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Abstract
Large unit cell calculations of the properties of charged point defects in
insulators largely neglect dielectric polarization of the crystal, because the
periodically repeated cells are so small. Embedded quantum cluster calculations
with shell-model crystals, representing a single defect in a large crystal, are able
to represent the polarization more realistically. For such embedded quantum
clusters, we evaluate the optical excitation energy for the nitrogen vacancy
in charge state (+3): v_N^{3+} in AlN. This is done with and without dielectric
polarization of the embedding crystal. A discrepancy of a few per cent is
found, when both ground and excited state orbitals are well-localized within the
vacancy. We show that the discrepancy rises rapidly as the excited state becomes
more diffuse. We conclude that an embedded cluster approach will be required
for transitions that involve even somewhat diffuse states. The investigation is
based on a new model for AlN that shows promise for quantitative accuracy.

1. Introduction

A charged point defect induces a long-range polarization field in a crystal insulator. The main
purpose of this work is to illustrate the effect on calculated properties of the defect arising
from neglect of this long-range polarization. The issue comes up in calculations based on
large unit cells with periodic boundary conditions. In such calculations, 'large' usually means

a unit cell consisting of tens of ions, corresponding to defect concentrations $\gtrsim 10^{-2}$. This must be compared with typical experimental defect concentrations $< 10^{-6}$. It is plausible that, for defects that are localized within a small number of interatomic spacings, such large unit cell calculations will give valid results for point defect properties. One kind of defect configuration that is not so well localized involves diffuse single-electron states. The prototypical examples are the F-centre excited states in KI [1] and KBr [2], where the diffuseness of the relaxed excited state is experimentally documented by ENDOR data, as well as possibly in BaF_2 [3], where only theoretical results are available. These F centres are anion vacancies binding single excess electrons. Their excited states span hundreds of ions neighbouring the vacancy, and clearly cannot be modelled by periodic unit cells of smaller dimension. For such problems, at low concentration (approaching zero), embedded quantum cluster methods [4–6] can be adapted to give physically reasonable modelling [3]. Such methods take account of the strong perturbation of nearby electronic structure by careful many-electron treatment of a small molecular cluster enclosing the point defect, and can deal with interaction of the diffuse electron with the surrounding crystal using a dielectric continuum, an effective band mass and Fröhlich's polaron theory [7]. In the case of an optical transition between an atomically localized state and a diffuse state, the embedding region for the localized state may be modelled in terms of the classical discrete-ion shell model, for greater accuracy.

For point defect processes that involve only atomically localized electron orbitals, there is a question whether polarization in the surrounding crystal has a significant effect. Specifically, consider optical absorption from a spherically symmetrical s-type orbital to a p-type orbital, subject to the Franck–Condon approximation, in the form such that the atomic positions and long-range polarization do not change from their ground state configuration during the transition. Then the excited-state p-type orbital interacts with an approximately spherically symmetric long-range polarization field. Now if we approximate the system by a spherical cavity in an infinite dielectric continuum, the potential seen by an electron within the cavity (in this case in a p-type orbital) is constant. Thus, to the extent that the ground-state s-type orbital and the excited-state p-type orbital both lie within the cavity, the effect of the polarization on both states will be the same. In a discrete-atom or all-electron treatment of the surrounding crystal, this will still be approximately the case, due to the relatively high symmetry of the crystal, and the strong localization of the states. It remains, however, to quantitatively estimate the accuracy of this approximation. In section 2 we give explicit results for the effect of neglecting polarization in the crystal in a model calculation of the optical excitation of the nitrogen vacancy in charge state +3 in AlN, where the excited state, as well as the ground state, is quite well localized within the vacancy. Qualitatively, the estimated absorption energy is increased by about 0.5 eV, in an excitation of 8 eV. While this is not a large amount, it is comparable with other effects that are usually not neglected. In cases where more diffuse states occur, we show that larger effects will be present.

The contents of this paper consist of two parts. The first, in section 2, is a quantitative discussion of the effect of long-range polarization on the optical excitation of a charged point defect. The second part, section 3, is a description of a new modelling scheme for the computation of point defect properties in group III nitrides. Although, logically, an account of the modelling method would be expected to precede the quantitative results, we have chosen to reverse the order so that the reader will understand that evaluating the optical excitation energy of the nitrogen vacancy in AlN is not the primary objective of the paper. The model used here is applied to a nearest-neighbour cluster of four Al atoms, whereas we feel that a fully convincing modelling would include the 12 second-neighbour nitrogen atoms. However, the present nearest-neighbour cluster is useful to quantitatively illustrate the role of polarization in the defect process. In section 4 we summarize and discuss our conclusions.

