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Temperature Dependence of Luminescence of F^+ and F Centers in CaO[†]

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The principal moments of the F^+-center absorption and emission bands in CaO have been studied as a function of temperature in the range 5–300 K. The absorption results are shown to be in excellent agreement with the very recent results of Escribe and Hughes. Moment analysis is less useful for emission than absorption bands and gives no further information about the nature of the dynamic Jahn–Teller effect in the excited state of the F^+ center. Nevertheless, certain features of the temperature dependence of the first four moments of the broad band shape indicate that the Jahn–Teller interaction is still important even though the luminescence process samples the orbitally nondegenerate ground state. Analysis of the results shows that in the range 5–78 K the moments $M_1(0)$ and $M_2(T)$ can be accounted for with an effective Huang–Rhys factor $S=6$, the phonon modes effective in broadening the transition having a mean frequency $\hbar\omega = 273$ cm^{-1}. The first four moments of the $^3P \rightarrow {}^1S$ transition of the F center have been measured between 5 and 300 K. The results are interpreted as being consistent with $S=5.5$ and $\hbar\omega = 155$ cm^{-1}. Surprisingly, the band shape, as indicated by the ratio $R=M_4/(M_2)^2$, varies with temperature, being Gaussian below 90 K ($R=3.1$) and rather asymmetric with $R<3$ between 90–300 K. The experimentally measured line shapes in electron-irradiated crystals are well represented by Voigt profiles, which is interpreted as a convolution of the Gaussian component of the unirradiated crystal and that Lorentzian component due to point-defect broadening. The shape, shift, and broadening due to electron irradiation are qualitatively in agreement with the statistical theory of strain broadening.

I. INTRODUCTION

The optical properties of the irradiated and additively colored oxides have been investigated in considerable detail.[1-4] In particular, the F^+ center[2,3] in CaO has attracted considerable interest owing to the Jahn–Teller interaction in the first excited $^2T_{1u}$ state. Hughes[5] has shown that the experimental results are consistent with the idea that the Jahn–Teller coupling of the $^2T_{1u}$ state to the E_g and T_{2g} vibrational modes is equally strong and dominant over coupling to the A_{1g} breathing mode. Presumably the sensitivity of the $^2T_{1u}$ state to Jahn–Teller distortions results from the excited-state wave function being fairly compact; this is reflected by the short lifetimes of the excited state.[6,7] The emission spectrum at 4 K should be somewhat simpler than the absorption spectrum since the emission process samples the vibronic structure of the ground state, in which no Jahn–Teller effect occurs. However, the sensitivity of this compact excited state to Jahn–Teller distortions of E_g and T_{2g} symmetry might be reflected in the temperature dependence of the emission band and particularly in the dichroism of this band under uniaxial stress.

The ground state of the F center is $(1s)^2$, ^1S, and the excited states will be spin singlets or triplets, as in two-electron atoms. The lowest-lying excited state[8] is $(1s)(2p)$, ^3P. However, the F band corresponds to the transition $^1S \rightarrow {}^1P$ ($^1A_{1g} \rightarrow {}^1T_{1u}$ in group-theoretical notation) and occurs at 3.10 eV.[9] The vibrational interactions in the excited P states are in principle similar to those in the F^+ center; thus we might expect coupling to noncubic modes to be dominant. However, there is less binding in the excited state for two electrons than for a single electron in the anion vacancy. Consequently, the coupling of the two-electron wave functions to the spectrum of lattice modes should be strong, and absence of sharp structure in the F-band absorption is not unexpected. The emission spectrum obtained by exciting in the 3.10-eV band includes a band at 2.0 eV which has been attributed to the spin-forbidden $^3P \rightarrow {}^1S$ transition on account of the long radiative lifetimes.[6] This luminescence band shows sharp structure below 77 K. Again the $^3P \rightarrow {}^1S$ emission samples vibronic interaction within the ground states at low temperatures.

In principle the Jahn–Teller coupling energies for both the F^+ and F centers can be determined from the temperature dependence of the broad bands[1] or more directly from the dichroism of the broad bands under external perturbations such as a magnetic field[10] or uniaxial stress.[11] Similar measurements on the zero-phonon line in the F^+ band gave the first indication of the two-mode Jahn–Teller effect.[5,12,13] Certain differences in the reported emission band of the F^+ center indicated that a further detailed investigation was in order.[6,7]

It is important to understand how defects interact with crystal-lattice modes in various materials. One of the better ways to evaluate this interaction is through optical-absorption and -emission studies. Therefore, in this paper we report detailed measurements on the absorption and emission band shape of the F^+ center as a function of temperature and on the temperature dependence of the $^3P - {}^1S$ emission from the F center. Escribe and Hughes[1] have also performed broad-absorption-band measurements and hence we do not discuss our absorption results in detail except for comparison with their measurements.

