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F center in BaF_2: Diffuse excited state

J. M. Vail, W. A. Coish,* H. He,† and A. Yang
Department of Physics and Astronomy, University of Manitoba, Winnipeg, MB, Canada R3T 2N2

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The optical properties of the F center in BaF_2 are of importance because the F center is a product of radiation damage when the material is used as a luminescent radiation detector. Its optical excitation energy is 2.03 eV, experimentally. We have applied computational modeling to study this process. Our method is based on a quantum molecular cluster containing the defect, embedded in a shell-model crystal. When the excess electron of the F center is kept localized in the molecular cluster, an excitation energy of 3.33 eV is found. When the F-center electron is allowed to become much more diffuse, the ground state remains within the vacancy, but the excited state delocalizes, and the excitation energy drops to about 2.56 eV, but the model is inaccurate because quantum-mechanical features of distant ions are omitted. A polaronic representation of the single diffuse electron is then carefully incorporated with the embedded quantum cluster treatment of the system. The polaron in BaF_2 is found to be beyond the intermediate-coupling regime. Feynman's path-integral results for Fröhlich's polaron model give an effective mass of 3.12, in units of band mass. The resultant estimate of F-center excitation energy is 2.04 eV. The successful combination of a quantum molecular cluster modeling element with bulk crystal modeling elements (band mass and polaron correction) warrants further study along these lines. Quantitative and physical limitations of the method and results are discussed.

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I. INTRODUCTION

Barium fluoride is a luminescent gamma-ray detector material, with intrinsic luminescence at 6.36 and 5.64 eV. Radiation damage degrades the crystal's luminescent efficiency. Thus it is important to understand the optical excitation processes of radiation damaged products. One set of products of interest consists of O^- ions and F centers, produced by gamma rays in the dissociation of O^{2-}-vacancy defect complexes:

$$\{\gamma+(O^{2-}\cdot v_F)\}\rightarrow\{O^-+F_c\}.$$

In this equation, v_F is a fluoride vacancy, and F_c is an F center, an electron bound in a fluoride vacancy.

We have previously studied the above dissociation process, and the optical excitation of O^-, obtaining excitation energies of 9.74 and 8.95 eV.[1] Radiation damage of BaF_2 by gamma irradiation causes the emergence of an optical-absorption band centered at 2.18 eV, ranging from ~1.9 to ~3.0 eV.[2] The band probably arises from overlapping lines from a variety of color centers and their aggregates. In additively colored BaF_2, this is certainly the case, where Cavenett, Hayes, and Hunter[3] have combined Faraday rotation with optical absorption to resolve the F center, finding an excitation energy of 2.03 eV. None of these defects, therefore, appears to strongly overlap the intrinsic luminescent frequencies. In this work we study F-center excitation computationally, in order to test agreement between theoretical modeling and experiment in such a system. We find an atomically localized ground state and a substantially diffuse excited state. This requires that the modeling method combines quantum molecular cluster features for the localized state with bulk crystal features for the diffuse state. The latter are implemented in terms of band-mass and polaronic effects. The excellent agreement of the computed with the experimental excitation energy encourages future work along the lines discussed herein.

Electronic features of point defects that are localized within a few ionic diameters can be computationally simulated by the ICECAP methodology,[4,5] in which the ions affected by the defect are treated along with the defect in a quantum molecular cluster which is embedded in a classical shell-model crystal. The molecular cluster is treated in a self-consistent field unrestricted Hartree-Fock approximation with many-body perturbation-theory correlation correction. Calculations can include core pseudopotentials, or can include all the cluster electrons explicitly. Nuclear positions and electronic structure in the molecular cluster are in equilibrium with polarization and distortion in the embedding shell-model crystal, for stationary states. For optical transitions, polarization and distortion of the embedding crystal taken from the initial state may be applied in the final state, in conformity with the Franck-Condon principle. In a wide range of point defect properties where experimental results are available, this method has provided satisfactory agreement.[6,7]

When we begin to examine, herein, the optical excitation of the F center in BaF_2 by the ICECAP method, we find that the excess electron in the ground state is well localized in the vacancy, but in the excited state it is not. When the excitation largely removes the electron from the vacancy, the electronic structure of near-neighboring ions is significantly affected, and so is the total energy. Indeed, electronic density associated with nearby ions should be thought of as participating in, rather than reacting to, the excitation. Since this effect is well represented in the ICECAP method, we want to retain the quantum molecular cluster in the excited-state calculation. However, in the excited state, as we have said, one electron is quite diffuse, though still bound to the vacancy. It is not practical, in terms of computational constraints, to extend the quantum cluster to include all ions that are significantly overlapped by this diffuse electron.

