various V centers.

$$V_1;\ g_{\parallel}=2.00327,\quad g_{\perp}=2.03859,$$
$$W;\ g_{\parallel}=2.0032,\quad g_{\perp}=2.0408\,,^4$$
$$V_{\mathrm{OH}};\ g_{\parallel}=2.0032,\quad g_{\perp}=2.0396\,,^1$$
$$V_{\mathrm{F}};\ g_{\parallel}=2.0031,\quad g_{\perp}=2.0388\,.^2$$

The quantity $g_{\perp}-2.0023$ is a measure of the orbital contribution to the g factor. If the hole were greatly delocalized into the equatorial oxygen orbitals, the substitution of OH^-, F^-, or O^- for $\mathrm{O}^=$ at the *nnn* site would be expected to perturb the hole orbital (and therefore $g_{\perp}$) significantly. However, the g factors of all the modified trapped holes are remarkably close to those of the V_1 center. This again suggests that the hole is largely localized on a single oxygen atom.

Note added in proof. Recently an improved $\mathrm{O}^=2p$ wave function due to Nagai[10] was brought to our attention. This function was developed for the calculation of hyperfine parameters in MnO, and in presenting it, Nagai mentions that Watson's orbital has been found to be too large in the tail for these calculations. The overlap calculated from this new function is $|\langle 2p(\mathrm{O}^=)|2s(F^-)\rangle|=0.00168$, which gives a value of $a=0.128$ MHz for the isotropic hyperfine coupling. This is much closer to the observed value of a than that obtained using Watson's orbital, and strengthens our argument regarding the tightly-bound hole model.

ACKNOWLEDGMENT

Philips-Aachen supplied the crystal used in this experiment.

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[10] S. Nagai, J. Phys. Soc. Japan **25**, 510 (1968).

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Magneto-Optical Structure of the MgO *F* Band*

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The paramagnetic Faraday-rotation pattern of the MgO F center has been investigated, using the ESR-optical double-resonance method, at 12 kG and 1.8°K. The rotation is centered precisely upon the familiar 4.95-eV absorption band, in agreement with the extrapolated position predicted from a previous observation on the extreme low-energy tail of the band. The p-state spin-orbit parameter λ is given as $-(12\pm3)\ \mathrm{cm}^{-1}$. The pattern is highly symmetrical, consistent with a very nearly Gaussian absorption band. The width of the pattern is about 30% less than the width which would correspond to a Gaussian absorption band with rigid magneto-optic shift, if the F band is assumed to be Gaussian with the accepted half-width of 0.48 eV. This implies that noncubic electron-lattice interaction is present: The third moment of the circular dichroism (computed from the observed rotation) in fact has a value such as to indicate that noncubic modes are strongly dominant. The same rotation spectrum is observed in samples of both neutron-irradiated and additively colored MgO. However, in the latter there are curious discrepancies between the apparent F-center densities as gauged by the absorption band intensity, the ESR signal strength, and the Faraday rotation amplitude. This is discussed in terms of a postulated near coincidence of the F and F' bands, and the occurrence of F'-F conversion during the measuring operation; the connection with other observations on the F-F' relationship in MgO is indicated.

I. BACKGROUND

THE utility of magneto-optic observations in isolating the F bands in the IIA oxides[1] was recognized over two years ago.[2] Well-defined Faraday rotation (FR) patterns believed characteristic of the F center were discovered in CaO [2–4] and in SrO and BaO.[4] These patterns were obtained from conventional measurements[4] of the spectroscopic Faraday rotation $\theta(E,H,T)$, and in the case of CaO by the magneto-optical double-resonance method.[2,3] The bands in these cases lie near 2 eV (BaO), 3.0 eV (SrO), and 3.7 eV (CaO), i.e., in the visible and near uv range.

The MgO F band is understood to be the familiar 4.9-eV band, at about 2500 Å. Rotation measurements on this band are difficult, first, because of the usual instrumental difficulties in the uv (weak light sources, etc.) and, second, because of the relatively weak paramagnetic rotation, i.e., the small rotation per unit sample absorbance (small spin-orbit coupling λ). Up to the present work, only a study of the rotation on the

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* Supported by the U. S. Air Force Office of Scientific Research.

[1] For the most recent review see B. Henderson and J. E. Wertz, Advan. Phys. (to be published).

[2] J. C. Kemp, W. M. Ziniker, and J. A. Glaze, Proc. Brit. Ceram. Soc. **9**, 109 (1967).

