PHYSICAL REVIEW B VOLUME 14, NUMBER 4 15 AUGUST 1976

Magneto-optical properties of F^+ centers in alkaline-earth oxides*

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(Received 8 March 1976)

The magneto-optical properties of F^+ centers in neutron-irradiated alkaline-earth oxide crystals were reexamined and further investigated. Magnetic circular dichroism, Faraday rotation, and optical absorption spectra were measured and analyzed, and the results are compared with those of previous studies. Values of -18 ± 3, -43 ± 4, -150 ± 30, and -380 ± 190 cm^{-1} were, respectively, found for the spin-orbit splittings in the F^+ bands of MgO, CaO, SrO, and BaO. Orbital magnetic moments very close to zero were found for the CaO and SrO excited states. Higher moments of the spectra were found unreliable but imply large contributions to the bandwidths by noncubic lattice modes. Optically detected paramagnetic resonance confirms assignment of the BaO 2.0-eV band to the F^+ center and assigns the 2.6-eV band to an axial defect. A calculated spin-orbit splitting for CaO is found in good agreement with experimental values if contributions from several shells of neighboring ions are included and renormalization is largely neglected.

I. INTRODUCTION

Previous magneto-optical studies[1-7] of one-electron F^+ centers in alkaline-earth oxides have been instrumental in identifying the optical bands of the centers and have given insight into details of their level spectroscopy. There are, however, questions and inconsistencies that have motivated further investigation.

The identification of F^+-center optical bands has been substantiated by Faraday-rotation (FR) or magnetic-circular-dichroism (MCD) spectra that reveal the F^+-center paramagnetism and level degeneracies. Moreover, these spectra have enabled optical detection of the electron-paramagnetic-resonance (EPR) spectrum. The centers were first identified using EPR, and optically detected EPR has given conclusive F^+-band assignments for MgO,[1,2] CaO,[3,4,6] and SrO,[7] but not for BaO. Since the BaO band identification has been questioned,[8,9] a spectrum verifying the band assignment was measured in this study.

Analysis of magneto-optical spectra yields values for both the spin-orbit splitting and the orbital magnetic moment in the unrelaxed optically excited state. However, studies[1-7] of F^+ centers in alkaline-earth oxides have usually not resolved the small orbital Zeeman splitting from the larger spin-orbit splitting. A determination of the orbital magnetic moment has been attempted only for SrO.[7] A very small moment was unexpectedly found, but the result was uncertain because some centers had combined with impurities to form F_a^+ centers. Measurements are reported here that imply very small orbital moments for both SrO and CaO. The values for spin-orbit splittings have also remained uncertain because independent results differed by as much as a factor of 2.[3,5,7] These discrepancies have been investigated and corroborative values were measured in this study.

Advances have also prompted this study. The quality of alkaline-earth oxide crystals has improved.[10,11] Instrumentation has advanced with MCD measurements largely supplanting Faraday-rotation measurements. Calculations of electronic structure have progressed.[12] Values for spin-orbit splittings can be computed from the wave functions generated in these calculations, and the values give a connection between the calculated structure and the magneto-optical experiments. Therefore, spin-orbit computations have been examined and a calculated value for the spin-orbit splitting in CaO is compared with the experimental result.

II. SAMPLE PREPARATION

The MgO, CaO, and SrO crystals were grown at the Solid State Division of the Oak Ridge National Laboratory (ORNL) by a variation of the submerged arc process.[10,11] The starting materials were high-purity-grade MgO powder from Kanto Chemical Company, Tokyo, Jpn. and reagent-grade $CaCO_3$ and $SrCO_3$ from Mallinckrodt Chemical Co., USA. BaO crystals were obtained from the University of Missouri, courtesy of Hensley and from Spicer, Winchcomb, Glouster, England. Irradiations were carried out in the ORNL Bulk Shielding Reactor at ~330 K. To maximize the ratio of defect to impurity concentrations, thin samples (0.2–2.0 mm) and high neutron doses (6×10^{15}–10^{18} neutrons/cm^2) were used. Several irradiated specimens of each oxide were investigated, in order to select those relatively free of impurities and strain birefringence.

III. EXPERIMENTAL APPARATUS AND PROCEDURES

The MCD apparatus essentially consisted of a xenon arc lamp, monochromator, dichroic polarizer, fused-quartz–crystal-quartz photoelastic modulator, magnet, cryostat, phototube, lock-in amplifier, and electronic circuitry to maintain constant polarization modulation and phototube current. General features of the apparatus have been described[13-15] and only a few details are given here.

Most measurements were made using a combined MCD-EPR spectrometer[13] that enables MCD, EPR (*K*-band), or optically detected EPR to be made without moving the sample. The spectrometer utilized a variable gap 15-cm electromagnet (Varian) with an axial bore. Magnetic fields to 6 kG were obtained at the 6.35-cm gap which accommodated a cold-finger cryostat (Sulfrian), used for temperatures between 4.2 and 77 K. Fields to 10 kG were obtained with a 3.8-cm gap and an immersion cryostat (Janis Research), mostly used at 4.2 K and below. A half-meter monochromator (Bausch and Lomb) was used with the electromagnet. Gratings blazed at 350 or 700 nm with, respectively, 1200 or 600 lines/mm were utilized as appropriate. Far stray light and the intensity in higher orders was controlled by filters (Corning Glass). The electromagnet and single monochromator proved unsuitable for MgO and a quartz-prism, double monochromator (Adam Hilger) was used with a superconducting solenoid (American Magnetics) which was horizontally mounted in a large immersion cryostat (Janis Research).

The efficiency of the dichoric polarizers (Polaroid HNP'B or Polacoat P1-40) was increased by aligning them to the polarization produced by the monochromators. When Faraday rotation was measured, a dichroic analyzer was placed before the phototube (EMI 9529B or 9798B) and procedures described previously[15] were used. Light depolarization caused by strained optical components was investigated. In the worst case a strain-induced retardation of 7° was measured[14] in the four rigidly epoxied windows of the smaller immersion cryostat. Most of this retardation was in the less important exit windows. Warm windows on rubber O rings and cold windows of a strain-free design[16] exhibited less strain and were used on other cryostats.

