

Pseudo-Stark effect and hole-burning spectroscopy of the 590-nm center in $\text{SrF}_2:\text{Na}^+$ crystals

F. Ramaz, F. Madéore, and J. C. Vial

Laboratoire de Spectrométrie Physique, Université Joseph Fourier, Grenoble I, Boîte Postale 87, 38402 St. Martin d'Hères CEDEX, France

S. C. Rand

Division of Applied Physics, University of Michigan, Ann Arbor, Michigan 48109-2122

A. Hachimi* and J. Margerie†

Laboratoire de Spectroscopie Atomique, ISMRA, Boulevard Maréchal Juin, 14050 Caen CEDEX, France

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The local structure of the color center responsible for the zero-phonon transition at 590 nm in $\text{SrF}_2:\text{Na}^+$ crystals has been investigated using hole-burning spectroscopy in an external electrostatic field applied along several crystallographic directions of the crystal. The experimental results and the theoretical interpretations indicate that this center may be an $\text{F}_{2A}\langle 110\rangle$ center, that is a neutral divacancy center oriented along $\langle 110\rangle$ similar to F_2 centers in pure SrF_2 crystals, but significantly modified by the presence of sodium at the nearest-neighbor strontium site.

I. INTRODUCTION

Color centers in metal fluoride MeF_2 -type crystals have been studied extensively in the past, partly because their large vibronic emission bands offer prospects for tunable lasers. This is, for example, the case with the F_{2A}^+ centers in alkali-doped CaF_2 and SrF_2 crystals.^{1,2} Their emissions are interesting and could supplement organic dyes for tunable sources in the red and near infrared, but problems with thermal or radiative stability exist. These centers tend to transform into others under temperature or irradiation perturbations.²⁻⁴ Consequently, further investigations are necessary to control their chemistry. Additionally, basic questions still persist concerning the microscopic structure of some centers, such as the defect in $\text{SrF}_2:\text{Na}^+$ associated with a zero-phonon line at 590 nm, which we shall call the "590-nm center," for brevity.

Color centers in $\text{SrF}_2:\text{Na}^+$ consist of electrons trapped on F^- vacancies. Doping with an alkali ion can stabilize the center and procedures to create different kinds of centers in $\text{MeF}_2:A^+$ ($A^+=\text{Na}^+, \text{K}^+, \dots$) have been studied.⁵ The 590-nm center is more stable than many others.

Many investigations have been performed on the 590-nm center, especially with magnetic circular dichroism (MCD) techniques on the associated vibronic bands,³ and by electron paramagnetic resonance (EPR).⁶ Its non-paramagnetic properties clearly show that it has an even number of optical electrons, most probably two. Regarding the local structure, Rauch⁷ suggested that the 590-nm center is made of two electrons distributed on three adjacent fluorine vacancies along $\langle 100\rangle$ direction close to an Na^+ dopant (C_s point-group symmetry, see Fig. 1). But other possibilities exist for two-electron color centers in $\text{SrF}_2:\text{Na}^+$. The aim of this paper is to present experimental results which support a new model for the 590-nm center: an $\text{F}_{2A}\langle 110\rangle$ (C_{2v} point-group symmetry).

Knowledge concerning local physical structure of color centers is often difficult to obtain due to the presence of broad vibronic bands which obscure zero-phonon lines. When observable, zero-phonon transition wavelength and splitting patterns in external fields provide key information about the local structure of the center. However, in