In the past, diffuse states in crystals have been described in terms of a semicontinuum model, with a single quantum-mechanical electron, where polarization effects, both static and dynamic, due to both the binding center and a single quantum-mechanical electron, are treated by describing the crystal as a dielectric continuum. For such a model to be realistic, the electron's effective mass must contain the effect of the crystal's periodic atomistic structure: the band mass must be introduced. In addition, the effect of crystal vibration on the electron's dynamics must be included: this introduces a polaron factor to further modify the electron's effective mass. The physical features involved in such a description are complicated, and many forms of theoretical analysis have been discussed, notably by Fowler[8–10] and by Stoneham.[11] In both of the latter works[10,11] also will be found extensive discussions of the optical transition process.

Theories of the polaron factor for the effective mass fall into four categories: weak coupling,[12] intermediate coupling,[13] strong coupling,[14] and the Feynman method,[15,16] the latter valid, in principle, for all values of coupling. For computational simulation, it is essential to apply the version of polaron theory that is appropriate for the material in question, BaF_2 in the present case. In Sec. V we shall see that the coupling constant for BaF_2 falls outside the ranges of applicability for weak-, intermediate-, and strong-coupling theories, leaving us to rely on the Feynman method. Fowler's discussion of diffuse F-center states[10] includes polaronic effects only in the effective dielectric constant and Stoneham's discussion extends over the whole range of coupling strengths. We shall return to a comment of Stoneham's in Sec. V.

In the semicontinuum theory of F-center excitation, there is one quantum-mechanical electron, and the entire crystal is modeled as a continuum, with the vacancy represented by a simple effective potential. Discrete ion methods also exist, ranging from point-ion[17] to the present embedded quantum cluster models. One method, that includes quantum-mechanical ionic features for a substantial number of ions, and that has been applied, *inter alia*, to the F center in BaF_2, is the method of Bartram and Stoneham.[18] In that work, systematic approximations are made to atomic pseudopotentials.[19] These pseudopotentials are applied in deriving the F-center excitation energy in the 17 rocksalt-type alkali halides, and in CaF_2, SrF_2, and BaF_2. In comparison with experiment, the results are not very good. However, introduction of a single scaling factor (‘‘$\alpha = 0.53$’’) into all of the pseudopotentials produces remarkable agreement with experiment across the whole range of crystals. Nearest-neighbor ionic displacements and ionic polarizations are included in the model. The success of this semiempirical ion-size effect in collating such a range of data was a significant achievement in showing that the quantum-mechanical structure of the nearby ions, along with distortion and polarization of the nearby crystal, is essential for quantitative modeling. The calculated excitation energy for the F center in BaF_2 with this method was 2.08 eV. The authors were unable to identify the physical source of the scaling effect, and later applications of the method[20–25] showed that it could not be extended consistently and uniformly to F-center emission, or to the absorption by impurity-related F_A and F_B centers, in the alkali halides.

In Sec. II, we describe our computational model for localized electronic states in BaF_2. In Sec. III we give our results for vacancy-localized ground and excited states of the F center. In Sec. IV we consider diffuse F-center states. We find the ground state to be localized in the vacancy, but the excited state to be diffuse, largely outside the vacancy. In Sec. IV also, we discuss a polaronic correction for the diffuse excited state. In Sec. V the evaluation of the effective mass is carried out in terms of band theory and Feynman's path-integral polaron theory. In Sec. VI the results are summarized, and our conclusions are stated.

II. COMPUTATIONAL MODEL

We approach the simulation of a point defect, the F center in BaF_2, in terms of a quantum molecular cluster embedded in a classical crystal. The BaF_2 crystal in the fluorite structure consists of a simple cubic fluoride sublattice of F^- ions, with a Ba^{2+} ion at the center of every other cube. The quantum cluster is centered on a fluoride site, and is treated in an unrestricted Hartree-Fock approximation. It consists of the four Ba^{2+} nearest-neighbor ions described in terms of effective potentials of the Kunz-Klein type,[26] and the six second-neighbor F^- ions with an all-electron treatment. The embedding is in terms of the shell model of Catlow, Norgett, and Ross.[27] The ICECAP method[4,5] is applied, in which polarization and distortion of the embedding crystal are consistent with ionic and F-center charges in the cluster region. The quantum cluster basis set has three parts. On the Ba^{2+} ions are 6*s* orbitals consisting of two Gaussian components initially fitted to the tail of a WTBS orbital,[28] and then optimized in the F-center ground state. The fluoride ions have (43/4) orbital sets originally from Huzinaga,[29] optimized iteratively between perfect-crystal embedded clusters, fluoride-centered $(Ba^{2+})_4\ (F^-)_7$ and Ba^{2+}-centered $(Ba^{2+})_1\ (F^-)_8$. Specifically, for a given perfect-crystal cluster, say fluorine centered, the atomic-orbital basis functions of the central ion are optimized, keeping all other orbitals fixed. The optimized fluorine basis set is then transferred to the other cluster, in this case barium centered. The basis functions of the central barium ion only are then optimized, keeping all others fixed. The optimized barium basis set is then transferred to the fluorine-centered cluster, where the previously optimized fluorine basis functions are also installed. The process is then iterated to convergence. Optimization of a given atomic orbital proceeds as follows. The most diffuse primitive atomic orbital (Gaussian localized) has its longest-range exponential coefficient fixed, to avoid spurious delocalization into the surrounding classical shell-model embedding region. Contraction coefficients and exponential coefficients are then successively optimized, going from the contraction coefficient of the second most diffuse primitive to its exponential coefficient, then to the next most diffuse primitive, and so on. The process is iterated to convergence for a given atomic-orbital basis function, before proceeding to another. The process is further iterated to convergence within the basis set for a given ion. Optimization in all cases is in terms of total-energy minimization. Convergence in all cases is to an accuracy of approximately 0.01 eV. In addition, fluoride $3s$, $3p$, and $3d$ orbitals are initially concocted by scaling from Kr, with tails of limited range to avoid basis-set superposition, and then optimized in the F-center ground state.