II. EXPERIMENTAL METHODS

High-purity CaO single crystals obtained from various sources were used. Measurements on the broad absorption and emission bands of the F^+ center were made on crystals grown at Oak Ridge National Laboratory, OR. In these cases suitable cleaved blocks were irradiated in the optical cryostat at 77 K using electrons with energy of 2 MeV from a Van de Graaff accelerator. The F-center luminescence was studied using crystals purchased from W. C. Spicers, Ltd., and contained both F and F^+ centers as a result of the reducing conditions in the arc furnace growth process. Zero-phonon lines were studied using electron-irradiated crystals and unirradiated crystals from Muscle Shoals Electrochemical Company, MS, as well as W. C. Spicers, S. Optical-absorption measurements on the broad F^+ band in the range 5–300 K were made using a Cary 14 spectrophotometer; the specimen temperatures were measured with a Chromel–Au-Fe thermocouple. For absorption measurements on the zero-phonon line and all luminescence studies a 1-m Czerny–Turner monochromator was used. The monochromator and the associated detection system were calibrated using a standard lamp supplied by the National Bureau of Standards. The instrument resolution was better than 3 cm^{-1} for the data. The emission was excited using the 3650-Å lines from a high-pressure Hg lamp and detection achieved using a cooled EMI 9558Q photomultiplier tube.

The measured absorption and emission curves were first corrected for background variation and then converted to a photon-energy scale. The moments of the band shapes were calculated on the computer using an energy interval of 5×10^{-3} eV in absorption and 2.5×10^{-3} eV in emission. The computer program is in terms of the shape function $f(E) = \alpha(E)/E^x$, where $\alpha(E)$ represents the absorption coefficient (cm^{-1}) or luminescence intensity (absolute units, $\mu W\,\mathrm{cm}^{-2}\,\mathrm{eV}^{-1}$), E the photon energy, and x is 1 for absorption and 3 for emission. The shape function $f(E)$ is then directly proportional to the transition probability.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Absorption and Emission Bands of F^+ Center at 5 K

The absorption band associated with the F^+ center is rather difficult to study in additively colored or neutron-irradiated crystals because of the overlapping absorption bands of other defects.[14,15] This is largely eradicated in the electron-irradi-

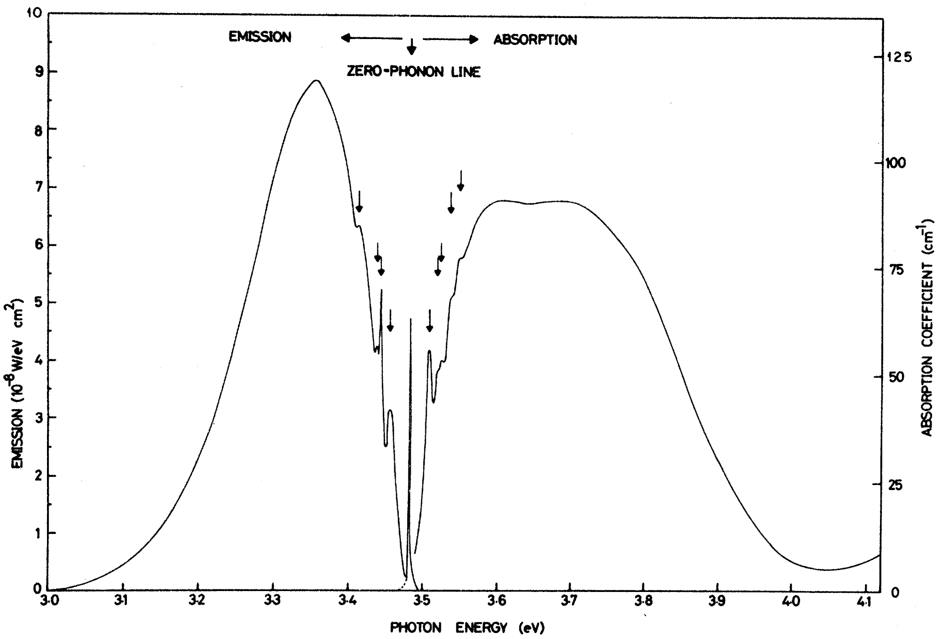

FIG. 1. Absorption and luminescence bands of the F^+ center in CaO at 5 K. The emission band was excited with the 3650-Å line from a high-pressure Hg lamp. Measurements were made using an electron-irradiated OR crystal in which the F^+ zero-phonon line was located at 28 098 cm^{-1}.

ated crystals, where the rising exciton edge on the low-wavelength side of the band is a relatively minor complication. In addition, the 3.10-eV band due to F centers is absent. Thus, the difficulties encountered by Escribe and Hughes[1] in making a sensible choice of background absorption are minimized. Figure 1 shows the absorption and emission bands of the F^+ center measured at 5 K. Well-resolved vibronic structure is evident in both cases. The positions of the vibrational sidebands and their frequency separation from the zero-phonon line are given in Table I. Note the absence on the emission band of the previously reported peaks at 99, 137, and 188 cm^{-1}.[6] This seems unlikely to be due to strain broadening or a resolution effect in the present experiments since the zero-phonon linewidth is only 12 cm^{-1} at 5 K. Thus, we conclude that such lines were peculiar to the additively colored crystals used in the earlier study and are associated with unknown defect species.