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

[4] R. G. Bessent, B. C. Cavenett, and I. C. Hunter, J. Phys. Chem. Solids (to be published).

far low-energy wing of the *F* band has been reported,[5] in a sample that was sensibly opaque within the band proper. The shape and paramagnetic character of this far-wing pattern, obtained by the double-resonance method, was in fact consistent with the assumed 4.9-eV *F*-band location; an estimate $\lambda \sim -15$ cm^{-1} of the spin-orbit parameter was made, believed to be appropriate in sign and magnitude for the MgO *F* center. A genuine picture of the rotation curve, throughout the absorbing region, was obviously desired. This became attainable after we completed technical improvements in our apparatus, and is reported herewith.

II. EXPERIMENTAL

A. Procedure

Faraday rotation here is measured by the electron spin resonance optical double-resonance method (FR-ESR), described more fully in previous papers.[2,3,5] This method has the dual virtues of showing a direct correlation with the ESR spectrum, and of eliminating various background Faraday rotation, since only the rotation θ_{para} of the atomic species excited by ESR is detected. The specific procedure used to obtain the present data is shown in Fig. 1. The polarization angle θ_t of a linearly polarized light beam, transmitted along the magnetic field through the sample, is measured by the spinning analyzer system[2] and monitored on a recorder, at discrete wavelengths λ_i. With the *H* field set at the spin-resonance value, in this case that appropriate for the MgO *F* center ($g=2.002$), saturating microwave power is applied, resulting in a shift $\Delta\theta_t = -\theta_{\text{para}}$ (*F* center). At each wavelength point λ_i we apply the power in a sequence of on-off steps, spaced sufficiently to permit full spin-lattice relaxation; this provides a rudimentary signal averaging and separates out apparatus drift.

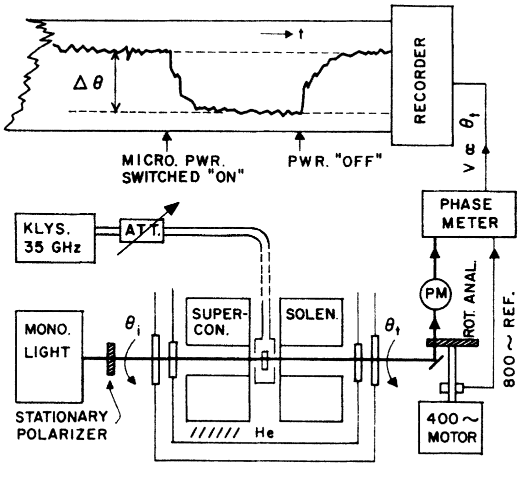

FIG. 1. Experimental arrangement and procedure used to obtain the double-resonance Faraday rotation data of the present paper. The microwave system, for saturating the *F*-center spin resonance, operates at 35 GHz; the cavity contains light ports of 2 to 3 mm diameter.

B. Sensitivity

The signal-to-noise ratio we work with in MgO is very poor, and reliable signals were obtained only after very careful optimization of all parts of the apparatus and proper selection of sample thickness. Because of optical losses, including constriction of the beam through the microwave cavity,[2] the chief noise component is shot noise (photon fluctuations): This decrees that one select an optimum sample thickness, corresponding to about unity absorbance (10% transmission) at the *F*-band peak. With such a choice the magnitude of the central peak of θ_{para}, at 2°K and at $H=11$ kG, in the case of the MgO *F* center turns out to be of the order 0.1°. In practice our best results were with a somewhat larger absorbance (note Fig. 2); this was