Table 1. Optical excitation energy of v_N^{3+} in a model of AlN, with and without long-range polarization of the embedding crystal: energies in eV.

	With polarization	Without polarization
UHF	8.3702	8.8884
Correlation	−0.1492	−0.1646
Total	8.22	8.72

2. Results for a model optical absorption process

We consider the nitrogen vacancy v_N^{3+} in charge state +3 in AlN. Details of the model will be given in section 3, in the cubic zinc-blende structure, but basically we consider the vacancy and its four nearest-neighbour Al ions as a quantum molecular cluster, embedded in an infinite classical shell-model crystal. The cluster is analysed in an all-electron self-consistent field unrestricted Hartree–Fock approximation with correlation correction in second-order many-body Rayleigh–Schrödinger perturbation theory. The method, which leaves electronic structure, atomic positions (deformation) and polarization of the crystal all in mutual equilibrium in the ground state, and which can evaluate the excited state in the presence of atomic positions and polarization of the ground state, is referred to as the ICECAP method [4, 5]. The whole analysis can also be carried out while keeping the embedding crystal unpolarized. The polarization comes about, of course, because the point defect has a net charge (+3 in the present case) relative to the perfect crystal without defects.

The calculated nature of the defect is that, in its ground state, approximately two electrons, spin paired, are drawn into the deep Coulomb potential well of the vacancy from the surrounding crystal: in the present case, from the nearest-neighbour Al ions, leaving them with very close to ten electrons (in terms of the calculated Mulliken population), i.e. approximately a filled shell atomic configuration. The dipole-allowed optical excitation involves one electron, say spin up, mainly involving the vacancy, essentially going from an atomic s-type orbital to an atomic p-type orbital. In table 1 are given the unrestricted Hartree–Fock (UHF) and correlation contributions, and the total excitation energies for two cases: with polarization of the embedding crystal, and without it.

From table 1 we see that neglect of polarization raises the transition energy by 0.5 eV, or about three times as much as neglect of correlation does. (The correlation corrections to the individual energy levels are ∼6–7 eV.)

We can see how the effect of polarization increases with diffuseness of the excited state by calculating the optical excitation energy when the vacancy-centred p-type orbital expands. This is discussed in detail at the end of section 3, but what emerges is that, when the orbital extends over a diameter of several nearest-neighbour distances, the calculated excitation energy at the Hartree–Fock level increases from 7.90 eV with polarization to 15.28 eV without it. The latter value of 15.28 eV is entirely unrealistic, suggesting that neglect of long-range polarization for such a diffuse state would be disastrous.

3. Computing local electronic properties in AlN

We want to apply the ICECAP method, which requires a shell-model for the embedding crystal and a molecular cluster for the local region containing the point defect. AlN is not a purely ionic material, but rather a partly-ionic wide-band gap covalent material. This should be taken into account in such a modelling scheme. There exists extensive literature of modelling group

III-nitride crystals using the large unit cell method. Specifically for point defects in AlN we cite here the *magnum opus* of Stampfl and Van de Walle [8]. In this section we describe a new modelling approach for group III nitrides, applied to AlN, including details for analysis of the nitrogen vacancy, and a discussion of the relationship between localization of the vacancy excited state and polarization of the embedding crystal.

3.1. Embedded cluster model for AlN

As a filled-shell ionic material, AlN would have ionicity 3, with nuclear charges 13 and 7 for Al and N respectively, and $1s^2 2s^2 2p^6$ configurations. However, the net charges associated with single ions in the crystal are not integral. In order to represent accurately the Madelung field seen by the electrons in the quantum molecular cluster, based on classical point ions for the embedding crystal, we determine the ionicity as follows. Beginning with the band structure (zinc-blende structure) [9], we use Bader's 'atoms in molecules' (AIM) method [10] to evaluate the net charges in the regions spanned by the ions. This yields an ionicity of 2.41. With this ionicity, a shell model is fitted to a set of bulk parameters, using Gale's GULP program [11]. The resulting shell-model parameters are as follows:

