the interstitial and vacancy mechanisms. We have evidence from two sources that strongly suggests that the vacancy mechanism is the one that applies to NiO. First, in general it is found that whenever an interstitial mechanism is applicable, ΔK is close to unity.[14] Second, Volpe and Reddy[1] showed that interstitial diffusion could account for only a fraction of the total diffusion in NiO; in addition, that fraction would vary (at 1 atm in O_2) from about 5% at high temperatures to about 20% at low temperatures. Inasmuch as the relative diffusion coefficient observed in this research was found to be independent of temperature, we conclude that interstitial diffusion cannot be important for NiO under our experimental conditions. The lack of temperature dependence of the relative diffusion coefficient also argues against the simultaneous occurrence of any other mechanism such as the interstitialcy, along with the vacancy mechanism.

The fact that ΔK is nearly the same for cation diffusion in both CoO and NiO, although both the activation energies and pressure dependencies differ, is notable. Evidently, the most important factor influencing kinetic-energy transfer to the lattice is the nature of the anion nearest neighbors.

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[1] M. L. Volpe and J. Reddy, J. Chem. Phys. 53, 1117 (1970).

[2] W. K. Chen, N. L. Peterson, and W. T. Reeves, Phys. Rev. 186, 887 (1969).

[3] J. R. Manning, *Diffusion Kinetics for Atoms in Crystals* (Van Nostrand, Princeton, New Jersey, 1968), p. 127ff.

[4] A. B. Lidiard, Phil. Mag. 5, 1171 (1960).

[5] L. W. Barr and A. D. LeClaire, Proc. Brit. Ceram. Soc. 1, 109 (1964).

[6] M. A. Wahlgren, M. G. Strauss, and J. J. Hines, Trans. Am. Nucl. Soc. 12, 67 (1969).

[7] K. J. Arrusavice, J. J. Pinajion, H. Oikawa, and R. T. DeHoff, Trans. AIME 242, 2027 (1968).

[8] A. Paulsen and H. Liskien, Nukleonik 7, 117 (1965); Nucl. Sci. Abstr. 19, 4405 (1965); A. Wjelberg and A. C. Pappas, Nucl. Phys. 1, 322 (1956).

[9] J. Crank, *Mathematics of Diffusion* (Oxford U. P., New York, 1956), p. 11.

[10] C. M. Lederer, J. M. Hollander, and I. Perlman, *Table of Isotopes* (Wiley, New York, 1967), 6th ed., pp. 191 and 201.

[11] N. L. Peterson, Solid State Phys. 22, 409 (1968).

[12] R. T. Overman and H. M. Clark, *Radioisotope Techniques* (McGraw-Hill, New York, 1960).

[13] M. O'Keeffe and W. J. Moore, J. Phys. Chem. 65, 1438 (1961).

[14] See Ref. 5 and references cited therein.

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Magneto-Optic Study of the Jahn-Teller Effect in the Excited Level of the F^+ Centers in CaO

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The magnetic circular dichroism was measured in both the zero-phonon line and the broad band of the F^+ centers in CaO. The spin-orbit coupling constant in the relaxed excited state was found to be $-0.58\ \mathrm{cm}^{-1}$. Comparison with the same constant measured in the broad band gives for the Ham reduction factor a value $K(T_1) = 0.02$. Analysis by the method of moments of the circular dichroism in the broad band allowed the determination of the coupling coefficients of the centers to cubic and noncubic modes of vibration. The values found for these coefficients explain quite well the observed shape of the band.

I. INTRODUCTION

It has been pointed out in a review article by Ham[1] that in the presence of Jahn-Teller coupling the ground vibronic level keeps the same degeneracy and symmetry as the orbital electronic level it originates from. The matrix elements of electronic operators taken inside the ground vibronic level are, however, reduced by a factor which depends only on the symmetry of the operator considered. We shall describe a method which allows a very direct measurement of these reduction factors. This method applies when the same electronic transition gives rise to both a zero-phonon line and a broad band. This is the case for many paramagnetic impurities[2] and color centers[3] in ionic crystals. If it is the ground level which is orbitally degenerate, it has already been shown[4-7] that measurement of circular (or linear) dichroism in a magnetic (or stress) field gives very direct information about the Ham reduction factors and the coupling coefficients of the centers to vibrational modes of various symmetries. Here we shall consider the case of the F^+ centers (one electron on an anion vacancy) in CaO, for which the excited level has an orbital degeneracy ($^2T_{1u}$) and the ground level is a Kramers doublet ($^2A_{1g}$). As first seen by Kemp *et al.*,[8] both a narrow zero-phonon line and a broad band can be associated with the transitions between these two levels. The zero-phonon line is due to transitions to the "relaxed" excited state, i.e., to the ground vibronic level, so that if one studies the effect of external perturbations such as magnetic field or stress, one measures coupling coefficients which are reduced by the Jahn-Teller effect. If, on the contrary, one measures the effect of these same perturbations on the absorption band, analyzing it by the method of moments, it has been shown by Henry, Schnatterly, and Slichter[9] that one measures the true (unreduced) coupling coefficients. The comparison of the two sets of results gives directly the reduction factors defined by Ham.[10,11]

