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In this paper we study the temperature-induced homogeneous broadening of the no-phonon line in the emission spectrum of the F center in CaO. The linewidth can be fitted to $\bar{n}(\bar{n}+1)$, where $\bar{n}$ is the thermally averaged occupation number of phonons with a frequency of 90 cm^{-1}. The results are characteristic of elastic scattering of pseudolocalized phonons at the defect site. These phonons also appear to dynamically couple the Jahn–Teller components of the F center in the photoexcited $^3T_{1u}$ state and thus give rise to a temperature dependence of the lifetime of this phosphorescent state. Finally, from experiments using laser-selective excitation it is concluded that the zero-phonon emission peaking at 571.1 nm does not originate in the F center.

I. INTRODUCTION

Recently, the problem of vibronic dephasing of an impurity in an optical inactive medium has received much interest.[1,2,3] Pure dephasing occurs because elastic phonon scattering is different in the impurity ground (i) and excited (f) levels. Actually, the disparity results from different impurity–lattice couplings in i and f. By a separation of "impurity" and "lattice" coordinates, one can show[1] that the strength of the impurity–lattice coupling depends on intramolecular electronic *and* vibrational motions. If, however, the optical probe lacks intramolecular modes, the coupling strength is solely determined by its electronic part and the vibronic dephasing process reduces to pure electronic dephasing; intramolecular anharmonicity is then irrelevant. In this paper, results representative of a pure electronic dephasing mechanism are reported for a color center system, namely, the luminescent F center in CaO.

In emission, the F center in CaO (i.e., an oxygen vacancy containing two electrons) is recognized by its narrow zero-phonon line at 574.2 nm, corresponding to the $^3T_{1u} \rightarrow {}^1A_{1g}$ transition.[4] As discussed later, analysis of the shape of the quasiline emission allows one to directly examine the homogeneous line broadening at high temperatures. Thus, to obtain the dephasing rates, the necessity of performing time-resolved coherence experiments[1,3,5] is not mandatory in this case. We also note that relatively few studies involving optical dephasing in color center systems have been reported.[6] The reason is that most work is concerned with defects in alkali halides and for these, sharp zero-phonon transitions are seldom observed.

From this work, several new findings for the F cen-

ter in CaO emerge. Population and phase relaxation (i.e., T_1- and T_2-type relaxation, respectively) could be independently studied as a function of temperature. It turns out that the corresponding relaxation rates have much different cross sections but both are thermally activated by phonons with $\hbar\omega \simeq 90$ cm^{-1}.

To explain the results, it is inferred that the F center defect is coupled to pseudolocalized modes. It will be shown that because of this coupling the observed effects of temperature on homogeneous linewidth and lifetime can be accounted for in a consistent way. Finally, by selective laser excitation a zero-phonon line emission peaking at 571.1 nm was observed. Since the 571.1 and 574.2 nm line emissions differ by about 90 cm^{-1}, it was thought worthwhile to examine the possibility that the 571.1 nm line (of which the origin has hitherto remained unclear[7,8,9]) originates in the F center. No evidence was found that this is actually the case.

II. EXPERIMENTAL

Yellow-colored CaO crystals (purchased from Spicer Ltd.) were mounted inside a Janis DT-10 variable temperature Dewar. The sample was cooled by a helium gas flow. The temperature, measured with a temperature sensing probe near the sample, was regulated between 4 and 120 K to within ±0.5 K using a Lakeshore Cryotronics DT-500 temperature controller. A Molectron DL II nitrogen pumped-dye laser was used for the optical excitation. The laser has a bandwidth of 0.2 cm^{-1} and a typical pulse energy of 0.5 mJ at 574.3 nm, the F-center excitation wavelength. The pulse duration is approximately 10 ns. The light emitted from the crystal was spectrally resolved with a Spex 3/4 m monochromator having a holographic grating with 1800 grooves/mm.