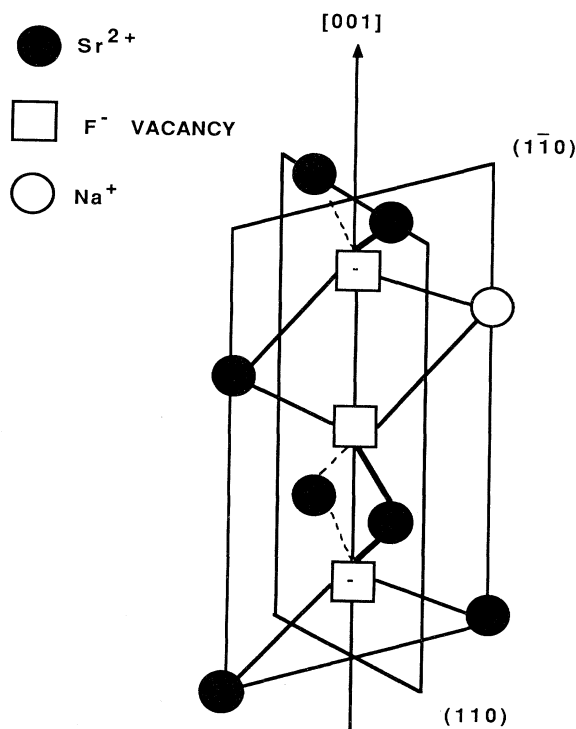


FIG. 1. Schematic diagram of the structure of a linear $\text{F}_{3,4}^+$ center. The point-group symmetry is C_s . The only mirror plane is $(1\bar{1}0)$.

the case of external electric fields (Stark effect) for example, very high field values are normally required to cause observable shifts or splittings of the zero-phonon line even at low temperature, due to a considerable residual width of the transition (inhomogeneous broadening). Nevertheless, such experiments have been performed with electrostatic fields on the $F_2\langle 110\rangle$ centers in SrF_2 ,⁸ and on $F_{2A}^+\langle 100\rangle$ one-electron centers⁹ in alkali-doped CaF_2 and SrF_2 .^{10,11} Here we have applied techniques of hole-burning Stark spectroscopy to overcome the need for large fields in studying the 590-nm center in $SrF_2:Na^+$.

Spectral hole-burning spectroscopy can be a very powerful technique for the study of color centers whenever it is possible to burn a persistent spectral hole in the zero-phonon line. Such a narrow feature, only a few MHz in width, behaves like a sharp, homogeneously broadened absorption line, and it makes possible the observation of spectral shifts and splittings in small electric fields, applied along different crystallographic directions at field strengths reduced by the ratio of the homogeneous to inhomogeneous linewidths of the zero-phonon transition. Under these circumstances, Stark fields of 1 kV cm^{-1} or less are normally sufficient for experimentation.

Selection rules, relating observed Stark splitting patterns to the polarization of the incident light and to the direction of the Stark field in the crystal frame, allow determination of the local symmetry of the center, as demonstrated in earlier experiments performed on NaF color centers.¹²

II. EXPERIMENTAL

Crystals of $SrF_2:Na^+$ were prepared using the procedure described in Ref. 6. The crystal structure is face-centered cubic with a cubic cell edge of $a = 5.8\text{ \AA}$,¹³ with easy cleavage along the $[111]$ direction. Each F^- ion is at the center of an Sr^{2+} tetrahedron (T_d point-group symmetry). All experiments were done at pumped liquid-helium temperature with samples immersed in the liquid. Conventional absorption spectra were recorded with a Perkin Elmer spectrophotometer providing a 0.8-\AA resolution, while hole-burning experiments on zero-phonon transition ($\lambda = 589.95\text{ nm}$) were performed using a Coherent 599-02 cw single-mode dye laser which was continuously tunable over a frequency range up to 30 GHz. The instrumental width of the laser was about 1 MHz. Fringes of a confocal Pérot-Fabry interferometer with 1.5-GHz free spectral range and a finesse of 350 were recorded simultaneously with our spectra for calibration.

Electric fields were supplied with transparent tin oxide electrodes on fused quartz windows in close contact with the sample surfaces. In order to reduce the effect of laser intensity fluctuations, hole-burning spectra were recorded using two GaAs photodiodes, and the light transmitted by the sample was normalized to the incident laser intensity. Persistent spectral holes were burnt in the zero-phonon line at zero field and subsequently read with low-intensity light in the presence of an electrostatic field ap-

plied along either the $[100]$, $[110]$, or the $[111]$ direction of the crystal. Relative orientations of the crystal axes, the polarization of light, and Stark field were recorded for each spectrum.