The F-center basis consists of vacancy-centered *s*- and *p*-type orbitals for ground and excited states, respectively, optimized in the embedded cluster. In BaF_2, the ionic sites are not centers of symmetry. Thus, the stationary states of the F center will not be of definite parity. However, in a calculation that includes both *s*- and *p*-type orbitals, the ground state is dominated by the *s*-type ($l=0$) component, since the *p*-type ($l=1$) components have zero amplitude in the Fock eigenvector that corresponds to the excess electron. Our use of an even-parity pure *s*-type ground state dictates a pure odd-parity *p*-type excited state, at the same level of approximation. It is then consistent to neglect the distortion of the ground-state embedded molecular cluster. In the excited state, as we have mentioned, the electronic distribution is changed from that of the ground state, although the ionic basis sets are unchanged. This corresponds to the situation in which the electronic structure of these ions responds instantaneously as part of the electronic excitation. On the other hand, the shell positions (as well as core positions), in these calculations, are held fixed through the excitation. This is the extreme form of the Franck-Condon principle. If one thinks of core-shell displacement as literally representing, approximately, distortion of the ion's electronic structure, then to be consistent with what happens in the quantum cluster in the excitation, one might allow the shells of shell-model ions to relax to equilibrium also, in the excited state. In fact, however, it is not clear just how to handle shell-model polarization in an optical transition. The reasons are twofold. First, it is well known that the shell model is a parametrized model, and that in particular there is no obvious relationship between the shells and the more malleable part of the ion's electronic structure. This is clear when one realizes that perfectly good shell models exist with positively charged shells. The other feature of the shell model that gives pause when it comes to too literal physical interpretation is the identically zero mass assigned to the shells. In any case, the approach that we use here, with frozen shells for the excitation, has been used successfully in other problems where detailed comparison with experiment is available.[30]

The perfect-crystal $(Ba^{2+})_4$ $(F^-)_7$ cluster with an optimized basis set is found to equilibrate with the embedding shell-model crystal with about 10% inward relaxations for both Ba^{2+} and F^-. This represents a mismatch of the modeling between the quantum cluster and its shell-model embedding. It should be taken into account when evaluating distortion due to the F center. The ground-state F-center cluster is found to equilibrate with the same relaxation, to two significant figures in the atomic displacements. We therefore proceed by assuming that distortion due to the F center is negligible in this system.

The computational model and method employed here are capable of evaluating a variety of experimental properties of F centers and other point defects. In general, spin densities can be evaluated at neighboring nuclei. They are proportional to isotropic hyperfine constants that can be measured, in some cases, by the ENDOR method,[31,32] for both ground and relaxed excited states. Such a comparison between computation and experiment has been carried out, for example, for the F-center ground state in NaF.[7] In the present case, BaF_2, such experimental data are unavailable, either for the F-center ground state or relaxed excited state. The fact that the barium nearest neighbors of the F center are treated here in terms of a rigid effective core potential means that spin polarization of these ions is not included in our model. This effect, of course, contributes to the spin density. While spin densities and spin-density plots can be generated, the lack of relevant experimental data renders such work uninteresting. Atomic positions adjacent to point defects may in some cases be directly obtainable experimentally from the extended x-ray absorption fine-structure method.[33] None are available experimentally for the F center in BaF_2, nor are we able to confidently predict them due to the mismatch that we mentioned between cluster and shell-model interionic forces. The relaxed excited state, and the optical emission to the unrelaxed ground state for F centers, can be determined from ICECAP studies, but experimental data are unavailable for the F center in BaF_2. The present work is an initial study of a diffuse electronic state in the context of a small embedded quantum cluster computation. Accordingly, other computational details of the F center in BaF_2 are not included.

