

Possibility of off-center-exciton formation in BaFBr

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(Received 17 March 1989)

Extended-ion calculations have been performed in order to test the possibility of spontaneous off-center motion of excitons in BaFBr. The off-center motion is a mode of decay to F, H centers in the material. The lattice distortion energy is computed self-consistently with the extended-ion method. It is energetically favorable to form off-center excitons displaced roughly 2 a.u. along the molecular axis for fluorine and bromine centers. The fluorine center is stabilized most due to its low-energy F -center ground state.

INTRODUCTION

When photons of energy exceeding the band-gap value irradiate an ionic crystal, the free electrons and holes which are created can interact to form a stable bound state called an exciton. In ionic solids such as alkali halides the hole is localized in the p orbitals of halogen and the electron is in a more extended orbital. This species becomes self-trapped at low temperature by virtue of lattice distortions. The self-trapped exciton has been viewed¹ as an electron bound to a V_K center (X_2^-) in alkali-halide crystals. Relaxation of the self-trapped exciton can lead to F and H centers as shown in various time-resolved spectroscopic studies.²

Various calculations of the self-trapped exciton in alkali halides have been presented. These include Hartree-Fock,³ pseudopotential,⁴ and complete neglect of differential overlap⁵ treatments. Good agreement of electron excited-state energies with experiment have been generally found. Recently the extended-ion model in the hybrid approximation⁶ has been applied⁷⁻¹⁰ to off-center configurations of the self-trapped exciton in alkali halides and alkaline-earth halides. It has been found in these calculations that the exciton spontaneously moves off center by approximately 2–4 a.u. along the axial direction, depending upon the crystal. A stabilization of a few electron volts is noted in the closely interacting F, H pair in the off-center configuration. Analysis of experimental excited-state transition energies and spin densities has provided support for the off-center model. The physical reason for the distortion has been explained as due to a deeper potential well for electrons at a F center relative to an exciton. Thus the electronic stabilization can account for the energy required to deform the crystal lattice as the off-center motion takes place. The purpose of this paper is to determine whether the off-center instability is possible in the alkaline-earth fluorohalide, BaFBr.

METHOD

The electronic energy of the self-trapped exciton is computed with a one-electron Hartree-Fock method known as the extended-ion model. Within this model the

electron is treated with a floating $1s$ Gaussian orbital basis. The Schrödinger equation is solved in the field of the ions surrounding the defect electron. These ions are represented by the hybrid method described by Song, *et al.*⁶ or the first-order pseudopotential terms introduced by Bartram *et al.*¹¹ The electron is described by a floating $1s$ Gaussian orbital ϕ_i orthogonalized to the core wave functions $\chi_{c,l}$:

$$\psi_i = \phi_i - \sum_{c,l} \langle \phi_i | \chi_{c,l} \rangle \chi_{c,l} . \quad (1)$$

The secular determinant is solved for this wave function where the core states include 349 ions and are represented by the pseudopotential ion-size parameters which treat screened Coulomb and exchange energies. The long-range Coulomb energy is treated by Ewald summation. We employ optimized Gaussian damping factors up to 0.10 a.u. on the molecular axis as in earlier implementations of this method.⁷⁻¹⁰ These calculations are performed with a version of the hybrid method code⁶ modified so as to treat the lower symmetry of the BaFBr crystal.

The X_2^- molecular ion is treated at the relaxed interatomic separation of the V_K center. This distance is determined in a classical atomistic calculation¹² using the HADES computer code.¹³ The pseudopotential parameters for the X^- and/or X^{2-} species are taken from earlier calculations⁴ with the pseudopotential method. Parameters needed for the hybrid method are computed from Hartree-Fock atomic orbitals.^{14,15} Madelung potentials appropriate to the off-center positions of the molecular species are computed by Ewald summations.