A Varian VP-100 PMT with a GaAs photocathode was used for detection. A PAR-162 boxcar integrator with a 164 plug-in unit was used for measuring lifetimes and time-resolved spectra. The spectra were digitized and computerized for data analysis. The fit of the data was done using a nonlinear least squares regression program. For analysis of the line shapes we have used the
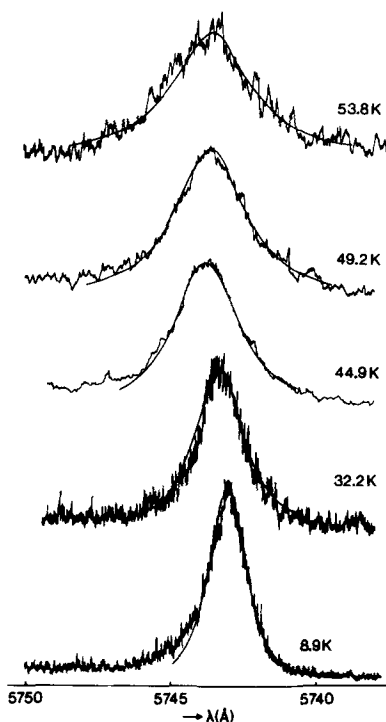
FIG. 1. Zero-phonon emission of the *F* center in CaO at the temperatures indicated. To compensate for the intensity lowering of the no-phonon line at the higher temperatures, spectrometer slit width, and instrumental gain were increased. Spectral resolution was always better than the actual linewidth by at least a factor of 5. Drawn curves represent computed Voigt profiles.
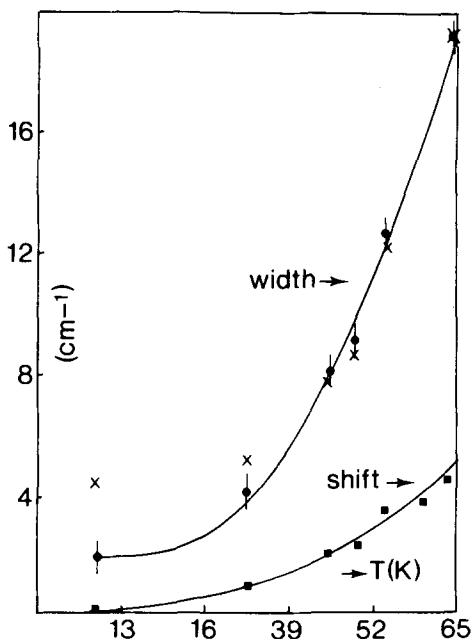

FIG. 2. Width and shift of the zero-phonon emission of the *F* center in CaO as a function of temperature. Dots represent the width of the Lorentzian component of the Voigt line shape fit. Error bars denote standard deviation of the calculated curve with respect to experimental line shape function. Crosses represent the total apparent width. The shift, indicated by squares, is into the red. Drawn curves are best fits using functions proportional to $\bar{n}(\bar{n}+1)$ with $\hbar\omega = 90$ cm^{-1} for the width, and $\bar{n}$ with $\hbar\omega = 75$ cm^{-1} for the shift.
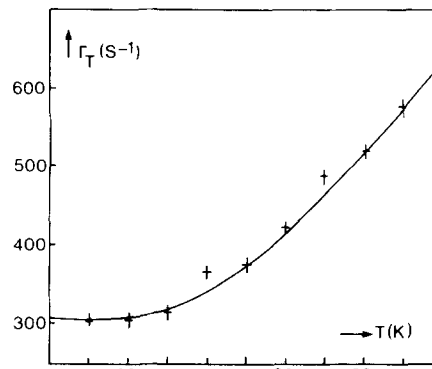

FIG. 3. Temperature dependence of the lifetime of the phosphorescent $^3T_{1u}$ state of the *F* center in CaO. Drawn curve is calculated for $\Gamma_T \propto \coth(\hbar\omega/2kT)$, where $\hbar\omega = 95$ cm^{-1}.

algorithm of Armstrong (see Sec. III) to separate the Lorentzian and Gaussian components of the Voigt zero-phonon line shapes.