The Faraday effect in the broad band of the F^+ centers in CaO gives[12] for the spin-orbit-coupling constant λ of the excited level a value of the order of -24 cm^{-1}. The fact that no structure is observed in the associated zero-phonon line, whose width is about 4 cm^{-1}, shows that the reduction factor $K(T_1)$ for the angular momentum is less than 0.05. Kemp *et al.*[8] measured the Faraday rotation of this line, but because of a lack of instrumental resolution they could not observe the spin-orbit structure. In the present paper we shall describe a high-resolution study of the circular dichroism which allowed us to measure this structure, and so to determine the reduction factor $K(T_1)$. The reduction factors $K(T_{2g})$ and $K(E_g)$ for operators transforming like T_{2g} and E_g might be determined from a comparison of the effect of stress in the broad band and in the zero-phonon line. The effect of stress is known only for the zero-phonon line.[13] The coupling coefficients to strains of E_g and T_{2g} symmetries are found to be of same order of magnitude[13] and are not much reduced with respect to the corresponding coefficients measured in the band of the F centers in alkali halides.[14] This together with the fact that $K(T_1)$ is very small can only be explained if the coupling coefficients of the excited states to E_g and T_{2g} vibrational modes are approximatively the same.[15,16]

Obviously the shape of the absorption band also depends on the strength of the coupling of the center to vibrational modes of various symmetries. Hughes[16] has recently shown that the peculiar shape of the absorption band of the F^+ centers in CaO could be understood if not only the coupling coefficients to T_{2g} and E_g modes are approximatively the same, but also if they are relatively larger than the coupling coefficient to A_{1g} modes. We carefully measured the circular dichroism in the broad band. Analysis of these results by the method of moments shows that this is indeed the case: The contribution of the noncubic modes (E_g and T_{2g}) of vibrations to the broadening of the band is about three times larger than the contribution of the cubic modes (A_{1g}).

After having briefly described the experimental conditions we shall show how optical detection of the paramagnetic resonance in the ground electronic level allows the identification of the zero-phonon line. Then we shall analyze the results of the circular-dichroism measurements in both the broad band and the zero-phonon line. We shall show how one can determine the reduction factor for the orbital angular momentum and the average coupling coefficients to vibrational modes of cubic and noncubic symmetries. An analysis of the shape of the broad band in terms of the moments is in very good agreement with the values determined for these coupling coefficients.

II. EXPERIMENTAL

If k_+ and k_- are, respectively, the absorption coefficients for left and right circularly polarized light (σ_+ and σ_-), the circular dichroism is defined by the relation $\Delta k = 0.5(k_+ - k_-)$. As analyzed by Margerie,[17] the magnetically induced circular dichroism of the F centers is due to two types of effects: One, the so-called diamagnetic effect, is temperature independent and is due to shifts of levels or variations in the transition probabilities when the magnetic field is applied; the other is due to variations in the populations of the two sublevels of the ground-state Kramers doublet. Experimentally there are two ways to distinguish between these effects: One can vary the temperature or one can saturate the paramagnetic resonance transitions in the ground state so that the population effect vanishes. Inversely, the temperature-dependent effect being proportional to the difference in the populations, it can be used to monitor these populations. Thus one can detect optically the paramagnetic resonance or the relaxation in the ground-state level.[18] In our experimental arrangement, provision was made for microwave irradiation at either 10 or 24 GHz.