The MCD spectra were calibrated against a 1-mg/ml water solution of *d*-10 camphorsulfonic acid, for which the difference in absorption coefficient of left and right circular polarization was taken as $+0.0215\ \mathrm{cm}^{-1}$ at 290 nm. Absorption spectra were measured with a spectrophotometer (Cary Model 14) accommodating the cold-finger cryostat. The cryostat was equipped with a germanium resistance thermometer (Cryocal CR 2500L) and a GaAs diode thermometer (Lake Shore Cryotronics). Temperature in the immersion cryostats was determined from helium-vapor pressure measurements.

IV. MAGNETO-OPTICAL SPECTRA

Measurements on the F^+ band in MgO proved difficult because of : (i) the band's position in the ultraviolet, (ii) a weak magneto-optical spectrum, and (iii) interfering spectra. The double monochromator and superconducting magnet, used for MgO, solved the first of these problems by producing stray-free ultraviolet intensity and a stronger spectrum. Unfortunately, the solenoid precluded measurements at higher temperatures. The problems with interfering spectra were alleviated by using crystals low in impurity Fe^{3+}.

Figure 1 shows MCD and optical density (OD) spectra of MgO. The MCD spectra of Figs. 1–4 are half the difference between scans made with the magnetic field parallel and antiparallel to the light beam. This procedure gives a correction for

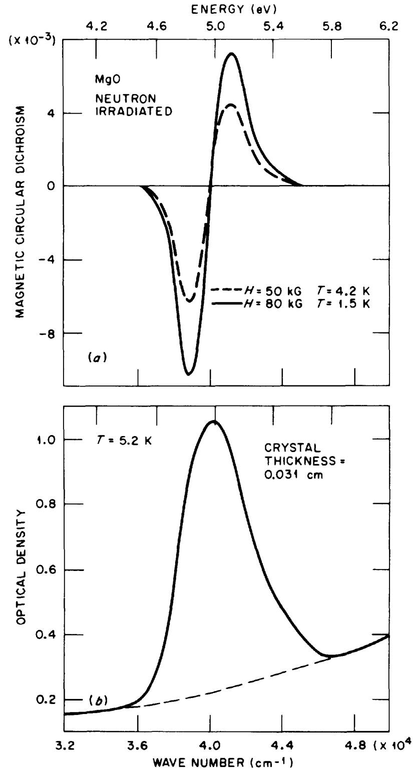

FIG. 1. Optical spectra of the F^+ center in MgO. The assumed background absorption is indicated. Units are base 10 absorbance.

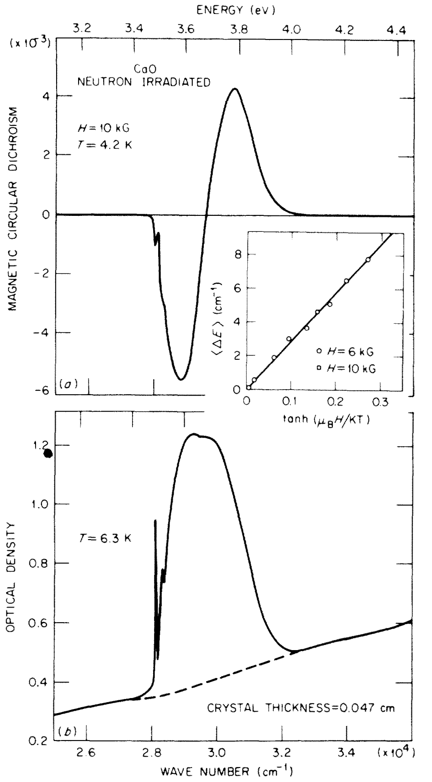

FIG. 2. Optical spectra of the F^+ center in CaO. The inset shows the temperature and field dependence of the MCD as determined from the first moment of the spectrum.

field-independent background contributed by imperfect optical elements or samples. Although background was usually negligible, it amounted to a few percent of the MgO spectra and was significant in some weaker spectra measured at higher temperatures for other crystals. The noise level was negligible on the low-energy peak but increased significantly at higher energy due to loss of light intensity. Any small MCD tail at higher energy was hidden by noise. The negative peak is more pronounced than the positive peak; this is characteristic of all F^+-band MCD reported here. The MgO spectra are more asymmetric in this respect than the spectrum computed by Kemp *et al.*[2] from combined Faraday rotation and EPR measurements.

Henderson *et al.*[17] decomposed an absorption spectrum of neutron-irradiated MgO and reported six absorption bands between 4 and 6 eV. Nevertheless, high-purity crystals showed little interfering absorption, except a small inflection on the high-energy side of the band. The band was therefore resolved by simply fitting a smooth curve to the background. This procedure gave a low-temperature half-width of 0.55 eV which is greater than the 0.48 eV computed by Henderson *et al.* but

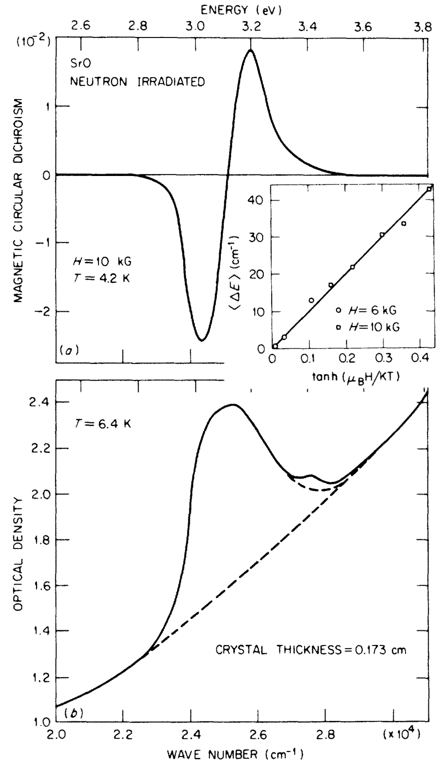

FIG. 3. Optical spectra of the F^+ center in SrO.