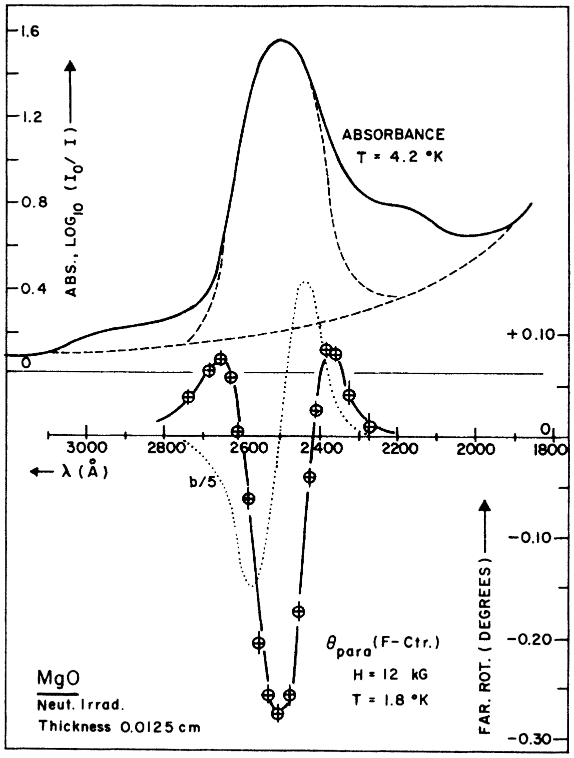

FIG. 2. Paramagnetic Faraday rotation pattern of the MgO *F* center, obtained by the FR-ESR method. Crosses on the data points (with circles) give very approximate magnitudes of error due to resolution width (horizontal) and noise (vertical). The dotted curve is the circular dichroism *b*, divided by 5, obtained by Kramers-Kronig inversion of θ; the same ordinate scale applies to θ and $\frac{1}{5}b$. The sample absorbance, taken on a spectrophotometer, is shown with a hand-sketched partial resolution of the absorption bands.

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[5] J. C. Kemp, W. M. Ziniker, and J. A. Glaze, Phys. Letters **22**, 37 (1966). In that paper an unfortunate error was made in interpreting the rotation signals; specifically the factor of two conversion from rotation angle to spinning analyzer signal phase was overlooked. Thus all rotations in the paper and the estimate of λ (given there as -30 cm^{-1}) should be multiplied by one-half.

because some noise other than that of shot-noise type is also present. The sketch of the recorder trace in Fig. 1 is a fair representation of the actual FR-ESR signals we obtained, at typical λ_i covered in Fig. 2, in the present experiment.

C. Calibration Accuracy

The influence of degenerating effects on the rotation signal was discussed previously, with reference to our type of rotation-measuring apparatus.[3] The usual care was taken here to control stray light, including fluorescence, which can effectively attenuate the measured changes in phase angle. In the MgO *F*-band region we had two new problems which had been unimportant at longer wavelengths, namely: (1) Strain birefringence in the Dewar windows, and (2) inhomogeneity in the Polacoat (PL-40) spinning analyzer disk. By the latter we refer to a variation in transmittance (or in transmitted polarized light) over a circular path around the face of the disk (see Fig. 1); this gave a spurious ac signal which competes with the true signal. Though the polarizing efficiency of the Polacoat units remains over 80% out to at least 2300 Å, the net transmittance decreases gradually beyond about 2500 Å, and the effect of any spatial nonuniformity increases. With our best unit we had a maximum ratio of false signal to true signal, from this effect, of about 1:3 at 2300 Å. In the worst possible case this means a systematic error in measured $\Delta\theta$ of some 30%.

Strain in the four fused-silica Dewar windows was the source of wavelength-dependent spurious rotation, plus degeneration of the beam polarization, in this spectral range. This was found to be largely a matter of the type of seal used for the windows, which had been at first cemented with epoxy cement. Fortunately, the outer windows, which were of larger diameter (Fig. 1) and were the main offenders, could be easily resealed with a nonrigid cement, and the problem was greatly reduced, though not eliminated.

A general check of systematic errors in rotation angle measurement due to the above effects was made by plotting the transmitted angle response; that is, the relation between the polarization angle θ_t of the transmitted beam and that of the incident beam, θ_i (Fig. 1), over a variety of conditions. More usefully we plotted the differential angular response $d\theta_t/d\theta_i$; and secondly the over-all differential response of the system $dV/d\theta_i$, where V is the phase-meter output voltage. Ideally, V is a linear function of θ_t, and $2\theta_t$ (relative to some zero) is readable directly on the calibrated meter scale. Deviations of the response $dV/d\theta_i$ from the ideal constant value, as a function of light wavelength and of input angle θ_i, were studied comprehensively. Such analysis helped isolate the worst sources of difficulty, e.g., one usually strained window. Since the effect of sequential birefringences in the several windows (and sample) is somewhat complex, an additional semiquantitative check of the angular response was made by measuring the bulk interband Faraday rotation of crystal samples. All of these observations aided in establishing a fairly reliable calibration of the output readings, and incidentally (and very significantly) in verifying the absolute *signs* of the measured rotation changes. (Under certain conditions, such as when a large spurious signal of appropriate phase due to imperfections in the spinning analyzer is present, the apparent sign of small rotation changes can be reversed.) In the final experimental run from which the data of Fig. 2 are taken, calibration corrections of from near zero to about +30% (obtained from measured deviations of $dV/d\theta_i$), over the range 2300–2800 Å, have been included in the plotted data points. We judge that a residual systematic error of at most ±20% may exist in these data.