The CaO crystals were grown by Spicer, Ltd. They were colored by irradiation in the swimming-pool reactor Melusine of the Nuclear Center in Grenoble. The integrated flux of neutrons ranged from 10^{16} to 10^{17}. Very few F centers (two electrons on an anion vacancy) were formed. In order to avoid problems with fluorescence, the optical densities of the samples were kept smaller than one in the broad band. The arrangement for the measurements of circular dichroism has been described elsewhere.[19] For the narrow-line measurements, a Spex II monochromator was used with a grating blazed at 7000 Å with 1200 lines/mm giving in second order a resolution of approximately 0.05 Å for a slit width of 15 μ. The magnetic field was given by a Varian 12-in. electromagnet with cylindrical poles and an air gap of 3 in.

III. OPTICAL DETECTION OF RESONANCE IN GROUND STATE

The identification of the line at 3557 Å with the zero-phonon line of the F^+ centers was done by Kemp *et al.*[8] by means of Faraday-effect experiments. The Faraday effect is related to the circular dichroism through Kramers-Krönig relations, so that it can also be used to monitor the populations in the ground state. Setting the microwave attenuation at a level such that the resonance of the F^+ centers is partially saturated, Kemp *et al.*[8] measured the variation of the Faraday effect when the field was swept through the resonance. The characteristics of the EPR line (g value and width), so detected at an optical wavelength corresponding either to the zero-phonon line or to the broad band, were found to be the same, and hence they concluded that both were due to the same center. However, the optically detected line was much broader (10 G) than the line detected by the ordinary technique of EPR (from 20 to 100 mG at these concentrations[20,21]). Thus, one cannot be absolutely sure that one is not saturating a different center coupled by cross relaxation to the F^+ centers. The variation of the relaxation times with the magnetic field does imply a cross-relaxation mechanism.[8] In view of the fact that the identification of the zero-phonon line was questioned for a time,[13] it seemed interesting to repeat the same type of double-resonance experiment but in better conditions: very homogeneous magnetic field, optical resolution good enough to resolve the dichroism in the zero-phonon line, good control of the very low microwave level necessary to saturate the transition (T_1 ranges from 10 to 50 sec). With microwave frequencies around 26 GHz we observed resonance linewidths of about 10 G and a line shape very similar to the one observed at 34 GHz by Kemp *et al.*[8] At 9.5 GHz, on the other hand, the limiting linewidth at low power was 0.65 G. As shown in Fig. 1, the position of the line, its width, and the saturation properties were exactly the same whether detected in the band or in the narrow line. This linewidth is still much larger than the one expected for F^+ centers at these concentrations. (Using the ordinary technique of EPR a linewidth of 70 mG was measured for this sample at room temperature.) The fact that it varies so much with the microwave frequency seems to imply that the broadening is experimental in its origin. As new evidence for the identification of the zero-phonon line came recently from experiment (observation of the same line in emission[22,23]) and from theory,[15,16] it was not felt necessary to push these double-resonance experiments further and to elucidate the origin of these abnormally wide lines.

IV. CIRCULAR DICHROISM IN BROAD BAND

A. Method of Moments

In the broad band, the circular dichroism is quite weak due to the smallness of the spin-orbit structure with respect to the bandwidth. In order to eliminate background effects which can be important[12] in this spectral region, the double-resonance technique was used. The signal was obtained as the difference of the dichroisms measured with microwave power off and on. In that way only the population effect is measured. The dichroism measured at a field of 3360 G and at a temperature of 1.55 °K is shown in Fig. 2. The shape of the signal is very different from the shape of the derivative of the absorption curve. This indicates that the rigid shift approxi-

