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Influence of random intrinsic strain upon the zero-field double-resonance spectra of the CaO F center in its excited Jahn-Teller states

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In previous studies of the photoexcited state of CaO F centers it was shown that the $^3T_{1u}$ state exhibits a Jahn-Teller coupling to e_g vibrational modes in the strong-coupling regime. The present work examines how, at low temperatures, coupling to a randomly distributed (intrinsic) strain affects zero-field optically detected magnetic resonance (ODMR) and phosphorescence microwave double resonance spectra. The ODMR spectra reflect microwave absorptive and emissive parts. As a result of this, different portions of the inhomogeneously broadened lines could be studied selectively as a function of the microwave-field polarization and small applied magnetic fields. The data are consistent with a proposed model in which the coupling between the vibronic system and randomly distributed strain is considered. It will be shown that singularities in the spectral density of the microwave resonances arise when a random angular distribution in the strain components e_θ and e_ϵ is adopted. It turns out that the resonances associated with these extrema are restricted to just a few subensembles of F centers. In each subensemble the vibronic degeneracy is lifted by the additional effect of the spectral distribution in strain magnitude, $(e_\theta^2 + e_\epsilon^2)^{1/2}$. This gives rise to the occurrence of several zero-phonon lines in the optical emission, inhomogeneous broadening of the ODMR line, population inversion, and the observations of internal conversion with conservation of spin state.

I. INTRODUCTION

The F center in a CaO lattice is characterized by two electrons trapped at an oxygen vacancy.[1] In the cubic crystal field the first excited state with a $1s2p$ configuration is an orbitally threefold degenerate $^3T_{1u}$ level and by virtue of the Jahn-Teller theorem this degeneracy can be removed by coupling of the motion of the electrons with vibrational modes of the crystal.[2]

Utilizing the technique of optical detection of magnetic resonance (ODMR) at high magnetic fields, Edel *et al.*[3] succeeded in observing transitions in the spin triplet with a tetragonal orbital symmetry. The optical polarization of the magnetically induced light changes is in agreement with a description in which the threefold orbital degeneracy is lifted by coupling to e_g lattice vibrations and is replaced by a threefold vibronic degeneracy.[4] The three degenerate vibronic states ξ, η, and ζ are characterized by different equilibrium positions of the oscillators (tetragonal distortions).

In the EPR experiment[3] the observed optical polarization of the induced light changes upon resonance indicated that the F centers are either in a ξ, η, or ζ Jahn-Teller (JT) state. However, some polarization effects were observed which showed that within the triplet-state lifetime the vibronic character can change.

Optically detected magnetic resonance (ODMR) and phosphorescence microwave double resonance (PMDR) in zero magnetic field revealed a more-complex situation.[5] The PMDR zero-phonon line at 5742 Å corresponding to an increase in phosphorescent light was induced by a microwave transition at 1.68 GHz. Two other PMDR zero-phonon lines at 5740 and 5743 Å were obtained from a resonance at 1.70 GHz and reflect a decrease in the emitted light. In this paper we will give a detailed experimental analysis of the ODMR and PMDR signals of the F center by making use of the polarization properties of the emitted light, different polarizations of the microwave field and small static magnetic fields directed along the principal axes of the crystal (Sec. III).

It will be shown hereafter that each of the observed PMDR zero-phonon lines apparently originates from three isoenergetic and isolated JT states (Secs. IV A–IV C). The results will be related to a previous study of the system under uniaxial external pressure.[6,7] The latter study showed that a rapid relaxation process is operative if the JT states are (almost) degenerate. The mechanism is a fast phonon-assisted internal conversion between different JT states subject to the condition that the spin state is conserved. Hence the emission in PMDR which behaves as if the three distortions could be treated as isolated, cannot be the response of degenerate vibronic levels. This paper will discuss in detail why only nondegenerate JT states are observed in zero-field ODMR and furthermore explain why three (no more or no less) isoenergetic distinct types of F centers are simultaneously under observation. It turns out that all observations could be explained consistently when it is assumed that F centers are predominantly affected by randomly distributed strain in

the crystal.[6] In Sec. IV D an outline will be given of the influence of random e_g-type strain upon the spectral density of the microwave resonance of an ensemble of F centers and in Sec. IV E the results of Sec. III and the EPR experiments in high magnetic fields will be discussed in relation to the random-strain model.

II. EXPERIMENTAL

Yellow-colored CaO crystals were purchased from Spicer Ltd. and mounted in a helium cryostat. F centers were excited by light from a 100-W Hg lamp filtered by a $CuSo_4$ solution. The experimental arrangement was that of a conventional zero-field ODMR spectrometer as described before.[7] The microwave H_1 field in the helix surrounding the crystal is polarized mainly along the helix axis. The helix could be directed along any one of the principal axes of a laboratory frame. This axis system is chosen in such a way that optical excitation is along the z axis and the detected phosphorescence is in the y direction (see Fig. 1). Static external magnetic fields up to 100 G could be applied along x, y, or z directions. Optical resolution of the split PMDR line was better than 0.1 Å. The experiments were performed at 1.5 K.

III. RESULTS

A. ODMR and PMDR in zero magnetic field

When at 1.5 K the zero-field ODMR spectrum is recorded with the detection wavelength around $\lambda = 5742$ Å (the maximum of the zero-phonon line of the directly detected phosphorescence) and using x-polarized microwaves, the magnetic resonance spectrum as represented in Fig. 2 is obtained. It manifests two spectral regions: the first corresponds to a light *increase* upon microwave pumping with a maximum at 1.68 GHz, the second reflects a light *decrease* peaked at 1.70 GHz.

While exposing the crystal to modulated resonant microwave fields at 1.68 and 1.70 GHz, respectively, two different phosphorescence (PMDR) spectra were obtained by phase-sensitive detection. First, the zero-field PMDR spectrum recorded with ν

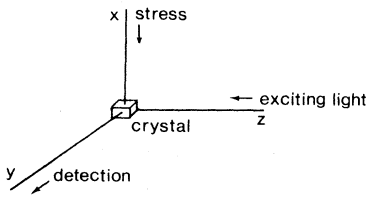

FIG. 1. Directions of the pumping light and the detected emitted light, respectively, in our axis convention.

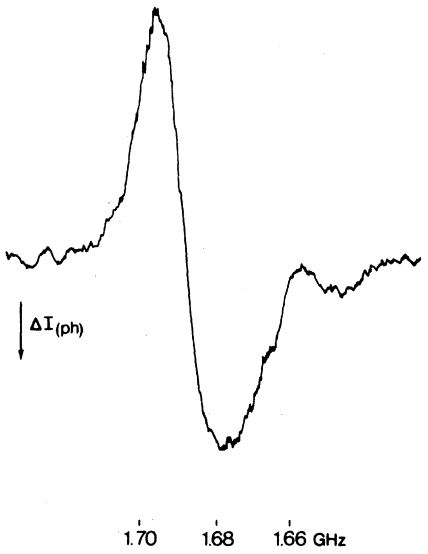

FIG. 2. Zero-field ODMR spectrum of the CaO: F center excited to its $^3T_{1u}$ state. Detection wavelength $\lambda = 5742$ Å; $T = 1.5$ K.

