PHYSICAL REVIEW B VOLUME 16, NUMBER 5 1 SEPTEMBER 1977

Laser selective excitation and double resonance in Jahn-Teller system: *F* center in CaO

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(Received 10 March 1977)

Reorientation processes in the relaxed excited state of the *F* center in CaO have been studied through optically detected paramagnetic resonance; difficulties usually encountered because of the random internal stresses are largely overcome by exciting selectively—with a dye laser, through the zero-phonon line—states which are subjected to a definite internal stress. The reorientation between vibronic states is confirmed to be faster than radiative decay, and for strongly stressed sites, it is shown not to involve any spin change. Finally, spin-lattice relaxation times are estimated experimentally. The model is discussed with constant reference to previous work which had required summations over the random strains.

A number of experiments have now demonstrated the interest of laser selective excitation of impurities in solids in order to overcome the inhomogeneous broadening of the optical lines: fluorescence-line narrowing (FLN) in ruby,[1] or in rare-earth-ion doped crystals[2] has led to the identification of diffusion processes or hyperfine structures hidden in the inhomogeneous width. More recently, evidence for Anderson localization was found in ruby by using laser selective pumping in the R_1 line.[3] Spectral diffusion occurring between impurities localized at different sites of the crystal is the main limitation to FLN techniques.

One may think that Jahn-Teller systems which exhibit a zero-phonon line can be good candidates for selective excitation. But the pumping selectivity may be cancelled if phonon-assisted fast reorientation between the Jahn-Teller wells split by the internal stresses occurs, giving rise to a change in the energy of the emitting state. It is, however, of great interest for such Jahn-Teller systems to identify the reorientation processes. In this paper we present our work on the *F* center in CaO in which the difficulty just mentioned is removed.[4] We show that whereas it is not possible to get the narrowed fluorescence of selected centers, we succeeded in measuring their paramagnetic resonance signal. A reorientation process may thus be identified unambiguously.

In Sec. I we briefly describe the experimental setup. Section II will recall the data on the *F* center in CaO. In the Sec. III we show how EPR experiments under excitation in various parts of the zero-phonon line bring further evidence for fast reorientation between the Jahn-Teller wells. In the Sec. IV, we identify the paramagnetic resonance of the optically selected centers. Section V presents a discussion of the reorientation processes by comparing our results to previous work.

I. EXPERIMENTAL

The sample is immersed in the pumped helium bath at the center of an X-band cavity. It is excited along a $\langle 001\rangle$ axis with a cw dye laser whose spectral width is about 1 cm^{-1}. The input light power is about 200 mW at 5740 Å. The polarization may be chosen parallel (π) or perpendicular (σ_X) to the magnetic field. The fluorescence takes place usually along the magnetic field, through thin slits opened in the cavity wall, and is collected by a large lens onto the photomultiplier. A neodymium heavily doped glass is used as a filter to get rid of the light scattered by the sample at 5740 Å.

The microwave power is modulated and the EPR signal is phase detected at the microwave modulation frequency by measuring the level of light emitted along the magnetic field (σ polarization). The sensitivity of this setup varies very much with the exciting wavelength. When pumping in the center of the zero-phonon line, we can measure signals which represent a variation of a few 10^{-5} of the total fluorescence flux with a time constant of 1 s.

II. RECALL OF DATA ON *F* CENTER IN CaO

A. Relaxed excited state

The relaxed excited state of the *F* center in CaO (two electrons in an anion vacancy) has been thoroughly studied by EPR using an optical detection technique.[5-7] The main results are the following: the degeneracy of the $^3T_{1u}$ metastable state is lifted by the Jahn-Teller coupling to E_g modes of vibration. For any of the three tetragonal distortions, the EPR spectrum leads to a usual $S=1$ tetragonal spin Hamiltonian. The zero-field splitting value is $D=(598\pm1)$ G. It must be attributed main-

TABLE I. Selection rules for polarized light. The magnetic field is applied along a ⟨001⟩ z axis (from Ref. 7).

x			y			z		
+1	0	−1	+1	0	−1	+1	0	−1
π	σ_y	π	π	σ_x	π	σ_+	···	σ_-

ly to spin-spin coupling.[7] The sign of the EPR signals is consistent with partially thermalized spin levels. This point will be discussed later. The emission spectrum consists of a zero-phonon line centered at 5740 Å and a large vibronic band extending up to 6400 Å. The radiative lifetime is 3 ms.[8] The selection rules are recalled on Table I.

