AB INITIO STUDY OF THE F CENTERS IN CaF$_2$: CALCULATIONS OF THE OPTICAL ABSORPTION, DIFFUSION AND BINDING ENERGIES

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The ground electronic state of the F center in CaF$_2$ crystal, its optical absorption energy, the activation energy of thermal diffusion and M center dissociation to pair of F centers are calculated using the Hartree–Fock embedded molecular cluster method. Different pseudopotentials, basis sets, boundary conditions and two computer codes, EMBED96 and Gaussian94, are employed and their results compared. © 1998 Elsevier Science Ltd. All rights reserved

1. INTRODUCTION

F centers in CaF$_2$ crystal, like in many ionic crystals, are fundamental primary defects created by ionizing radiation along with H and V_K centers. The F center diffusion and their interaction governs the process of their aggregation with subsequent metallic colloid formation in heavily irradiated and thermally annealed crystals. The latter process is responsible for unrecoverable radiation damage and destruction of the materials in CaF$_2$ optical devices. On the other hand, it finds a positive application in the electron beam lithography of CaF$_2$ insulating layers in microelectronics [1]. The activation energy for the F center diffusion, the binding energy for the F_2 dimer (M center) and the larger aggregate formation are the key parameters required as input for the statistical simulation of the kinetics of metallic colloid formation and growth.

Optical absorption of the F centers (3.3 eV) is well established experimentally [2] and can serve as a test for theory. F centers in alkaline-earth fluorides have been studied theoretically with the Xα method [3]. Agreement with experiment has been achieved in optical adsorption energy and hyperfine interaction constants.

Thermally stimulated luminescence (TSL) measurements [4] provide an experimental value for the H center diffusion energy of 0.46 eV. However, a reliable diffusion energy for the F center is not yet available. A tentative interpretation of a luminescence peak at 230 K as a recombination caused by the F center yields an activation energy of 0.7 eV. This interpretation only is supported by indirect evidence from the M center growth in CaF$_2$ [5]. There is only the study of the M center thermal decay [5] indicating that the M_{Na} centers in CaF$_2$ are stable up to 350 K. This data can be used to estimate the dissociation energy of the M center into the pair of F centers. Note that very few theoretical studies deal with the F center diffusion in ionic solids, such as KCl [6] and MgO [7] and none of them are done from first-principles.

The objective of this paper is to evaluate theoretically the above mentioned F center properties using the best available modern quantum chemical techniques.

2. METHODS OF CALCULATION

Two computational methods and corresponding computer codes have been used in the present study. In the Gaussian-94 calculations [8] the small (18 atom) quantum cluster with the defect in its center has been embedded into the finite array of host lattice ions. A standard D95 + basis set has been used for the F$^-$ ions

and LANL2DZ basis and pseudopotential [9] for Ca^{+2} ions within the quantum cluster. The cluster wave function has been calculated in the Hartree–Fock (HF) approximation. The ionic cage surrounding the quantum cluster was taken large enough to reproduce correctly the spatial dependence of the Madelung potential in the cluster region. Negative F$^-$ ions have been simulated by a bare Coulomb potential whereas positive Ca^{+2} ions have been replaced by LANL1 pseudopotentials to prevent unphysical delocalization of the cluster wave function.

The EMBED96 computer code [10] is based on the Perturbed-Cluster method. This approach is formulated in the framework of the HF method and contains the following sequence of steps in calculation:

(i) subdividing the entire defect system into a molecular cluster containing the defect region and an outer region, the indented crystal;

(ii) calculating the wave function for the molecular cluster in the crystal field of the indented crystal;

(iii) correcting for the right propagation of the wave functions into the indented crystal while generating the density matrix of the defect system.

Steps (ii) and (iii) are repeated to self-consistency. The corrective terms in step (iii) are evaluated by assuming that the density of states projected onto the indented crystal is the same as in *perfect* closed-shell host crystal. This is the fundamental approximation of the method. The Calculations presented here are similar to the *F* center calculations in LiF [11] and MgO [12] crystals where the details of the method and emerging technical problems are thoroughly discussed. In order to save the computation time, the semilocal pseudo-potentials given by Durand and Barthelat with corre-sponding basis sets [13] have been used for both F$^-$ and Ca^{+2} ions. For a better comparison, some of EMBED calculations have been made with the same pseudo-potentials and basis sets as those used in our Gaussian calculations.