III. RESULTS: VACANCY-LOCALIZED STATES

The ground and excited states for the F center have vacancy-centered orbitals with radial dependencies of the form $\exp(-\alpha r^2)$, with exponential coefficients α_s and α_p, respectively. The radial dependence of the vacancy-centered orbital amplitude squared is represented in terms of range R:

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

R is the distance at which the square of the *s*-type orbital with α_s has a value $e^{-1}=0.368$ of its maximum, while the square of the *p*-type orbital with α_p has its maximum at R, with over 60% of the electron's charge lying beyond this distance. The nearest-neighbor spacing of the fluoride sublattice, 3.100 05 A, is here referred to as the unit of SCALE. Thus the four nearest neighbors of the F center are Ba^{2+} ions at a distance of $\frac{1}{2}\sqrt{3}=0.8660$ SCALE, and the six second-neighbor F^- ions are at 1.0 SCALE.

For values of α such that $R<1$, there are minima of the total energy with respect to variations of α_s and α_p for ground and unrelaxed excited states, respectively. These minima can be seen in Fig. 1. The respective ranges are $R_s=0.4183$ and $R_p=0.4459$ SCALE. When these are compared with the nearest-neighbor distance of 0.8660 SCALE, we see that they both represent wave functions that are well localized within the vacancy. They correspond to a calculated excitation energy of 3.33 eV, which compares badly with the experimental value of 2.03 eV.[3] However, from Fig. 1 we see that the excited state has a second minimum at a much larger

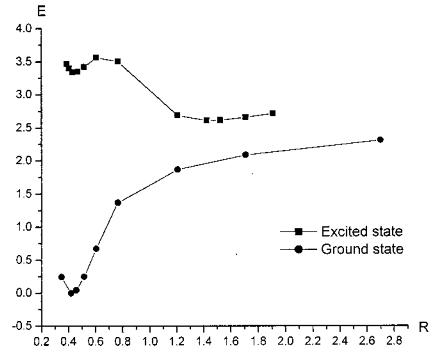

FIG. 1. F center in BaF_2: total energy E (eV) of ground and unrelaxed excited states as a function of range R (SCALE), relative to the ground-state minimum, without polaronic correction.

value of R. This leads us to question the vacancy-localized picture of the F-center excited state.

IV. DIFFUSE STATES: A POLARONIC MODEL

Diffuse states, particularly excited states, are common in color centers. However, the model described in Sec. II is not suitable for such states because it does not contain quantum-mechanical features of the ions beyond the quantum cluster. These quantum-mechanical effects, at the Hartree-Fock level, are first, the spatial extent of the electronic distribution of the ions, and second, the Pauli repulsion or exchange effect. The first contributes to a potential that alternates between attractive and repulsive as the electron passes from cation to anion over a distance of the order of SCALE. The second is consistently repulsive.

We begin by considering total energy E vs range R for both ground and unrelaxed excited states: See Fig. 1. We find E rising monotonically with R for $R \lesssim 1$ for the ground state, suggesting that this state is indeed vacancy localized. For the excited state, however, a second, lower minimum occurs at $R = 1.4709$ SCALE, corresponding to an excitation of 2.56 eV, a drop of 0.77 eV from the vacancy-localized excited-state result.

We now undertake to correct in some approximate way for the inadequacy of the model for diffuse states. We propose to do this by removing the contribution $\varepsilon^{(1)}$ to the total energy from the excited-state electron, and replacing it by the energy of a polaron in a dielectric continuum, based on the effective band mass of the crystal.

Thus, if E_{exc} is the excited-state energy calculated with the original model and $\tilde{\varepsilon}$ is the polaron energy, then the corrected excited-state energy $\tilde{E}_{\mathrm{exc}}$ is

$$\tilde{E}_{\mathrm{exc}}(R) = \{E_{\mathrm{exc}}(R) - \varepsilon^{(1)}(R) + \tilde{\varepsilon}(R)\}. \tag{2}$$

The original total energy $E_{\mathrm{exc}}(R)$ includes the Fock eigenvalue for the excited-state electron, which turns out to be the highest occupied spin-up eigenvalue: we denote it as $\varepsilon_{31,\uparrow}$. It corresponds to the only occupied Fock eigenstate that is dominated by the vacancy-centered p-type orbital ψ_p. This eigenstate, however, is a true molecular orbital, containing small but significant contributions from both Ba^{2+} $6s$ orbitals, and from some F^- orbitals. Correspondingly, ψ_p contributes a small amount to many molecular orbitals that predominantly describe the fluoride ions. It is therefore not justified to identify $\varepsilon^{(1)}$ as $\varepsilon_{31,\uparrow}$.