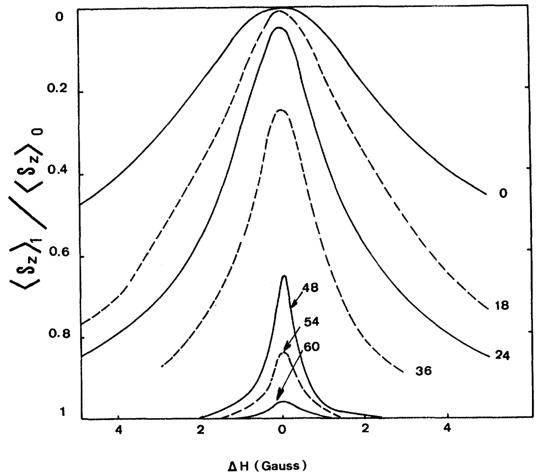
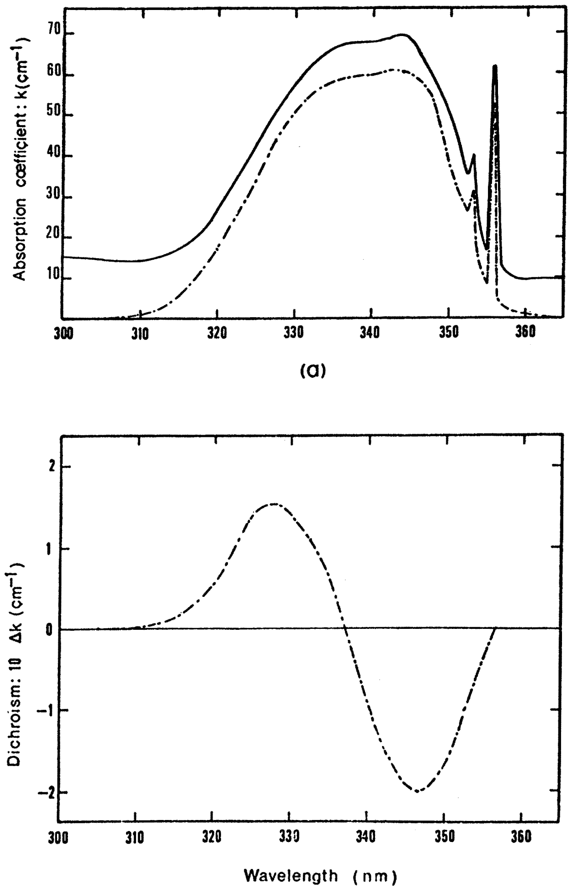


FIG. 1. Relative variation of spin polarization in the ground state on sweeping the field through resonance. The numbers 0, 18, ..., 60 refer to the attenuation of the microwaves (in dB). Solid line is optical detection in the broad band (346 nm), dashed line is optical detection on the low-energy side of the zero-phonon line.



(a)

(b)

FIG. 2. F^+ band in CaO at $T = 1.55$ °K. (a) Absorption coefficient with a resolution of 0.5 Å, solid line is uncorrected, dashed line is after substraction of the background. (b) Dichroism signal in a magnetic field $H = 3360$ G, resolution 10 Å.

mation is not valid. Henry *et al.* showed[9] that in such a case the experimental results can be analyzed in terms of the moments of the shape function

$$f(\nu) = \nu^{-1} k(\nu)$$

of the absorption coefficient $k(\nu)$ and their variations when a magnetic field (or any external perturbation) is applied. They showed that if mixing to other electronic excited states of the center is ignored, the variations in the moments of the shape function of the absorption curve of circularly polarized σ_+ light, when the magnetic field is applied, are as follows:

(i) The variation of area is zero,

$$\Delta A_b / A_b = 0 . \tag{1}$$

(ii) The variation $\langle \Delta E_b \rangle$ of the first moment E_b is

$$\langle \Delta E_b \rangle = g_0 \mu_B H + \lambda \langle S_z \rangle , \tag{2}$$

where μ_B is the Bohr magneton, g_0 is the Landé factor of the excited level

$$g_0 = | \langle x | L_z | y \rangle | , \tag{3}$$

λ is an effective spin-orbit coupling constant in which the matrix element (3) has been included, and

$$\langle S_z \rangle = -\tfrac{1}{2} \tanh(\mu_B H / kT)$$

is the spin polarization created by the magnetic field in the ground state.

(iii) The variation of the third moment $\langle \Delta E_b^3 \rangle$ is

$$\langle \Delta E_b^3 \rangle = 3 \langle \Delta E_b \rangle \left(\langle E^2 \rangle_{\mathrm{C}} + \tfrac{1}{2} \langle E^2 \rangle_{\mathrm{NC}} + \tfrac{1}{4} \lambda^2 \right) , \tag{4}$$

where $\langle E^2 \rangle_{\mathrm{C}}$ and $\langle E^2 \rangle_{\mathrm{NC}}$ are the contributions to the second moment from cubic (A_{1g}) and noncubic $(E_g$ and $T_{2g})$ modes of vibrations, so that the second moment is given by

$$\langle E_b^2 \rangle = \langle E^2 \rangle_{\mathrm{C}} + \langle E^2 \rangle_{\mathrm{NC}} + \tfrac{1}{2} \lambda^2 . \tag{5}$$