III. THEORETICAL BACKGROUND

The theoretical context of our work may be understood by considering the general nature of the eigenstates and eigenvalues of a two-electron center, starting with a point group of the highest possible symmetry and then analyzing level shifts and splittings as the symmetry is lowered in keeping with experimental conditions. We therefore begin the problem of determining the energy levels of a two-electron center by considering it to be a H_2 molecule, with axial and inversion symmetry ($D_{\infty h}$ point group), in an isotropic medium. When anisotropies of the real local environment are taken into account, the different electronic states of the H_2 molecule must be decomposed with respect to irreducible representations (Γ_i) of the new symmetry group. For each point group associated with a particular structure of the center, the representations corresponding to energy levels have a precise symmetry dictating selection rules for the electric dipole transitions, as indicated, for example, in Refs. 14 and 15.

Surprisingly good results about F_2 and F_2 -like color centers are obtained by the very naive model, first introduced by Herman, Wallis, and Wallis,¹⁶ of the H_2 molecule embedded in a dielectric continuum. The ground level is a nondegenerate $^1\Sigma_g^+$ state. Intense optical absorptions are expected only toward other spin-singlet levels (excited spin-triplet states are metastable and can be observed by EPR). The two first spin-singlet excited states of the H_2 molecule are nondegenerate $^1\Sigma_u^+$ and doubly degenerate $^1\pi_u$; the corresponding transitions from the ground level are polarized, respectively, parallel and perpendicular to the molecular axis (here the line that joins the two vacancies). Of course, the symmetry of the real problem is not $D_{\infty h}$, but one of its subgroups. Therefore, the $^1\pi_u$ level degeneracy is often lifted and the selection rules may be slackened. We shall tentatively assume that the spectra of F_{3A}^+ and F_{2A} centers are coarsely similar, since both of these centers have two optical electrons.

The probability of optical transition between Γ_i and Γ_j states is determined by the square of the relevant transition matrix element between these states, namely $\langle \Gamma_i | -\boldsymbol{\mu} \cdot \mathbf{E}_L | \Gamma_j \rangle$ ($=\boldsymbol{\mu} \cdot \mathbf{E}_L$), where $\boldsymbol{\mu} = \sum_i e \cdot \mathbf{r}_i$ is the electric dipole transition moment of the center and \mathbf{E}_L the electric field of the light. From group theory, one may predict for light of a given polarization the natures of the states Γ_i and Γ_j for which the above matrix element is nonzero. The information brought by the observed selection rules are all the more accurate that the color center point group has a higher symmetry.

In an external electrostatic field, each state Γ_i is shifted (in first order) by a Stark term of the form $\langle \Gamma_i | -\boldsymbol{\mu} \cdot \mathbf{E}_S | \Gamma_i \rangle$. Observation of the optical transition between Γ_i and Γ_j states should, therefore, reveal a shift of the transition energy given by

$$\delta\mu \cdot \mathbf{E}_S = (\langle \Gamma_j | -\mu | \Gamma_j \rangle - \langle \Gamma_i | -\mu | \Gamma_i \rangle) \cdot \mathbf{E}_S.$$

The shift vanishes in the presence of inversion symmetry, since then diagonal matrix elements of polar vectors, such as μ , are zero. Hence, the Stark shift of the transition energy is zero or nonzero in first order, depending sensitively on local symmetry, the optical transitions of interest, in the framework of the H_2 molecular model, are allowed both in the presence and absence of inversion symmetry. If more than one symmetry-equivalent orientation exists for a set of low symmetry centers, an electric field will in general cause a different Stark shift for different subsets of centers. This lifting of configurational degeneracy, or pseudo-Stark¹⁷ effect is revealed by a splitting of spectral lines. The pseudo-Stark splittings are sensitive to the local symmetry of the crystal, and in this work we have used pseudo-Stark results for various polarizations and electrostatic field orientations to attribute a local symmetry to the 590-nm center in $\text{SrF}_2:\text{Na}^+$.