$= 1.68$ GHz is given in Fig. 3(a), where a zero-phonon line peaked at 5742 Å was observed. Second, when the PMDR spectrum was recorded with $\nu = 1.70$ GHz the spectrum of Fig. 3(b) was obtained. The latter consists of *two* zero-phonon bands with maxima at 5740 and 5743 Å, respectively. It is to be noted from Fig. 3 that the 5742-Å zero-phonon line overlaps with both the 5740- and 5743-Å bands.

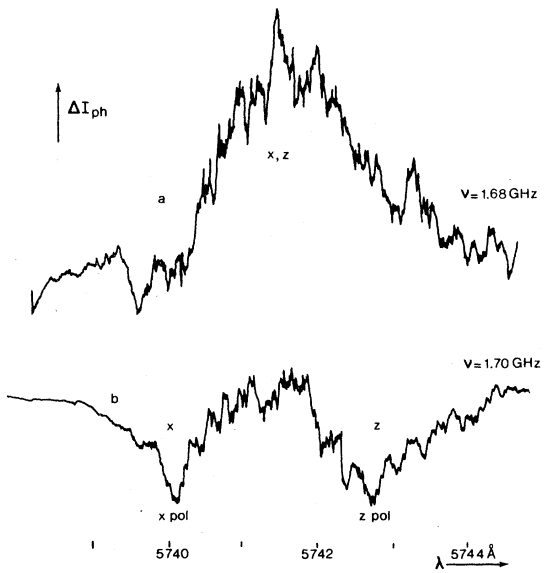

FIG. 3. (a) Zero-field PMDR spectrum showing only the zero-phonon line taken with $\nu = 1.68$ GHz, the microwave H_1 field being polarized (mainly) along the x axis; $T = 1.5$ K. (b) Zero-field PMDR zero-phonon lines taken with $\vec{H}_1 \| \vec{x}$, $\nu = 1.70$ GHz, $T = 1.5$ K.

Detection of the emission with a polarizer in either the x or z direction revealed that the ratio of x- to z-polarized light of the 5742-Å zero-phonon PMDR line ($\nu = 1.68$ GHz) is about 2, while the zero-phonon PMDR line at 5740 and 5743 Å ($\nu = 1.70$ GHz) are x and z polarized, respectively.

B. Effects of a magnetic field upon the ODMR of the 5742-Å emission

In agreement with the polarization of the zero-phonon PMDR line at 5742 Å, the line around 1.68 GHz also showed an x- to z-polarization ratio of about 2. Application of a magnetic field of 38 G along the z axis and detection of the emitted light at 5742 Å gives two additional resonances occurring at 1.786 and 1.574 GHz and corresponding with the Zeeman splitting of formerly degenerate x and y levels within a spin triplet state and mixed by the magnetic field along z.

PMDR on the 1.69-GHz resonance shows a zero-phonon line at 5742 Å which is now unpolarized [Figs. 4(a) and 4(b)]. The zero-phonon line corresponding to the new resonances also occuring at 5742 Å, is x polarized [Figs. 5(a) and 5(b)].

By applying the magnetic field along the y direction, the unshifted ODMR line at 1.69 GHz becomes x polarized while the outer resonances now become unpolarized (Fig. 6). The light decrease at 1.70 GHz in Fig. 6 gives rise to PMDR lines at 5740 and 5743 Å and will be dealt with in Sec. III C.

No Zeeman splitting was observed when the small magnetic field was directed along the x axis and the unshifted ODMR line with a maximum at 1.68 GHz exhibits, as in the zero-field case, an

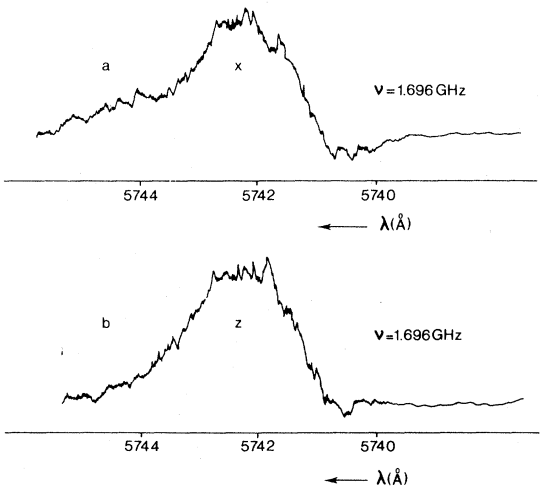

FIG. 4. Optical polarization of zero-phonon line in PMDR spectrum taken in the presence of a (small) magnetic field ($H_z = 38$ G) and with $\vec{H}_1 \| \vec{x}$, $\nu = 1.696$ GHz. (a) x polarization; (b) z polarization.

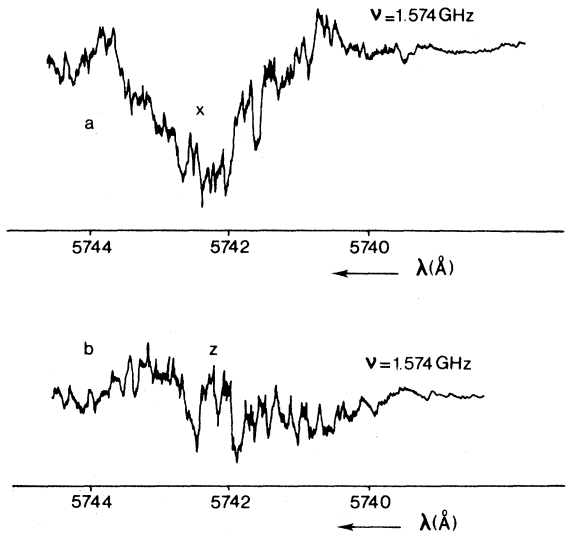

FIG. 5. Zero-phonon line in PMDR showing only x polarization [(a) x polarization; (b) z polarization], when $H_z = 38$ G, $\nu = 1.574$ GHz, and $\vec{H}_1 \| \vec{x}$.

x- to z-polarization ratio of about 2.

With y-polarized microwaves and a magnetic field along the x axis, the light changes at 5742 Å induced by pumping the outer Zeeman resonances was purely z polarized and the polarization of the light changes induced by the microwave transition at 1.68 GHz, was purely x polarized. Table I summarizes the results of this subsection.

C. 5740- and 5743-Å PMDR lines

The first five columns of Table II show representative data of the effects of microwave polarization and magnetic field upon the optical polarization.

With an x-polarized microwave field and the application of a magnetic field along a ⟨100⟩ axis, the optical polarization does not change with the magnetic field direction. Note that the 5743-Å emission is not observed in case $H = H_z$.

With a magnetic field of ~43 G along the z direction, two ODMR resonances reflecting a light de-

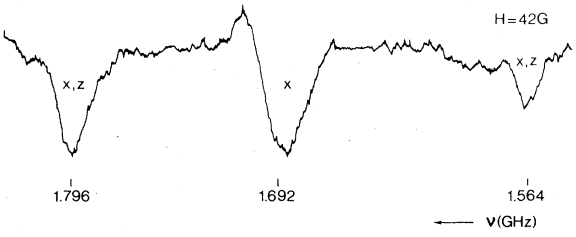

FIG. 6. ODMR spectrum of F center in CaO in the presence of a small magnetic field along y ($H_y = 42$ G). The optical polarization of the resonance lines is as indicated.