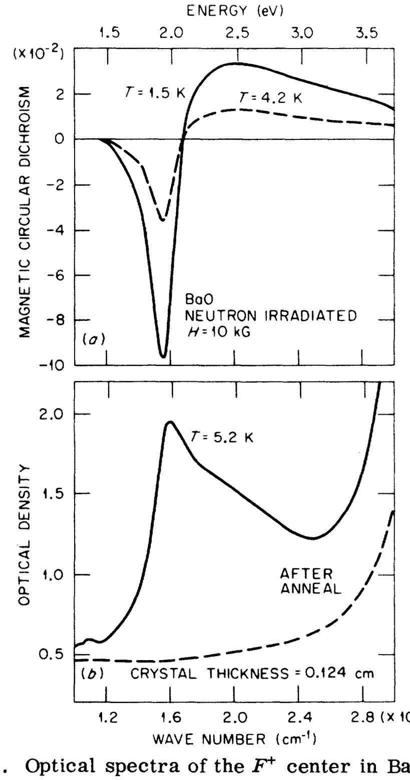

FIG. 4. Optical spectra of the F^+ center in BaO. The absorption spectrum after thermally annealing the crystal at 200 °C for 1 h is also shown and reveals considerable interfering absorption.

less than the 0.78-eV value reported by Kappers *et al.*[18]

More studies have been made of the F^+ band in CaO than in the other alkaline-earth oxides. The vibronic structure and optically detected EPR of the center have been studied in detail[4,6] and present efforts were restricted to examining the broad-band MCD and its temperature dependence. However, for comparison a few Faraday rotation measurements were also made.

The MCD spectra of better samples exhibited no measureable asymmetry with magnetic field reversal and were noise free when made at 4.2 K with a 10-kG magnetic field using 1-nm spectral resolution and a 1-sec lock-in time constant. The effect of stray light and luminescence on the shape of the MCD was checked by using interference filters and found to be negligible. Low-temperature spectra, as in Fig. 2, have a shape, including a ratio of positive to negative peak height, that is nearly identical to that reported by Merle d'Aubigné and Roussel.[6] At high energy, the MCD was found to have a small tail that may be associated with the center, but it is clearly not part of the F^+ band. The temperature dependence of the MCD as measured by its first moment is shown as the inset to Fig. 2.

Some CaO crystals exhibited an interfering MCD associated with an absorption spectrum too weak to measure. The MCD coincides with the F^+ band but it is of a positive sign throughout and distorts the F^+ spectrum. This may explain some of the early discrepancies regarding the shape and magnitude of the F^+-band Faraday rotation spectrum.[4,5] The curious MCD can be measured even in unirradiated crystals, and those not exhibiting the MCD were selected.

Measurements on SrO were made as for CaO. The optical quality of the samples was not as good as that of CaO, but the accessible position of the F^+ band and its stronger MCD gave the comparable results of Fig. 3. None of the SrO samples exhibited spectra showing a prominent high-energy tail or the structure attributed to F_a^+ centers by Modine *et al.*[7] Therefore, it is probable that F_a^+ centers in SrO have the enhanced higher-energy absorption known for their alkali halide counterparts.[19] Although the MCD spectrum is well resolved, the absorption band is on a rising background, partly due to light scattering, and is accompanied by at least one other absorption band, found at 3.4 eV. Separation of the bands requires judgment.

Barium oxide attracted early attention because of its electronic properties,[20] but only recently has progress been made toward identifying the defects giving these properties.[21] Several problems have hampered the understanding of BaO. Optical-quality crystals are difficult to obtain. Fortunately, good crystals were obtained from two sources. The crystals are very hygroscopic, and therefore difficult to handle. The handling problem is compounded by the radioactivity of neutron-irradiated samples. Irradiated crystals exhibit overlapping absorption bands that are difficult to resolve and also conductive microwave losses making EPR difficult.

Figure 4 shows spectra for BaO. The striking features of these spectra were their widths and asymmetry, and in this respect the spectra differ significantly from the FR and OD spectra of proton irradiated BaO reported by Bessent *et al.* Since Bessent *et al.* found a FR spectrum, which suggests a larger positive MCD peak, a detailed study of several crystals was made and Faraday rotation measurements were included. However, a broad absorption was always found, and all MCD and FR spectra showed relatively small positive peaks that extend to the band edge. Inflections in the MCD suggest small overlapping absorption bands at low energy.

The OD spectrum in Fig. 4 shows the 2-eV band attributable to the F^+ center and another band at 2.6 eV that tended to increase with time after irradiation. All of the irradiated samples exhibited a 2.6-eV band, although it was not possible to examine the crystals immediately after irradiation because of their radioactivity. The absorption after annealing the crystal is also shown and reveals considerable underlying absorption.

V. PARAMAGNETIC RESONANCE OF BaO

The questioned identity of the BaO optical bands together with the irregular shape of the optical spectra motivated study of the EPR associated with these bands. Carson *et al.*[22] first studied the EPR of defects in BaO. Because no correlation was found between the 2.0-eV band and the F^+-center EPR, they concurred with a prior assignment by Sproull *et al.*[23] and attributed the optical band to the two-electron *F* center. Later, Bessent *et al.*[5] showed the 2-eV band to be due to a paramagnetic center and identified it as the F^+ center. Nevertheless, questions regarding identity have persisted, based upon (i) lack of correlation of the 2.0-eV band with the EPR, (ii) a theoretical calculation[24] which predicted the F^+ band to be near 3 eV, and (iii) Mollwo-Ivey plots suggesting that the 2-eV band is due to the *F* center and that the F^+ band is at 2.6 eV.[8]

Figure 5 shows an EPR spectrum of a neutron-irradiated BaO crystal. Many of the lines are attributable to the F^+ center. The hyperfine lines indicated on the figure derive from the 40% of the

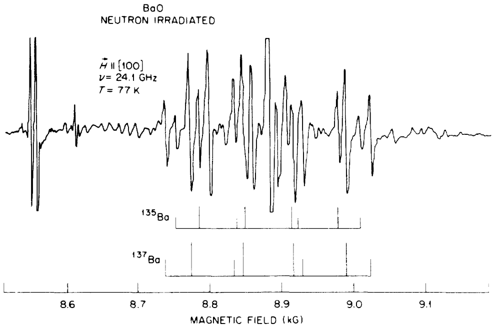

FIG. 5. Electron paramagnetic spectrum for BaO. Hyperfine lines corresponding to F^+ centers having a single near-neighbor magnetic isotope are indicated.