IV. RESULTS

Figure 2(a) shows absorption bands at $T = 1.5$ K arising from the different color centers in $\text{SrF}_2:\text{Na}^+$. The

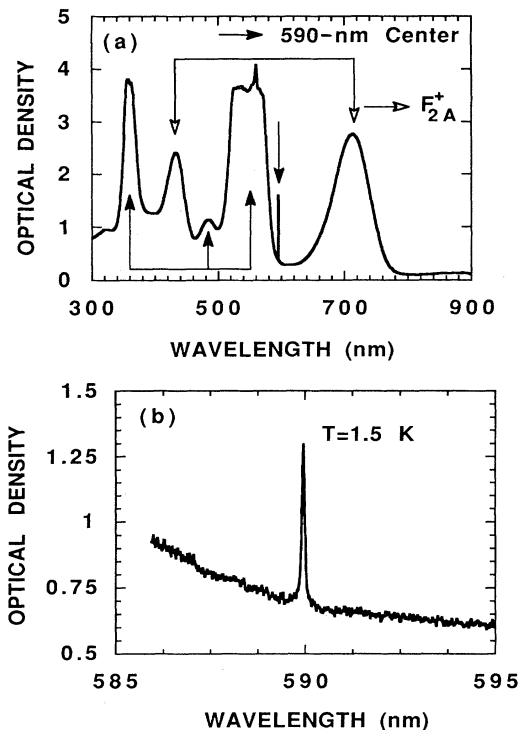


FIG. 2. (a) Absorption spectrum of $\text{SrF}_2:\text{Na}^+$ crystal at $T = 1.5$ K measured in optical density $\text{OD} = \log_{10}(I_i/I_t)$, where I_i and I_t are, respectively, the incident and transmitted light through the crystal. The attribution of the different bands are taken from Ref. 5. (b) Magnified section of the absorption spectrum around the 590-nm zero-phonon line at $T = 1.5$ K measured in optical density $\text{OD} = \log_{10}(I_i/I_t)$, where I_i and I_t are, respectively, the incident and transmitted light through the crystal.

center of current interest has two broad absorption bands centered at 490 and 555 nm. The former corresponds to a transition of the type $s \rightarrow p_z$, and is nonmagnetic, whereas the latter corresponds to a nearly degenerate $s \rightarrow (p_x, p_y)$ -type transition.⁵ A hole can be burnt inside the zero-phonon line of the long-wavelength band, located at $\lambda = 589.95$ nm as shown in Fig. 2(b). The decay of excitation at this wavelength exhibits three different lifetimes. The fluorescence lifetime has been measured as 4 ns.¹⁸ Second, metastable decay from triplet levels of the center reached by intercrossing occurs with an observed decay time of less than 100 ms. Measurements of similar phenomena have been performed at 77 K on analogous centers in CaF_2 ,¹⁹ and on F^+_3 centers in NaF at 4.2 K;²⁰ the decay times were, respectively, 0.83 and 2.5 s. Third, persistent hole burning may be observed (with monochromatic excitation) which decays on the time scale of several hours.

While mechanisms of persistent hole burning in this system have not yet been determined and are not discussed here, the spectra of Fig. 3(a) clearly reveal

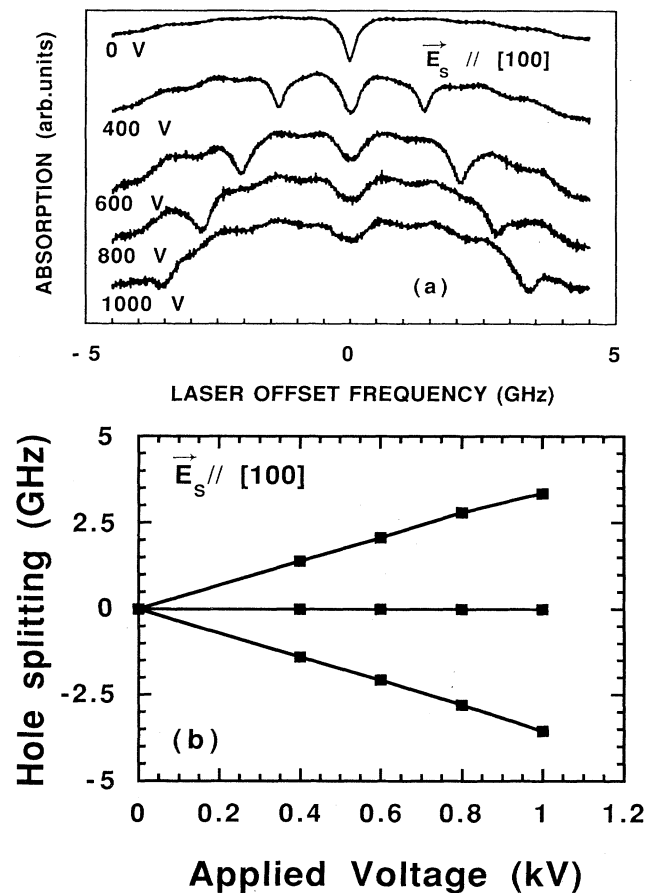


FIG. 3. (a) Pseudo-Stark splitting for different values of the electric field applied along the [100] direction for a crystal thickness of 1.58 mm. The light polarization has no simple relationship with the crystallographic axes. (b) Plot of the hole splitting vs the applied voltage for an electric field oriented along the [100] direction.