TABLE I. Frequencies and optical polarization of ODMR resonances detected at $\lambda = 5742$ Å as a function of the orientation of the microwave field and magnetic field vectors. The assignments based on the random-strain model are given in the last column.

Microwave field polarization	Magnetic field (G)	ODMR frequency (GHz)	Optical polarization	Intensity ratio x- to z polarized light	Assignment emitting level
x	···	1.68	x and z	~2	$\eta(90°)$ and $\zeta(150°)$
x	$H_z = 24$	1.747 and 1.613	x		ζ
		1.68	x and z	~1	$\eta(90°)$
x	$H_y = 24$	1.747 and 1.613	x and z	~1	η
		1.68	x		$\zeta(150°)$
x	$H_x = 24$	1.68	x and z	~2	$\eta(90°)$ and $\zeta(150°)$
y	···	1.68	x and z	~1	$\xi(270°)$ $\zeta(210°)$
y	$H_x = 24$	1.68	x		$\zeta(210°)$
		1.747 and 1.613	z		ξ

crease are observed at $\nu = 1.58$ GHz and $\nu = 1.82$ GHz, respectively (see Fig. 7). The corresponding PMDR lines at 5740 and 5743 Å show x and z polarization, respectively.

The behavior of the 5743-Å zero-phonon line is quite different at the unshifted resonance when the microwave field is y polarized. In this case the optical polarization changes with the magnetic field direction.

Observe also that for the y polarized microwave field no PMDR line at 5740 Å is detected.

IV. DISCUSSION

A. 5742-Å emission

Like in the optically detected magnetic resonance at high magnetic fields,[3] the characteristic properties of the 5742-Å emission induced by an x-polarized microwave field at zero or low magnetic fields can easily be ascribed to transitions of F centers which are either in an isolated η or ζ state.

Isolated spin vibronic levels, as depicted in Fig. 8, are characterized by a specific polarization of the light emitted in the optical transition to the ground state. This is due to the selective mixing between the $^3T_{1u}$ and $^1T_{1u}$ levels on account of spin-orbit coupling, whereas the $^1T_{1u}$ admixtures determine the emission properties of the states.[3]

With an x-polarized microwave field in zero-magnetic field only the $\eta y \rightarrow \eta z$ and $\zeta z \rightarrow \zeta y$ transitions can be induced (cf. Fig. 8). As both the ηz and ζy states give rise to x-polarized emission, one would expect purely x-polarized ODMR and PMDR lines. Experimentally, however, an intensity ratio of x- to z-polarized light of about 2 has been measured. This can be understood when we

TABLE II. Effects of the orientation of microwave field and magnetic field vectors on the optical polarization of the 5740- and 5743-Å PMDR zero-phonon lines.

Microwave field polarization	Magnetic field	Resonance frequency (GHz)	Optical polarization 5740 Å	Optical polarization 5743 Å	Assignment 5740 Å	Assignment 5743 Å
z	···	1.70	z	x	$\xi y(150°)$ $\eta x(210°)$	$\xi y(150°)$
y	···	1.70	···	unpolarized	$\xi z(90°)$ $\zeta x(30°)$	$\eta z(90°)$ $\eta x(30°)$
x	···	1.70	x	z	$\eta z(270°)$ $\zeta y(330°)$	$\xi y(330°)$
x	H_x	1.70	x	z	$\eta z(270°)$ $\zeta y(330°)$	$\xi y(330°)$
x	H_y	1.70	x	z	$\zeta y(330°)$	$\xi y(330°)$
x	H_z	1.70	x	···	$\eta z(270°)$	
x	H_z	1.58 + 1.80	x	z	ζy	ξy
y	H_x	1.70	···	z		$\eta x(30°)$
y	H_y	1.70	···	unpolarized		$\eta z(90°)$ $\eta x(30°)$
y	H_z	1.70	···	x		$\eta z(90°)$

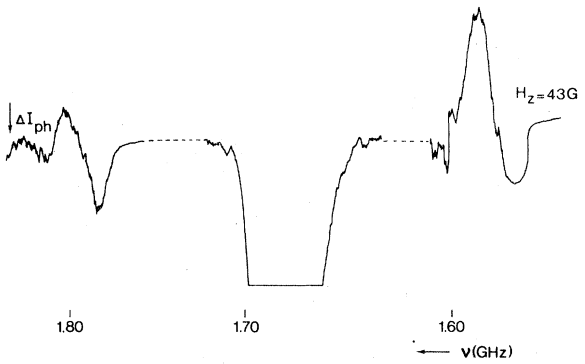

FIG. 7. ODMR spectrum of F center in CaO in the presence of a small magnetic field along z ($H_z = 43$ G). The resonance lines at $\nu = 1.58$ GHz and $\nu = 1.80$ GHz partly reflect a light decrease.

assume the upper spin levels of, respectively, the η and ξ states to be degenerate within the homogeneous linewidth of the resonance at 1.68 GHz. Then light with different polarization can be emitted with equal probability. In the experimental arrangement the y-polarized light from the ξ state cannot be detected and only emission from the ηx (z-polarized), ηz, and ξy (x-polarized) states can be observed, which accounts for the intensity ratio of about 2.

In agreement with this picture is the effect of a magnetic field along the z direction (Table I). This gives two additional resonances, which in PMDR induce an x-polarized zero-phonon line at 5742 Å (Fig. 5). In terms of isolated JT states these resonances can only be attributed to the ξ state (the x polarization arising from the fact that in the experimental arrangement no y-polarized emission can be observed). Since an isolated ξ state will not be pumped by an x-polarized microwave field, the resonance at 1.68 GHz is left to the η state. At these low fields ($H_z \sim 40$ G) the splitting between the ηx and ηz levels apparently remains unresolved and accordingly the emitted light is unpolarized (Fig. 4). Otherwise, when ξ was also pumped, the light should have been completely x polarized when the upper spin levels were not degenerate, or in case they are degenerate the ratio of x- to z-polarized light should have been smaller than one.

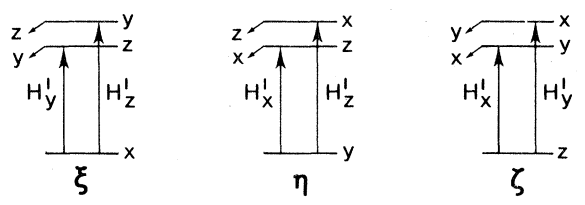

FIG. 8. Polarization of microwave transitions and spontaneous emission from CaO F centers in the excited $^3T_{1u}$ state.

When the microwave field is x polarized the assignment of the 5742-Å line as an emission from an isolated ξ or η state is further confirmed by the behavior under a magnetic field in the y direction (cf. Table I). In this case the η state gives rise to the outer resonances and due to equal mixing of the ηz and ηx levels, the induced light changes are unpolarized. The unshifted resonance at 1.68 GHz can be attributed to the ξ state with an x-polarized emission.

No Zeeman splitting is observed at low magnetic field (≤ 40 G) along the x direction indicating, once again, that an x-polarized microwave field cannot induce transitions in the ξ state. The ratio of x- to z-polarized light, emitted by the ξ and η state and induced by the 1.68-GHz transition is then about 2, as in the zero-field case.