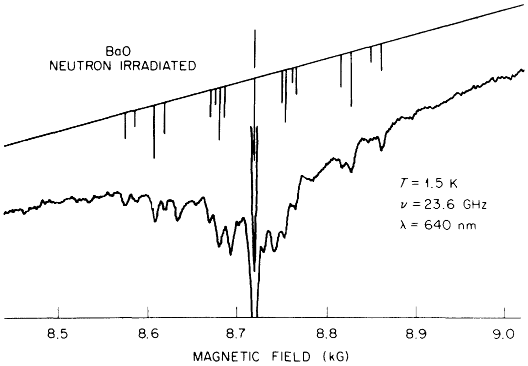

FIG. 6. BaO paramagnetic resonance spectrum that was obtained by measuring changes in the MCD. Lines assignable to the F^+ center are indicated.

centers having only one near-neighbor magnetic ($I = \frac{3}{2}$) isotope, either 6.6% abundant ^{135}Ba or 11.3% abundant ^{137}Ba. Roughly 30% of the centers have no neighboring magnetic isotopes and give the large central line. Many weaker, more widely distributed lines can be attributed to F^+ centers with two or more magnetic near neighbors. The spectrum also exhibits prominent lines not attributable to F^+ centers, notably one near 8.8 kG, a pair flanking the central line and lines at lower field.

Since the F^+ center spectrum has previously been analyzed in detail, it need not be reconsidered here. It is sufficient to note that a first order computation of the g value and hyperfine parameters clearly favors the values of Mann *et al.*[25] over earlier results.[22,26]

Figure 6 shows an optically detected EPR spectrum of the same sample. The hyperfine splittings clearly identify the F^+ center. A nearly, but not exactly, identical spectrum can be measured at any wavelength giving a strong MCD. A correlation between the 2.0-eV optical band and F^+-center EPR definitely exists. However, even the optically detected EPR exhibits lines that are not attributable to F^+ centers. These lines are seen because other bands underlie the F^+ band, and because of cross relaxation. Figure 7 illustrates the quenching of the MCD obtained by partially saturating the central EPR line. The fraction of the MCD that is quenched by saturating an EPR line is not wavelength independent, verifying that bands other than the F^+ band contribute to the MCD. Figure 7, for example, shows that partial saturation of the central line decreases the height of the 1.9-eV MCD peak relative to the 2.7-eV MCD peak.

The absorption bands and EPR lines were further investigated by making measurements on thermally annealed crystals. Figure 8 shows optical spectra measured before and after annealing a sample that exhibited a large 2.6-eV band. After the anneal, about 95% of the F^+ centers are gone, and spectra of defects having greater thermal stability than the F^+ center are better resolved. The OD spectrum more clearly reveals the 2.6-eV band and another band is resolved at 1.5 eV. The MCD shows two negative peaks after anneal; the 2.1-eV band is a remnant of the F^+ band and the 1.7-eV peak suggests a band that is unresolved in the OD spectrum. The shape of the MCD of the bands is probably discernible. The 1.5- and 1.7-eV bands appear to have absorptionlike shapes. Absorptionlike MCD results from a magnetically induced admixture of resolved bands, or from magnetic splitting in an orbitally degenerate ground state.[27] The MCD of the 2.6-eV band is asymmetric and may be comprised of both an absorptionlike and an absorption-derivative-like component. Absorption-derivative-like MCD results from magnetic splittings or possibly from a near superposition of bands having MCD of opposite sign.[27]

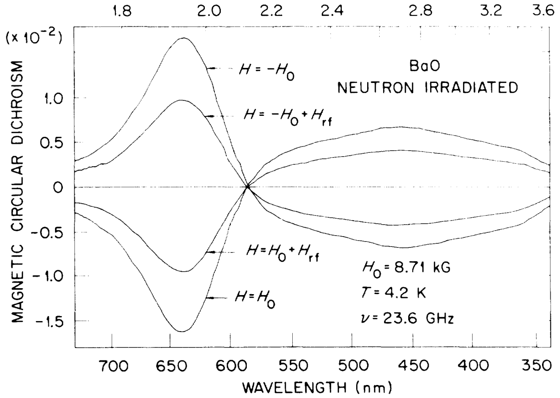

FIG. 7. MCD spectra of BaO measured with the magnetic field parallel and antiparallel to the light beam and with and without microwave power. The central line of the F^+-center spectrum was displayed on an oscilloscope during the scans with the microwave power applied.

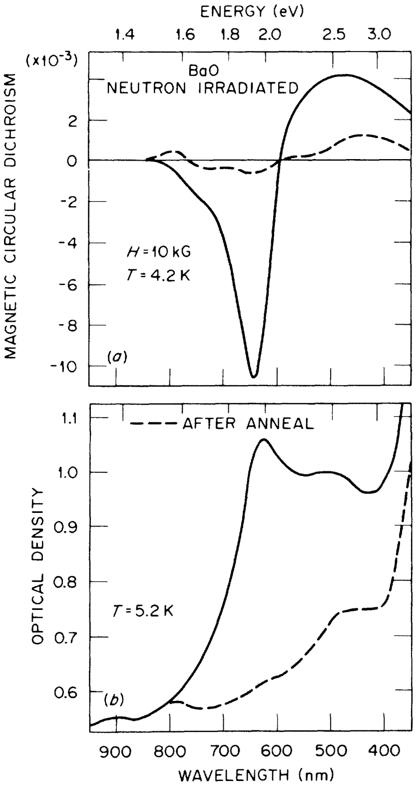

FIG. 8. Optical spectra measured before and after annealing a BaO crystal for 10 min at 150 °C.