pseudo-Stark splitting of spectral holes within the zero-phonon line for different values of the electrostatic field oriented along the [100] direction. The splitting is linear, with a pseudo-Stark coefficient of 3.5 GHz/kV, as is shown in Fig. 3(b). Splitting coefficients observed with electric fields in directions different from [100] have smaller magnitudes they are approximately proportional to the cosine of the angle between the electric field and the nearest [100] direction.

This means that the Stark dipole moment $\delta\mu$ of the differently oriented centers is along the $\langle 100 \rangle$ direction.

In Figs. 4 and 5 spectra are shown which reveal important information about the orientations of the optical and Stark dipoles. In these spectra particular polarizations of the light have been chosen. Figure 4(a) shows that no

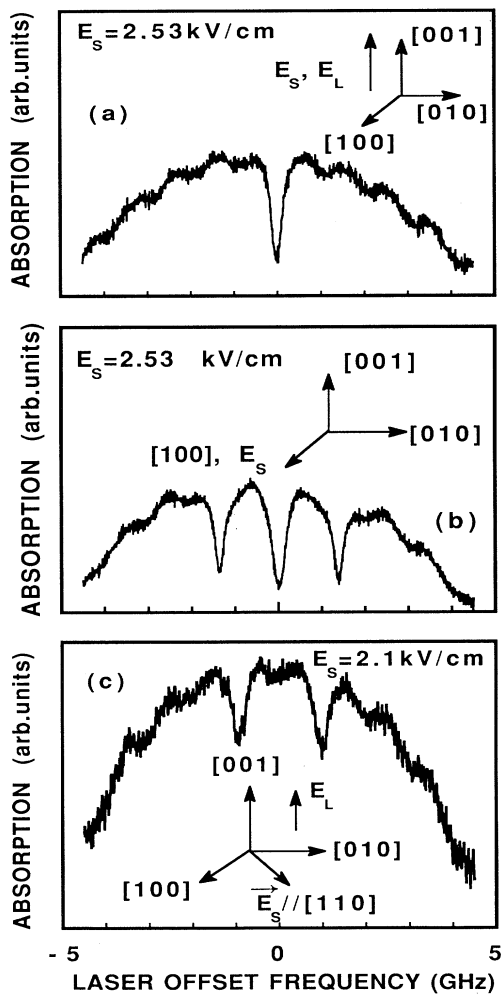


FIG. 4. Hole-burning spectra of the 590-nm zero-phonon line for different orientations of electric field E_s and light polarization E_L with respect to crystallographic axes. The crystal thicknesses are 1.58 nm for spectra (a) and (b), and 1.9 mm for spectrum (c). The central hole on the spectra (a) and (b) reveals the presence of centers, selected by light, but with a Stark dipole orthogonal to E_s . Spectrum (c) indicates that all centers excited by light polarized along [001] have the same nonzero Stark dipole component along [110].

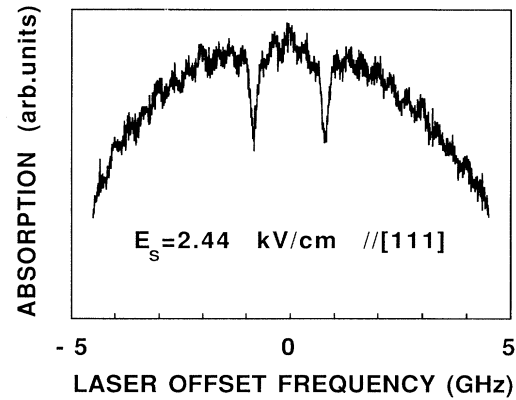


FIG. 5. Hole-burning spectrum for an electrostatic field applied along [111] and an arbitrary light polarization (crystal thickness is 1.84 mm). Since the Stark dipole is along [100], it has the same projection along [111] for each selected center and we only observe two holes.