B. Origin of the width of optical and EPR lines

The crystal field at the F-center site varies from one point of the crystal to the other; these microscopic deformations are conviently called "internal stresses." They are responsible for two phenomena:

One is the first-order splitting of the Jahn-Teller vibronic states. Uniaxial stress studies[4] have shown the effect of a trigonal stress to be negligible and the coupling to a totally symmetric stress to be an order of magnitude smaller than the coupling to a tetragonal stress. We will therefore just consider the effect of the tetragonal internal stresses. The splitting of the vibronic states $|x\rangle\!\rangle$, $|y\rangle\!\rangle$, and $|z\rangle\!\rangle$ may then be illustrated in Fig. 1. We notice that the centroid of the line is not displaced. Both the statistical distributions of e_θ and e_ϵ lead to the inhomogeneous width of the zero-phonon line. In the samples we have studied, the half-height width is about 7 cm^{-1}.

The second-order effect of the tetragonal internal stresses takes place within the spin states $|S, M_S\rangle$ of $|x\rangle\!\rangle$, $|y\rangle\!\rangle$, and $|z\rangle\!\rangle$. We are not really concerned by the physical origin of this effect, which may involve any operator coupling the orbit and the spin. In fact, the effect is easily understood just by group theory and illustrated by the following Hamiltonian, written for the $|z\rangle\!\rangle$ state on an $|S, M_S\rangle$ basis in cubic symmetry:

$$\begin{pmatrix} +1 & -1 & 0 \\ g\mu_B H + \frac{1}{2}\mathcal{B}_2 e_\theta & \frac{1}{2}\sqrt{3}\,\mathcal{B}e_\epsilon & 0 \\ \frac{1}{2}\sqrt{3}\,\mathcal{B}e_\epsilon & -g\mu_B H + \frac{1}{2}\mathcal{B}e_\theta & 0 \\ 0 & 0 & -D - \mathcal{B}e_\theta \end{pmatrix} .$$

For a given set (e_θ, e_ϵ) this gives the resonance condition

$$h\nu = \pm D + g\mu_B H \pm \tfrac{3}{2}\mathcal{B}e_\theta . \tag{1}$$

This upper sign corresponds to the low-field line, the lower sign to the high-field line. We have neglected $\frac{1}{2}\sqrt{3}\,\mathcal{B}e_\epsilon$ which is a second-order contribution with respect to $g\mu_B H$.

Now if the center is optically pumped in an upper excited state and relaxes nonradiatively to the metastable state,[5] populating all the sites, the $|z\rangle\!\rangle$ resonance line, according to Eq. (1), is inhomogeneously broadened, due to the superposition of the lines corresponding to all values of e_θ associated to the random distribution of internal stresses, and as we shall see later, weighted by the thermalization processes.

III. EVIDENCE FOR FAST REORIENTATION BETWEEN JAHN-TELLER VIBRONIC STATES

A. Experimental results

The dye laser is tuned in order to excite at different energies in the zero-phonon line, with a σ_X polarization. Our results are shown on Fig. 2 for the Z low-field line. The asymmetry has been previously observed[7] and we shall comment on this point later. When we vary the energy E of the exciting light, starting from the low-energy side of the zero-phonon line and sweeping E through it, the EPR line is displaced. We have checked that

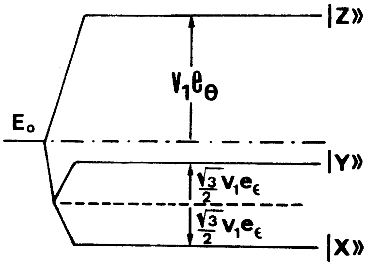

FIG. 1. Splitting of the vibronic state $|T_{1u}\rangle\!\rangle$ by a tetragonal stress with e_θ, e_ϵ components. V_1 is the coupling coefficient to the stress.