The apparent isolation of the JT states emitting at 5742 Å is most clearly demonstrated in the experiments where microwave resonance is restricted to a single vibronic state as selected by the application of an external magnetic field, e.g., when H is along the z direction, the outer resonances are observed to be strictly x polarized. If, in the latter case, communication existed between the ξ and η states emitting at 5742 Å, this would have been reflected in z-polarized light changes due to rapid $\xi x \rightarrow \eta x$ radiationless transitions.[7] Similarly the isolation is also demonstrated by the strict polarization of the light increase induced at the different y-polarized microwave transitions in the presence of a magnetic field along the x axis, i.e. (cf. Table I), pure z-polarized light at the outer resonances from ξ and pure x-polarized light at 1.68 GHz from ξ.

We thus find that the emitting states that contribute to the emission at 5742 Å may be identified as isolated states of either ξ, ζ, or η character. The mere fact that the emitting vibronic states can be considered as isolated, i.e., show no rapid dynamical coupling among themselves within the triplet lifetime, excludes a vibronic degeneracy per F-center site. This conclusion emerges from previous experiments[7] in which a rapid phonon assisted internal conversion process ($k \sim 10^6$ sec^{-1}) was shown to be operative when the vibronic states are degenerate. Therefore the simultaneous phosphorescence emission at 5742 Å from ξ, η, and ζ states must originate from *different* groups of F-center sites rather than from vibronic degeneracy at each F-center site.

Since the vibronic states emitting at 5742 Å are nondegenerate, we expect the remaining JT states to emit at different wavelengths. As will be discussed in Sec. IV E, the PMDR zero-phonon lines

at 5740 and 5743 Å can indeed be associated with such emissions.

B. 5740- and 5743-Å emission

First we will discuss the "5740-Å" emission in terms of the six radiative spin vibronic levels. The absence of mixed optical polarization in the 5740-Å PMDR line makes, as before, an interpretation of this line in terms of isolated and therefore nondegenerate states obvious. We thus find (cf. Table II) that for a z-polarized microwave field in zero-magnetic field the emission has to be assigned to ξy and ηx levels in different groups of F-center sites.

In agreement with this is the lack of any trace of a 5740-Å emission when the microwave field is y polarized. In this case a y-polarized emission will be induced from the ξz and ζx levels. Light with this polarization cannot be detected in the experimental arrangement used and accordingly no 5740-Å emission is observed.

In contrast to the 5740- and 5742-Å emissions, the properties of the "5743-Å" emission cannot be explained in terms of a direct response of a vibronic level upon microwave induced transitions between the spin levels. For example the z-polarized emission (in case of an x-polarized microwave field, see Table II) should involve the ξy and ηx levels (cf. Fig. 7). However, these levels are not involved in x-polarized microwave transitions. The same feature is also valid when y- and z-polarized microwave transitions are considered. This indicates that within a description of a response from single spin vibronic levels (the strict optical polarization points to nondegenerate spin levels), the population change of the levels emitting at 5743 Å is not a direct response to the perturbing microwave field, but the result of a communication with another vibronic state in which the steady-state population is changed by the spin transitions. The appearance of the 5743-Å emission at the same microwave frequency as the 5740-Å emission favors a coupling between these two nondegenerate vibronic levels.

Moreover, the levels emitting at 5743 Å have in common with those emitting at 5740 and 5742 Å, that, because of the strict optical polarization and thus the absence of internal conversion with other vibronic levels of the *same* energy, they are also nondegenerate with other vibronic levels of the F center and that different groups of F centers contribute simultaneous to the 5743-Å emission.

C. Preliminary conclusions

Summarizing we can say that for the 5740- and 5742-Å emission, the correlation between the observed optical polarization on the one hand and the polarization of the applied microwave field and the direction of an applied magnetic field on the other is in complete agreement with a description in terms of nondegenerate vibronic JT states (ξ, η, ζ) resulting from Jahn-Teller coupling of an orbitally degenerate ^3P state to an e_g vibrational mode in the static limit. The strict optical polarizations show that no trigonal effects have to be included.

Moreover the experiments show that different vibronic levels contribute simultaneously to the zero-phonon line emission. It was inferred from the observed polarization in PMDR in relation with previous work that the double resonance spectra originate from F centers in nondegenerate vibronic states.

At this moment we may as well set out the program of the discussion to follow. Having identified the ODMR and PMDR spectra as being due to *perturbed* F centers (i.e., F centers in which the vibronic degeneracy between the JT states is lifted) we pursue by answering the two main questions: (i) why do we see predominantly perturbed instead of unperturbed excited F centers, and (ii) why do the spectra contain absorptive and emissive parts?

It is well known that the vibronic JT states of a F center are very sensitive to only e_g strain.[8] e_g strain will lift the vibronic degeneracy without changing the spin vibronic character of the levels and therefore the occurrence of e_g strain in the crystal might be a plausible explanation for the observed phenomena. The lower-lying vibronic state will then appear as isolated and will give a light increase, while the population of the spin levels in the higher vibronic levels may deviate from a Boltzmann distribution, resulting in a light decrease upon microwave pumping.

To arrive at different subensembles of F centers one needs e_g strain whose components vary both in magnitude and direction in the crystal.

The concept of random static intrinsic strain,[9] which arises from dislocations, inhomogeneities, nearby point defects, etc., has long been recognized as being very important for inhomogeneous line-broadening effects in EPR.[9-12] Therefore, we will first try to investigate the effect of random strain on magnetic resonance frequencies and the vibronic energies.

D. Random-strain model

The selection of F centers, giving rise to the emission at 5740, 5742, and 5743 Å, is essentially made by the *microwave*-induced transitions. Therefore, we have to consider first of all the effect of random strain upon the zero-field splitting of the spin-vibronic levels and to determine which

subensemble will have the highest spectral density in the magnetic resonance. From this the level ordering of the responding F centers and the optical polarization of the zero-phonon lines can be deduced.

In the static limit the effect of strain upon the vibronic energies is given by[4]

$$H_1 = V_2[(-\tfrac{1}{2}e_\theta + \tfrac{1}{2}\sqrt{3}\,e_\epsilon)L_x^2 + (-\tfrac{1}{2}e_\theta - \tfrac{1}{2}\sqrt{3}\,e_\epsilon)L_y^2 + e_\theta L_z^2]\,. \quad (1)$$