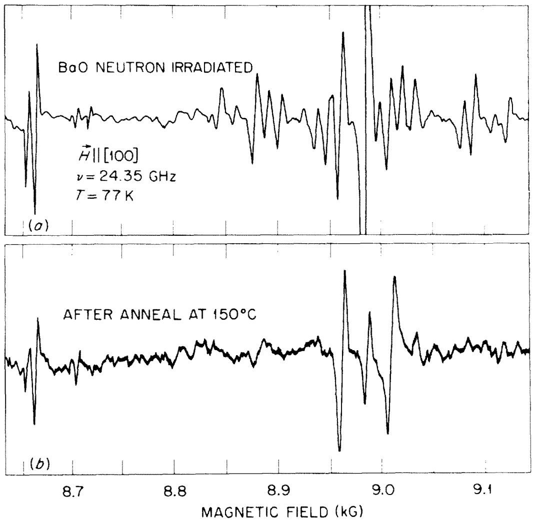

FIG. 9. Paramagnetic resonance spectra measured before and after annealing a BaO crystal.

Figure 9 shows changes in the EPR spectrum that accompany changes in the optical spectrum shown in Fig. 8. The central line of the F^+ center is greatly reduced and the F^+ hyperfine structure is largely lost after the anneal. The extra line at about 8.9 kG is lost, but the two lines flanking the F^+ central line persist as do some at low field. The angular variation of the EPR spectrum reveals that the two lines are due to $\langle 100\rangle$ axial centers. Moreover, these axial lines belong to two sets. The low-field line is a double perpendicular with a $g_\perp = 1.940 \pm 0.002$. The higher-field line is the parallel line of this set with $g_\parallel = 1.930 \pm 0.002$ and the superimposed double perpendicular of another set with $g_\perp = 1.930 \pm 0.002$. The parallel line has $g_\parallel = 1.886 \pm 0.002$ and is found at higher field than shown in Fig. 9. The low-field lines near 8.66 kG are isotropic.

Optically detected EPR spectra of the annealed sample are shown in Fig. 10. The spectra are complicated by the overlapping bands and cross relaxation; moreover, the measurements are made difficult by a long relaxation time, $T_1 \approx 56$ sec at 8.8 kG and 1.5 K. Nevertheless, the result is revealing. The 640-nm MCD peak shows the strongest EPR response to the F^+ central line, verifying the assignment of this peak to the F^+ center. A relatively stronger EPR response to the axial lines is found for the MCD peaks at 720 and 440 nm, implying that bands at 1.7 and 2.6 eV are associated with axial centers. The 1.5-eV band correlates with none of the strong lines. In fact, the MCD at 800 nm increases rather than decreases. However, the MCD displays a decrease near 8.88 kG which probably correlates with an EPR line that is too broad to appear in a microwave absorption-derivative spectrum.

There is sufficient evidence to associate tentatively the 2.6- and 1.7-eV peaks with the same axial defect which may be a variant of the F^+ center. It is tempting to assign the 2.6-eV band to an orbital doublet and the 1.7-eV band to an orbital singlet, where a spin-orbit interaction splits the doublet and admixes the doublet and singlet.[28] However, the spectra are complicated, and de-

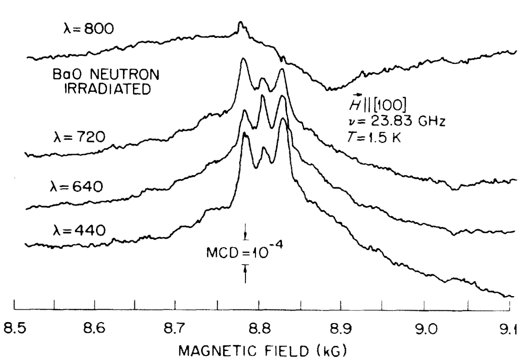

FIG. 10. Optically detected paramagnetic resonance spectra measured for an annealed BaO crystal. The phase of the $\lambda = 440$-nm signal was inverted to give a more compact presentation.

finite assignments will require further investigation.

Although the bands found under the F^+ band explain many irregularities of the optical spectra, the true shape of the F^+-center spectra is not apparent. Annealing yields difference spectra that are also broad and asymmetric. Hence, the true F^+-center spectra are either inherently asymmetric, or the difference in the thermal stability of the various defects is insufficient to reveal a true shape. Moreover, because of the large hyperfine interactions in BaO, optically detected resonance cannot resolve the F^+-center MCD.

VI. ANALYSIS AND RESULTS

The optical spectra were interpreted by the method of moment analysis which has been described by Henry *et al.*[29] and by Osborne and Stephens.[30] Moments were calculated by using a Simpson's rule integration scheme to evaluate integrals in the form

$$M_n=\frac{(-1)^{n+1}}{\bar{\lambda}^n}\int\frac{(\lambda-\bar{\lambda})^n}{\lambda^{n+1}}F(\lambda)\,d\lambda\,. \qquad (1)$$

M_n denotes the nth moment of a spectrum $F(\lambda)$, which is either the OD or MCD. λ is the wavelength and $1/\bar{\lambda}$ is the energy centroid $\bar{E}$ of the absorption band. Adopting the approximations and terminology of Henry *et al.*, the ratio of the second to the zeroth moment of the absorption band gives the mean-square width of the band $\langle E^2\rangle$, which is a sum of cubic mode $\langle E^2\rangle_c$, noncubic mode $\langle E^2\rangle_{nc}$, and spin-orbit contributions

$$\langle E^2\rangle=\langle E^2\rangle_c+\langle E^2\rangle_{nc}+2(\tfrac{1}{3}\Delta)^2\,, \qquad (2)$$

where Δ is the spin-orbit splitting of the unrelaxed excited state. Ratios of the first and third moments of the MCD to the zeroth moment of the absorption, respectively, give

$$\begin{aligned}\langle\Delta E\rangle &\equiv\langle\Delta E_+\rangle-\langle\Delta E_-\rangle\\ &=2g_L\mu_B H-2(\tfrac{1}{3}\Delta)\tanh(\mu_B H/kT)\end{aligned} \qquad (3)$$

and

$$\langle\Delta E^3\rangle=3\langle\Delta E\rangle\,[\langle E^2\rangle_c+\tfrac{1}{2}\langle E^2\rangle_{nc}+(\tfrac{1}{3}\Delta)^2]\,, \qquad (4)$$

where $\langle\Delta E\rangle$ has been defined as twice the $\langle\Delta E_+\rangle$ of Henry *et al.* and g_L is the g factor which measures the orbital moment in the excited state. The temperature dependence of Eq. (3) distinguishes between the orbital moment and the spin-orbit splitting. $\langle E^2\rangle_c$ and $\langle E^2\rangle_{nc}$ are found by combining Eqs. (2)-(4).