effect occurs when E_L and E_s are parallel. This result can occur only if the optical transition dipole and the Stark dipole are perpendicular, and give rise in the figure to a central hole which does not shift or split at all. Shifted holes can appear together with unshifted central holes if two orientational classes of centers are simultaneously excited by the incident light. As an example, the central hole in Fig. 4(b) is due to the excitation of 590-nm centers which have their Stark dipole moment along [001] or [010], but have nevertheless a significant projection of their optical dipole moment along E_L , which direction has not been aligned along a particular crystallographic axis. (The ratio of area for shifted and unshifted spectral components allows us to calculate the proportion of centers whose levels have been shifted by the electrostatic field.) In Fig. 4(c), all centers exhibit the same nonzero splitting (there is no central hole at all) in the presence of the Stark field. Hence all centers which can be excited by [001] polarization have the same projection of $\delta\mu$ along [110]. Figure 5 is the hole-burning spectrum for an electrostatic field applied along the [111] direction. This spectrum clearly shows that the differently oriented centers all have their $\delta\mu$ along $\langle 100 \rangle$ directions, because, despite arbitrary light polarization, every excited center exhibits the same projection of $\delta\mu$ along the diagonal of the cube. This explains why we observe only two holes for Stark fields applied along the cube diagonal ($E_s \parallel [111]$).

We have also briefly tested the Zeeman effect of the 589.95-nm line. The hole was observed to remain unshifted under the influence of an external 0.5-kG magnetic field.

V. DISCUSSION

One may conclude from these results that the orientation of the Stark dipole $\delta\mu$ of the center is along a tetragonal axis of the crystal, while the optical transition dipole

μ_L is in a perpendicular plane. These simple results have important implications for possible models of the physical structure of this center.

A. Linear F_{3A}^+ model

As mentioned in the introduction, the 590-nm center has long been assumed to be a linear F_{3A}^+ center (Fig. 1). However, this hypothesis is in contradiction with the combined results of Refs. 3 and 21:

(i) By MCD experiments, Martin, Hamaidia, and Margerie³ have shown that the first excited state of the center (vibronic 555-nm band associated with the 589.95-nm zero-phonon line) is nearly doubly degenerate.

(ii) Using the hydrogen molecular ion (H_3^+) model, Amara *et al.*²¹ have predicted that the first spin-singlet excited state of the linear F_3^+ should be, as in the case of the F_2 center, a nondegenerate $^1\Sigma_u^+$ level (Γ_4 in the D_{2d} group), very far below the doubly degenerate $^1\pi_u$ (Γ_5 in D_{2d}). It seems dubious that perturbation by the sodium ion should be strong enough to invert the energy positions of these Γ_4 and Γ_5 levels.

Section IV results yield another argument to discard Rauch's⁷ identification of the 590-nm center: the Na^+ impurity introduces a charge anomaly in the lattice and therefore it should play an important role in the center electric dipole moment. This impurity lies out of the [001] axis of the fluorine vacancies (Fig. 1). Therefore, it seems strange that the center Stark dipole moment $\delta\mu$ should be along [001], as experimentally observed.

B. Angular F_{3A}^+ model

Another possible structure for the 590-nm center is three fluorine vacancies forming a right-angle isosceles triangle, decorated by two electrons, in near vicinity to a substitutional Na^+ ion (Fig. 6). Such a structure has been proposed by Arkhangelskaya and Shcheulin²² for a color center observed in $CaF_2:Na^+$. In order to use here the hydrogen molecular ion model,¹⁶ we need to know the spectrum of the right-angle isosceles H_3^+ molecule. Hirschfelder's²³ calculations are much too crude and, unfortunately, contrary to the case of the linear F_{3A}^+ center, no more reliable theoretical calculations have been performed (to the best of our knowledge) to find whether an angular F_{3A}^+ center should have, or not, a quasidegenerate first excited spin-singlet level. Because of the low point symmetry (C_s), a quasidegenerate level