The influence of strain upon the zero-field splitting between the spin levels in vibronic JT state has been shown to be of the form[7]

$$\begin{aligned} H = {} & V_2[(-\tfrac{1}{2}e_\theta + \tfrac{1}{2}\sqrt{3}\,e_\epsilon)L_x^2 + (-\tfrac{1}{2}e_\theta - \tfrac{1}{2}\sqrt{3}\,e_\epsilon)L_y^2 + e_\theta L_z^2] - D(L_x^2S_x^2 + L_y^2S_y^2 + L_z^2S_z^2) \\ & + e_\theta[\tfrac{1}{3}(G_{11} - G_{12} - G_{33})(2L_z^2S_z^2 - L_x^2S_x^2 - L_y^2S_y^2) + (-\tfrac{1}{2}G_{11} - G_{12} - \tfrac{1}{4}G_{33})(L_x^2S_y^2 + L_y^2S_x^2) \\ & + \tfrac{1}{3}(-\tfrac{1}{2}G_{11} - G_{12} - \tfrac{1}{4}G_{33})(L_x^2S_x^2 + L_y^2S_y^2 + L_z^2S_z^2) + (\tfrac{1}{2}G_{11} + G_{12} - \tfrac{1}{4}G_{33})S^2L_z^2 + \tfrac{1}{2}G_{33}L^2S_z^2] \\ & + (e_\epsilon/\sqrt{3})\{(L_x^2S_x^2 - L_y^2S_y^2)(G_{11} - G_{12} - G_{33}) + (L_x^2 - L_y^2)[(\tfrac{1}{2}G_{11} + G_{12} - \tfrac{1}{4}G_{33})S^2 + (\tfrac{1}{2}G_{11} + G_{12} + \tfrac{1}{4}G_{33})S_z^2] \\ & + (S_x^2 - S_y^2)[\tfrac{1}{2}G_{33}L^2 + (\tfrac{1}{2}G_{11} + G_{12} + \tfrac{1}{4}G_{33})L_z^2]\}\,. \end{aligned} \quad (2)$$

H operates within the basis $|\nu i\rangle$, with $\nu = \xi$, η, or ζ and $i = x$, y, or z the spin functions of the $S = 1$ system. V_2 is the strain coupling coefficient, e_θ and e_ϵ are defined in terms of the strain tensor elements e_i by $e_\theta = e_3 - \frac{1}{2}(e_1 + e_2)$ and $e_\epsilon = \frac{1}{2}\sqrt{3}\,(e_1 - e_2)$, and elements G_{ij} stem from the magnetoelastic tensor G. It is readily seen that only matrix elements of the type $\langle \nu i | H | \nu i \rangle$ have nonzero values as required in the extremum of the static Jahn-Teller coupling case.

From experiments under uniaxial external strain it was determined that $G_{12} = G_{33} = -2G_{11}(= 2G)$ and in terms of the parameters ϕ and e, defined by $\tan\phi = e_\epsilon/e_\theta$ and $e = (e_\theta^2 + e_\epsilon^2)^{1/2}$, the frequencies for the transitions between the spin levels can be calculated to have the simple form as given in Table III.

The characteristics of random strain are as follows: (i) e varies from one site to another and it is customary to adopt a spatial distribution P of the form $P(e) = (e/\sigma^2)P\exp[-\frac{1}{2}(e/\sigma)^2]$; and (ii) an equal probability for each value of ϕ within the interval $0° \leq \phi \leq 360°$.

Assuming for the moment a fixed value for e, a random strain distribution then implies a ϕ-dependent spread in the energies of the spin levels and therefore also a dispersion of the zero-field microwave transition frequencies. Since the spectral density $g(\nu)$ is related to the resonance frequency ν by $g(\nu) \sim (\delta\nu/\delta\phi)^{-1}$, and since ν is a goniometric function of ϕ (Table III), one expects singularities in $g(\nu)$ (Fig. 9).

As an explicit example we consider now the case of x-polarized microwave transitions. Then two microwave transitions are possible, namely, $\eta y \rightarrow \eta z$ and $\zeta z \rightarrow \zeta y$. According to Table III we can write, for the resonance frequencies,

$$h\nu(\eta y \rightarrow \eta z) = D - 2\sqrt{3}\,eG\sin\phi$$

and

$$h\nu(\zeta z \rightarrow \zeta y) = D + eG(3\cos\phi - \sqrt{3}\sin\phi)\,.$$

The spectral density achieves an extreme value when $|\delta\nu/\delta\phi| = 0$. This occurs for the $\eta y \rightarrow \eta z$ transition when $\cos\phi = 0$, i.e., $\phi = 90°$ or $270°$ and for the $\zeta z \rightarrow \zeta y$ transitions when $\mathrm{tg}\,\phi = -1/\sqrt{3}$, i.e., $\phi = 150°$ or $330°$; the transition frequencies at the extrema are

$$h\nu(\eta y \rightarrow \eta z, 90°) = h\nu(\zeta z \rightarrow \zeta y, 150°) = D - 2\sqrt{3}\,eG\,,$$

$$h\nu(\eta y \rightarrow \eta z, 270°) = h\nu(\zeta z \rightarrow \zeta y, 330°) = D + 2\sqrt{3}\,eG\,.$$

TABLE III. Frequencies of the zero-field microwave transitions in the $^3T_{1u}$ state expressed in terms of the strain parameters $e = (e_\theta^2 + e_\epsilon^2)^{1/2}$ and $\phi = \arctan(e_\epsilon/e_\theta)$ as calculated from Eq. (2). The values for ϕ giving rise to singularities in the spectral density function $g(\nu)$ [$g(\nu) \rightarrow \infty$] are also given.

Microwave transition	Microwave polarization	Transition frequency	ϕ for $\delta\nu/\delta\phi = 0$
$\xi x \rightarrow \xi y$	z	$D + eG(-3\cos\phi + \sqrt{3}\sin\phi)$	330°, 150°
$\xi x \rightarrow \xi z$	y	$D + 2\sqrt{3}eG\sin\phi$	90°, 270°
$\eta y \rightarrow \eta x$	z	$D + eG(-3\cos\phi - \sqrt{3}\sin\phi)$	30°, 210°
$\eta y \rightarrow \eta z$	x	$D - 2\sqrt{3}eG\sin\phi$	90°, 270°
$\zeta z \rightarrow \zeta x$	y	$D + eG(3\cos\phi + \sqrt{3}\sin\phi)$	30°, 210°
$\zeta z \rightarrow \zeta y$	x	$D + eG(3\cos\phi - \sqrt{3}\sin\phi)$	150°, 330°

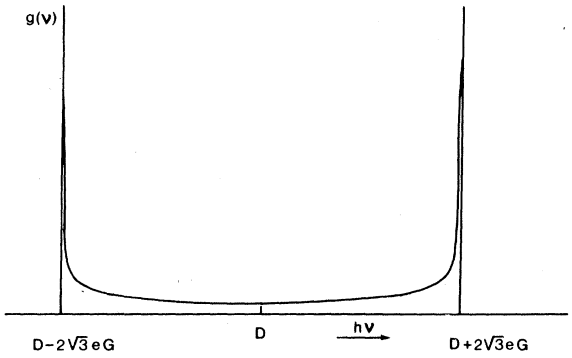

FIG. 9. Variation of the spectral density $g(\nu)$ with the resonance frequency ν of the $\eta y \rightarrow \eta z$ ODMR transition under conditions of (i) equal probability for each ϕ in the interval $0 \leq \phi \leq 2\pi$ and (ii) a constant strain magnitude e.

Considering the magnetic resonance at the region of high spectral density around $h\nu = D + 2\sqrt{3}eG$, we see that the microwave selects (i) a subensemble of F centers all subject to a strain with ϕ around 270° in which case the η vibronic state is in resonance, and (ii) another subensemble of F centers subject to a different strain with ϕ around 330° in which case the ζ state is affected by the microwaves.

Consequently, the light emission induced at that microwave frequency will be a superposition of the emission from different spin vibronic states connected with different subensembles of F centers.