Ionic charges, ± 2.41 (units: proton charge e)

$$(K, Y) = (7.59 \text{ eV Å}^{-2}, -2.46e), \qquad \text{(Å is ångström unit of length)}$$

$$B_{12} = 6.59 \times 10^2 \text{ eV}, \qquad \rho_{12} = 0.363 \text{ Å}, \qquad C_{12} = 0;$$

$$B_{22} = 1.60 \times 10^3 \text{ eV}, \qquad \rho_{22} = 0.296 \text{ Å}, \qquad C_{22} = 1.94 \times 10^2 \text{ eV Å}^6.$$

In the above, K and Y are the force constant for core–shell interaction and the shell charge, respectively, for the nitrogen ion; the aluminium ion is rigid; $(B_{ij}, \rho_{ij}, C_{ij})$ are parameters of the Buckingham short-range interionic potentials V_{ij}:

$$V_{ij} = \{B_{ij} \exp(-R/\rho_{ij}) - C_{ij} R^{-6}\} \tag{1}$$

where R is the interionic shell–shell distance, with $i = 1$ for Al, $i = 2$ for N, and the same for j. The Al–N interaction has no van der Waals term ($C_{12} = 0$), and Al–Al short-range interactions are neglected, but N–N are not, relative to nearest-neighbour Al–N interaction. Thus Al–N interactions act between Al cores and N shells, while N–N interactions are shell–shell interactions. Dielectric constants used in deriving this shell model are for the wurtzite structure, as we are unaware of values for cubic AlN. The accepted ranges for low and high frequency dielectric constants are 8.5–9.1 and 4.6–4.8, respectively. Our shell model gives corresponding values of 9.97 and 5.20, respectively [12]. This represents discrepancies of about 10%, which is as close a fitting as we could get without producing unacceptably bad calculated mechanical properties.

The fractional ionicity raises a problem for the specification of the local molecular cluster, which must have an integral number of electrons. Consider the nitrogen-centred perfect-crystal cluster Al_4N. With the given nuclear charges and ionicities, N has 9.41 electrons and Al has 10.59. Thus Al_4N should have 51.77 electrons. In order to have a cluster with an integral number of electrons, and zero spin in the ground state, we round this off to 52 electrons, 26 each of spin up and spin down. The discrepancy of 0.23 electrons introduced in this way needs to be borne in mind as an inaccuracy of the model. The inaccuracy does not extend to the polarization field, however, except indirectly. The reason is that, in our calculations, the polarization field is induced by point charges that do not include the extra ($-0.23e$) of electronic charge (see section 3.2).

We first consider equilibration in this model between the perfect-crystal nitrogen-centred nearest-neighbour embedded cluster Al_4N and the embedding crystal. The result is a nearest-neighbour equilibrium distance of 0.992 times the perfect-crystal distance, with only 0.007 eV

of relaxation energy. This shows that, at least with respect to cluster-embedding compatibility, our model is quite reasonable. This is further supported by the Mulliken populations found in Al_4N, of 10.69 for Al and 9.24 for N, to be compared with corresponding Bader charges of 10.59 and 9.41 respectively, from band structure, bearing in mind that our cluster contains 0.23 too many electrons, as mentioned earlier.

3.2. The nitrogen vacancy v_N^{+3}: ground state and optical excitation

We create the nitrogen vacancy v_N^{3+} by removing from Al_4N (52 electrons) a nitrogen nucleus and ten electrons, leaving 42 electrons. For the Al ions, we begin with the basis set of [9], consisting of Gaussian-type orbitals, of the form (8511/511/1): see for example [13]. We add single s- and p-type orbitals centred in the vacancy, to allow for the possibility of electrons being drawn into the vacancy from the neighbouring Al ions. The total energy of the model system, cluster plus embedding crystal, is systematically minimized with respect to four features:

  (i) the polarization field;
 (ii) the vacancy-centred orbitals;
(iii) the polarization orbitals (3s, 3p, 4s, 4p);
(iv) the nearest-neighbour distance.

The polarization field is set up by an array of point charges representing approximately the charge distribution of the cluster. These charges add up to the total charge of the cluster, and minimize the total energy. In our case, they coincide with atomic sites, including the vacancy site. When we want to do a defect calculation without polarization, we choose these point charges to simulate a perfect-crystal cluster. All of the orbitals have Gaussian radial dependence, $\exp(-\alpha r^2)$. For vacancy-centred and polarization orbitals, the total energy is minimized with respect to the α-values. In our case, variation of the nearest-neighbour distance to minimize the total energy has all shell-model cores and shells in equilibrium at each distance.

