

## Calculation of the electronic structure and magnetic hyperfine contact terms of interstitial hydrogen in alkaline-earth fluorides\*

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The electronic structure of the interstitial hydrogen atom in alkaline-earth fluorides has been studied using the self-consistent-field multiple-scattering  $X\alpha$  method. In the calculations we have used a cluster constituted by the hydrogen atom and its first anion and cation neighbors. The contact parameters with the proton and the fluorine nuclei have been evaluated. The agreement obtained with the experimental results is in general good and indicates that this method is also appropriate to study defects in ionic crystals.

### I. INTRODUCTION

Interstitial hydrogen atoms in  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  were detected, using EPR and ENDOR techniques, by Hall and Schumacher,<sup>1</sup> Welber,<sup>2</sup> and Bessent *et al.*,<sup>3</sup> respectively.

To our knowledge the only theoretical treatment concerning the electronic structure of this defect in alkaline-earth fluorides was proposed by Hagston,<sup>4</sup> who used ligand field theory. Within his restricted scheme the wave function of the color center is strictly associated to that of the unpaired electron. Therefore this formulation is only able to take into account mechanisms such as Pauli repulsion (overlap core polarization) and charge transfer (covalence). Of course when we are interested in calculating hyperfine interactions, mainly in the case of magnetic contact terms, it is essential to include the possibility of closed-shell spin polarization in the description of the electronic structure. Ikenberry *et al.*<sup>5,6</sup> have used a perturbation technique<sup>7</sup> (moment perturbed method) in order to estimate the effects due to spin polarized closed shells in the evaluation of the contact terms of nearest-neighbor nuclei to the  $V_k$  and  $F$  centers in  $\text{LiF}$ . In these works the exact symmetry of the defect was not respected, as should be, the description involving basically a "central structure" ( $\text{F}_2^-$  molecule ion in the case of the  $V_k$  center and the unpaired electron in the case of the  $F$  center) and the ion for which the calculations have been performed. Schirmer,<sup>8</sup> studying the contact interaction with the Li nucleus in the  $V_{\text{Li}}$  center in  $\text{BeO}$ ,  $\text{ZnO}$ ,  $\text{MgO}$ , and  $\text{CaO}$ , has shown that a more realistic description of the spin polarization can be obtained by including ions other than those constituting the central structure of the defect ( $\text{O}^-$ - $\text{Li}^+$  complex). Therefore from his calculations

it is possible to infer that the inclusion of a large number of ions, together with the real local symmetry of the defect, is necessary if we expect to reproduce accurately the experimental results. This would be extremely difficult within the moment perturbed method.

Recently, Yu *et al.*<sup>9</sup> have used the SCF multiple-scattering  $X\alpha$  method to calculate the electronic structure of the  $U_2$ ,  $U$ ,  $U_1$ , and  $F$  centers in  $\text{KCl}$ . For the first time this method was applied for such kind of defects. They have calculated optical absorption bands and contact terms.

In the present work we will use this same method to study the interstitial hydrogen center in the alkaline-earth fluorides. Our purpose is to calculate its electronic structure and the contact term associated to the proton and the  $\text{F}^-$  ion nuclei neighboring it; as no optical-absorption bands have been associated to this center we were not concerned about optical transitions. The SCF multiple-scattering  $X\alpha$  method, developed by Johnson,<sup>10-12</sup> has been extensively discussed by several authors that applied it to many molecular systems.<sup>13-15</sup> We can briefly mention some advantages of this theoretical approach over LCAO-MO SCF methods. The SCF multiple-scattering  $X\alpha$  method takes into account spin polarization (within a mono-electronic formalism) together with the possibility of inclusion of a great number of ions reflecting the proper local symmetry of the physical system; most important is the fact that this scheme is faster computationally by something of the order of magnitude of a factor of a hundred to a thousand than an equivalent LCAO-MO SCF method, which could in principle reach the same purposes (within a configuration interaction procedure).