What should be done, ideally, is to identify $\varepsilon^{(1)}$ as the energy of an electron in the orbital ψ_p, interacting with the shell-model ions of the embedding region, and with the quantum-mechanical ions of the quantum cluster. The latter interaction is dominated by the Coulomb field of the ionic charges in the quantum cluster. Several facts tend to support the approach that neglects the non-point-charge parts of the self-consistent field (scf). A p-type orbital ψ_p, oriented along the z axis, say, is zero at four of the six second-neighbor F^- ion sites. The contribution of these ions to the scf seen by the excess electron is therefore very small. The four nearest-neighbor Ba^{2+} ions are modeled by the KKLP effective potentials,[26] which are spherically symmetric, quite compact, and include exchange only intraionically. The two F^- ions that are most strongly overlapped by the orbital ψ_p are located well within the distance at which this orbital achieves its maximum value, and they span a small spatial region compared to that spanned by the excess electron.

On the basis of the preceding considerations, we have evaluated the energy of an orbital ψ_p in the presence of a crystal with a vacancy where all of the ions are represented by the shell model. This energy as a function of R, as with $\varepsilon_{31,\uparrow}(R)$, has a finite, positive-energy asymptote as $R \to \infty$ (with different asymptotes for one-electron and many-electron cases). The polaronic correction, which we shall introduce shortly, gives an energy $\tilde{\varepsilon}(R)$, Eq. (2), with a zero-energy asymptote. The asymptotic energy from the discrete, shell-model-based calculation must therefore be added to $\tilde{\varepsilon}(R)$, or alternatively subtracted from the one-electron energy $\varepsilon^{(1)}$ in a shell-model crystal with a vacancy. The result of the latter procedure is an estimate of $\varepsilon^{(1)}(R)$, with a zero-energy asymptote, which has been fitted as follows:

$$\varepsilon^{(1)}(R) = (-BR^{-N} + CR^{M}), \tag{3}$$

with energy in eV and R in SCALE, where

$$B = 1.499\,18, \quad N = 3.482\,33,$$

$$C = 1.168\,82, \quad M = 3.804\,55.$$

The χ^2 value of the fit is 0.0126 (see any textbook on data analysis, for example, Bevington and Robinson[34]).

Following the approach of Fröhlich,[12] we now represent the excess electron's energy $\tilde{\varepsilon}$ in terms of a polaronic single-particle Hamiltonian h, as follows:

$$\tilde{\varepsilon} = \langle \psi | h | \psi \rangle, \tag{4}$$

where ψ is the normalized single-particle excited-state orbital,

$$\langle \mathbf{r} | \psi \rangle \equiv \psi(\mathbf{r}) = 3^{1/2}(2\alpha/\pi)^{3/4} e^{-\alpha r^2} \cos\theta, \tag{5}$$

and

$$h=\left\{\frac{p^2}{2m^*}-\frac{e^2}{4\pi\varepsilon_0 Kr}\right\}\quad (SI). \tag{6}$$

In Eq. (6) m^* is the effective mass and K is the effective dielectric constant. This model assumes that the diffuse electron sees the crystal essentially as a dielectric continuum. In Hartree-Bohr atomic units, Eq. (6) becomes

$$h=\left\{-\frac{m}{m^*}\times\frac{\nabla^2}{2}-\frac{1}{Kr}\right\}. \tag{7}$$

Now from Eq. (5),

$$\frac{m}{m^*}\langle\psi|-\frac{\nabla^2}{2}|\psi\rangle=\frac{9}{2}\times\frac{m}{m^*}\times\alpha\quad (Hy), \tag{8}$$

and

$$-\frac{1}{K}\langle\psi|\frac{1}{r}|\psi\rangle=-\frac{2}{K}\left(\frac{2\alpha}{\pi}\right)^{1/2}. \tag{9}$$

We must convert Eqs. (8) and (9) from Hartree-Bohr units to eV-SCALE units. Now

$$1(\text{SCALE})=\left(\frac{3.100\,05\text{ A}}{0.529\text{ A}/a_0}\right)=5.8602a_0, \tag{10}$$

where a_0 is the Bohr radius. From Eq. (1), let R' be $(2\alpha)^{-1/2}$, where α is in a_0^{-2} and thus R' is in units a_0. Equations (4) and (7)–(9) now become

$$\tilde{\varepsilon}=2.72\left\{\frac{m}{m^*}\times\frac{9}{2}\times\frac{1}{2R'^2}-\frac{2}{K}\left(\frac{2}{\pi}\right)^{1/2}\times\frac{1}{2^{1/2}R'}\right\}\text{ eV}. \tag{11}$$

Now from Eq. (10),

$$\frac{R'(a_0)}{5.8602}=R\quad(\text{SCALE}). \tag{12}$$

Thus Eq. (11) becomes

$$\tilde{\varepsilon}=27.2\left\{(0.065\,52)\,\frac{m}{m^*}\times\frac{1}{R^2}-(0.1925)\times\frac{1}{KR}\right\}\text{ eV}, \tag{13}$$

with R in units of (SCALE). Equations (3), (2), and (13) give us our corrected excited-state energy $\tilde{E}_{\text{exc}}(R)$.