The first peak in the vibronic structure at 206 cm^{-1} has roughly the same form in both absorption and emission, whereas the ~300-cm^{-1} peaks are clearly different, that in emission being especially sharp. That this peak is so narrow suggests that a sharp local mode of the F^+ center is involved.[4,6] It seems reasonable to attribute the 206-cm^{-1} sidebands to A_{1g} modes since no interaction with the Jahn–Teller effect is involved. The ~300-cm^{-1} sideband apparently involves noncubic modes, either E_g or T_{2g}, since transitions may be broadened by the excited-state Jahn–Teller effect sampled only in absorption. This assignment has recently been made by Hughes *et al.*[11] and Duran *et al.*[16]

B. Moments of F^+-Center Band Shapes

In this section are presented our measurements of the moments of the optical band shape of the F^+ center in absorption and emission. Recently, the method of moments was applied to the F^+-center absorption band in CaO and used to calculate the Jahn–Teller coupling energies and strengths.[1,10] Such analyses were possible because the singlet ground-state wave function can be written as a simple product of an electronic wave function $|\epsilon\rangle$ and a lattice-vibrational function $|\lambda\rangle$. The orbital degeneracy of the excited states enters into the moments calculation as a sum over the states $|b\rangle$

TABLE I. Vibronic sidebands attending the F^+ absorption band and the F^+ and F emission bands in CaO. Note that line positions were measured using an untreated MS crystal in which the zero-phonon linewidths were 7 and 5 cm^{-1} for the F^+ center in absorption and emission, respectively, and 7.5 cm^{-1} for the F center $^3P \rightarrow {}^1S$ emission.

F^+ center				F center	
Absorption		Emission		Emission	
Peak position (cm^{-1})	Energy separation (cm^{-1})	Peak position (cm^{-1})	Energy separation (cm^{-1})	Peak position (cm^{-1})	Energy separation (cm^{-1})
28 117 ± 5		28 117 ± 5		17 407 ± 5	
28 324 ± 15	207	27 912 ± 10	206	17 209 ± 20	196
28 420 ± 15	303	27 813 ± 5	304		
28 449 ± 20	332	27 790 ± 20	327	17 087 ± 20	320
28 548 ± 50	431	27 624 ± 30	493		
28 637 ± 50	520			16 900 ± 50	507
		27 517 ± 50	600		

TABLE II. Moments of F^+ and F bands at 5 K.

	Centroid M_1 (cm^{-1})	M_2 ($\times 10^4$ cm^{-2})	M_3 ($\times 10^8$ cm^{-3})	$R = M_4/M_2^2$	
F^+ absorption	29 650 ± 40	68.6 ± 3	2.0 ± 0.3	2.48 ± 0.08	Ref. 1
F^+ absorption	29 630 ± 30	70.5 ± 2	2.0 ± 0.2	2.38 ± 0.06	Present work[a]
F^+ emission	26 790 ± 30	47.1 ± 2	3.3 ± 0.2	3.38 ± 0.06	Present work[a]
F emission	16 300 ± 30	20.4 ± 1	0.48 ± 0.05	3.10 ± 0.04	Present work[b]

[a] Results for OR crystal irradiated with 2-MeV electrons at 5 μA cm^{-2}.

[b] Results for untreated S crystal.

which can be converted to a sum over the electronic states $|\beta_i\rangle$ by use of spectroscopic stability. When the initial state is orbitally degenerate, as in luminescence studies, the wave functions are linear combinations of products $|\beta_i\rangle|\lambda\rangle$, where $|\beta_i\rangle$ are the several electronic states. These states now enter into the moments equations as a thermal average over states $|\beta_i\rangle|\lambda\rangle$, each state being weighted by a Boltzmann factor. Consequently, the principle of spectroscopic stability cannot be applied. In the absence of an external perturbation the important terms in the electronic Hamiltonian for an F-like center are due to the electron-lattice interaction and the spin-orbit interaction. The latter is entirely negligible in the present case. Furthermore, the zeroth (M_0) and first (M_1) moments as well as changes in the second moment (M_2) are independent of electron-lattice interaction in the limit of linear coupling. Evidently, it is reasonable to apply the moments methods to luminescence results within certain restrictions. The zeroth moment M_0 is simply the area under the band and measures directly the number of centers involved for both absorption and emission. M_1 represents the band centroid, while M_2 is a measure of the band half-width. For the F^+ center in absorption,[1]

$$M_2(T) = \sum_i a_i S_i \hbar^2 \omega_i^2 \coth(\hbar\omega_i/2kT) , \qquad (1)$$