The Mulliken population of the vacancy-centred s-type orbital in the ground state is found to be 0.81 in both spin up and spin down states (see table 2). One would therefore say that roughly two spin-paired electrons are drawn into the vacancy from the Al nearest-neighbours in this model. The nearest-neighbour equilibrium distance in v_N^{3+} is 1.00 times the perfect-crystal distance. The fact that there is no significant outward relaxation associated with creation of the charged vacancy is contrary to conventional wisdom, and to other calculations [8]. The conventional wisdom is that the repulsion among the four nearest-neighbour cations, no longer balanced by Coulomb attraction to the central anion, will cause expansion. However, the short-range cation–anion repulsion has also been removed in creating the vacancy. The two opposite effects, along with new values associated with electron transfer into the vacancy from the cations, all cancel almost exactly in the present model.

The dipole-allowed optical excitation is taken to be from the s-type ground state to the p-type virtual state, both being Hartree–Fock many-body states in the spin-up manifold. The Franck–Condon approximation is applied by maintaining nearest-neighbour positions and the associated polarization from the ground state. The resulting Hartree–Fock excited state is contaminated with a lower-energy, dipole-forbidden spin-flip transition, from a vacancy s-type spin-down state to a pure vacancy p-type spin-up state. The pure allowed state has spin zero; the forbidden state has spin one; the mixed state has spin 0.488. When we refer to vacancy s-type or p-type states, we actually mean Fock eigenstates that are predominantly, but not exclusively, of this character, being in fact molecular orbitals with contributions from neighbouring Al ions. Let E_0, E_a and E_b be total energies of ground, spin-flip and pure spin-up excited states,

Table 2. Mulliken populations of vacancy centred s- and p-type orbitals, spin up (↑) and spin down (↓) in optical excitation of v_N^{3+} in AlN.

State	With polarization		Without polarization	
	s↑, s↓	p↑, p↓	s↑, s↓	p↑, p↓
Ground	0.81, 0.81	0.00, 0.00	0.88, 0.88	0.00, 0.00
Spin-flip	0.82, 0.00	0.69, 0.00	0.88, 0.00	0.87, 0.00
Spin-up, mixed	0.12, 0.83	0.30, 0.00	0.22, 0.89	0.64, 0.01

Table 3. Ranges R (see equation (3)) of vacancy centred s- and p-type orbitals in optical excitation of v_N^{+3} in AlN. Units: nearest-neighbour distance.

State	With polarization		Without polarization	
	s	p	s	p
Ground	0.55	—	0.56	—
Spin-flip	0.53	0.49	0.55	0.53
Spin-up, mixed	0.52	0.49	0.56	0.56

respectively, and let E_b' and S_b' be the mixed state total energy and spin respectively. Then one can show that:

$$E_b = \frac{[E_b' - \frac{1}{2}S_b'(S_b' + 1)E_a]}{[1 - \frac{1}{2}S_b'(S_b' + 1)]}. \tag{2}$$

The excitation energies given in table 1 are then given by $(E_b - E_0)$.

To illustrate the molecular orbital character of the Fock eigenstates, and the nature of contamination in the mixed state, we present in table 2 the Mulliken populations of the vacancy-centred orbitals, s- and p-type, both spin up and spin down, with and without polarization. The deviations from values 1 and 0 constitute the illustrations.

3.3. Extent of localization of the excited state

Let us now examine the localization of the vacancy orbitals involved in this analysis. Let α_s and α_p be the Gaussian exponential coefficients of vacancy-centred s- and p-type orbitals, respectively. The range R of a Gaussian wavefunction's probability density will be defined here to be:

$$R = (2\alpha)^{-1/2}. \tag{3}$$

The values obtained in ground, spin-flip and mixed spin-up excited states are given in table 3, in units of nearest neighbour Al ion distance. The p-type orbital is essentially unoccupied in the ground state, and was therefore omitted from the energy minimization process.