In Sec. II we shall discuss the theory and the

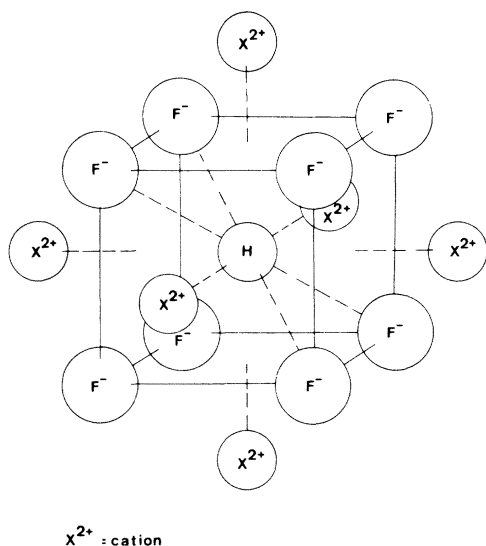


FIG. 1. Cluster used in calculations.

results obtained; Sec. III presents our conclusions.

## II. THEORY AND RESULTS

### A. Electronic structure

We have used the SCF multiple-scattering  $X\alpha$  method in the usual muffin-tin approximation, which is believed to be appropriate in describing crystalline systems with a predominant degree of ionic binding as is the case of the alkaline-earth fluorides. In this work the structure of the defect is approximated by the cluster shown in Fig. 1, which has  $O_h$  symmetry. Within such approximations the potentials and charge densities in the spheres containing the interstitial hydrogen atom and the ions surrounding it are spherically averaged. Outside the whole cluster the potential and charge density are spherically averaged. For the intersphere region volume averages of the charge density and potential are used, giving a constant value for the final intersphere potential. It is worthwhile mentioning that in a preliminary calculation a smaller cluster comprising only the eight  $F^-$  nearest neighbors to the H atom was chosen; the results indicated that a large fraction of the hydrogen-atom electronic charge "escapes" through the faces of the fluorine cube to the outer-sphere region which is physically unjustified. It is then obvious that for this small cluster the muffin-tin approximation is not adequate. The inclusion of the cations in the description of the defect improved the results as was expected since it greatly reduces constant potential region.

The choice of the ionic radii in order to define the inner spheres was made in the following man-

ner: (a) In the case of the  $F^-$  ions the radius was chosen in such a way that the spheres were tangent to each other compatible with the lattice parameter.<sup>16</sup> (b) the criterion used in item (a) makes possible to define uniquely all the other sphere radii if we impose that the nearest spheres be tangent to each other. Choosing the radii in this manner the intersphere muffin-tin region is minimized, the outer sphere radius is defined to be tangent to the anion and cation inner spheres, and the radii of all inner spheres are approximately proportional to the ionic radii tabulated<sup>17</sup> for the different elements of the cluster. In Table I are present all the data concerning this discussion.

The cluster considered has a total positive charge +4. In order to stabilize the cluster we used the idea of Watson<sup>18</sup> replacing the potential due to the rest of the crystal by a uniformly charged sphere such that the whole system would be neutral. Using for the outer sphere a Watson charge -4 we verified by simple calculations that the energy levels that interested us would not be bounded. Noticing that a Watson charge -1 did not present this inconvenience we firstly carried out complete calculations using this value. The results obtained for the potentials and charge densities were used as input to new calculations varying the charge in the outer sphere. It is important to note that all the results are essentially independent of the values used for the outer sphere charge, except for a corresponding uniform shift of the energy levels.

The nonlocal correlation potential present in the Hartree-Fock equations satisfied by the one-electron orbitals is replaced by the  $X\alpha$  statistical exchange potential.<sup>19,20</sup> The  $\alpha$  values used for the ions were those calculated by Schwarz<sup>21</sup> and for the hydrogen atom we used the obtained from a spin-polarized calculation.<sup>22,23</sup> A weighted average for the intersphere and the outer region was used; this follows the suggestion of Yu *et al.*<sup>9</sup>

Figures 2-4 present the one-electron energy levels for the defect in  $CaF_2$ ,  $SrF_2$ , and  $BaF_2$ , re-

TABLE I. Lattice parameters  $a$ , muffin-tin  $R$ , and ionic  $R'$  radii. Values are all in atomic units.