where $\sum_i$ runs over the A_{1g}, E_g, and T_{2g} modes; $a_A = a_E = 1$ and $a_T = \frac{3}{2}$. In emission the coefficients a_i differ owing to the thermal average over the linear combinations of $|B_i\rangle|\lambda\rangle$ required for the initial state. Thus we can at best write $M_2(T) = S\hbar^2\omega^2 \coth(\hbar\omega/2kT)$, where S and ω represent average values over all coupled modes. When the coupling to A_{1g} modes is neglected, O'Brien[17] shows that the energy separation Δ between the emission peak and the zero-phonon line is $(S-1)\hbar\omega$. The inclusion of the A_{1g} coupling gives approximately

$$\Delta = (S_A + S - 1)\hbar\omega . \qquad (2)$$

The absorption and emission band shapes were measured over the temperature range 4–300 K. The broad emission band (Fig. 1) clearly lacks the flat-topped appearance so obvious in absorption. Nonetheless, there is a pronounced tail on the low-energy side of the band. M_0 is expected to be temperature insensitive provided that the quantum efficiency remains constant. In fact, as Fig. 2 indicates, M_0 increases slightly up to about 200 K, above which it decreases. As shown in Fig. 3, the absorption band broadens more rapidly with increasing temperature than does the emission band. In contrast, the shift in the band centroid is greater for the emission band than the absorption band. The ratio $R = M_4/M_2^2$ has a value of 3.38 ± 0.25 up to 190 K. At higher temperature, R decreases and at 300 K reaches a value of 2.75. As noted above, analytic expressions for the moments of the emission band shape have not been derived. Using Eq. (2) and $M_2(0)$ with the emission results in Table II we find $S_A + S = 5.5$ and $\hbar\omega = 293$ cm^{-1}. The calculated $M_2(T)$ using these values are in error by only

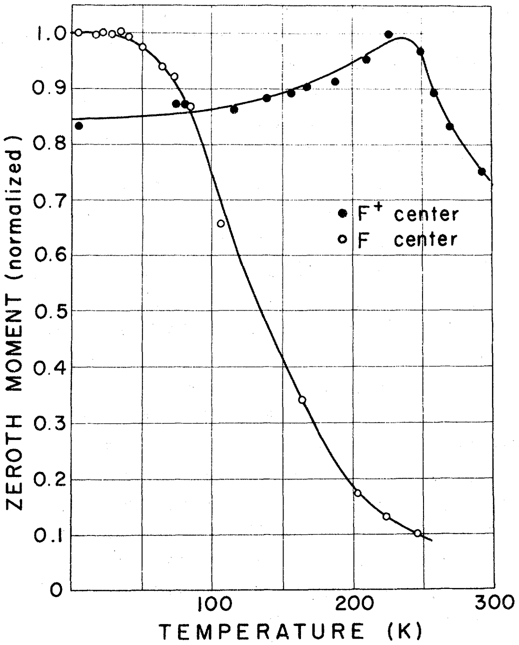

FIG. 2. Zeroth moment M_0 of the F^+ and F luminescence bands as a function of temperature. F^+-center data were recorded using electron-irradiated OR crystals and F-center data using additively colored S crystals.

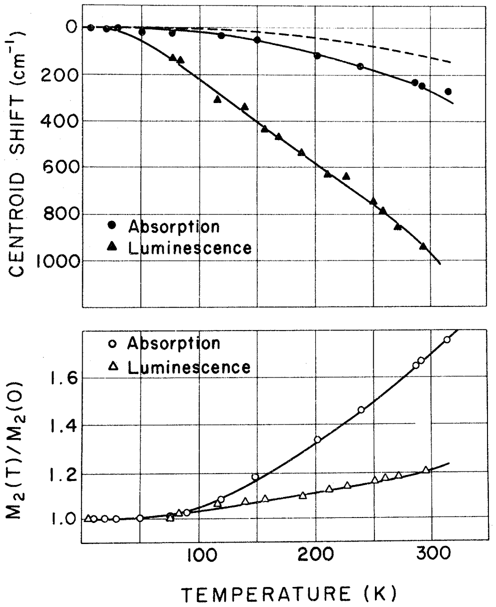

FIG. 3. Temperature dependence of the band centroid M_1 and second central moment M_2 for the F^+ absorption and luminescence bands. For M_1 the estimated contribution due to thermal expansion (Ref. 1) is indicated by the broken line. The full lines refer to the fit to Eqs. (3) and (4) using the values of ω discussed in the text. The full line for the M_2 data in absorption represents a two-frequency fit to Eq. (1). The full line drawn through the emission data is of no physical significance since no satisfactory fit to the data was obtained.

1–2% up to 78 K. At 300 K the error is as large as 12%, and no satisfactory fit to the $M_2(T)$ data in emission (Fig. 3), over the temperature range 5–300 K, was obtained.