In Fröhlich's formulation of polaron theory,[12] he concludes that the appropriate value of the dielectric constant K is

$$K=(K_\infty^{-1}-K_0^{-1})^{-1}, \tag{14}$$

where K_∞ and K_0 are high- and low-frequency dielectric constants, respectively. Values calculated from our shell model[27] are given in Table I, along with experimental values.[35] The values of K are not significantly different in the two cases: we use the shell-model value. The question of effective mass will be discussed in the next section. Whatever value we adopt, we must then find the value of R which minimizes $\tilde{E}_{\text{exc}}(R)$, Eq. (2), with Eqs. (3) and (13).

TABLE I. Experimental and calculated values of dielectric constants (Eq. 14) of BaF$_2$.

	Calculation	Experiment
K_0	6.76	7.19
K_∞	2.18	2.16
K	3.22	3.09

V. DIFFUSE EXCITED STATE: RESULTS

The difference between effective mass m^* in the continuum model single-particle Hamiltonian, Eq. (6), and free-electron mass m has two sources. First it must account for the fact that the particle moves in the periodic potential of the crystal, outside the defect region. This requires the free-electron kinetic energy to be replaced by an expression involving the band mass m_b:

$$\frac{p^2}{2m}\rightarrow\frac{p^2}{2m_b}. \tag{15}$$

The band mass m_b is discussed in all textbooks of solid-state theory: see, for example, Grosso and Pastori Parravicini.[36] The band mass represents the effect of fully quantum-mechanical ions on the excess electron's dynamics, in place of the classical point-ion effects of the shell model represented in Fig. 1 for $R>1$. From Eq. (15), we see that, for given momentum, the kinetic energy is reduced if the effective mass is increased. We prefer to think in terms of given velocity. From Eq. (6), with m^* replaced by m_b, we see that

$$\frac{\text{p}}{m_b}=\vec{\text{v}}, \tag{16}$$

so that the kinetic energy is

$$\frac{p^2}{2m_b}=\frac{1}{2}m_b v^2, \tag{17}$$

which increases with m_b for given velocity. Experimental band masses for common semiconductors range from 1 to 10^{-2}: see, for example, Marder.[37] The band mass of BaF$_2$ has been calculated using our basis set along with the CRYSTAL program[38] for band structures, by Jiang and Franco,[39] to be 0.5552, in units of m. This is similar to calculated or inferred values for alkali halides: see, for example, Knox and Teegarden.[40]

The second property affecting the effective mass m^* arises from electron-phonon interaction. This is the polaron effect. It is analyzed in terms of a dimensionless coupling constant α [not to be confused with the exponential coefficient in Eq. (1)] defined as

$$\alpha=\frac{e^2}{4\pi\varepsilon_0}\times\frac{1}{2^{1/2}K}\times\left(\frac{m_b}{\omega\hbar^3}\right)^{1/2}. \tag{18}$$

In Eq. (18), *Système International* units are to be used, and ω is a frequency characteristic of the phonon spectrum, which, according to Fröhlich,[12] is approximately determined by

$$\omega = \left(\frac{K_0}{K_\infty}\right)^{1/2} \omega_t , \tag{19}$$

where ω_t is the reststrahl frequency. From the phonon-dispersion relation for BaF_2, based on a shell model by Hurrell and Minkiewicz,[41] we deduce

$$\omega_t = 2.935 \times 10^{13}\ \mathrm{s}^{-1}, \tag{20}$$

whence

$$\omega = 5.186 \times 10^{13}\ \mathrm{s}^{-1}. \tag{21}$$

We therefore estimate that for BaF_2

$$\alpha = 4.627. \tag{22}$$

The polaron coupling strength $\alpha = 4.63$, Eq. (22), is beyond the range ($\alpha \lesssim 3$) appropriate to intermediate-coupling theory,[13] and falls in the range that requires numerical integration of an effective-mass formula by Feynman.[15] The formula is

$$\frac{m^*}{m_b} = \left\{ 1 + \tfrac{1}{3} \pi^{-1/2} \alpha v^3 \int_0^\infty dx [F(x)]^{-3/2} \times e^{-x} \times x^2 \right\}, \tag{23}$$