	$CaF_2$	$SrF_2$	$BaF_2$
$a$	10.32	10.96	11.72
$R_{out}$	7.05	7.60	8.01
$R_{cation}$	1.88	2.00	2.14
$R_{F^-}$	2.58	2.74	2.93
$R_H$	1.88	2.00	2.14
$R'_{cation}$	1.87	2.12	2.53
$R'_{F^-}$	2.51	2.51	2.51
$R'_H$	1.5	1.5	1.5

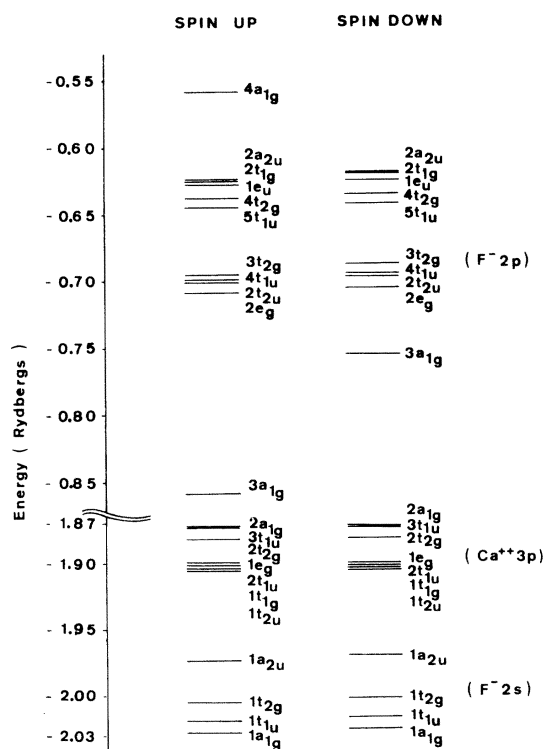


FIG. 2. One-electron energy levels from the ground-state calculation of the interstitial hydrogen atom in  $\text{CaF}_2$ .

spectively. We are only showing the levels that are not essentially atomic. All results presented in this work were obtained using a Watson charge  $-4$ .

The occupied  $3a_{1g}$  and  $4a_{1g}$  spin-up wave functions are mixed states from both hydrogen and neighboring fluorine ions. From the analysis of the charge distribution of the set of wave functions for each cluster we obtain that the most hydrogen-like orbital with spin up,  $3a_{1g}$ , is below the group of levels predominantly characterized by  $\text{F}^- 2p$  states. On the other hand the unoccupied hydrogen-like  $4a_{1g}$  spin-down orbital is above the fluorine levels. This is a result with the same feature as that of the  $U_2$  center in  $\text{KCl}$ .<sup>9</sup>

Table II presents the percentual amount of charge inside fluorine and hydrogen spheres arising from the spin up wave function associated to the energy level  $3a_{1g}$  for the three crystals.

Table III indicates the total amount of charge in the different regions of the cluster, including the outer sphere.

#### B. Magnetic hyperfine contact interaction

The magnetic hyperfine contact interaction with a given nucleus has a correct relativistic treat-

TABLE II. Percentual amount of charge inside hydrogen  $Q_H$  and fluorine  $Q_{F^-}$  spheres arising from the spin-up wave function associated to the energy level  $3a_{1g}$  for the three crystals. The fluorine charge is obtained by adding the charges in each of the eight spheres around hydrogen.

	$\text{CaF}_2$	$\text{SrF}_2$	$\text{BaF}_2$
$Q_H$	0.41	0.53	0.62
$Q_{F^-}$	0.44	0.32	0.17

ment,<sup>24</sup> and the Hamiltonian which describes it is

$$\mathcal{H} = \frac{2}{3} \pi g_e g_n \mu_B \mu_N \vec{I} \cdot \sum_i \vec{S}_i \delta(\vec{r}_i), \quad (1)$$

where  $g_e$  is the  $g$  factor of the free electron ( $g_e = 2.0023$ ),  $g_n$  the  $g$  factor of the nucleus,  $\mu_B$  the Bohr magneton ( $\mu_B = e\hbar/2m_e c$ ;  $m_e$  = electron mass),  $\mu_N$  the nuclear magneton ( $\mu_N = e\hbar/2m_p c$ ;  $m_p$  = proton mass),  $\vec{r}_i$  the position vector of the  $i^{\text{th}}$  electron with respect to the nucleus,  $\vec{S}_i$  the spin operator of the  $i^{\text{th}}$  electron, and  $\vec{I}$  the spin operator of the nucleus.