In Fig. 3 are also compared the shifts in the centroids of absorption and luminescence bands. These temperature-dependent shifts are at least partially dependent upon the thermal expansion of calcium oxide. Approximate allowance can be made for this expansion since the hydrostatic-strain coupling coefficient for the F^+ band is known[12]; the correction is identical in absorption and emission, although it is probably only about 30% accurate since the thermal expansivity was determined from the Grüneisen relation.[1] The remaining shift is determined by changes in force constant between the oscillators in the ground and excited states.

The zeroth moment M_0 represents the number of centers involved in the transition. In Fig. 1 the heights of the zero-phonon lines in absorption and emission were normalized and thus act as a scale for the total transition probability. The areas under the two curves are approximately equal, representative of the fact that the fraction of the intensity appearing in the zero-phonon line $e^{-S_{\mathrm{eff}}}$ is roughly the same in absorption and emission. For emission a careful comparison of the integrated area under the zero-phonon line relative to the whole band yields a mean Huang–Rhys factor of $S = 5.3$. The shape of the curve for M_0 vs T in Fig. 2 seems unlikely to result from changes in the transition quantum efficiency. A more likely explanation is that the initial albeit slight increase in M_0 is due to the temperature dependence of the efficiency of $F \rightarrow F^+$ photoconversion by the 365-nm Hg line. The rapid decrease of M_0 with T above 230 K probably represents a real decrease in the quantum efficiency.

One further important consideration indicated by the moments analysis of the emission band is that M_3 and $R = M_4/(M_2)^2$ are temperature dependent at high temperature. M_3 and R, respectively, qualitatively describe the skewness of the band and the quantum-mechanical band shape.[5] These results indicate that the over-all band shape changes at high temperature rather than simply the half-width and band centroid. A tentative suggestion is that thermal occupation of higher-lying vibronic levels in the excited electronic state becomes important. Such an effect might conceivably result in a larger shift of the emission band peak with temperature than is apparent in absorption.

From the experimental absorption results the zeroth and first moments as well as the second, third, and fourth central moments were calculated on the computer. Escribe and Hughes[1] have discussed such measurements in detail and our purpose here is to compare our results with these earlier measurements. The moments at 5 K are presented in Table II. The errors are somewhat smaller than in earlier data[1] owing to the weaker background absorption in the electron-irradiated samples. The zeroth moment of the absorption band is found to be temperature independent within about ± 3%, and the third central moment to within ± 5%. The ratio $R = M_4/M_2^2$ is 2.38 ± 0.06 and is also temperature independent. Our measurements of the variation with temperature of the band centroid M_1 and the central moment M_2 are also in good agreement with the earlier results, which were interpreted in terms of a two-mode Jahn–Teller effect in which the coupling coefficients to E_g and T_{2g} modes are approximately equal.[4,5] According to this model, simplified to only a single effective frequency, we find from the temperature variation of M_2 a value of $\hbar\omega = 275$ cm^{-1} using Eq. (1). From the value of M_2 at 5 K and the separation of band centroid from the zero-phonon line we determine $S_{E,T} = 3.2 \pm 0.7$ and $S_A = 1.4 \pm 0.7$. Above 200 K a better fit to the experimental results is obtained using Eq. (1) with $\hbar\omega_A = 215$ cm^{-1} and $\hbar\omega_{E,T} = 297$ cm^{-1}. In all respects the present results are in excellent agreement with values de-

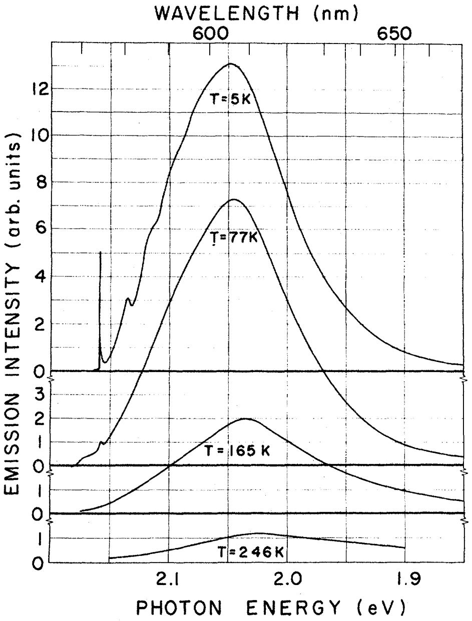

FIG. 4. Shape function of the F-center luminescence at several temperatures.

termined by Escribe and Hughes[1] for F^+ centers in neutron-irradiated crystals.