III. RESULTS

We first consider the temperature-induced broadening of the no-phonon emission around 574.2 nm of the CaO *F* center. Figure 1 is illustrative of the observed broadening of the *F*-center line emission after pulsed laser excitation ($\lambda = 504$ nm) at a number of different temperatures. Below 20 K, the zero-phonon line is asymmetrically shaped with a typical FWHM of 4.6 cm^{-1}. The asymmetry is caused by the effect of internal strain fields in the crystal on the vibronically triply degenerate $^3T_{1u}$ level.[10] As the temperature is increased, the line becomes more symmetric and becomes a good Lorentzian above 40 K. Overlap with the phonon side band is negligible for temperatures lower than 50 K and severe above 65 K. To determine the inhomogeneous width, we fit the high-energy side of the line, which showed the steepest edge, to a Voigt function (i.e., a Lorentzian convoluted with a Gaussian).[11] At 4.2 K the best fit gave a Gaussian width of 1.3 ± 0.5 cm^{-1}. At higher temperatures, the line was fitted by convolve-and-compare using the algorithm of Armstrong.[12] The drawn curves in Fig. 1 represent the computed Voigt profiles.

The width of the Lorentzian component is considered representative of the homogeneous broadening.[13] The temperature dependence of the homogeneous width of the *F*-center zero-phonon line is given in Fig. 2, together with the apparent FWHM and the shift of the line center. As shown in Fig. 2, a residual homogeneous width of ~1.8 cm^{-1} at the lowest temperatures is found.

In a separate experiment the contribution of the population decay out of the $^3T_{1u}$ state to the homogeneous broadening was determined. Figure 3 shows our data for the temperature dependence of the $^3T_{1u}$ state lifetime in the temperature region of interest. It is seen that the lifetime always remains on the order of milliseconds. However, a significant temperature effect is also evident.

Laser excitation at 503.8 nm yielded in addition to

the *F*-center phosphorescence, a sharp-line emission with a peak at 571.1 nm. Figure 4(a) shows the well-known *F*-center spectrum ($T = 4.2$ K) gated 1 ms after the laser pulse, whereas Fig. 4(b) shows the spectrum gated 50 ns after the excitation pulse. [Note that the intensity scales in Figs. 4(a) and 4(b) are much different due to a difference in experimental conditions (slit widths and apparatus gain). The 571.1 nm is much stronger than the 574.2 nm line emission.] The excitation spectra of the 574.2 and 571.1 nm lines were monitored also. These spectra, shown in Fig. 5, were obtained by scanning the dye-laser wavelength from 480 to 580 nm. For the excitation spectrum of the 574.2 nm line, an asymmetric broad absorption band peaking at 510 nm was observed. On the other hand, the excitation spectrum of the 571.1 nm line [cf. Fig. 5(b)] consists of two bands, a relatively weak band with its maximum near 510 nm and a strong band with a maximum at 550 nm. As mentioned in Sec. I, it seemed of interest to investigate the possibility that the 571.1 nm emission originates in the *F* center.

As already noted, the $^3T_{1u}$ state lifetime typically is in the millisecond range. By contrast, the time decay of the 571.1 nm emission appeared too short to be measured within the time resolution of our equipment (~50 ns). The orders of magnitude difference in the decay time of the 571.1 and 574.2 nm emissions shows that the population flow, if any, between the emitting states is slower than the millisecond decay of the $^3T_{1u}$ level. Thermal isolation was also found in another experiment.

Upon direct excitation of the crystal at 571.1 nm ($T < 10$ K), no emission is observed at 574.2 nm. Thus, now we find that the level, which emits at 571.1 nm, has decayed before any relaxation to the $^3T_{1u}$ level has occurred. In our initial experiments, the temperature dependence of the intensity of the emission at 571.1 nm was measured while the crystal was pumped optically with light of 574.2 nm wavelength. It was found that, as the temperature raises from 4 up to 100 K, the 571.1 nm emission becomes more intense. This suggests that during the lifetime of the $^3T_{1u}$ state, thermal equilibra-
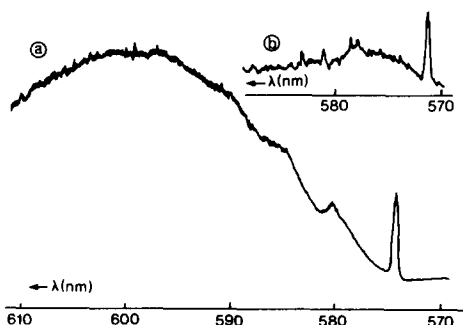