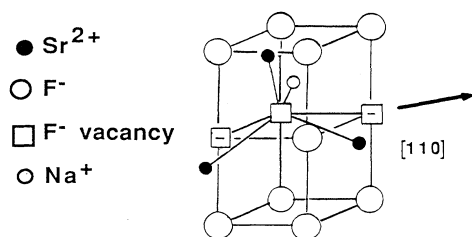


FIG. 6. Structure of an angular " F_{3A}^+ " center. Associated point-group symmetry is C_s .

would require an accidental near-coincidence. On the other hand, there is no geometrical reason why the Stark dipole of the angular F_{3A}^+ center should lie along the [001] direction. The fact that we observe such a direction for $\delta\mu$ would thus require a second accidental coincidence. We think it, therefore, improbable that the 590-nm center should be the angular F_{3A}^+ defect.

C. F_{2A} [110] model

The 590-nm center is one of the most commonly and easily observed in $SrF_2:Na^+$. Therefore, it seems strange that this very common center would be a complex one like linear or angular F_{3A}^+ . Moreover, it is very simple to convert F_{2A}^+ centers into 590-nm centers, or the reverse.³ These "reactions" are easier to understand if both centers have the same number of anionic vacancies, i.e., if the 590-nm center has only two vacancies. Since the 590-nm center is diamagnetic,³ it should consist of two electrons decorating two vacancies, i.e., it should be an F_{2A} center.

In pure SrF_2 , two kinds of F_2 center are known:⁸ a $\langle 100 \rangle$ variety (C_{2h} symmetry), where the two vacancies are nearest neighbors, and a $\langle 110 \rangle$ variety (C_{2v} symmetry), where they are second neighbors. The former cannot present a pseudo-Stark effect because C_{2h} symmetry has an inversion center. The C_{2v} center is the most abundant in the case of SrF_2 , where it is associated with the 605.3-nm zero-phonon line. We propose tentatively the 590-nm center in $SrF_2:Na^+$ to be the $\langle 110 \rangle F_2$ center perturbed by a neighboring Na^+ ion either in a substitutional or in an interstitial location. In both cases the symmetry is C_{2v} since Na^+ lies on the [001] binary axis of the [110] F_2 center (see Fig. 7).

This structure agrees with our experimental results:

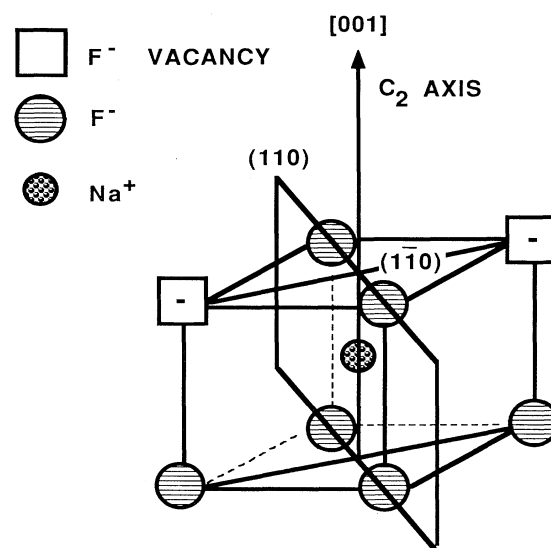


FIG. 7. Proposal of a model for the 590-nm center in $SrF_2:Na^+$: this is an F_{2A} [110] center with point-group symmetry C_{2v} .

TABLE I. Electric dipole selection rules in C_{2v} symmetry.

Light polarization	Γ_1	Γ_2	Γ_3	Γ_4
$\mu_x(\parallel[1\bar{1}0])$	Γ_3	Γ_4	Γ_1	Γ_2
$\mu_y(\parallel[110])$	Γ_4	Γ_3	Γ_2	Γ_1
$\mu_z(\parallel[001])$	Γ_1	Γ_2	Γ_3	Γ_4