Evaluating the matrix element  $\langle \psi | \mathcal{H} | \psi \rangle$ , where  $\psi$  is the many-electron wave function of the cluster, and performing only the integration over the space coordinates we get the spin Hamiltonian

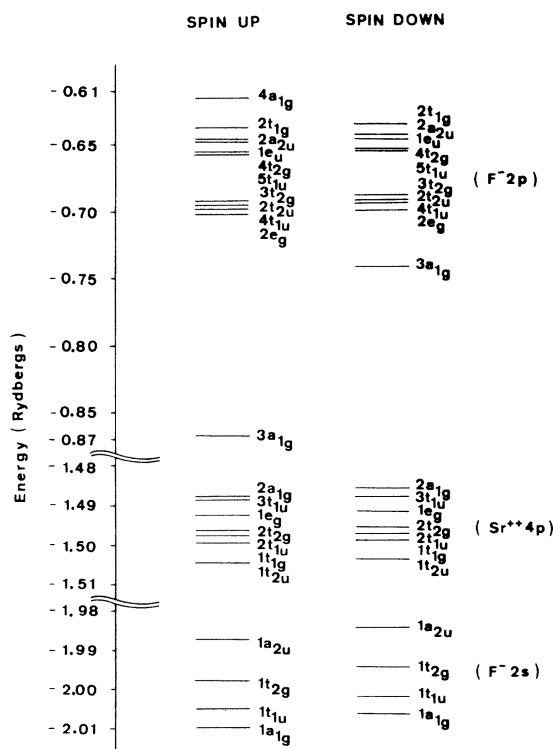


FIG. 3. One-electron energy levels from the ground-state calculation of the interstitial hydrogen atom in  $\text{SrF}_2$ .

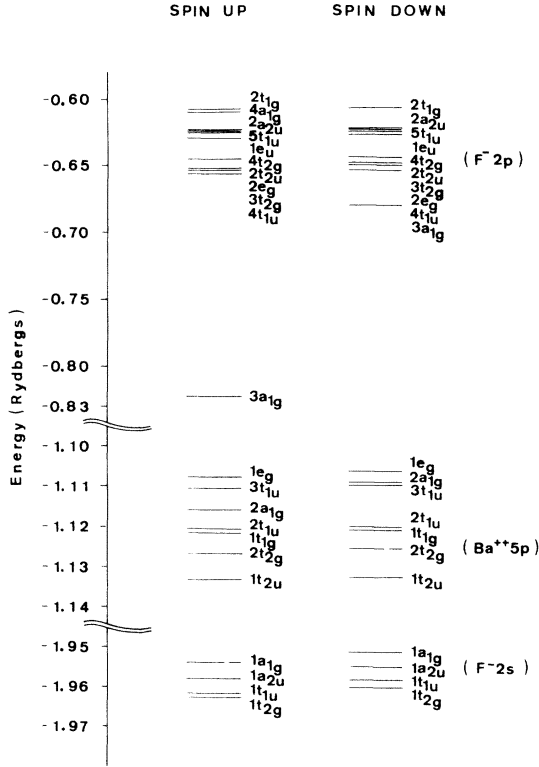


FIG. 4. One-electron energy levels from the ground-state calculation of the interstitial hydrogen atom in  $\text{BaF}_2$ .

$$\mathcal{H}_{ef} = a\vec{I} \cdot \vec{S}, \quad (2)$$

where

$$a = \frac{8}{3} \pi g_e g_n \mu_B \mu_N \sum_i [n_{i\uparrow} |\phi_{i\uparrow}(0)|^2 - n_{i\downarrow} |\phi_{i\downarrow}(0)|^2]. \quad (3)$$

$n_{i\uparrow, \downarrow}$  is the occupation number of the one-electron molecular orbital  $\phi_{i\uparrow, \downarrow}$  associated with spin up ( $\uparrow$ ) or down ( $\downarrow$ ).

TABLE III. Total charge for different regions of the cluster.  $Z \equiv$  atomic number;  $Q_\beta \equiv$  total charge inside  $\beta$  sphere.

	$\text{CaF}_2$ $Z - Q_\beta$	$\text{SrF}_2$ $Z - Q_\beta$	$\text{BaF}_2$ $Z - Q_\beta$	Ionic model ion charge
H	+0.07	+0.06	+0.05	0
$\text{F}^-$	-0.64	-0.75	-0.87	-1
Cation	+2.63	+3.12	+3.91	+2
Intersphere charge	6.13	8.20	11.62	...
Outersphere charge	0.58	0.54	0.92	...

TABLE IV. Proton contact term; comparison between experimental and theoretical results ( $a_{\text{H}_i}$  values are all in MHz). All parameters are defined in the text.