FIG. 4. (a) *F*-center phosphorescence spectrum gated 1 ms after laser excitation at 503.8 nm ($T = 4.2$ K). (b) Emission as observed for additively colored CaO, 50 ns after laser excitation at 503.8 nm ($T = 4.2$ K). Due to different experimental conditions (slit width and apparatus gain), the intensity scales of (a) and (b) are different.
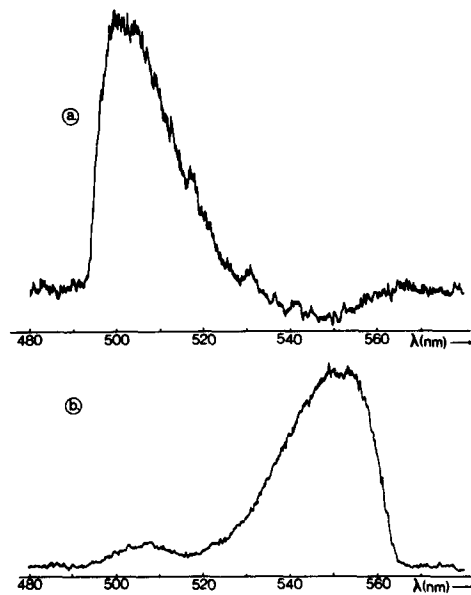

FIG. 5. (a) Excitation spectrum of *F*-center emission peaking at 574.2 nm, gated 1.5 ms after excitation ($T = 20$ K). (b) Excitation spectrum of zero-phonon line with peak at 571.1 nm, gated 50 ns after photoexcitation ($T = 20$ K). The spectra were not corrected for system response.

tion among the two emitting levels is achieved and indeed, the 571.1 nm emission intensity was found to be exponentially enhanced with an activation energy of 95 cm^{-1}. However, from the time-resolved experiments we know now that thermalization does not take place and the alternative explanation for the temperature induced increase of the 571.1 nm line intensity must be that the 574.2 nm light is absorbed in the hot electronic ground state of some unknown defect.

IV. DISCUSSION

The dephasing times that correspond to the homogeneous linewidths of Fig. 2, range from 5 to 0.4 ps. These times are much shorter than the lifetime of the $^3T_{1u}$ state, which never drops below the value of 300 μs (cf. Fig. 3). Consequently, "pure" dephasing (and not population relaxation) is responsible for the observed homogeneous line broadening.

When pure dephasing is caused by phonon scattering at the impurity levels, the general expression for the rate of dephasing is given by[1,2]

$$(T_2')^{-1} = (\pi/\hbar) \sum_{p,p'} W_p |\langle p | \Delta V | p' \rangle|^2 \delta(E_p - E_{p'}), \quad (1)$$

where $\Delta V = \langle i | V | i \rangle - \langle f | V | f \rangle$, V is the potential operator that couples the defect states i and f to the bath, p and p' are the states representative of the phonon reservoir, and W_p is the occupation probability of state p. As is apparent from Eq. (1), phonon-induced dephasing evolves from a disparity in the cross section for phonon scattering in the electronic initial and final states.

When Eq. (1) is considered for different densities of phonon states, one obtains either a T^7-Raman type tem-

perature dependence for $1/T_2'$, or, in the case where the phonon density of states is sharply peaked, the homogeneous width will be proportional to $\bar{n}(\bar{n}+1)$, where $\bar{n}$ is the thermally averaged occupation number of the relevant phonons. As reflected by the drawn curve in Fig. 2, the *F*-center zero-phonon linewidth follows the $\bar{n}(\bar{n}+1)$ temperature dependence, the effective mode frequency being 90 cm^{-1}.

The change in the $^3T_{1u}$-state lifetime is striking. As illustrated by the drawn curve in Fig. 3, the lifetime appears proportional to $\coth(\hbar\omega/2kT)$, for $\hbar\omega = 95$ cm^{-1}. The results are in agreement with the experimental data obtained by Welch *et al.*[14] for the same temperature range.