The second moment depends both on the average energy of the vibrational modes which are coupled to the center, and on the magnitude of this coupling. In the approximation of linear coupling this magnitude is often measured in terms of the Huang-Rhys parameter[24] which is the average number of quanta emitted when a photon is absorbed. If $\omega_{\mathrm{C}}, \omega_E, \omega_T$ and S_{C}, S_E, S_T are the average frequencies and Huang-Rhys factors for the A_{1g}, E_g, T_{2g} modes of vibration, respectively, one has

$$\langle E^2 \rangle_{\mathrm{C}} = S_{\mathrm{C}} (\hbar \omega_{\mathrm{C}})^2 , \tag{6}$$

$$\langle E^2 \rangle_{\mathrm{NC}} = S_E (\hbar \omega_E)^2 + 1.5 S_T (\hbar \omega_T)^2 . \tag{7}$$

B. Experimental Results

We have evaluated the moments of the shape function of the absorption coefficient and of the dichroism signal shown on Fig. 2. Within the experimental uncertainties, Eq. (1) was verified. Evaluation of the first moment variation $\langle \Delta E_b \rangle$ gives $\lambda = -31 \pm 6$ cm^{-1} in relatively good agreement with previous Faraday-effect results[8,12] and with the calculated value of Bessent *et al.*[12] (see Table I). In our measurements, the main source of error probably comes from the determination of the absorption shape function. There are at least two bands (the F band and a band centered at 250 nm) which may overlap the F^+ band. The contributions of these various spectra to the absorption in the F^+ region vary from sample to sample. The choice we made for the background absorption is illustrated in Fig. 2. For the measurement of the dichroism we do not have this problem of the choice of the base line, since with our double-resonance technique we measure only the dichroism due to the F^+ centers. The values of the second moment $\langle E_b^2 \rangle$ of the absorption shape function and of the ratio $\langle \Delta E_b^3 \rangle / 3 \langle \Delta E_b \rangle$ are given in Table I. Application

TABLE I. Spin-orbit coupling constants in the excited level of the F^+ centers in CaO. FR: Faraday rotation; FRS and CDS: Faraday rotation and circular dichroism with elimination of the background effect by double-resonance technique; C: calculated.

Method	$\lambda(\mathrm{cm}^{-1})$	$\lambda'(\mathrm{cm}^{-1})$	Reference
FRS	-55		8
FR	-24		12
CDS	-31	-0.58	This work
C	-20		12

of formulas (4) and (5) gives $\langle E^2\rangle_C = 16\times10^4\ \mathrm{cm}^{-2}$ and $\langle E^2\rangle_{NC} = 62\times10^4\ \mathrm{cm}^{-2}$. One sees that the contribution of the noncubic modes of vibration to the second moment is about 80% compared to about 50% for the F centers in the alkali halides.[14]

Hughes has recently shown[16] that the stress effects on the zero-phonon line can only be understood if the Jahn-Teller stabilization energies for E_g and T_{2g} modes are approximatively the same. We shall assume that they are equal and moreover that

$$\omega_E = \omega_T = \omega_{NC} . \tag{8}$$

Then from the definition of these stabilization energies one has[1]

$$S_T = S_E = S_{NC} , \tag{9}$$

and Eq. (7) becomes[16]

$$\langle E^2\rangle_{NC} = 2.5 S_{NC}(\hbar\omega_{NC})^2 . \tag{10}$$

If we take for $\hbar\omega_C$ and $\hbar\omega_{NC}$ the average energy $280\ \mathrm{cm}^{-1}$ determined by Bessent[25] from the thermal broadening of the band, we get from the experimental values of $\langle E^2\rangle_C$ and $\langle E^2\rangle_{NC}$, $S_C = 2.05$ and $S_{NC} = 3.15$. We shall see in Sec. VI that these values explain very well the shape of the absorption band.