Table I summarizes the values, obtained in this and previous studies, for the spin-orbit splittings and orbital magnetic moments of the F^+-center unrelaxed excited states. To within the limits of uncertainty, the values determined in this study agree with one or more of the previously determined values. In the MgO case, the exact agree-

TABLE I. Summary of the data on magnetic splittings in unrelaxed excited states of F^+ centers in alkaline-earth oxides.

Crystal	Spin-orbit splitting (cm^{-1})	Orbital magnetic moment (μ_B)	Source	Reference
MgO	≈− 22.5		FR-EPR [a,c]	1,2
	− 18 ±4.5		FR-EPR	2
	− 18 ±3		MCD [b]	This work
CaO	≈− 70		FR-EPR	3
	− 80 ±10		FR-EPR	4
	− 36		FR	5
	− 30		TC [d]	5
	− 46.5 ±9		MCD-EPR	6
	− 35 ±10		FR	This work
	− 43 ±4	0 ±0.2	MCD	This work
	− 39.2		TC	This work
SrO	−277.5		FR	5
	−120		TC	5
	−141.8	≈0	MCD	8
	−150 ±30	0 ±0.2	MCD	This work
BaO	−397.5		FR	5
	−270		TC	5
	−380 ±190		MCD	This work

[a] FR: Faraday rotation.

[b] MCD: magnetic circular dichroism.

[c] -EPR: as optically detected paramagnetic resonance.

[d] TC: theoretical calculation.

ment is fortuitous because different assumptions were made in analyzing the absorption spectra. Kemp *et al.*[2] assumed a Gaussian band having the 0.48-eV half-width determined by Henderson *et al.*[17]

The Δ values for CaO are reasonably consistent if the values determined by Kemp *et al.*[3,4] are disregarded. The value obtained from the temperature dependence of the MCD is in good agreement with that obtained by Merle d'Aubigné and Roussel[6] using combined MCD and EPR. Nevertheless, a value obtained from a FR measurement is in good agreement with the result of Bessent *et al.*[5] There is no fundamental basis for different MCD and FR results and the MCD values are considered more accurate. Background rotation is a problem in the FR measurements, and error may be introduced in the Kramers-Kronig inversion that converts rotation data to MCD before the moments analysis.

The value obtained for the spin-orbit splitting in SrO is consistent with the value previously found from MCD, even though the previous result was obtained from a spectrum partly attributed to F_a^+ centers. This is not too surprising, since the spin-orbit splitting of the F_a^+ center is expected to be similar to that of the F^+ center and moments analysis yields an averaged splitting for such spectra.[28,29] No explanation of the large difference between the MCD and FR values is known.

The BaO spectra cannot be clearly resolved and therefore cannot be rigorously analyzed. The greatest difficulty is associated with the high-energy MCD tail. The extent of this tail could not be measured and it extends well beyond the absorption band, that is resolved by making a smooth fit to the background absorption. The MCD spectrum can be made to correspond with the region of the band absorption, either by fitting to a background that extends the absorption band, or by truncating the MCD tail. However, if only reasonable adjustments are made, the tail still gives an apparently inordinate contribution to the moments.

Approximate methods which avoid the problem are the only recourse. A method that appears reasonable consists of analyzing only the lower-energy portion of the spectrum. The region where the MCD is negative is assumed to contribute half the zeroth moment of the absorption and half the first moment of the MCD. Moments are calculated about the energy at which the MCD changes sign, assumed the energy centroid of the band. The method, which gives approximate values for Δ in the other alkaline-earth oxides, yields $\Delta \simeq -380$ cm^{-1} for BaO. Another method which avoids problems associated with the tails of the spectra is to apply rigid shift formulas[31] that predict Δ from the spectra peak heights and the absorption band half-width. In BaO, such formulas give $\Delta \simeq -800$ cm^{-1}. However, the formulas overestimate Δ by about a factor of 2 in the other oxides, and therefore again $\Delta \simeq -380$ cm^{-1}. Although such estimates are not satisfying, they appear to confirm the previous FR result.

No orbital Zeeman splitting is found for either the CaO or SrO F^+ band. The result is unexplained but corresponds with the previous SrO result and appears to be valid. The sensitivity of the measurements to an orbital Zeeman splitting was verified by cursory measurements of the KCl F band. Analysis gave $g_L = 0.9 \pm 0.1$ and $\Delta = -60 \pm 10$ cm^{-1}, both in good agreement with previous results.[32] Unfortunately, the temperature dependence of the MgO spectra could not be measured, and the BaO spectra are too uncertain to permit a reliable analysis.

A complete study of all moments of the spectra did not appear warranted because of problems with interfering absorption and the uncertainty of the MCD tails. However, moments through the third were calculated for several of the low-temperature spectra and the results deserve comment. Excepting BaO, the zeroth moments of the MCD spectra are consistently negative in sign and about six percent of the first moment in magnitude. This could indicate improper treatment of the high-energy tails, but it more probably reveals a spin-orbit induced configuration mixing of the excited state with other states. In principle, the second moments of the MCD spectra can also give the spin-orbit splittings, but these were found to be completely unreliable.

Table II gives parameters for the absorption bands, together with cubic and noncubic mode contributions to the bandwidths that are implied by moments of the MCD spectra. In the MgO case, the

TABLE II. Absorption band parameters: energy centroid, mean-square width, and the cubic and noncubic mode contributions to the width computed from moments of the MCD and OD spectra.