The energy of crystal-ion distortion is computed classically with the HADES code. This method uses a shell model to describe ions interacting by Coulomb and short-range potentials. Such potentials have been derived for BaFBr.¹² The ion distortions are computed for the charge distribution of the defect electron. This quantity is determined by the extended-ion calculation. It is found that when the molecular species is displaced along its axial direction, the electron becomes concentrated in the region being vacated. For example, a displacement of 1.3 a.u. of the F_2^- center gives 83% of the defect electron in

the vacated region as estimated from coefficients in the wave function. The lattice ion displacements due to the V_K off-center motion and the defect electron computed from the HADES method are reintroduced in the extended-ion method. This achieves a rudimentary self-consistency between the two calculations. The change in total energy of the system versus displacement is the sum

$$\Delta E = \Delta E^S(\bar{\mathbf{R}}) + \Delta E^Q(\bar{\mathbf{R}}), \quad (2)$$

where $E^S(\bar{\mathbf{R}})$ is the steric or crystal distortion energy and $E^Q(\bar{\mathbf{R}})$ is the lowest eigenvalue in the quantum-mechanical calculation.

RESULTS

The structure of BaFBr is tetragonal with layers of ions as shown in Fig. 1. We observe that the layers normal to the c axis consist of close-packed fluoride-ion planes separated by barium ions and two adjacent bromine-ion planes. There are three distinct pathways for exciton decay to F, H pairs which we will consider. These involve off-center motion of the V_K center along the direction of its molecular axis. These are sketched in Fig. 1 and consist of (110) motion of the fluorine center, (100), and an out-of-plane motion of the bromine center.

We consider the energy change involved in relaxation of the F_2^- exciton by (110) motion in Fig. 2. The initial F_2^- ion has an internuclear distance of 3.82 a.u. As the ion is moved the steric energy increases and the electronic energy computed in the hybrid method decreases. The total stabilization is 3.5 eV for an equilibrium off-center

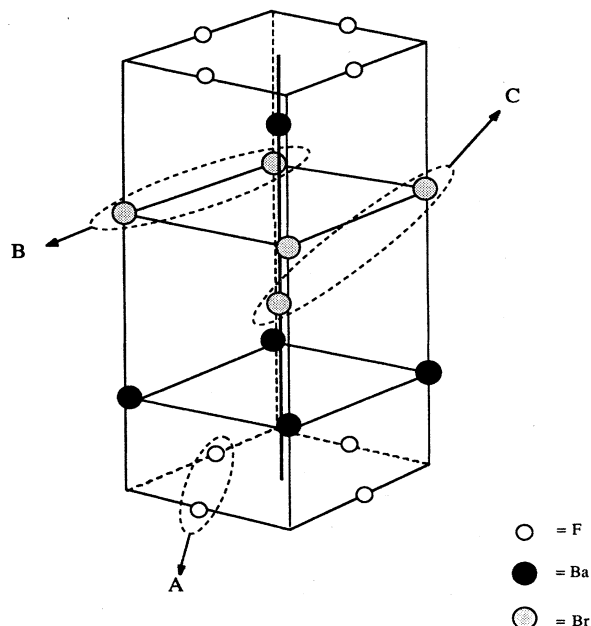


FIG. 1. The unit cell of BaFBr is shown along with three possible displacement pathways for the self-trapped exciton: A, fluorine (110) motion; B, bromine (100) motion; C, bromine out-of-plane motion.

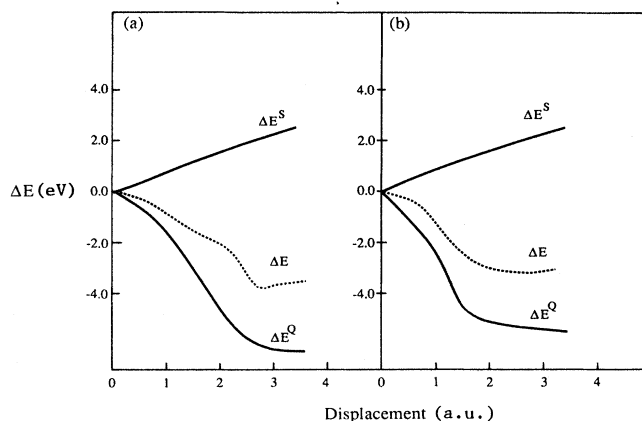


FIG. 2. Energy profile vs displacement of center of mass of F_2^- species in (110) direction. (a) Full hybrid method; (b) pseudopotential method.

displacement of 2.13 a.u. When the pseudopotential calculation is performed for this system (using only A, B parameters of Bartiam *et al.*¹¹) we find a stabilization of 3 eV with a displacement of 2.1 a.u. as shown in Fig. 2(b). Both levels of computation predict a stabilization of the exciton can occur if the molecular axis moves off center.