The quantum cluster employed in the calculation by both methods (Fig. 1) has been centered in the middle of the line connecting the two nearest F$^-$ ions in the fluorite lattice and contains two central F$^-$ ions together with two spheres of nearest neighbors (6Ca^{+2} and 10F$^-$ ions). This results in the stoichiometric, Ca$_6$F$_{12}$ cluster. Next, one or both of the central F$^-$ ions have been removed while simulating the *F* or *M* center, respectively. The floating Gaussian orbitals have been centered on the created fluorine vacancies. Their exponents have been independently optimized for the ground (1*s*) and excited (2*p*) states of the *F* center as well as for the saddle point configuration of the *F* center diffusion hop.
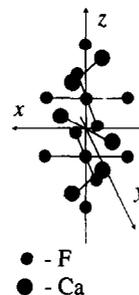
Fig. 1. Quantum cluster used in calculations.

3. RESULTS AND DISCUSSION

The wave function of the *F* center in its ground state is well localized in the vacancy. The optimal exponential of the floating Gaussian was found to be 0.15 a.u. with the Durand and Barthelat pseudopotential and 0.09 with LANL pseudopotentials in both EMBED and Gaussian calculations. Both methods and both pseudopotentials almost gave the same values for the *F* center formation energy and the position of the *F* center level in the band gap with respect to the top of the valence band calculated as a difference between Hartree–Fock eigenvalues (see Table 1). The *F* center electron binding energy with respect to the valence band maximum can be determined more precisely using the ΔSCF method as a difference between ionization potentials of the perfect cluster and that containing one *F* center. This has been done with the Gaussian code and the binding energy was found to be 9.5 eV above the top of the valence band.

The relaxation of the lattice around the *F* center was found to be very small. Four nearest Ca^{+2} ions have an inward displacement of 0.6% of the lattice constant ($a_0 = 2.77$ Å). The hopping of the *F* center has been studied with the EMBED method. We found that the motion of the F$^-$ ion along a straight path between two lattice sites is energetically not favorable. In the saddle point configuration the ion is displaced towards the empty interstitial site by 45% of a_0, which is about half way to the interstitial. This displacement gives an energy gain of 1 eV, about half of the overall relaxation energy. The coordinates of the saddle point configuration are given in Table 2. The calculated activation energy is in qualitative agreement with the experimental fact that the F centers are stable at least up to the room temperature [1].

The *F* center excitation energies listed in the Table 1 have been calculated by the EMBED method as a difference in Hartree–Fock energies between 1*s* and 2*p* states. In the case of Gaussian, the CIS MP2 method (Configuration Interaction with Single substitutions plus 2-nd order Moller–Plesset perturbation correction), has been used. Both values are higher than experimental absorption energy. The discrepancy can be attributed to the fact that the excited state wave function is more

Table 1. Energetic properties of the *F* center and *M* center calculated with different basis sets, pseudopotentials and cluster boundary conditions

Method	EMBED		Gaussian
Pseudopotential	Durand–Barthelat	LANL	
F center:			
Formation energy (eV)	6.55	6.40	6.50
Position of the level with respect to the top of the valence band (eV)	10.37	10.18	10.11
			9.50
Exponent of the floating Gaussian (a.u.)	0.15	0.09	0.09
Excitation energy (eV)	5.12		4.76
Diffusion activation energy (eV)	1.69		
M center:			
Dissociation energy (eV) singlet	0.31		
triplet	0.03		0.04

diffuse than that of the ground state and much larger clusters should be used in order to reproduce correctly the excited state of the *F* center.

The *M* center dissociation energy is defined as a difference in formation energy between the *M* center and the pair of separated *F* centers. It has been calculated using the Unrestricted Hartree–Fock method for both singlet and triplet states. The singlet state is more stable due to the chemical bonding between two *F* centers. The triplet state dissociation energy is 10 times smaller than that of singlet and can be attributed to the elastic interaction between *F* centers.