	$\bar{E}$ (10^4 cm^{-1})	$\langle E^2\rangle$ (10^5 cm^{-2})	$\langle E^2\rangle_c$ (10^5 cm^{-2})	$\langle E^2\rangle_{nc}$ (10^5 cm^{-2})
MgO	4.060	36	$\simeq 0$	$\simeq 36$
CaO	2.965	7.3	1.7	5.5
SrO	2.525	8.8	0.9	7.9

moments unrealistically imply a small negative contribution to the bandwidth from cubic modes. Possibly this results because there is interfering absorption in the tails of the band and too large a bandwidth has been computed. Nevertheless, the band half-width is as small as any actually observed for MgO. Alternatively, it is possible that an underestimate has been made of the tails of the MCD which contributed sizeably to the third moment.

The CaO energy centroid, mean-square width, and implied mode contributions are in good agreement with the results of other studies. The width is slightly greater than reported by Escribe and Hughes[33] and by Henderson *et al.*[34] however, it is somewhat less than that reported by Merle d'Aubigné and Roussel.[6] The ratio of cubic to noncubic mode contribution is nevertheless identical to that deduced by the latter.

For SrO, both the energy centroid and bandwidth are significantly greater than reported by Hughes and Webb.[35] The mean-square width is almost 30% greater than they report, which is disturbing, since a narrower width is expected to be more correct. The difference can probably be attributed to the interfering band at 3.4 eV, which Hughes and Webb found more prominent in neutron irradiated crystals than in the proton irradiated crystals used for their study. An overestimate of the bandwidth gives an underestimate of the cubic mode contribution and the value reported here does appear low. A different decomposition of the absorption could change the values reported, but at the risk of forcing a result. An overestimate of the band width can also decrease the computed spin-orbit splitting but to a lesser extent than the cubic mode contribution.

VII. CALCULATED SPIN-ORBIT SPLITTING FOR CaO

F-band spin-orbit splittings have been calculated with reasonable success for alkali halides.[36,37] Moreover, such calculations have been used for alkaline-earth oxides by Bessent *et al.*,[5] and rough agreement was obtained between values computed from a simplified model and the results of their Faraday-rotation measurements. These results together with recent electronic structure calculations have prompted the present calculation. CaO was chosen because it has been most studied, and is better known than any other alkaline-earth oxide.

The calculation applies the model previously employed by Smith[36,37] to calculate spin-orbit splittings in the alkali halides. The CaO F-center wave functions, core orbitals and potentials of the host lattice ions were computed from a model based upon that used by Wood and Öpik[38,39] for alkali-halide F centers. In this model, the electronic structure of the first nearest neighbor (1nn) ions is explicitly included in the calculation. Beyond the 1nn shell, an effective-mass approach is used.

The form of the wave function used in these calculations is given by

$$\psi(\vec{r}) = \sum_{i=1}^{n} C_i \psi_i(\vec{r}) , \tag{5}$$

where the orbitals have the form

$$\psi_i(\vec{r}) = N_i \left(f_i(\vec{r}) - \sum_{\nu,k} \phi_{\nu k}(\vec{r}) S_{\nu k,i} \right) . \tag{6}$$

The vacancy centered function $f_i(\vec{r})$ is given by the product of a single Slater-type radial orbital with an appropriate spherical harmonic, and $\phi_{\nu k}(r) = \phi_k(\vec{r} - \vec{R}_\nu)$ is the kth occupied core orbital on the νth lattice ion. $S_{\nu k,i} \equiv \langle \phi_{\nu k} | f_i \rangle$ is the overlap integral between the vacancy centered function f_i and the core orbital $\phi_{\nu k}$. The renormalization of the orbital ψ_i resulting from the orthogonalization of the function f_i to the core states of the lattice ions is given by

$$N_i \equiv \left(1 - \sum_{\nu,k} | S_{\nu k,i} |^2 \right)^{-1/2} .$$

The linear parameters C_i and the nonlinear parameters appearing in the expressions for the functions $\psi_i(\vec{r})$ are optimized variationally at several outward displacements of the 1nn ions for each state of the F^+ center. The linear coefficients C_i obtained in this way correspond to using orbitals of the type given in Eq. (6) in which the sum over the lattice ions is limited to the 1nn shell. The $^2T_{1u}$ wave function was constructed using four orthogonalized Slater-type orbitals having p-like symmetry, and the calculation was made with the 1nn ions displaced outwards by 7% of the 1nn distance, which corresponds to the calculated minimum in the ground-state configuration coordinate curve.

Only the "ion-ion" contribution was kept in the calculation of the spin-orbit splitting. Smith has shown that the "vacancy-vacancy" and "vacancy-ion" contributions are about three orders of magnitude smaller than that of the ion-ion term. The spin-orbit splitting Δ can be expressed in terms of the expectation value of the spin-orbit Hamiltonian $\mathcal{H}_{so}$ for the $j = \frac{3}{2}$, $m_j = \frac{3}{2}$ function, and is given by

$$\Delta = 3 \langle \mathcal{H}_{so} \rangle_{3/2,3/2} = N^2 \, 3 \langle \psi | \mathcal{H}_{so} | \psi \rangle \equiv N^2 \tilde{\Delta} , \tag{7}$$

where

$$\langle\psi|\mathcal{H}_{so}|\psi\rangle \simeq \sum_{i,j} C_i C_j N_i N_j \sum_{\nu} \sum_{k,l} S_{i,\nu k} S_{\nu l,j} \langle\phi_{\nu k}|\mathcal{H}_{so}|\phi_{\nu l}\rangle \tag{8}$$

$$N^2 = \left[\sum_{i,j} C_i C_j N_i N_j \left(\langle f_i|f_j\rangle - \sum_{\nu,k} S_{i,\nu k} S_{\nu k,j}\right)\right]^{-1}. \tag{9}$$

The form of the spin-orbit operator used here is given by

$$\mathcal{H}_{so} = (2m^2c^2)^{-1} \sum_{\nu} |\vec{r} - \vec{R}_\nu|^{-1} \frac{\partial V_1(|\vec{r} - \vec{R}_\nu|)}{\partial |\vec{r} - \vec{R}_\nu|} \vec{L}_\nu \cdot \vec{S}. \tag{10}$$

The potential V_1 is the $l = 1$ component of the l-dependent potential for the νth ion that was used in the F^+-center calculations.[38,39] The potential for the O^{-2} ion was generated using the local orbitals obtained by Pantelides, Mickish, and Kunz[40] in their MgO band-structure calculation.