C. Dichroism of F^+-Center Luminescence under Stress

The F^+ luminescence band is unpolarized irrespective of whether excitation is accomplished using polarized or unpolarized light. However, when uniaxial stress P is applied parallel to the $\langle 100\rangle$ or $\langle 110\rangle$ crystal axes, the emission spectrum is strongly dichroic. The emission spectrum was measured from the illuminated surface to minimize effects due to self-absorption of the zero-phonon line. At zero stress the zero-phonon line is observed at 28 102.0 ± 10 cm^{-1} with a half-width of 10 cm^{-1}. The zero-phonon line splittings and dichroism under stress are as expected for a $T_{1u} \rightarrow A_{1g}$ transition at a site with cubic symmetry.[12] The temperature of measurements under stress was of order 7–10 K. With a stress P of 6.82 kg/mm^2 directed along a $\langle 100\rangle$ axis a single strong line was observed at 28 101.0 cm^{-1} for light with the electric vector ξ perpendicular to the applied stress (σ component). With the ξ vector parallel to the applied stress (π component), a single line of intensity approximately one-fifth of the σ component is observed at 28 111.2 cm^{-1}. In this orientation, there was no evidence of leakage of transitions that should be completely σ polarized into the π polarization. With a stress of 7.10 kg/mm^2 parallel to the $\langle 110\rangle$ axis three components were observed, a π polarization component at 28 111.3 cm^{-1} and σ-polarized transitions at 28 100.8 cm^{-1} ($\langle 110\rangle$ view and 28 104.0 cm^{-1} ($\langle 100\rangle$ view). The results are easily analyzed in terms of the stress coupling parameters of the T_{1u} state using Kaplianskii's tables.[18] From this we find $A = 0.35$, $B = 0.50$, and $C = 1.03$ in units of $\text{cm}^{-1}\,\text{kg}^{-1}\,\text{mm}^2$; these parameters agree well with the absorption-band data of Hughes and Runciman,[12] although they are probably less accurate since they were evaluated at a single stress value in each orientation.

Preliminary stress measurements were also made on the broad-band spectrum. For $\vec{P} \parallel \langle 111\rangle$ (8.20 $\text{kg}\,\text{mm}^{-2}$) the dichroism was found to be strongly wavelength dependent. This percentage dichroism, defined at $(I_\sigma - I_\pi)/I_0$, was 27% at 27 250 cm^{-1}, 19% at 27 000 cm^{-1}, 13% at 26 200 cm^{-1}, and 11% at 25 400 cm^{-1}. These results agree qualitatively with the more extensive results of stress experiments.[11]

D. F Center in Emission

The ${}^3P \rightarrow {}^1S$ emission band of the F center is shown in Fig. 4, which also shows the temperature dependence of the shape function. Weak structure on the high-energy side of the peak was reported earlier.[6] These peaks are observed displaced from the zero-phonon line by energy separations quite close to those observed for the F^+ center (Table I). However, the shape function of the F band suggests that no sharp local mode is involved in the vibronic structure. The first few moments of the broad band, including the zero-phonon line, were calculated on the computer. As in the case of the F^+ center the band shape appears to be temperature dependent. At temperatures below 180 K the ${}^3P \rightarrow {}^1S$ band is reasonably Gaussian since $R = 3.1 \pm 0.15$. Above 180 K, R decreases to a value of 2.53 at 300 K. The zeroth moment M_0 decreases rapidly above 40 K, as can be seen in Fig. 2. Figure 5 portrays the temperature dependence of M_1 and M_2. At 5 K we set the Stokes shift $\Delta = S\hbar\omega$ and $M_2(0) = S\hbar^2\omega^2$ and obtain $S = 6.2$ and $\hbar\omega = 156$ cm^{-1} from the results in Table II and Fig. 5. The half-width data alone yield $S = 5.2$ and $\hbar\omega = 168$ cm^{-1}. From the fraction of the intensity in the zero-phonon line, e^{-S}, we find $S = 5.7$. The solid line through the experimental results represents a least-squares fit to

$$M_2^2(T) = M_2^2(0)\,\coth(\hbar\omega/skT)\ , \tag{3}$$

with $S = 5.5$ and $\hbar\omega = 160$ cm^{-1}. The line is seen to give reasonable representation of the experimental values of $M_2(T)$ up to 300 K.

E. Line-Shape Measurements on F^+- and F-Center Zero-Phonon Lines

We have measured carefully the temperaure variation of the peak position, half-width, and integrated intensity of the F^+-center zero-phonon

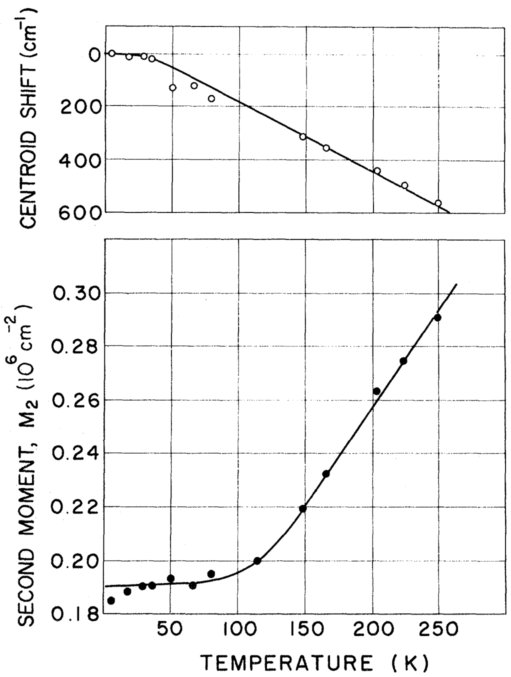

FIG. 5. Temperature dependence of band centroid M_1, and second central moment $M_2(0)$ of the F luminescence band in an S crystal. The full line through the experimental M_2 points represents a fit to Eq. (4) using $S = 5.5$ and $\hbar\omega = 160$ cm^{-1}.