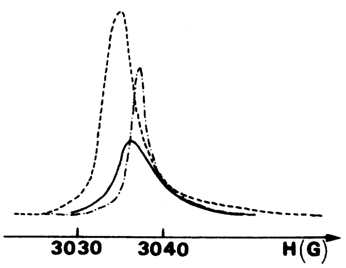

FIG. 2. Behavior of the Z low field where the center is excited at the centroid of the line E_0 (----), at E_0 $-4.3\ \text{cm}^{-1}$ (—·—·—), and $E_0 + 4.3\ \text{cm}^{-1}$ (——). T $= 1.1$ K.

the dependence of this displacement versus the energy difference $\Delta E = E - E_0$ (E_0 being the centroid of the zero-phonon line) is roughly linear. However, it has always the same sign, whatever the sign of ΔE.

B. Discussion

This behavior cannot be understood if EPR is assumed to occur in the optically excited $|z\rangle\rangle$ states before they relax or fluoresce. Referring to Fig. 1 and Eq. (1), the displacement of the line should then be reversed when the sign of ΔE changes. If, on the contrary, the thermalization between the vibronic states occurs before resonance takes place within the Zeeman sublevels, we can give the following explanation:

When exciting with a σ_X polarized beam within the zero-phonon line, we populate $|z\rangle\rangle$ and $|y\rangle\rangle$ states (the "selected" zones) at a given energy $E_0 + \Delta E$; according to the internal stress present at their site, some $|z\rangle\rangle$ states may reorient to an $|x\rangle\rangle$ or $|y\rangle\rangle$ state lower in energy, which will give no contribution to the Z EPR line; some $|y\rangle\rangle$ states will also reorient to an $|x\rangle\rangle$ or $|z\rangle\rangle$ state, the latter contributing to the resonance ("relaxed" Z state).

If the excitation takes place in the high-energy side of the zero-phonon line ($\Delta E > 0$), the reorientation will concern all the selected $|z\rangle\rangle$ and $|y\rangle\rangle$ states, the former being lost for resonance. The "relaxed" $|z\rangle\rangle$ states will then be the only ones contributing to the EPR signal. Their respective energies correspond to a distribution of e_θ values which at 0 K, should be given by $V_1 e_\theta < -\frac{1}{2}E$. (This comes from the property previously mentioned: the centroid E_0 of the zero-phonon line is not moved by tetragonal stresses.)

If the excitation takes place in the low-energy side of the zero-phonon line ($\Delta E < 0$) the resonance line may involve selected $|z\rangle\rangle$ states whose corresponding $|x\rangle\rangle$ and $|y\rangle\rangle$ states are higher in energy and relaxed $|z\rangle\rangle$ states, depending upon the distribution of internal stresses. At 0 K, the values of e_θ are defined by $V_1 e_\theta < \Delta E$.

Therefore the resonance line must be associated only with negative values of e_θ, which explains why the displacement has always the same sign.

We can now comment on the shape of the low-field line. It is sharp on the low-field side and exhibits a long "tail" towards the high-field side. As we just saw, the resonance line must be associated to a range of e_θ values [Eq. (1)] corresponding to all the relaxed $|z\rangle\rangle$ states which are populated by the reorientation of the $|y\rangle\rangle$ selected states. (In the case $\Delta E < 0$, we have also the contribution of some selected $|z\rangle\rangle$ states.) Now assuming some statistical distribution for e_θ, the larger $|e_\theta|$ is, the less numerous the $|z\rangle\rangle$ states are. Therefore, the EPR line is expected to be the most intense for the largest e_θ values (low-field side) and to expand towards the high-field values with a decreasing intensity. At 1.2 K the low-field side is very sharp because very few states at $V_1 e_\theta < \Delta E$ (or $\frac{1}{2}\Delta E$) are thermally populated. In the case $\Delta E < 0$, the presence of selected $|z\rangle\rangle$ states increase this sharpness.