Now we can calculate from (1) and (2) the level ordering in each of the subensembles with $(\delta\nu/\delta\phi) = 0$. This leads to three equidistant vibronic levels in each subensemble, separated by $\frac{1}{2}e|V_2|\sqrt{3}$. However, as depicted in Fig. 10, the microwave transitions for the 270° and 330° subensembles occur in the highest vibronic state and for the 90° and 150° subensembles in the lowest-lying vibronic states. All information concerning the resonant states is compiled in Table IV.

TABLE V. Relative vibronic energies and resonance fields of the subensembles with $\phi = 0°$ and $\phi = 180°$ which contribute to the low- and high-field Z lines in the X-band EPR spectrum as deduced from the random-strain model.

	$\phi = 0°$	$\phi = 180°$
ξ	$-\frac{1}{2}e\|V_2\|$	$+\frac{1}{2}e\|V_2\|$
η	$-\frac{1}{2}e\|V_2\|$	$+\frac{1}{2}e\|V_2\|$
ζ	$+e\|V_2\|$	$-e\|V_2\|$
Resonance field of:		
H^{low}	$(h\nu - D - 3eG)/g\mu_B$	$(h\nu - D + 3eG)/g\mu_B$
H^{high}	$(h\nu + D + 3eG)/g\mu_B$	$(h\nu + D - 3eG)/g\mu_B$

E. Interpretation with random strain

1. 5740-Å emission

At this stage we make an attempt to interpret the experimental results qualitatively in terms of the random strain model. First we can assign the 5740-Å emission in case of an x-polarized microwave field to a resonance in the upper vibronic η states of F centers in the 270° subensemble and in the upper ζ states of the 330° subensemble (Fig. 10). Since the ηz and ηx as well as the ζy and ζx levels will be splitted by an amount of $eG\sqrt{3}$, the ηz and ζy states can be selectively pumped and both levels will exhibit an x-polarized light emission (cf. Table II).

When a magnetic field is applied along the z axis the model requires that the light change at the 1.70-GHz resonance is due to the η state of the $F(270°)$ centers and at 1.58 GHz (the Zeeman-split line) to the ζ state. Both induced light changes have to appear at the same wavelength with the same polarization. Changing the magnetic field to the y direction will leave the resonance at 1.70 GHz to the $F(330°)$ centers in the ζ state and the η states will respond upon resonance in a Zeeman component. Again the emission at both resonances will occur at the same wavelength and with the same polarization. Also with a magnetic field along the x axis the 1.70-GHz resonance will give an x-polarized zero-phonon line at 5740 Å. This is all in agreement with the experimental results given in Table II.

From Table IV it follows that when the microwave field is y polarized the random-strain model predicts the 5740-Å emission to be y polarized which, in agreement with Table II, cannot be detected in the experimental arrangement used. Furthermore, Table IV shows that in the random-strain model the 5740-Å line induced by z-polarized microwaves, should have a z polarization.

Also the decrease in light intensity of the 5740-Å emission upon microwave pumping is understandable. All three spin levels within either the $\eta(270°)$ or the $\zeta(330°)$ state have a rapid internal conversion to the lower-lying vibronic JT states.

Only the upper spin levels of the $\eta(270°)$ or $\zeta(330°)$ state are populated by intersystem crossing from the ${}^1T_{1u}$ state. Now when the spin lattice relaxation within the upper JT state is slow as compared to the internal conversion rate, a surplus in the population of the upper spin levels is built up and consequently a decrease in light intensity is induced upon microwave pumping. This condition is the more valid the higher the strain magnitude,

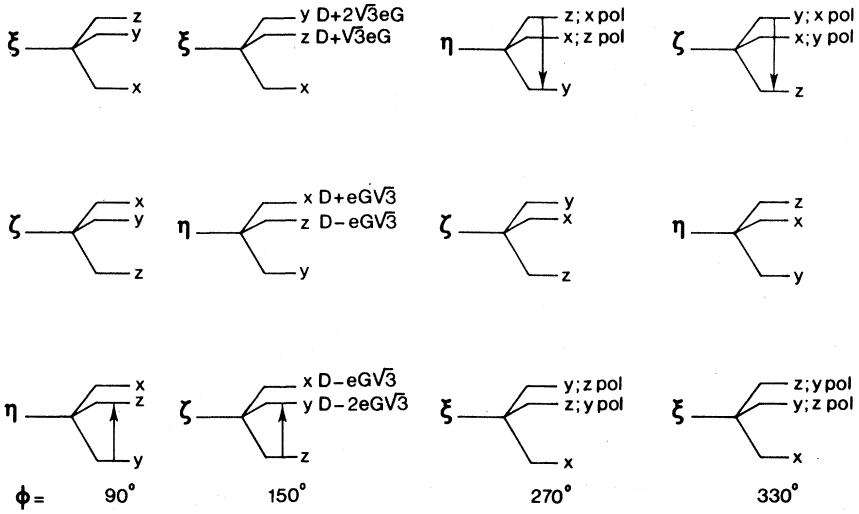

FIG. 10. Level ordering in subensembles, with $|dv/d\phi|^{-1}=0$ and arbitrary chosen strain magnitude, which are involved in the ODMR observations when x-polarized microwaves are used.

because the relaxation rate in a single vibronic state is determined by the vibronic splitting.[7]

Note: As explained in Sec. V E, the outer Zeeman components of the ζ states originate from another subensemble than the ζ states responding at 1.70 GHz in zero field.

2. 5742-Å emission

The population of the spin levels in the *lowest*-lying vibronic states of the different subensembles is determined by a direct feeding by intersystem crossing from the ${}^1T_{1u}$ state, by the radiationless cascade with spin alignment memory from the higher-lying vibronic states and by the spin lattice relaxation within a JT state. Only the upper spin levels of the lowest vibronic JT state have a radiative probability for a transition to the electronic ground state. This means that when the lowest spin level of an isolated JT state has no other decay channel than a radiationless transition to the electronic ground state, a population surplus is collected in the lowest spin state with respect to the upper spin states. In that case a microwave transition from the lower to an upper spin state will induce a light increase. This situation was actually found to be present under uniaxial stress.[7]

When, guided by these considerations, the increase in the 5742-Å emission is assigned to those subensembles of F centers where the resonance proceeds in the lowest vibronic state, a good agreement with the experimental data is obtained. It has to be assumed, however, that the upper spin levels are still degenerate within the homogeneous linewidth of the resonance.

For example with x-polarized microwaves and a magnetic field along z, the Zeeman components from ζy are x polarized (cf. Table IV and Fig. 5). The 1.68-GHz resonance with emission from the degenerate $\eta z(90°)$ and $\eta x(90°)$ state is unpolarized (Table IV and Fig. 4).

With a y-polarized microwave field and a magnetic field along x, the x-polarized light at 5742 Å (Table I) arises from $\zeta y(210°)$ and the z-polarized light induced at the Zeeman components from upper spin levels of the ξ state (Table IV) which will split by the magnetic field along x.

3. 5743-Å emission

We are then left with the appearance of a PMDR zero-phonon line at 5743 Å. A few peculiarities emerge. First, the random-strain model predicts the resonance of the *low*-lying vibronic levels with the highest spectral density at *low* microwave frequencies. The 5743-Å emission, however, still appears at the higher microwave frequency with which the 5740-Å emission can also be generated. Second, if the lowest vibronic state were to be pumped directly, we expect a light increase instead of a decrease. Third, the optical polarization of the 5743-Å emission indicates that just those spin levels are involved which cannot be affected by the microwave field.