	$\text{CaF}_2$	$\text{SrF}_2$	$\text{BaF}_2$
$a_{\text{H}_i}^{\text{expt}}$	1464	1442	1425
$a_{\text{H}_i}^{\text{theor}}$	+1523	+1485	+1440
$\delta^{\text{expt}}$	3,1%	1,5%	0,4%
$\delta^{\text{theor}}$	7,3%	4,6%	1,4%
$\epsilon$	4,0%	3,0%	1,1%

### 1. Interaction with proton

It is usual to define the quantity

$$\delta = (a_{\text{H}_i} - a_{\text{H}}) / a_{\text{H}},$$

where  $a_{\text{H}_i}$  is the proton hf constant for the interstitial hydrogen atom and  $a_{\text{H}}$  the proton hf constant for the free hydrogen atom

$$(a_{\text{H}} = 1420 \text{ MHz}).$$

Table IV compares the experimental results with our theoretical calculations concerning the parameters  $\delta$  and  $a_{\text{H}_i}$ ; also the percentual deviation

$$\epsilon = (a_{\text{H}_i}^{\text{theor}} - a_{\text{H}_i}^{\text{expt}}) / a_{\text{H}_i}^{\text{expt}}$$

between experimental and theoretical values is given. We can notice that the experimental trend for  $\delta$  is reproduced in our calculations with a very reasonable absolute quantitative agreement. This is confirmed by the values obtained for  $\epsilon$ .

The most important contributions for the calculated values arise from the wavefunctions associated to the  $3a_{1g}(\uparrow)$ ,  $3a_{1g}(\downarrow)$ , and  $4a_{1g}(\uparrow)$  levels.

### 2. Interaction with fluorine nuclei

The theoretical and experimental results for the contact term, together with the value of the quantity

$$\epsilon = (a_{\text{F}}^{\text{theor}} - a_{\text{F}}^{\text{expt}}) / a_{\text{F}}^{\text{expt}}$$

are presented in Table V.

The most important contributions to this contact interaction arise in general from the wave functions associated to the  $3a_{1g}(\uparrow)$ ,  $3a_{1g}(\downarrow)$ ,  $4a_{1g}(\uparrow)$ , and

TABLE V. Fluorine contact term; comparison between experimental and theoretical results ( $a_{\text{F}}$  values are in MHz).  $\epsilon$  is defined in the text.

	$\text{CaF}_2$	$\text{SrF}_2$	$\text{BaF}_2$
$a_{\text{F}}^{\text{expt}}$	104	75	41
$a_{\text{F}}^{\text{theor}}$	+74	+50	+30
$\epsilon$	-29%	-33%	-27%

the spin polarized fluorine 2s and 1s wave functions.

As it is shown in Table V, the present calculation gives a fairly reasonable quantitative agreement between theory and experiment which would be difficult to be obtained by methods other than the SCF multiple-scattering  $X\alpha$ . To treat the problem using perturbation theory, trying to describe the defect as realistically as it was done in this work, would require a very complex mathematical formulation and an extremely large computational time. A possible improvement in the calculated results could eventually be obtained by increasing the size of the cluster as is indicated in the work of Schirmer.<sup>8</sup>

It is worthwhile to note that the calculation done was a static one. As shown by Spaeth<sup>25</sup> the consideration of the hydrogen zero-point vibration can contribute significantly to increase the value of the calculated contact term. The inclusion of such behavior would improve the agreement between theory and experiment.

### III. CONCLUSIONS

Usually one tries to describe the electronic structure of this kind of defect by the wave function of the unpaired electron corrected, taking into account its overlap with wave functions cen-

tered on the nearest neighbors, and eventually assuming a small degree of covalence.<sup>4, 26, 27</sup> Our results show that this procedure must be carefully reexamined since there exists a large degree of mixture between hydrogen and fluorine wave functions in the description of the  $3a_{1g}$  spin-up molecular orbital. We would like to emphasize that it was essential to include the cations in the cluster so that the constant potential muffin-tin region could be reduced.

Any attempt to correctly calculate contact interactions must realistically take into account complex mechanisms such as Pauli repulsion, charge transfer, and spin polarization since these interactions depend on the value of the one-electron wave functions in a specific point. The present calculations, using the SCF multiple-scattering  $X\alpha$  method, indicate that the wave functions obtained seems to be adequate to describe the electronic structure of the interstitial hydrogen atom in alkaline-earth fluorides. We believe that, when calculating dipolar interactions, these wave functions would reproduce the experimental results more accurately than when calculating contact interactions.

Other very good tests for this method are the study of the substitutional hydrogen ion  $H^-$  and atom in these same crystals. This study is in progress.

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