line in emission. The results are shown in Fig. 6. For the zero-phonon lines considered here the peak shift with increasing temperature is approximately the same as the broad-band centroid. This is to be expected.[1]

The half-width and shape of the zero-phonon lines are of some interest, since they vary with source of materials, concentration of centers, irradiation, or heat treatment, etc. The narrowest lines investigated were observed in the MS crystals. In one crystal at 5 K the F^+-center zero-phonon lines had full widths at half-height of 7 cm^{-1} in absorption and 5 cm^{-1} in emission. The line shape in both cases is approximately Gaussian, as can be seen for the luminescence line in Fig. 7(a). In the same crystals the zero-phonon line of the F-center $^3P \rightarrow {}^1S$ transition is somewhat broader with the full width at half-height being typically of order 7.5 cm^{-1}. The half-widths of the zero-phonon line of the F^+ center at 5 K are about four orders of magnitude larger than would be expected for an allowed electric dipole transition. For the F center the half-width, owing to uncertainty principle broadening, is even smaller, since the $^3P \rightarrow {}^1S$ transition is forbidden. In both cases the excess half-width is due to inhomogeneous broadening due to random strains in the crystals. Actually, even in the MS crystals the linewidth varied by up to a factor of 2. At the larger linewidths the line shape was no longer Gaussian, being almost Lorentzian in some cases. Crystals with very small linewidths had the lowest dislocation densities. The MS specimen with the narrowest linewidth had a dislocation density of only 4×10^5 cm^{-2}. This crystal was also remarkably free from dislocations concentrated in the polygon cell walls which typifies the microstructure of oxide crystals grown by the arc-fusion method. In the following discussion the linewidths of the zero-phonon lines in this crystal are taken as the "perfect" crystal linewidths.

A statistical theory of line broadening has been developed by Stoneham.[19] He shows that in elastically isotropic crystals the line shape is approximately Gaussian when the dislocation distribution is statistically isotropic and homogeneous. The non-Gaussian shape of untreated crystals is attributable to the complexity of the real dislocation structure as compared with the simple model. The experimental linewidth and shape of the F^+ center in electron-irradiated crystals are shown in Fig. 7. Electron irradiation creates point interstitials as well as F^+ centers, and these contribute to the linewidth and line position. In cases where broadening is caused by point imperfections (including impurities) the line shape is a Lorentzian of full half-width $\rho I_0 |A|$, shifted by an amount

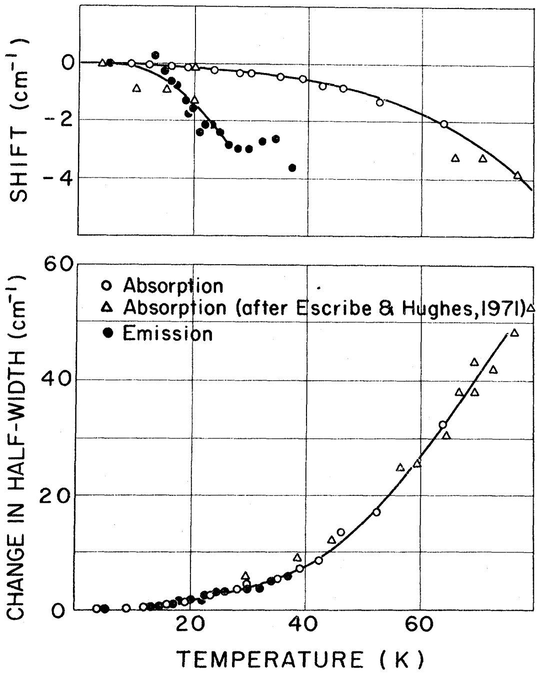

FIG. 6. Temperature dependence of shifts and half-widths of the F^+-center zero-phonon line in absorption and emission and the F-center zero-phonon line in emission.