We note that R is the distance at which an s-type Gaussian drops to $e^{-1} \sim 0.37$ of its maximum value, while for a p-type orbital it is the distance at which the orbital reaches maximum particle density, with $\geqslant 60\%$ of the integrated particle density beyond this range. From table 3 we see that, in all cases, the orbitals are quite well localized within the vacancy. It is against this background that we see a 0.5 eV difference in optical excitation energy due to the neglect of polarization (table 1), even with an excited state of range R only $\sim 0.5 \times$ nearest-neighbour distance. Calculations with much more diffuse excited state orbitals show that the only total-energy minimum is with $R_p = 0.49 \times$ nn, so the excited state is not diffuse. We have, in fact, calculated the optical excitation energy with a vacancy-centred p-orbital whose

range is $3.0 \times$ (nearest-neighbour distance), i.e. $\alpha_p = 0.004\,35\,a_0^{-2}$. While the mixed-state excited state energy rises only slightly compared to that with the optimal value $\alpha_p = 0.165\,a_0^{-2}$, namely by 0.29 eV, when polarization is included, it rises much more strongly, by 6.34 eV, when polarization is neglected. In both cases, contamination by the pure spin-flip state is stronger than with the short-range p-type orbital. The result, as stated in section 2, is that the estimated excitation energy at the Hartree–Fock level rises from 7.90 to 15.28 eV when polarization is neglected. The modelling for this calculation is deficient in that the diffuse orbital, to the extent that it is occupied by an electron, interacts only with the point charges of the embedding shell-model crystal, thereby neglecting quantum-mechanical features of the electrons of the embedding crystal. For this reason, correlation correction is not included in the above results. The electron–phonon effect, which is important for diffuse states [3], is also neglected. However, our work on the F-centre diffuse excited state in BaF_2 [3] shows that the shell-model results qualitatively track the more realistic modelling. We are therefore confident in the large effect obtained for significantly diffuse states.

4. Conclusions and discussion

We have shown that, in a nearest-neighbour embedded molecular cluster model of v_N^{3+} in AlN, the dipole-allowed optical excitation energy of 8.22 eV is increased by 0.50 eV when long-range polarization in the embedding crystal is neglected. The excited state electron is quite well localized in the vacancy. In systems with more diffuse excited states, our calculations indicate that the discrepancy is much larger. Regarding AlN specifically, we have introduced a new modelling scheme for such partly ionic materials, and have demonstrated how to include in the calculation the full process of total energy minimization, projection onto a pure excited state, and correlation correction. To obtain what we consider to be results of predictive value, we need only to extend the model to include second-neighbour nitrogen ions in the molecular cluster, to see the role, if any, of nitrogen electrons in forming the spin-paired two-electron vacancy configuration of the ground state, and in the optical excitation process. From one viewpoint, one might expect the two vacancy-centred electrons to come from the relatively less tightly bound nitrogen anions rather than from the aluminium cations. On the other hand, taking electrons from nitrogen, which nominally has 9.41 of them, drives the nitrogen farther from the filled-shell configuration of ten, whereas taking them from Al, nominally with 10.59, drives the Al ions closer to the filled-shell configuration. Thus the issue is not obvious.

A comparison of embedded quantum cluster and large unit cell approaches to optical excitation of v_N^{3+} is in order. A second-neighbour cluster is $v_N^{3+} \cdot Al_4 \cdot N_{12}$, whereas a large unit cell would be typically $v_N^{3+} \cdot Al_{16} \cdot N_{15}$. The latter therefore contains 12 Al ions beyond nearest-neighbour sites, and 3 N ions beyond second-neighbour sites. With the nearest-neighbour embedded cluster, the four nearest-neighbour quantum-mechanical Al ions, and all more distant shell-model ions, are polarized by the defect's charge. With the large unit cell, all ions are represented quantum mechanically. However, those on the cell's periphery, barely beyond second-neighbour distance, are essentially unpolarized, because the electric field from one cell's defect is largely cancelled out by that from the defects in the other cells. The polarization of all other neighbours is similarly affected, to a lesser degree. In the present work, when we neglect polarization, we do so only for shell-model ions; i.e. ions beyond nearest neighbours. In a second-neighbour cluster analysis, neglect of polarization would apply only to ions beyond second neighbours. The second-neighbour distance is 1.63 times the nearest-neighbour distance. We find that, even with an excited-state p-type orbital whose maximum density is at a distance of only 0.49 times the nearest-neighbour distance, the neglect of polarization for second-neighbours and beyond affects the excitation energy by 0.5 eV, or

6%, and the effect grows rapidly for more diffuse excited states. Qualitatively, the larger the number of polarized ions that are significantly overlapped by the excited state orbital, the larger the error in neglecting polarization. Thus, for large unit cell treatment, we can expect the error due to poor representation of polarization to be small only if overlap of the excited state electron with second neighbours and beyond is small, assuming that polarization of nearest-neighbours is reasonably well-represented by that model. For more diffuse excited states, analysis of optical absorption will require an embedded cluster approach.

Acknowledgments

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