In the Appendix, it is shown that when a level decays due to a vibronic transition, the temperature dependence of its lifetime is given by the function $\coth(\hbar\omega/2kT)$. In fact, a Herzberg–Teller coupling in the initial electronic level induced by a mode of frequency ω gives rise to the vibronic character of the decay; all other lattice modes are treated within the usual adiabatic approach for the defect-lattice coupling. In view of the fact that the *F*-center $^3T_{1u}$ level refers to a Jahn–Teller state,[15] it may seem surprising that the adiabatic description is valid.

However, for the particular case of the *F* center in CaO it is well established that the $^3T_{1u}$ level is strongly coupled to e_g modes[15] in which case the exact vibronic solutions (in the linear coupling limit) can still be written as Born–Oppenheimer states, $\Psi(r, q_0)F_{n,m}(q_\theta, q_\epsilon)$.[16] Note that the phase relaxation of the $^3T_{1u} \rightarrow {}^1A_{1g}$ no-phonon transition as well as the decay out of the $^3T_{1u}$ level both are activated by 90 cm^{-1} modes. On this basis, we infer that the pseudolocal modes that affect the optical dephasing process are also involved in the vibronic mixing among the Jahn–Teller levels in the excited $^3T_{1u}$ state. This vibronic mixing is readily visualized as follows. Three tetragonal distortions exist for the *F* center in the $^3T_{1u}$ state, due to the strong linear coupling of the latter to an e_g mode. For the system in one of these distorted configurations i ($=x, y, z$), the coupling to t_{2g} modes causes a vibronic mixing among the Jahn–Teller states according to

$$\Psi_i'(r, q_e^{(i)}) = \Psi_i(r, q_e^{(i)}) + \sum_j \lambda_{ij}\Psi_j(r, q_e^{(i)})q_t ,$$

where $\Psi_i(r, q_e^{(i)})$ is the uncorrected electronic wave function for distortion i and $q_e^{(i)}$ is short for the equilibrium positions of the q_θ and q_ϵ coordinates of the e_g (Jahn–Teller) mode corresponding to distortion i; λ_{ij} is representative of the vibronic mixing between Ψ_i and Ψ_j as induced by the t_{2g} mode with coordinate q_t. Presumably, the relative small energy spacing among the states $\Psi_i(r, q_e^{(i)})$ and $\Psi_j(r, q_e^{(i)})$ is most effective in promoting the temperature dependence of the $^3T_{1u}$-state lifetime.

Finally, we comment on the small shift to the red of the *F*-center zero-phonon emission when the temperature is raised. As shown in Fig. 2, the shift δ can be fitted to $\delta \propto \bar{n}$, where $\bar{n}$ is the thermally averaged occupation number of a lattice mode with $\hbar\omega = 75 \pm 10$ cm^{-1}. Consequently, in contrast to the two-phonon effects on the linewidth, the shift is typical for a *one*-phonon as-

sisted process. Evidently, again low-frequency pseudolocal modes are involved. A general expression for δ appears to comprise the sum of two terms[2]: the first of these (the incoherent term) is of the order of $|H_{int}|^2/\Delta E$, where ΔE is the energy difference of the states mixed by H_{int}.

The second (the coherent term) is determined by the coherence in the dynamic frequency shift of the two resonant levels and demands that no change in the phonon state occurs during the electron-phonon interaction ("elastic scattering"). The latter condition implies that only terms second order in the expansion of H_{int} in phonon coordinates contribute to δ. On the other hand, no such restriction applies for the incoherent shift and therefore the latter is predominantly determined by first order terms in the electron–phonon interaction. One readily shows that then $|H_{int}|^2 \propto \bar{n}$.

V. CONCLUSION

In this paper, a laser-selective study concerning the mechanism for optical dephasing of the $^3T_{1u} \rightarrow {}^1A_{1g}$ transition within the *F* center in CaO is presented. The homogeneous width of the no-phonon line is found to be proportional to $\bar{n}(\bar{n}+1)$. This behavior is characteristic of a process of elastic scattering of pseudolocalized phonons at the defect site. The presence of pseudolocalized modes is independently concluded from temperature effects on the no-phonon line position and the lifetime of the emissive $^3T_{1u}$ state. In both these series of measurements we find changes proportional to $\bar{n}$, in which case it can be shown the temperature behavior is determined by terms linear in the electron-phonon coupling.