where, near $\alpha = 5$, to an accuracy $\lesssim 3\%$,

$$v = \left\{ 1 + 1.14 \left(\frac{\alpha}{10}\right) + 1.35 \left(\frac{\alpha}{10}\right)^2 + 1.88 \left(\frac{\alpha}{10}\right)^3 \right\}, \tag{24}$$

and

$$F(x) = \left\{ x + \frac{(v^2 - 1)}{v} (1 - e^{-vx}) \right\}. \tag{25}$$

With $\alpha = 4.627$, v is equal to 2.0027, and numerical integration in Eq. (23) yields

$$\frac{m^*}{m_b} = 3.1161. \tag{26}$$

We conclude that

$$\begin{aligned} \frac{m}{m^*} &= \left(\frac{m}{m_b}\right) \times \left(\frac{m_b}{m^*}\right) \\ &= (0.5552 \times 3.1161)^{-1} = 0.5780. \end{aligned} \tag{27}$$

When this is applied in Eq. (2) with Eqs. (3) and (13) we obtain a minimum excited-state energy $\widetilde{E}_{\mathrm{exc}}(R)$ for $R = 1.5024$ (SCALE). This produces an estimated excitation energy ΔE, including polaron correction:

$$\Delta E = 2.04\ \mathrm{eV}. \tag{28}$$

The almost exact agreement of our calculated result, Eq. (28), with the experimental value of 2.03 eV, cannot be taken seriously. Earlier, we have discussed the physical approximations upon which our modeling is based, and these approximations will be reflected in the total energies calculated for the F-center ground and excited states, and presumably to some extent in the resultant excitation energy. Our application of Feynman's polaron theory requires further explanation, which may cast some light on the accuracy of the modeling for the excited state. Since it is not involved in our treatment of the ground state, it is directly reflected in the excitation energy.

Feynman's theory is a variational procedure that applies to a polaron in a Gaussian-localized *s*-type ground state. We have applied it to a *p*-type Gaussian-localized excited state. The uncertainty in so doing is not known. We note parenthetically Stoneham's statement (Ref. 11, p. 239) that the Gaussian-localized wave function is never favored for the bound polaron ground state. This is plausible for a truly diffuse F center, which at a large distance sees the vacancy to be much like a point charge, because we are familiar with the fact that electronic states of the hydrogen atom have Slater-type exponential tails $\sim e^{-\lambda r}$. We have mentioned the intermediate-coupling polaron theory of Pines.[13] It is accurate for $\alpha \ll 6$, and is formulated perturbatively in relation to polaron momentum rather than localization: it applies for low momentum, and presumably for low kinetic energy. Now for BaF_2 we have determined a value of $\alpha = 4.63 \lesssim 6$. Pines points out that, for $\alpha \lesssim 3$, the method can be used with confidence in an accuracy ~5%, and he presents a perturbative correction for larger values of α. Referring to Eq. (13), we see that the effective mass m^* affects only the polaron's kinetic energy (ke), as follows:

$$(\mathrm{ke}) = 1.782 \frac{m}{m^*} \times \frac{1}{R^2}, \tag{29}$$

where from Eq. (27),

$$\frac{m}{m^*} = \frac{m}{m_b} \times (\text{polaron factor}), \tag{30}$$

where $m_b = 0.5552m$. So far, we have determined the polaron factor, (m_b/m^*), only from the Feynman theory, as in Eqs. (23)–(25). Pines' intermediate-coupling theory gives, in first order,

$$\frac{m_b}{m^*} = \frac{1}{\left(1 + \dfrac{\alpha}{6}\right)}, \tag{31}$$

and to second order,

$$\frac{m_b}{m^*} = \left\{ \frac{1}{\left(1 + \dfrac{\alpha}{6}\right)} + \frac{0.02\alpha^2}{\left(1 + \dfrac{\alpha}{6}\right)^2} \right\}. \tag{32}$$

Note that "orders" in Eqs. (31) and (32) are defined in terms of the parameter $(1 + \alpha/6)^{-1}$. From Eq. (26), we have, from Feynman theory,

$$\frac{m_b}{m^*} = 0.3209. \tag{33}$$

From Eq. (32), we have, from intermediate-coupling theory,

$$\frac{m_b}{m^*} = (0.5646 + 0.1365). \tag{34}$$

In Eq. (34), we see that with $\alpha = 4.627$, the second-order term, 0.1365, is ~24% of the first-order term. We therefore conclude that intermediate-coupling theory is inappropriate for the polaron in BaF_2. With a polaron factor of unity, $m^* = m_b$, the effective mass is the band mass, with phonon effects neglected. In that case, from Eq. (29) we get a kinetic energy of 1.43 eV. As the polaron factor varies from ~0.3, the Feynman-based value, to unity, the optimal energy rises as the optimal value of R decreases, meaning that the excited state becomes less diffuse, to the point that at unity it is largely overlapping the first and second neighbors of the vacancy. In that case, the continuum and band-mass approximations of Sec. IV become inappropriate.