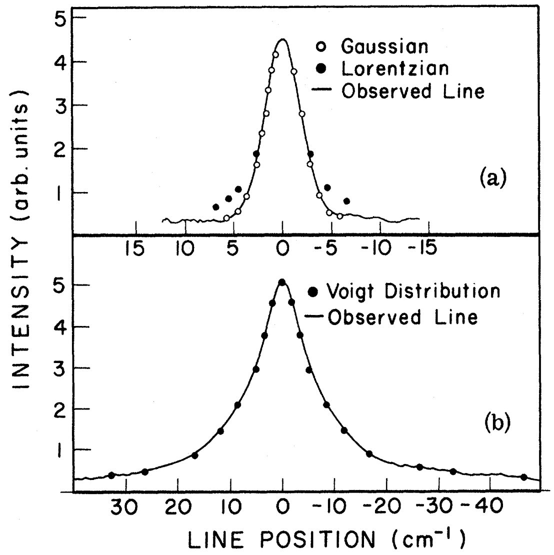

FIG. 7. (a) Pure crystal line shape of F^+-center luminescence measured using MS crystals and (b) Voigt profile of the observed line in an electron-irradiated MS crystal. These are representative results, similar line shapes being observed for OR and S crystals, for the absorption line and the F-center luminescence line.

$\rho I_1 A$ from the position in a perfect crystal. In these expressions, ρ represents the density of centers, A is the elastic strength, and I_0 and I_1 are integrals related to the probability distribution of strain set up by the imperfections. For several species of defects, uncorrelated in their distribution, the observed line shape is a convolution of the effects of each defect species present. In the electron-irradiated crystals the observed line shape is a convolution of the perfect-crystal line shape (Gaussian) and that due to point-defect broadening (Lorenzian). The result is a Voigt profile, from which the point-defect contribution to the half-width may be unfolded only when the perfect-crystal linewidth is known. The reconstruction of the line shape in Fig. 7(b) requires Lorentzian and Gaussian components in the ratio 1.5:1. The enhanced intensity in the wings of the line is very marked.

According to Stoneham[19] the peak position shift and the half-width vary linearly as the change in the lattice parameter, $\Delta a/a$ of the crystal. $\Delta a/a$ has not been measured in the present case. However, for low irradiation doses there should be a linear relationship between the concentration of defects produced, $\Delta a/a$, and the irradiation dose as observed by Henderson and Bowen[20] in neutron-irradiated MgO. On three crystals irradiated at 77 K for 5, 10, and 15 h at 5 $\mu A/cm^2$, we observe linewidths of 8, 10.5, and 12.5 cm^{-1}. The corresponding line shifts are −7, −12, and −19 cm^{-1}. The red shift is commensurate with an expansion of the lattice by the irradiation. Since electron irradiation produces interstitial ions as well as F^+ centers, such a result is not unexpected.

IV. CONCLUDING REMARKS

Detailed measurements of the broad absorption and emission bands of the F^+ band and the emission band as a function of temperature are reported and analyzed in terms of the moments of the band shape. The vibronic sidebands of the F^+ band in absorption and emission are closely similar apart from the very sharp 304-cm^{-1} line in the emission. This line is assigned to a resonance mode of the F^+ center, and has been shown to have mixed E_g and T_{2g} character.[11] In the $^3P \rightarrow {}^1S$ transition of the F center the sidebands are less prominent. However, structure can be discerned at 196, 320 and 507 cm^{-1}. The breadth of these lines seems to rule out resonance modes of the F center. However, the peaks at 196 and 320 cm^{-1} are close to peaks in the pure lattice density of states.[21] Recent magnetic-resonance results[22] suggest that E_g vibrational modes should be important. The peak near 197 cm^{-1} in the phonon density of states occurs at the $TA(X)$ and $TA(L)$ critical points,[21] which contains both E_g and T_{2g} modes. However, the peak in the density of states near 330 cm^{-1} contains neither E_g nor T_{2g} modes. In the absence of stress polarization data it is unreasonable to suggest a more detailed assignment of these rather broad vibronic sidebands. A multimode synthesis of the band shapes which generates these features with partial success is described by Evans and Kemp.[7]

The moments analysis of the F^+ band in absorption gives results for the coupling constants which are in good agreement with those of Escribe and Hughes.[1] The shape and first four moments of the emission bands of both F^+ and F band as a function of temperature are also reported. These results give less information than the absorption results since they can only be interpreted in terms of "effective" Huang–Rhys factors and coupling frequencies. Hence, they give no specific information concerning the nature of the Jahn–Teller interactions in the orbitally degenerate excited states of the F^+ and F center. However, the change in band shape with temperature for both centers, as evidenced by the values of $R = M_4/(M_2)^2$, suggests that the Jahn–Teller modes are important despite the emission sampling orbitally nondegenerate ground states of A_{1g} symmetry. Measurements of the temperature-dependent properties of the F- and F^+-center zero-phonon lines cannot be interpreted in terms of conventional theories. These results suggest that more sophisticated treatments of the electron-phonon interactions will be necessary to achieve a more reasonable agreement. The techniques developed by Mostoller and his associates[23,24] may go some way to resolving the discrepancies reported here, although it will require specific adaptation to include the Jahn–Teller interaction.

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