Finally, we emphasize that the temperature dependence of the coherence decay rate and the dynamic frequency shift differ by a factor of $(\bar{n}+1)$. This result eliminates for the *F* center the applicability of the conventional exchange model.[3] In the latter, an exchange process involving different vibronic transitions is invoked, thereby producing line broadening and line shifts. However, for such an exchange mechanism one can show that the ratio of the temperature-induced shift and broadening should be temperature independent.

APPENDIX

To derive the temperature dependence of the lifetime (τ) of an emitting level $|\text{I}i\rangle$, the vibronic transition $|\text{I}i\rangle \rightarrow |\text{II}f\rangle$ is considered. Here I and i denote the initial electronic and phonon states, II and f denote the respective final states. The radiative decay rate (τ^{-1}) is related to the integrated vibronic transition probability according to

$$\tau^{-1} \propto \sum_f \langle W(\text{I}i \rightarrow \text{II}f)\rangle_T . \tag{A1}$$

In Eq. (A1), $W(Ii \rightarrow IIf)$ represents the probability for the $|Ii\rangle$ to $|IIf\rangle$ transition, $\langle \ldots \rangle_T$ expresses thermal averaging of W over all occupied initial phonon states i and the summation is over all possible final phonon states f. Consider now the electronic transition moment

$$M_{I\ II}(R) = \int dr\ I(r, R)\, M(r)\, II(r, R) , \qquad (A2)$$

which is assumed to exhibit a weak dependence on q_p, the normal coordinate of a pseudolocal mode, only. Thus,

$$M_{I\ II}(q_p) = M_{I\ II}^{(0)} + M_{I\ II}^{(1)} q_p + \cdots \qquad (A3)$$

and Eq. (A1) becomes

$$(\tau^{-1}) \propto \sum_{f_p} \langle W(Ii_p \rightarrow IIf_p)\rangle_T \sum_{f_s} \prod_{s \neq p} \langle J_{i_s f_s}\rangle_T . \qquad (A4a)$$

Here $\langle W(Ii_p \rightarrow IIf_p)\rangle_T$ is the probability for the $|Ii_p\rangle$ to $|IIf_p\rangle$ vibronic transition thermally averaged over all occupied initial pseudolocal mode states i_p, and the Franck–Condon overlap is given by

$$J_{i_s f_s} = \left| \int dq_s\, \chi_{Ii_s}^*(q_s)\, \chi_{IIf_s}(q_s) \right|^2 ,$$

where $\chi_{Ii_s}(q_s)$ is the harmonic vibrational function for mode s in the electronic state I. Since, $\sum J_{i_s f_s} = 1$ (closure relation), Eq. (A4a) becomes

$$\tau^{-1} \propto \sum_{f_p} \langle W(Ii_p \rightarrow IIf_p)\rangle_T . \qquad (A4b)$$

To evaluate the right-hand side of Eq. (A4b) we assume the same equilibrium configuration for mode p in states I and II (i.e., no shift in the equilibrium positions of the lattice atoms). Furthermore, no additional distortions in II for mode p are assumed ($\omega_{Ip} = \omega_{IIp} = \omega_p$). Then, by substitution of Eq. (A3) in Eq. (A4b) and making use of the properties of the harmonic oscillator functions {viz, $\langle \chi_{v+1} | q | \chi_v \rangle = (v+1)^{1/2} [\hbar/(2\mu\omega)]^{1/2}$}, one readily obtains

$$\tau^{-1} \propto \left| M_{I\ II}^{(0)} \right|^2 + \frac{\hbar}{2\mu\omega_p}\left| M_{I\ II}^{(1)} \right|^2 \langle (2i_p + 1)\rangle_T$$

$$= A + B \coth(\hbar\omega_p / 2kT) , \qquad (A5)$$

where μ is the reduced mass of pseudolocal mode p.

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