, R.; Rubio, A., "Bound excitons in time-dependent density-functional theory: optical and energy-loss spectra". Phys. Rev. Lett. 2003 91, 256402.

Sander, T.; Maggio, E.; Kresse, G., "Beyond the Tamm-Dancoff approximation for extended systems using exact diagonalization". Phys. Rev. B 2015 92, 045209.

Chen, S.; Raha, M.; Phenicie, C.M.; Ourari, S.; Thompson, J. D., "Parallel single-shot measurement and coherent control of solid-state spins below the diffraction limit". Science 2020 370, 592.

Khan, M.; Leuenberger, M. N., "Ab initio calculations for electronic and optical properties of ErW defects in single-layer tungsten disulfide". J. Appl. Phys. 2021 130, 115104.