V. ZERO-PHONON LINE

A. First-Order Effect

The absorption coefficient and the circular dichroism measured in a field of 9090 G and at a temperature of 1.57 °K are shown in Fig. 3. A small structure is observed in absorption. It is sample dependent and is probably due to the combined effect of spin-orbit coupling and internal strains. As already noted, the dichroism signal is the sum of a population and a diamagnetic effect. The latter was directly measured when the population effect was suppressed by saturation of the paramagnetic resonance in the ground state. It has a rather complicated spectral dependence, which probably results from a second-order effect of the Zeeman and spin-orbit interactions; it should also depend on the internal strains. Once it is subtracted from the observed signal the population effect, shown by a dashed line in Fig. 3, is obtained. As was the case for the broad band, this signal may be interpreted in terms of changes of the moments of the shape function. Because the excited level which gives rise to the zero-phonon line is a vibronic T_{1u} triplet, the calculation of the moments is very similar in the two cases. Since the width of the zero-phonon line is mainly due to static strains, one has only to replace thermal averages of the dynamical distortions of the lattice by an average of the static deformations (which are supposed to be randomly distributed in the crystal). One gets for the change in the first moment of the zero-phonon line $\langle \Delta E_0\rangle$ an expression similar to (2) where the Landé factor g_0 and the spin-orbit constant λ are replaced by their reduced value

$$g_0' = K(T_1)g_0, \quad \lambda' = K(T_1)\lambda , \tag{11}$$

where $K(T_1)$ is the reduction factor for the orbital angular momentum defined by Ham.[10]

B. Second-Order Effect

The excited vibronic states are mixed by the spin-orbit and Zeeman interactions into the ground vibronic states. As a result there is a change in

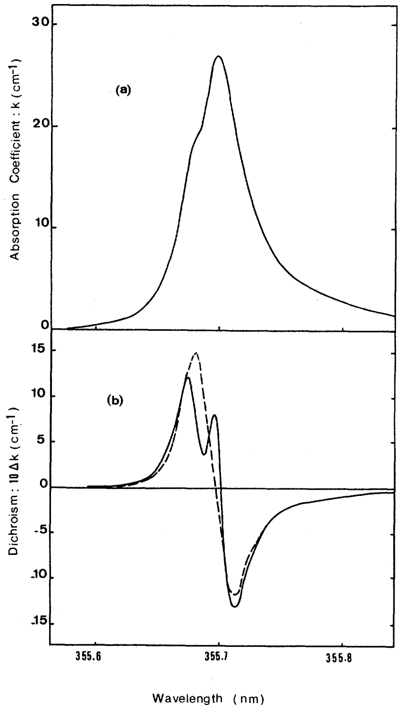


FIG. 3. Absorption coefficient (a), and dichroism signal (b), in the region of the zero-phonon line. $H = 9090$ G, $T = 1.57$ °K, resolution 0.05 Å. Solid line is sum of the diamagnetic and population effects, dashed line is population effect. The results illustrated in Figs. 2 and 3 were obtained with two different crystals. The concentration in F^+ centers were in the ratio 3.1 to 1.

the intensity of the zero-phonon line (for circularly polarized light) when the magnetic field is applied. The dichroism signal associated with this effect has approximately the shape of the absorption curve.[19] The corresponding Faraday effect was observed by Kemp *et al.*[8] These second-order effects are easily calculated if one assumes that the center is only coupled to one pair of E_g modes (and eventually to A_{1g} modes, but not to T_{2g} modes). Then we can show that Eq. (1) must be replaced by

$$\Delta A_0/A_0=(\hbar\omega_E)^{-1}\,2(g_0\,\mu_B H+\lambda\,\langle S_z\rangle)G(u)\,e^{-u}\,, \qquad u=3E_{JT}/2\hbar\omega_E\,, \tag{12}$$

where E_{JT} is the stabilization Jahn-Teller energy for the coupling to E_g modes, $G(u)$ is the function defined by Ham,[10] which is approximately $u^{-1}e^{u}$ when u is large.

Using the adiabatic approximation, Kemp *et al.*[8] obtained a slightly different expression for $\Delta A_0/A_0$. For coupling to E_g modes only, the reduction factor $K(T_1)$ is given by[10]

$$K(T_1)=e^{-u}\ . \tag{13}$$

The spin-orbit splitting could also be evaluated in second order. It can be shown that for a spin $S=\frac{1}{2}$ the effective Hamiltonian operating inside the ground vibronic triplet keeps the same form ($\lambda'\,\vec{L}\,\vec{S}$) but a small correction must be added to expression (11) giving λ'. For $\lambda\ll\hbar\omega_E$ this correction may be neglected.