Energy changes accompanying Br_2^- off-center displacement are shown in Fig. 3. We consider the (100) motion in Fig. 3(a). A stabilization of 0.5 eV is predicted at an equilibrium displacement of 2.5 a.u. as computed by the hybrid method. A larger stabilization of 1.2 eV is computed by the pseudopotential method as shown in Table I. In both cases an activation barrier of a few tenths of 1 eV is observed. It is unclear how accurate this barrier value is since it reflects the balance of two energies. Lastly, we note that the energy change accompanying the Br_2^- off-center motion is less than in the previous case of the F_2^- off-center motion.

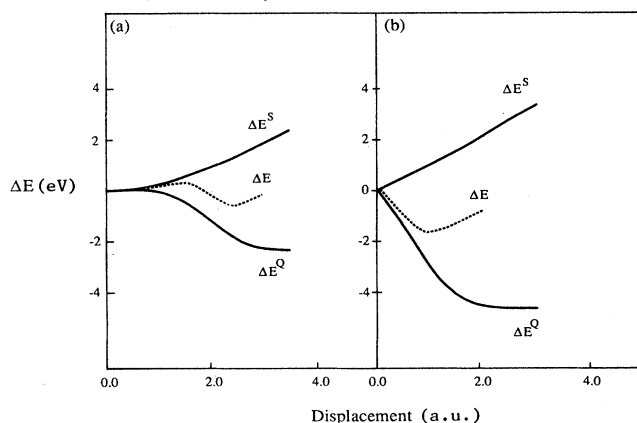


FIG. 3. Energy profile vs displacement of center of mass of Br_2^- species. (a) (100) direction computed by hybrid model; (b) out-of-plane direction computed by pseudopotential model.

TABLE I. Computed properties of the off-center exciton.

| Species | Decay path | Internuclear distance (Å) | Pseudopotential | | Hybrid | |
|------------------------------|--------------|---------------------------|----------------------------------|-------------------|----------------------------------|-------------------|
| | | | Displacement ^a (a.u.) | ΔE^b (eV) | Displacement ^a (a.u.) | ΔE^b (eV) |
| F ₂ ⁻ | (110) | 2.02 | 2.1 | 3.0 | 2.1 | 3.5 |
| Br ₂ ⁻ | (100) | 3.13 | 2.5 | 1.2 | 2.5 | 0.5 |
| Br ₂ ⁻ | out-of-plane | 2.92 | 1.5 | 0.5 | 2.0 | 0.9 |

^aDisplacement of the center of mass of the molecule from the on-center site.

^bSee Eq. (2).

The off-center motion of a Br₂⁻ center in an out-of-plane direction is considered in Fig. 3(b). A stabilization energy of 0.5 eV is computed for a displacement of 1.5 a.u. Activation barriers for this motion are not observed. We note that the degree of stabilization for off-center motion is similar to that for the (100) motion and much less than for the F₂⁻ off-center motion.

DISCUSSION

The possibility of formation of the off-center exciton in the alkaline-earth fluorohalides seems plausible based upon these calculations. In the case of fluorine and out-of-plane bromine excitons there is no energy barrier to motion from the centered position. The off-center fluorine exciton is stabilized more than the bromine exciton versus the centered position. This result is reasonable since the ground state of the fluorine *F* center is at least 2 eV deeper than the ground state of the bromine *F* center as shown in extended-ion calculations¹⁶ in this system. Thus the nearest neighbor (*F,H*)-center pair is more stable if the *F*-center ground state is deeper.

The mode of (*F,H*)-center production from band-gap

irradiation of BaFBr can clearly involve an exciton which undergoes an off-center motion. Once the near-neighbor *F,H* center is formed, diffusion of the *H* center must occur in order to avoid recombination. This diffusion is known to take place in alkaline-halide crystals with a low activation energy on the order of 10 meV. Thus the *F,H* near-neighbor pair can separate and lead to free charged defect species in the crystal.

These calculations are a first step in providing some plausible arguments for the off-center exciton in alkaline-earth fluorohalides. The method of calculation is approximate and is viewed as qualitative at this stage. It would be important to treat the electronic and lattice distortion components within the framework of a single method. The three directions of off-center motion are somewhat restricted and even more complicated motion might occur in these low-symmetry materials.

ACKNOWLEDGMENTS

I am grateful to K. S. Song for many helpful discussions on this work.

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