This brings us to the idea that the 5743-Å emission arises from levels for which the population is changed in an indirect way and is connected to the resonance in the levels which give the emission at 5740 Å. As has been shown previously, a vibronic JT state can relax into another JT state by absorption or emission of a phonon.[7] In this conversion process the spin state is conserved. Now, assuming that a resonance in the upper vibronic level (5740 Å) changes in this way the population of the spin levels in a lower vibronic state (5743 Å), the selection rule dictates that only those spin levels are influenced which have that same spin state as

the ones involved in resonance in the upper vibronic state. Moreover, when in case of nondegeneracy the spin lattice relaxation within a single JT state is slow as compared to the fast internal conversion process; consequently the internal conversion will be observed only from the spin levels, selected by the microwaves.

That this view holds becomes clear when we examine the data for a y-polarized microwave field in detail (Table II). In zero magnetic field the random-strain model predicts (Table IV) that with the resonance at the higher microwave frequency the $\xi z(90°)$ and $\zeta x(30°)$ levels are involved. The internal conversion process with conservation of spin state will then produce a population change in the low-lying $\eta z(90°)$ and $\eta x(30°)$ levels, respectively. This results in an x- and z-polarized light change at 5743 Å. Experimentally, the light at 5743 Å was found to be unpolarized (cf. Table II).

A magnetic field along x will detune the $\xi x \leftarrow \xi z$ resonance from 1.70 GHz and only the $\zeta z \leftarrow \zeta x(30°)$ resonance is left at 1.70 GHz. Accordingly the 5743-Å emission from $\eta x(30°)$, due to internal conversion from $\zeta x(30°)$, has to be z polarized. When the magnetic field is along z, resonance at 1.70 GHz occurs for the $\xi x \leftarrow \xi z(90°)$ transition and concurrently with a decrease in the $\xi z(90°)$ population we expect a decrease of $\eta z(90°)$ (x polarized).

As follows from Table II, these polarization changes with the magnetic field along different crystal axes have been actually observed.

However, we have only observed that a population decrease of the upper spin level in the upper vibronic state ($\nu = 1.70$ GHz) is reflected in a population decrease of a level with the same spin state in the *lowest* vibronic state. Decrease of the same spin level of the vibronic state in between has not been found. Clearly, the spin levels of the lowest vibronic state have a much larger population than the spin level of the vibronic state in between and will therefore act as the main source to replenish a population decrease in the upper vibronic state. Moreover, an effect in the middle vibronic state will be hidden in the wing of the 5740- and 5743-Å zero-phonon lines.

No transfer of the increase in population to lower vibronic states has been observed after resonance in the upper vibronic state. This, however, will appear in the region where there is a strong overlap with the 5742-Å emission, which itself is also an increase in light intensity, and one cannot distinguish between the different origins of these light changes.

4. 5742- and 5743-Å emission

Now the question arises why the lowest vibronic state in the subensembles emitting at 5743 Å, is still lower than the lowest vibronic state of the subensembles where the light change was a direct result of the magnetic resonance (5742 Å). This problem is intimately connected with the nondegeneracy of the JT states selected by the microwaves, the strain magnitude e (vibronic splitting), the selective internal conversion, and the resulting population distribution over the spin vibronic levels under steady state illumination.

Let us first discuss the 5742-Å emission. In the random-strain model this corresponds with a resonance in the lowest-lying vibronic state of those subensembles which have the highest spectral density. Experimentally, a light increase is found and a population surplus in the lowest spin vibronic level is not an astonishing fact (cf. Sec. IV E 2). However, only in the lowest JT states we are sure that regardless of the strain magnitude such a situation exists. This in contrast to the upper vibronic state where the population differences are much more determined by competitive processes as feeding from ${}^1T_{1u}$, conversion to lower spin vibronic levels, thermal feeding from lower vibronic states, radiative and or radiationless transitions to the electronic ground state.

Up to now we have only considered the effect of ϕ in selecting subensembles with a high spectral density. Now assuming also a distribution in the strain magnitude e (cf. Sec. IV D), the shape of the ODMR line can be constructed from the regions of high spectral density with respect to ϕ for every e, weighted by the probability $P(e)$ and taking also in account the homogeneous width of a resonance and the population difference as a function of e. Indeed, when recording the PMDR at different frequencies in the frequency interval comprised by the inhomogeneously broadened ODMR line, the top of the zero-phonon line shifts slightly.

Now we focus our attention to subensembles where the highest vibronic JT state is selected by the magnetic resonance. First, given a fixed optical pumping rate and microwave power, the light response is governed by the initial steady-state population difference between the spin levels, involved in the resonance experiment. The population of the highest spin vibronic levels is strongly dependent upon the energy separation ΔE of the vibronic states since the ratio of the upward to the downward internal conversion rates, assuming microscopic reversibility, is determined by $e^{-\Delta E/kT}$. Thus for a low-strain magnitude the steady-state population difference between the spin levels in the upper vibronic state can be such that a microwave-induced transition between these levels will result in an *increase* of emitted light. Certainly such contributions may be present in the high-energy tail of the 5742-Å zero-phonon band

TABLE IV. Subensembles involved in the zero-field microwave resonance experiment in the F center $^3T_{1u}$ state as follows from the random-strain model in which only the strain parameter ϕ is allowed to vary ($0° \leq \phi \leq 360°$) and e is taken as a constant. The sixth column shows states of which the population is affected by internal conversion from an upper state involved in resonance at highly stressed sites [type (a)] and states which respond also to resonance because of near degeneracy in lowly stressed sites [type (b)].

Microwave polarization	Energy shift of PMDR zero-phonon line	Microwave frequency	Emitting state involved in resonance	Optical polarization	Connected by (a) internal conversion (b) spin-degeneracy to:	Energy shift of PMDR zero-phonon line	Optical polarization
x	$+\frac{1}{2}\sqrt{3}e\lvert V_2\rvert$	$D+2\sqrt{3}eG$	$\eta z(270°)$	x	(a) $\xi z(270°)$	$-\frac{1}{2}\sqrt{3}e\lvert V_2\rvert$	y
			$\zeta y(330°)$	x	(a) $\xi y(330°)$		z
	$-\frac{1}{2}\sqrt{3}e\lvert V_2\rvert$	$D-2\sqrt{3}eG$	$\eta z(90°)$	x	(b) $\eta x(90°)$	$-\frac{1}{2}\sqrt{3}e\lvert V_2\rvert$	z
			$\zeta y(150°)$	x	(b) $\zeta x(150°)$		y
y	$+\frac{1}{2}\sqrt{3}e\lvert V_2\rvert$	$D+2\sqrt{3}eG$	$\xi z(90°)$	y	(a) $\eta z(90°)$	$-\frac{1}{2}\sqrt{3}e\lvert V_2\rvert$	x
			$\zeta x(30°)$	y	(a) $\eta x(30°)$		z
	$-\frac{1}{2}\sqrt{3}e\lvert V_2\rvert$	$D-2\sqrt{3}eG$	$\xi z(270°)$	y	(b) $\xi y(270°)$	$-\frac{1}{2}\sqrt{3}e\lvert V_2\rvert$	z
			$\xi x(210°)$	y	(b) $\xi y(210°)$		x
z	$+\frac{1}{2}\sqrt{3}e\lvert V_2\rvert$	$D+2\sqrt{3}eG$	$\xi y(150°)$	z	(a) $\zeta y(150°)$	$-\frac{1}{2}\sqrt{3}e\lvert V_2\rvert$	x
			$\eta x(210°)$	z	(a) $\zeta x(210°)$		y
	$-\frac{1}{2}\sqrt{3}e\lvert V_2\rvert$	$D-2\sqrt{3}eG$	$\xi y(330°)$	z	(b) $\xi z(330°)$	$-\frac{1}{2}\sqrt{3}e\lvert V_2\rvert$	y
			$\eta x(30°)$	z	(b) $\eta z(30°)$		x

or in the low-energy tail from the lowest vibronic JT states of these subensembles where the population is influenced by internal conversion to the upper state. Unfortunately, these superimposed emissions from different subensembles cannot be resolved.