We have just checked that the Jahn-Teller states reorient each to one another within the zero-phonon line in a time shorter than the radiative lifetime.[9]

IV. EVIDENCE FOR RESONANCE IN SELECTED STATES

If the microwave power available in the cavity is large enough, the microwave induced transition rate can become large enough compared to the reorientation rate. We might then observe an extra line associated to the $|z\rangle\rangle$ selected states, beside the contribution of the $|z\rangle\rangle$ relaxed states coming from the reorientation of the $|y\rangle\rangle$ selected states.

Our experimental results in these conditions [Figs. 3(a) and 3(b)] indeed exhibit two lines. The result is only noticeable when ΔE is positive because the two lines are separated.

In order to check that the observed extra lines must be attributed to the resonance of selected z centers, we have turned the excitation polarization from σ_X to π. According to the selection rules (Table I) the only states thus selected are then $|y\rangle\rangle$ and $|x\rangle\rangle$. Figure 3 shows that the extra line disappears. Moreover, we can measure the displacement ΔH of this extra line when varying ΔE. We find

$$\Delta H = +3.9 \pm 0.2 \text{ G},$$

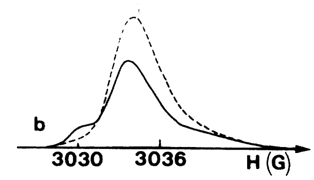

FIG. 3. (a) Z high-field line at $T = 1.1$ K. The excitation energy is $E_0 + 6\ \text{cm}^{-1}$. The line at 4235 G corresponds to an increase of the I_σ light, the line at 4229 G to a decrease. (b) Z low-field line. The excitation energy is $E_0 + 4.3\ \text{cm}^{-1}$. Both lines correspond to an increase of I_σ light. The solid line refers to σ_X excitation, the dashed line to π excitation. The microwave modulation frequency is 1000 Hz, and the microwave field amplitude is about 0.6 G .

for

$$\Delta E = +6 \text{ cm}^{-1}$$

This is consistent with previous measurements and theoretical calculation of the displacement ΔH versus $V_1 e_\theta$.[10] The extra line must therefore be attributed to the selected z centers, and will be called the "selected" line. The term "relaxed line" will refer to the resonance of the relaxed $|z\rangle\rangle$ states.

We would now like to emphasize one more point. Whereas the half-height width of the lines is usually 4–5 G, the width of the selected line is 2.3 G.

We would find the homogeneous width if we could really isolate only one e_θ value. Actually, we still select a distribution of e_θ values because of: (a) the spectral width of the laser (~1 cm^{-1}); (b) the totally symmetric internal stresses whose effect is certainly small, but which are not really known. So this selected line is still inhomogeneously broadened. From its width, we can estimate an upper limit to the A_{1g} contribution to the optical line: we find 2.5 cm^{-1}.

V. REORIENTATION PROCESSES AND THERMALIZATION

A. Characterization of the processes

It is possible to study the reorientation processes of the selected highly stressed sites. We will discuss the high field $|z\rangle\rangle$ line but the arguments would be the same, *mutatis mutandis*, for the low-field one. From Sec. IV for the selected center at sufficiently high microwave level, the nonradiative reorientation from $|z\rangle\rangle$ to $|y\rangle\rangle$ or $|x\rangle\rangle$ follows immediately the microwave absorption between $|z, M_S = -1\rangle\rangle$ and $|z, M_S = 0\rangle\rangle$. If there exist selection rules for the nonradiative decay from the $|z, M_S\rangle$ states, then a change in the population of the $|y\rangle\rangle$ Zeeman sublevels is induced, and thus the level of emitted σ light is modified. It turns out that the observed increase of σ light is only possible *if reorientation without spin flip is more efficient than reorientation involving a spin flip* [Fig. 4(a)]. In order to be able to resolve the selected line we have to select sites which are submitted to large internal stresses. The evidence for reorientation without spin flip concerns these strongly stressed sites.