C. Experimental Results

From the measured value of the change in the first moment $\langle\Delta E_0\rangle$ as defined by Eqs. (2) and (11) we get $\lambda'=-0.58\pm0.06\ \text{cm}^{-1}$. Comparing this value with the unquenched parameter $\lambda=-31\ \text{cm}^{-1}$ measured in the broad band, we get $K(T_1)=0.02$, and using Eq. (13) we obtain

$$S_E=E_{JT}/\hbar\omega_E=\tfrac{2}{3}u=2.7\ \ .$$

This value of S_E, determined for a model in which coupling to the T_{2g} mode is neglected, is found to be rather close to the value determined in Sec. IV B, $S_E=S_{NC}=3.2$. This shows that, as predicted by Ham,[1] if coupling to E_g modes is strong, an additional coupling to T_{2g} modes does not reduce much further the matrix elements of the angular momentum $K(T_1)$ in the ground vibronic triplet. In the same way, second-order effects are not much affected by introduction of the coupling to the T_{2g} modes. This is shown by the fact that our measured values of $\Delta A_0/A_0$ are in good agreement with the expression given by Eq. (12) when one takes $u=4$, $\lambda=-31\ \text{cm}^{-1}$ (as determined in Sec. IV B), and $\hbar\omega_E=280\ \text{cm}^{-1}$.

In concluding this section, we wish to stress the fact that the reduction factor $K(T_1)$ we determined would keep its meaning even in a much more elaborate model in which, for instance, couplings to modes of various energies and symmetries were taken into account.[10,26]

VI. BROAD-BAND SHAPE

In Sec. IV B we determined various parameters defining the coupling of the center to the vibrational modes of the lattice. We shall now see that the values of these parameters explain very well the observed shape of the broad band. In the absence of a more detailed theory this shape will be interpreted in term of its moments. The striking fact about the optical spectra of the F^+ centers in CaO is the existence of the zero-phonon line. F-center (one-electron center) spectra are known in most of the alkali halides and alkaline-earth oxides and fluorides, but this is the only case where one observes a zero-phonon line. The ratio A_b/A_0 of the intensities of the band and of the zero-phonon line corresponds to a Huang-Rhys factor S of the order of 5.[8] A value of the same order is determined[8] from the difference in energy E_b-E_0 between the centers of gravity of the band and of the zero-phonon line (half the Stoke shift in the approximation of linear coupling) when the energy of the vibrational modes is taken to be 280 cm^{-1}.[25] On the other hand, the Huang-Rhys factor determined from the second moment of the band would be approximatively twice as large. Using a theoretical model developed by O'Brien,[15] Hughes[16] has shown that this may be explained if one assumes that the coupling to noncubic modes of vibration is large and that the coupling coefficients to T_{2g} and E_g modes are approximatively equal. Then one can show[16] that, if as expected both T_{2g} and E_g modes contribute to the second moment, the intensity of the zero-phonon line and the separation E_b-E_0 are approximatively the same as if only E_g (or T_{2g} modes) were coupled to the center. So, if Eqs. (8) and (9) are satisfied, one has

$$A_0/A_b\simeq e^{-S_C-S_{NC}}\,, \qquad E_b-E_0\simeq S_C\hbar\omega_C+S_{NC}\hbar\omega_{NC}\,, \tag{14}$$

and the second moment is as given by Eqs. (5), (6), and (10).

The moments of the shape function of the absorption band which we measured at 1.6 °K are given in Table II. They are in good agreement with the values given by Eq. (14) when one takes for S_C and S_{NC} the values determined in Sec. IV and sets $\hbar\omega_C=\hbar\omega_{NC}=280\ \text{cm}^{-1}$ as determined by Bessent[25] (see Table II). This value for the average frequency of the vibrational modes is probably not very precise. As shown in Table II, we obtain a better fit to the experimental results if we take $\hbar\omega_C=\hbar\omega_{NC}=265\ \text{cm}^{-1}$. This good fit may be considered as

TABLE II. Moment analysis of the absorption and dichroism shape functions. (a) Experimental results. (b) Calculated for $\hbar\omega = 280$ cm^{-1} and fitting $\langle E^2\rangle_C$ and $\langle E^2\rangle_{NC}$ to the experimental values. (c) Best fit of all the moments. Hence one obtains $\hbar\omega = 265$ cm^{-1}.