However, experimentally the resonance in the upper vibronic states could emerge so distinctly in the observation of the 5740-Å line by virtue of the light decrease. For these subensembles of F centers in the higher spin levels a population surplus with respect to the lower spin level is built up under steady state conditions. This can be reached (cf. Sec. IV E *1*), when the feeding by internal conversion from the lower vibronic states slows down, i.e., when the strain magnitude and so the energy gap between the vibronic levels becomes larger. Thus in studying the subensembles which respond by a light *decrease* at 5740 Å, the additional requirement of an inverted population makes that we are already selecting F centers which are subject to the larger strain magnitudes. This in contrast to the resonance in the lower vibronic states (5742 Å), when *all* subensembles over the e distribution can contribute to the light increase.

Thus the average e at the top of the inhomogeneously broadened ODMR line corresponding with the light increase is smaller than that at the top of the ODMR line which is connected to the light decrease. Consequently, the vibronic energy of the lowest vibronic state, which is coupled by internal conversion with the resonance in the highest vibronic state is determined by a higher average value of the strain magnitude which corresponds to a lower average vibronic energy (5743 vs 5742 Å).

From expression (1) we calculate the strain induced splitting between the 5740- and 5743-Å emitting levels (9 cm^{-1}) to be $\sqrt{3}eV_2$. The strain-coupling coefficient V_2 can easily be calculated from the results presented in Ref. 7. $V_2 \sim -3.95 \times 10^4$ cm^{-1}. Hence, for the magnitude of the strain corresponding to the subensemble 5740 and 5743 Å we find $e \simeq 1.3 \times 10^{-4}$.

The position of the zero-phonon line for unstrained crystals should be 5741.5 Å. Thus the subensemble emitting at 5742 Å is subjected to internal strain with $e \simeq 4.5 \times 10^{-5}$.

F. Magnetic resonance under high magnetic fields

In studying the F center in EPR at high magnetic fields, Edel *et al.*[3] have noted that in the EPR spectra the polarization of the emission induced by the microwave transitions, was not in complete agreement with what has to be expected from the site under resonance.

Very recently we learned about a similar study[13] in which the X-band EPR was studied under nar-

row-band excitation in the zero-phonon absorption line of the triplet states. It was concluded that the observed phenomena have to be explained by the presence of strain and inclusion of a reorientation process without spin flip for highly stressed states. This view is in perfect agreement with the interpretation we gave before for the zero-field phenomena and for the experiments under uniaxial stress.[6,7] In fact we will show that a similar treatment as for the zero-field case is also consistent with the results obtained in X-band EPR.

In interpreting the high-field EPR experiments of F centers under random-strain conditions one has first to determine which subensemble will give a high spectral density. With restriction to the Z low- and high-field lines (only the resonance in the ζ state are then considered), it can easily be shown from Table III that the resonance will occur at $H_z^{\text{low}} = (h\nu - D - 3eG\cos\phi)(g\mu_B)^{-1}$ and $H_z^{\text{high}} = (h\nu + D + 3eG\cos\phi)(g\mu_B)^{-1}$. Extrema in the spectral density are reached for $\phi = 0°$ and 180°; the vibronic energies of the JT states in these subensembles and the position of the low- and high-field Z line are given in Table V.

Due to the positive sign of G, the resonances in the subensembles where ζ is the lowest vibronic state ($\phi = 180°$) will appear at the high-field wing of the low-field Z line and at the low-field wing of the high-field Z line. A resonance in the subensemble where ζ is the upper vibronic state ($\phi = 0°$) is to be found at the low-field side of the low-field Z line and at the high-field side of the high-field Z line.

With excitation in the high-energy wing of the zero-phonon absorption line, the upper vibronic states of strongly strained F centers are optically selected. From these the EPR experiment selects the ζ states which may be in either the $\phi = 0°$ subensemble (then the ζ state is an upper vibronic "selected" state) or the $\phi = 180°$ subensemble in which case the ζ "relaxed" states becomes populated by internal conversion with conservation of spin state from the upper lying optically prepared ξ and η states. When the polarization of the excitation light is such the ζ state cannot directly be prepared by optical excitation, the resonance of the 0° subensemble in the high-field wing of the high-field Z line has to disappear. These phenomena have actually been found by Bontemps-Moreau *et al.*[13]

Returning to the work of Edel *et al.*, rather strong changes in circularly polarized light were found at the low- and high-field resonances of the ξ and η states, which can only originate from a response of a ζ state. Now, working along similar lines as before, we find that the highest spectral density for the resonance in the ξ state is obtained for $\phi = 60°$ and 240°. The level ordering is such that in both cases the vibronic ξ and ζ states are degenerate with each other. This situation is exactly the same as that studied under uniaxial stress along a principle axis,[7] where internal conversion with spin memory is also responsible for *large* changes in the simultaneous response of two degenerate vibronic levels when one of the states is on resonance.

With this, the small change in $z(\pi)$ polarized light observed in the resonance of the ζ state has to be compared. From Table V it follows that the resonant state is nondegenerate and the microwave-induced light changes in the other states are now, due to different (Boltzmann, phonon-density) factors in the rate constant, much smaller.

No attempt was made to explain the sign of the light changes. The population distribution is the steady state balance of many dark processes in the optical-pumping cycle of the nine-spin vibronic states which themselves are perturbed by strain and the magnetic field. A quantitative analysis would require a detailed knowledge of all the kinetics involved and cannot as yet be given.

V. CONCLUSIONS

We have shown in this paper that with (i) the assumption of static random strain of the e_g type in the crystal, (ii) a description of the F centers in terms of tetragonally distorted spin vibronic Jahn-Teller states in the static limit, (iii) phonon-assisted conversion of vibronic character with conservation of spin state, the rather complicated optically detected magnetic resonance phenomena can be described qualitatively in a satisfactory way.

Of major importance in understanding the data is that with random strain only a part of the excited F centers is observed. The selection of subensembles is determined by the conditions used in the magnetic resonance experiment, e.g., microwave polarization, direction magnetic field, zero field. With this specific selection of a subensemble the level ordering of the three JT states and the position of the resonant state with respect to the others are fixed. This then in turn will determine the wavelength and sign of the induced light changes in the resonant and in the other states.

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