for there to be a pseudo-Stark effect, $\delta\mu$ must have nonzero diagonal matrix elements. In C_{2v} symmetry, the $\delta\mu$ must transform like Γ_1 , which means it must lie along the symmetry axis of the defect, i.e., along [001] for a center oriented which has its two vacancies along [110], precisely as observed. As for the optical dipole for the 589.95-nm transition, it can be along [110], $[1\bar{1}0]$, or [001], depending on the symmetry of the first excited state (see Table I). Experimental results of Sec. IV rule out [001]. Thus the optical dipole may be along [110] or $[1\bar{1}0]$; in the latter hypothesis, it would be along the line joining the two vacancies, as is usual for the first spin-allowed transition of F_2 and F_2 -like centers. C_{2v} has no two-dimensional irreducible representation. Thus, all levels are expected to be nondegenerate and it is natural that we observe no Zeeman splitting of the holes burnt in the 589.95-nm line. However, it is possible that two different excited levels should be close enough to yield unresolved (broad) vibronic bands, leading to a quasidegeneracy of the first excited state inferred from Martin, Hamáidia, and Margerie's³ MCD experiments.

Let us point out that if the current $F_{2A}\langle 110 \rangle$ hypothesis is correct, the symmetry of the first excited state is different for the F_{2A} center in $SrF_2:Na^+$ and for the $F_2\langle 110 \rangle$ center in pure SrF_2 (see Fig. 8). In the latter case, both the Stark dipole and the optical dipole lie along the same [001] direction,⁸ whereas in $SrF_2:Na^+$ the optical dipole is in a plane perpendicular to [001]. Probably the perturbation by Na^+ is strong enough to invert the two first spin-singlet excited levels.

Our Stark experiments cannot determine whether the sodium perturber is in a substitutional or in an interstitial site, because the symmetry is the same in both cases. This problem could benefit significantly from theoretical calculations of the relative stabilities of various configurations.

VI. CONCLUSION

We have shown by hole-burning spectroscopy with external electrostatic fields that the local structure of the 590-nm two-electron color center in $SrF_2:Na^+$ could be $F_{2A}\langle 110 \rangle$ with C_{2v} point-group symmetry. The Stark dipole of the center lies along [001]. Not surprisingly,

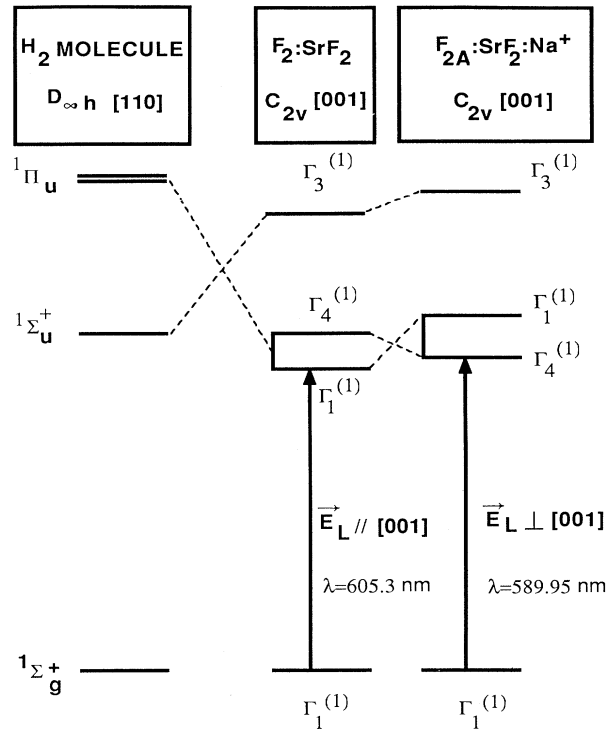


FIG. 8. From left to right, energy levels and correspondence diagrams for a two-electron center in free space (H_2 molecule), in pure SrF_2 (Ref. 8), and in $SrF_2:Na^+$. Note the inversions of excited states in the crystal environments compared with the H_2 model.

this structure is the same as that of analogous, two-electron centers in the pure crystal, apart from the presence of the impurity ion. These results serve to emphasize the very useful role which can be played by hole-burning Stark spectroscopy in crystals with observable zero-phonon lines. They also indicate that mechanisms for the interconversion of color centers in $SrF_2:Na^+$ need to be reconsidered.

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*Present address: Département de Physique, Faculté des Sciences de Tétouan, BP 2121, Tétouan, Morocco.

†Also at UFR de Sciences, Université de Caen, 14032 Caen CEDEX, France.

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