	(a)	(b)	(c)
$\langle \Delta E_b^3\rangle/3\langle\Delta E_b\rangle$ (10^4 cm^{-1})	47		49
$\ln(A_b/A_o)$	5.6	5.2	6.0
$E_b - E_o$ (cm^{-1})	1620	1460	1590
$\langle E_b^2\rangle$ (10^4 cm^{-1})	78		79
$\langle E^2\rangle_{NC}$ (10^4 cm^{-2})	62		61
$\langle E^2\rangle_C$ (10^4 cm^{-2})	16		18

accidental since the model is oversimplified and the experimental evaluation of the moments is not very precise. Underlying bands of impurities or other defects may introduce distortions of the observed band shape. Moments are very sensitive to the absorption in the wings of the band so that a very precise knowledge of the spectra is needed for this evaluation. However, these experiments give a good quantitative check of Hughes's model and show that his assumption of strong coupling to E_g and T_{2g} modes is justified. They also give a good confirmation of the value determined by Bessent[25] for the average frequency of the modes coupled to the lattice.

VII. CONCLUSION

The spin-orbit structure in the "relaxed" excited state of the F^+ centers in CaO was measured. It was found to be strongly reduced by the Jahn-Teller effect $[K(T_1) = 0.02]$. The contribution of the noncubic modes of vibration to the second moment of the band was found to be more than three times larger than the contribution of the cubic modes. This explains the fact that a zero-phonon line is observed in the absorption spectra. A quantitative analysis of the shape of the broad band and of the intensity of the zero-phonon line was given in terms of the moments of the shape function. Due to the existence of the zero-phonon line in the absorption and emission spectra, these centers appear to be very promising for the optical study of the Jahn-Teller effect. For example, measurements of linear dichroism under stress in the broad band would allow one to determine separately the average energies and coupling coefficients of the E_g and T_{2g} modes. Then it would be possible to calculate the Ham reduction factors $K(T_1)$, $K(E_g)$, and $K(T_{2g})$ and compare them with the experimental values. Similar measurements in emission would give information about the second-order terms of the electron lattice coupling.

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[1] F. S. Ham, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, 1970).

[2] M. D. Sturge, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1967), Vol. 20, pp. 92–211.

[3] D. B. Fitchen, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), pp. 294–350.

[4] R. H. Silsbee, Phys. Rev. 138, A180 (1965).

[5] Y. Merle d'Aubignè and P. Duval, J. Phys. (Paris) 28, Suppl. C 4, 112 (1967).

[6] I. W. Shepherd, Phys. Rev. 165, 985 (1968).

[7] W. Burke, Phys. Rev. 172, 886 (1968).

[8] J. C. Kemp, W. M. Ziniker, J. A. Glaze, and J. C. Cheng, Phys. Rev. 171, 1024 (1968).

[9] C. H. Henry, S. E. Schnatterly, and C. P. Slichter, Phys. Rev. 137, A583 (1965).

[10] F. S. Ham, Phys. Rev. 138, A1727 (1965).

[11] F. S. Ham, Phys. Rev. 166, 307 (1968).

[12] R. G. Bessent, B. C. Cavenett, and I. C. Hunter, J. Phys. Chem. Solids 29, 1523 (1968).

[13] A. E. Hughes and W. A. Runciman, J. Phys. C 2, 37 (1969).

[14] S. E. Schnatterly, Phys. Rev. 140, A1364 (1965).

[15] M. C. M. O'Brien, Phys. Rev. 187, 407 (1969).

[16] A. E. Hughes, J. Phys. C 3, 627 (1970).

[17] J. Margerie, J. Phys. (Paris) 28, Suppl. C 4, 103 (1967).

[18] N. V. Karlov, J. Margerie, and Y. Merle d'Aubignè, J. Phys. Radium 24, 717 (1963).

[19] Y. Merle d'Aubignè and P. Duval, J. Phys. (Paris) 29, 896 (1968).

[20] B. Henderson and A. Tomlinson, J. Phys. Chem. Solids 30, 1801 (1969).

[21] J. C. Dumais and Y. Merle d'Aubignè, in Proceedings of the Sixteenth Ampere Colloquium, Bucharest, 1970 (unpublished).

[22] B. D. Evans, J. C. Cheng, and J. C. Kemp, Phys. Letters 27A, 506 (1968).

[23] B. Henderson, S. E. Stokowski, and T. C. Ensign, Phys. Rev. 183, 826 (1969).

[24] K. Huang and A. Rhys, Proc. Roy. Soc. (London) A204, 406 (1950).

[25] R. G. Bessent (private communication to B. Henderson); see Ref. 23.

[26] K. W. H. Stevens, J. Phys. C 2, 1934 (1969).