Convergence of $\tilde{\Delta}$ to 0.1 cm^{-1} was achieved by including contributions from the first 24 shells of neighbors (618 ions). Results are summarized in Table III. Good agreement is obtained with the experimental values reported in Table I, if the renormalization term N^2 that corrects for the overlap of the vacancy centered function with the core orbitals beyond the 1nn shell is ignored. If it is included, the calculated value is about four times larger. Smith has argued that neglecting renormalization corrections may give a sufficiently good approximation since it is compensated by the neglect of overlap corrections to the free-ion core orbitals. Although the N^2 terms were neglected in Smith's treatment of the F center in NaCl,[36] he found it necessary to include them in his treatment of the F center in RbCl,[37] in order to obtain agreement with the measured value. The large N^2 indicates that the neglect of core-core overlap is probably unjustified in a CaO calculation. The size of N^2 is primarily due to a more diffuse character of O^{-2} orbitals compared to the more compact halide ion wave functions. The value of N^2 for the unrelaxed excited state of the F center in a typical alkali halide is ~2.0 using free-ion orbitals to approximate the halide ion cores. It may be possible to overcome the problem through the use of symmetrically orthogonalized core orbitals.[41,42] If vacancy centered functions are orthogonalized to an orthogonalized set of core orbitals, third-order overlap corrections are introduced that tend to reduce the size of the expectation value of $\mathcal{H}_{so}$ and the size of N^2. Thus, the net effect is to reduce the size of Δ. Only an actual calculation of these corrections would reveal whether or not they are adequate.

The results differ in several respects from the earlier calculation by Bessent *et al.*[5] They calculated ion-ion contributions from only the 1nn shell of Ca^{+2} ions, which were fixed in their perfect lattice positions, neglected all renormalization and obtained a value of -24 cm^{-1}. Table III shows that the 1nn shell gives only 28% of the total splitting. Actually, this contribution is strongly dependent upon the outward displacement of the 1nn shell of ions. For an outward displacement of 2%, $\tilde{\Delta}_{1nn} = -79.9$ cm^{-1}, and for 5%, $\tilde{\Delta}_{1nn} = -29.2$ cm^{-1}. Thus, the agreement between their calculated and measured values appears mostly fortuitous.

TABLE III. Computed results for the spin-orbit splitting in the F^+ band in CaO.

Shell	$\tilde{\Delta}$ (cm^{-1})	% of total
1nn(6 Ca^{+2})	-11.13	28.41
2nn(12 O^{--})	-4.96	12.65
3nn(8 Ca^{+2})	-3.33	8.50
4nn(6 O^{--})	-1.71	4.36
5nn(24 Ca^{+2})	-5.09	12.99
6nn(24 O^{--})	-4.29	10.96
Σ(24 shells)	-39.18	100.00

$\langle\psi|\psi\rangle = 0.2362$, $N^2 = 4.23260$

VIII. DISCUSSION AND CONCLUSIONS

This study was largely motivated by the uncertainties persisting after previous studies and these have surely been reduced. The spin-orbit splittings are more certain because there are now comparable independent values. Even the approximate value agreeing with the BaO FR result of Bessent *et al.* is reassuring. The MgO MCD result agreeing with the previous FR result is also reassuring and was unforeseen. Prior to this study, only the disparate MCD and FR results for the spin-orbit splittings in CaO and SrO had been found.

That no orbital Zeeman splitting was found in either the CaO or SrO F^+ bands contrasts with alkali halide F-band results and may indicate a significant difference in the electronic structure of the oxide and halide centers. It is probably significant that a negative orbital moment has been reported for the two-electron F center in CaO,[43] and orbital moments close to zero have been reported for F centers in alkaline-earth halides.[44,45]

The higher moments of the spectra appear to give useful information regarding both the defects and the quality of the results. Some sample problems are indicated, and in no case does the accuracy and consistency of the results appear to approach that attained for some alkali halide F centers.[29] However, higher moments of LiF F-center spectra have shown complications that were attributed to a breakdown of the approximations usually made to interpret these moments.[30]

The study shows that sample imperfections make isolation of the F^+-band spectra difficult. Indeed, the differences in the results of the various magneto-optical studies may be largely attributable to samples rather than technique. Some variation is due to sample strain and impurities. There also appears to be a difference between the properties of neutron- and proton-irradiated crystals. The optical spectra reported here for neutron-irradiated SrO and BaO differ significantly from those reported elsewhere[5,35] for proton-irradiated crystals. Aparently, this is due to a difference in constituent defects that is not understood.

The BaOF^+ spectra could not be resolved for the neutron-irradiated crystals used in this study and it may be that their true shape was not discerned by Bessent *et al.* A large positive FR in the high-energy portion of the absorption band does not appear consistent with the shape of the band, even as reported by Bessent *et al.* Also, both the zero in the MCD and the negative peak of the FR appear too far removed from the peak of the absorption band to give symmetrically shaped magneto-optical spectra. Moreover, an explanation was not found for the high-energy tails of the magneto-optical spectra of this study. The proximity of the band to the fundamental absorption edge may give complications not seen in the other oxides.

The optically detected resonance study of BaO eliminates any further doubt regarding the identity of the F^+ band. Moreover, since Rose and Hensley[21] have identified the two-electron F band at 2.3 eV and this study clearly refutes its assignment at 2.6 eV, all questions[8,9] regarding the identity of the optical bands appear to be answered.

The calculated spin-orbit splitting for CaO brings the alkaline-earth oxide spin-orbit calculations at least to the level of sophistication attained for the alkali halides. Moreover, the calculation shows that the previously applied models are almost as inadequate for the oxides as they would be for alkali halides. Further progress will primarily require better treatment of the O^{-2} ions.

ACKNOWLEDGMENTS

The authors are indebted to E. B. Hensley for some of the BaO crystals and to M. M. Abraham for aid in examining the angular dependence of the EPR spectra.

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*Research sponsored by the U. S. Energy Research and Development Administration under contract with Union Carbide Corporation.

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