The applicability of a continuum dielectric model for the polaronic correction may be questioned for an excited-state wave function as compact as the one that we have used, even though it is diffuse in relation to the size of the vacancy. The p-type orbital's range R is 1.5024 (SCALE), and more than 60% of its probability density lies outside this range. Let us say that it spans a radius $r \sim 4$ (SCALE). This corresponds to a volume $\sim \frac{4}{3}\pi r^3 \sim 270\,(\mathrm{SCALE})^3$. Thus the orbital's diffuseness spans ~130 primitive unit cells.

The combination of band mass and Feynman's polaron correction brings the calculated excitation down by 0.52 eV from the value (2.56 eV) given by point-charge ions outside the quantum cluster, and the correction is in the right direction, in comparison with experiment (2.03 eV). Inclusion of the polaron correction with the band mass gives an optimal polaronic wave function whose diffuseness is compatible with the corrections. From all of the above we conclude that while the calculated agreement with experiment to an accuracy of 0.01 eV must be in part fortuitous, the corrections implemented here are physically reasonable, of the correct order of magnitude, and in the right direction.

VI. SUMMARY AND CONCLUSIONS

We have studied the unrelaxed excited state of the F center in BaF_2. The experimental optical excitation energy is 2.03 eV. Our basic model consists of a second-neighbor quantum molecular cluster embedded in a classical shell model of point charges. In calculating the optical excitation energy of the F center in BaF_2, we have found the excess electron to be stable within the vacancy in the ground state, and metastable within the vacancy in the excited state. The estimated excitation energy from these two states is 3.33 eV. The stable unrelaxed excited state has a diffuse excess electron, overlapping $\gtrsim 100$ primitive unit cells. Even this model, unsatisfactory as it is for a quantum-mechanical electron outside the cluster, gives a predicted excitation energy of 2.56 eV, within 30% of the experimental value. Corrections are made to the excess electron's energy, both for band (periodic-crystal) and polaron (electron-phonon) effects, treating the crystal as a dielectric continuum. The effective band mass m_b has been calculated using the basis set of the present work, giving $m_b = 0.5552m$. The effective dielectric constant was evaluated from data derived from our shell model, in agreement with experimental data. The dimensionless polaron coupling constant α has been evaluated, giving $\alpha = 4.63$, outside the ranges of weak-, intermediate-, and strong-coupling theories. In evaluating α, the reststrahl frequency has been taken from the BaF_2 phonon-dispersion relation derived from a shell model (not the same as the one used herein). The value $\alpha = 4.63$ gives a polaron effective mass, including band-mass correction of $m^* = 1.7301m$, based on Feynman's path-integral theory for Fröhlich's polaron model, applicable to all coupling strengths. When this polaron correction is applied to the embedded quantum cluster result, a predicted excitation energy of 2.04 eV is obtained. Since the Feynman theory, which we have used, is for an s-type Gaussian wave function, and is therefore not strictly applicable to our p-type excited state, the degree of agreement with experiment is not to be relied upon. What we can say is that application of the band-mass approximation alone, without polaron correction, is inconsistent with the assumption of diffuseness. When the polaron correction is included, the calculated results change from those based on point-ion embedding, in the right direction, and in the right order of magnitude.

The results are sufficiently promising that the method should be further developed and applied to other systems. Principal features of the present work, not represented by earlier works, include (i) Fröhlich polaron theory with the Feynman results for the region beyond intermediate-coupling theory, and (ii) accurate treatment of many-electron effects adjacent to the vacancy, in both ground and excited states. A major improvement in the method, conceptually if not quantitatively, would be the development of Feynman polaron theory for other than s-type Gaussian orbitals, especially for p-type Slater-type orbitals, whose radial dependence can be represented as a linear combination of Gaussians. An important test of the method would be to see whether the good agreement with experiment obtained here is repeated for systems that are known experimentally to have diffuse excited states. We intend to apply it to the relaxed excited state of the F center in one of the alkali halides for which resonance experiments that determine spin densities at nuclear sites have shown quantitatively the diffuseness of the state. Specific cases are KI (Ref. 42) and KBr.[43] In order to accurately simulate a relaxed excited state, the quantum cluster and the shell model need to be compatible. We propose that this be included as one of the criteria in developing a shell model, along with agreement with bulk and phonon characteristics of the crystals.

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[*] Present address: Department of Physics, McMaster University, Hamilton, ON, Canada L8S 4M1.

[†] Permanent address: Department of Materials Science, Lanzhou University, Lanzhou Gansu 730000, People's Republic of China.

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