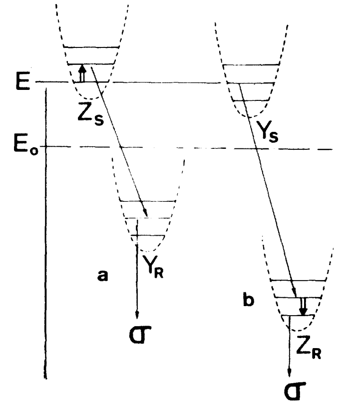

FIG. 4. Reorientation model for highly stressed sites: (a) the reorientation of selected Z states after the microwave absorption (⇒) leads to an increase of σ light (→σ). (b) Selected highly stressed $|y\rangle\rangle$ states reorient in Z states which absorb microwaves (⇒) before thermalizing, thus leading to an increase of σ light (→σ).

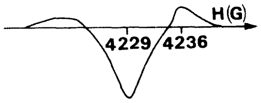

FIG. 5. Z high-field line line at low modulation frequency (300 Hz).

Now we may look at other highly stressed $|z\rangle\rangle$ centers, those which are populated by the reorientation of the $|y, 0\rangle\rangle$ selected states (Table I). Fig. 4(b) illustrates the behavior. If reorientation without spin flip is predominant the $|z, 0\rangle\rangle$ state should be much more populated than $|z, -1\rangle\rangle$. The microwave then should induce an increase of the σ light emitted by $|z, -1\rangle\rangle$. Figure 5 shows that it is indeed the case for the low-field side of the relaxed line, which corresponds to the largest $|e_\theta|$ values (the reason why Figs. 3(a) and 5 are different for the low-field side is related to the relaxation times. We shall come back to this point further).

The situation must be different for less stressed sites since the largest part of the relaxed line corresponds to a decrease of the σ light. We cannot draw any unambiguous conclusion from this sign: either the spin levels are mostly thermalized before resonance occurs or reorientation of $|y\rangle\rangle$ states involves a spin flip. In these two cases, the result would be qualitatively the same. It is worthwhile comparing the above results to those of Ref. 11 where reorientation processes have also been studied. We recall them briefly:

The experiments described in Ref. 11 are measurements of a microwave pulse decay for a given magnetic field. The process thus studied concerns one set of relaxed $|z\rangle\rangle$ states, and among them the weakly stressed centers, which give the largest contribution to the EPR line. For these centers, reorientation was found to be more efficient when involving a spin flip. In the detailed analysis of all one phonon processes which may possibly contribute to the reorientation, tunneling and direct processes must be discriminated. The probability of the former depends linearly upon the energy of the phonon involved. All spin-flip reorientations are tunneling processes. The latter is induced by

T_{2g} phonons, its probability increasing with the cube of the energy of the phonon.

Considering the energy dependence of the direct and tunneling processes, for small internal stresses and large ones the respective efficiency of the two processes may very well be reversed, the non-spin-flip reorientation becoming predominant. Then, up to this point we see no inconsistency between our model and the results of Ref. 11.

B. Measurement of relaxation times and discussion

For a better understanding of the processes, it is interesting to get an idea of spin-lattice relaxation times for the selected and relaxed $|z\rangle\rangle$ states.

When we increase the modulation frequency of the microwave power, the EPR signals are reduced and dephased. If the system has only one characteristic time, it is possible to measure it this way. Although this is not the case here, nevertheless the system behaves on the selected line as well as on the relaxed one, as if it involved one main relaxation time.

On the high-field line, we find for the relaxed line (at 1.2 K), $\tau_R = 20\ \mu s$. In Ref. 11 two times of 5 and 20 μs were found. Now, for the selected line, when $\Delta E = 4.4\ cm^{-1}$,

$$\tau_S = 110\ \mu s \text{ at } 1.2\ K.$$

It is not clear at once whether τ_S is the spin-lattice relaxation time between the Zeeman sublevels of $|z\rangle\rangle$ or not. We recall that there are two steps in the detection of the resonance. In the first one, the transfer of population from $|z,-1\rangle\rangle$ to $|z,0\rangle\rangle$ may or may not be modulated according to a relaxation time τ_1 of the $|z\rangle\rangle$ states. If τ_1 is short enough, the decay to the $|y\rangle\rangle$ Zeeman sublevels is modulated. In this second step, the level of emitted σ light will only be modulated if the relaxation time τ_2 between the $|y,M_S\rangle\rangle$ states is short enough compared to the microwave modulation frequency. Now we think τ_S must be the spin-lattice relaxation time within the Zeeman sublevels of $|y\rangle\rangle$ for the following reasons:

In the same experimental conditions, the relaxed line is very much saturated by the microwave whereas the variation of the selected line intensity still increases linearly with the microwave power. The time which determines the degree of saturation for the relaxed line is $\tau_R = 20\ \mu s$. For the selected line, this time should therefore be much shorter and can be reasonably identified as the reorientation time. The time τ_S which is much larger is then the spin-lattice relaxation time of $|y\rangle\rangle$ spin levels.

This time is surprisingly slow. We will refer once more to the theoretical analysis of Ref. 11 where it is shown that $|y\rangle\rangle$ spin states cannot relax with ΔM_S changes equal to ±1 except by reorienting hrough the $|z\rangle\rangle$ spin states. For the $|y,M_S\rangle\rangle$ levels considered, the available $|z,M_S'\rangle\rangle$ are the selected ones. The splitting Δ between $|y,M_S\rangle\rangle$ and $|z,M_S'\rangle\rangle$ is thus fairly large compared to the Zeeman splittings δ. Then in the assumption that the $|z,M_S'\rangle\rangle$ states are fast decaying levels, it is possible to get an analytical result for τ_S if we momentarily restrict to 3 levels.

We find (in the approximation $\delta \ll \Delta$)

$$1/\tau_S = [4W_{31}W_{32}/(W_{31}+W_{32})^2]e^{-\Delta/kT},$$

where W_{31} and W_{32} are the probability of emission of a phonon between the levels 3 and 1, and 3 and 2, respectively.

The interesting result in this simplified situation is to show that we must be very close to the situation where an Orbach process takes place. This explains qualitatively why τ_S is so slow compared to τ_R which has no exponential dependence. We point out that the highly stressed relaxed centers already mentioned [Fig. 4(b)] have qualitatively the same long relaxation time; this is natural since the situation, although symmetric ($|z,M_S'\rangle\rangle$ relaxes through $|y,M_S\rangle\rangle$) is exactly analogous. [At 300 Hz, the tail has a weak positive sign (Fig. 5). At 1000 Hz, it is too small to be clearly detected (Figs. 2 and 3).]

A serious difficulty remains to check experimentally the exponential factor law for τ_S in the temperature range (1.1–2 K). The reason is that the laser beam heats the sample (about 0.2 K for 50 mW at 5740 Å) and that a poor signal-to-noise ratio prevents us from operating at low pumping levels. Nevertheless, the variations of τ_S for various temperatures and power levels were found to be in agreement with an Orbach type process.

VI. CONCLUSION

Our experiments establish unambiguously that for large stresses ($\Delta \sim 5\ cm^{-1}$) reorientation between Jahn-Teller states does not involve a spin flip. This process is therefore assisted by T_{2g} phonons. These results agree satisfactorily with the Jahn-Teller model: for low internal stress splittings, the coupling to T_{2g} phonons is very much quenched and according to Ref. 11, tunneling processes are more efficient. When the energy of the phonon involved increases, the direct process becomes more efficient.

Among the Jahn-Teller systems, the *F* center in CaO was a favorable one because the one-to-one correspondence between the *Z* EPR line and the stress value e_θ is almost realized.

It is worthwhile noticing that though internal stresses have always been an obstacle to the study of relaxation processes, our work shows that it is possible to use them in a controlled manner.

ACKNOWLEDGMENT

We are grateful to M. Sturge for fruitful remarks and to Y. Merle d'Aubigné, R. Romestain, and J. Cibert for stimulating discussions.

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[10] Le Si Dang (private communication). The displacement of the EPR line has been measured through EPR experiments under uniaxial stress and confirmed by selecting two different wavelengths (spectral resolution 0.2 cm^{-1}) within the emission spectrum of the zero-phonon line. This gave: $\Delta H = 4$ G for $\Delta E = -6$ cm^{-1} for the low-field line. The theoretical calculation predicts $H = 4.4$ G. Our results are consistent with those measurements.

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