The activation energy for the thermal decay of the *M* center is approximately the sum of the *F* center diffusion energy and *M* center dissociation energy. The activation temperature for the *M* center decay can be roughly estimated assuming that for the similar processes the activation temperature is proportional to the activation energy. If we take the experimental values for the *F* center diffusion temperature (300 K [1]) and calculated values for the F center diffusion and the M center dissociation energies (Table 1), then we found 360 K

Table 2. Coordinates of ions in the saddle point configuration for the *F* center motion. Notations as in Fig. 1. Units $a_0 = 2.77$ Å

Ion	*x*	*y*	*z*
F$_{int}$	−0.307	0.307	0.0
Ca$_1$	−0.521	−0.491	0.0
F$_2$	−1.011	−0.024	0.532
F$_3$	0.000	−1.000	0.500
Ca$_2$	0.500	−0.500	0.500
Ca$_3$	−0.500	0.500	0.500
F$_4$	0.0	0.0	1.500

activation temperature for the *M* center decay in agreement with experimental observation [5].

4. CONCLUSIONS

Calculated properties of the *F* centers are in qualitative agreement with available experimental data. However, the error in excitation (absorption) energy is about 1 eV. The dependence of the results on the embedding model, pseudopotentials and basis set of atomic orbitals have been studied. We can exclude that the results can be improved by changing these parameters. The main source of error is that the *F* center wave function is rather diffuse in its excited state and at the saddle point configuration. The larger clusters should be used in order to solve this problem. Electron correlation correction is expected to be rather small, because only one electron is participating directly in the considered processes. However, it could increase the *F* center electron binding energy in both ground and excited states and lower the barrier for the *F* center diffusion.

REFERENCES

1. Stenzel, E., Bouchala, N., Gogoll, S., Klotzbucher, T., Reichling, M. and Matthias, E., *Mater. Sci. Forum*, **239–241**, 1997, 591.
2. Hayes, W. and Stoneham, A.M., *Defects and defect processes in nonmetallic solids*, John Wiley & Sons, New York, 1985.

3. Taurian, O.E. and Kai, T., *J. Phys. Chem. Solids*, **48,** 1987, 513; Feltham, P., *Phys. Status Solidi*, **20,** 1967, 675.

4. Atobe, K., *J. Chem. Phys.*, **71,** 1979, 2588.

5. Lisytsin, V.M., Habilitation dissertation, Riga, 1980.

6. Broun, R.J. and Vail, J.M., *Phys. Status Solidi*, **B49,** 1972, K33; Vail, J.M., Brown, R.J. and Ong, C.K., *J. Physique*, **C9,** 1983, 83; Kuklja, M.M., Kotomin, E.A. and Popov, A.I., *J. Phys. Chem. Sol.*, **58,** 1997, 103.

7. Popov, A.I., Kotomin, E.A. and Kuklja, M.M., *Phys. Status Solidi (b)*, **195,** 1996, 61.

8. Gaussian 94, Revision D.3, Frisch, M.J., Trucks, G.W., Schlegel, H.B., Gill, P.M.W., Johnson, B.G., Robb, M.A., Cheeseman, J.R., Keith, T., Petersson, G.A., Montgomery, J.A., Raghavachari, K., Al-Laham, M.A., Zakrzewski, V.G., Oritz, J.V., Foresman, J.B., Cioslowski, J., Stefanov, B.B., Nanayakkara, A., Challacombe, M., Peng, C.Y., Ayala, P.Y., Chen, W., Wong, M.W., Andres, J.L., Replogle, E.S., Gomperts, R., Martin, R.L., Fox, D.J., Binkley, J.S., Defrees, D.J., Baker, J., Stewart, J.P., Head-Gordon, M., Gonzalez, C. and Pople, J.A., Gaussian, Inc., Pittsburgh PA, 1995.

9. Hay, P.J. and Wadt, W.R., *J. Chem. Phys.*, **82,** 1985, 270; Wadt, W.R. and Hay, P.J., *J. Chem. Phys.*, **82,** 1985, 284; Hay, P.J. and Wadt, W.R., *J. Chem. Phys.*, **82,** 1985, 299.

10. Pisani, C., Birkenheuer, U., Cora, F., Nada, R. and Casassa, S., EMBED96 User's Manual, University of Torino, Torino, 1996.

11. Pisani, C. and Birkenheuer, U., *Comp. Phys. Commun.*, **82,** 1996, 221.

12. Scorza, E., Birkenheuer, U. and Pisani, C., *J. Chem. Phys.* (submitted).

13. Bouteiller, Y., Mijoule, C., Nizam, M., Barthelat, J.C., Daudey, J.P., Pelissier, M. and Silvi, B., *Mol. Phys.*, **65,** 1988, 295.