It was easily verified that complete saturation of the *F*-center spin resonance was attained in this experiment, so that the induced $\Delta\theta$ values accurately represent θ_{para}. With microwave power from the 100-mW klystron (Fig. 1) "on," reduction of the power by 10 dB gave no noticeable signal change. The "microwave off" condition represents about 60 dB attenuation; additional attenuation from that level gave no significant signal change. The estimated spin-lattice relaxation time (at 1.8°K) was of the order of 1 sec; we did not measure this systematically since it is felt, as in CaO,[3] that T_1 here is dominated by extrinsic, sample-dependent effects of no very fundamental significance. The interaction width in H field, i.e., the width ΔH over which saturation was sustained with full microwave power applied, was several Gauss, which as in the CaO experiments is several times the ESR linewidth.[3]

III. RESULTS AND DISCUSSION

A. Neutron-Irradiated Cystals

Samples used here were neutron-irradiated at or above ambient reactor-core temperatures (Oak Ridge ORR reactor), with *F*-center density of about $6\times10^{17}/\text{cm}^3$. Such samples, in this density range, show the correlation in ESR-determined and optically determined densities studied by Henderson and King.[6]

The curve of θ_{para} of the MgO *F* center, made from FR-ESR signals at discrete λ_i, is shown in Fig. 2, along with the sample absorbance curve. The striking feature is the almost symmetric shape, with central peak sensibly coincident with the peak of the 4.95-eV absorption band. When plotted on a scale linear in energy rather than in λ, the rotation appears even more symmetric than appears in the figure. Any asymmetry in fact is probably within the error bars of the data. The horizontal error in these data, governed by the monochromator resolution (slit width) used, was about ±12 Å and was roughly the same for all points.

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[6] B. Henderson and R. D. King, Phil. Mag. 13, 1149 (1966).

For comparison with the magneto-optic pattern we have sketched a partial resolution of the absorbance curve in Fig. 2, with the F band drawn approximately as a Gaussian. This follows a more detailed numerical resolution by Henderson, King, and Stoneham[7] of the several bands thought to coexist (obviously with variable sample-dependent relative intensities) in this region. For quantitative application we made use of their value $\Gamma = 0.48$ eV for the residual low-temperature F-band half-width; to compute the F-band area (zeroth moment) we used the Gaussian relation $A = a_0\Gamma/[2(\ln 2)^{1/2}] \cong 1.06 a_0 \Gamma$, and took only the peak height a_0 from our hand-sketched resolution. [For the absorbance in Fig. 2 we take $a_0 = (\ln 10) \times 1.35 \cong 3.1$.] It appears that our error in A is not greater than about 15%.

By idealizing the Faraday rotation data with a smooth curve we computed the circular dichroism $b(E)$, essentially the Kramers-Kronig conjugate of $\theta(E)$. Here $b(E)$ is the difference between the absorptions $a_\pm(E)$ for right versus left circularly polarized light, and is simply the sample thickness t times the specific circular dichroism $\beta(E)$ defined in Ref. 3.[8] We have[3]

$$b(E) \cong \frac{4}{\pi} \int \frac{\theta(E')}{E'-E} dE' \qquad (1)$$

and we sketch $b(E)$ in Fig. 2 (for convenience we actually display $\frac{1}{5}b$).

The use of $b(E)$ is to apply the relations of Henry, Schnatterly, and Slichter[9] for the magneto-optic moments. From the first moment relation (ignoring the diamagnetic term)

$$A^{-1} \int (E-\bar{E}) b(E) dE = \tfrac{4}{3}\Delta\langle S_z\rangle = -\tfrac{2}{3}\Delta \tanh(\mu H/kT), \qquad (2)$$

we find from the data of Fig. 2

$$\Delta \cong -18 \text{ cm}^{-1}, \quad \text{or} \quad \lambda = \tfrac{2}{3}\Delta \cong -12 \text{ cm}^{-1}.$$

This result is in essential agreement with the crude estimate made earlier.[5] It is in keeping with the trend noted among the other three alkaline earth oxides,[4] i.e., with λ increasing in magnitude from MgO to BaO.

A very clear feature of the rotation pattern is the relative narrowness. If one had rigid-shift conditions,[2,9] with a Gaussian absorption curve of half-width Γ the separation between the two zeros of $\theta(E)$ should be closely 1.1Γ. For $\Gamma = 0.48$ eV such a separation is 260 Å; the observed value in Fig. 2 is about 175 Å. The quantitative meaning of this is obtained by examining the third moment of the circular dichroism, or specifically the ratio $\langle E_\pm^3\rangle/\langle E_\pm^1\rangle$ between the third and first moments.[9] For a rigidly shifted Gaussian band this ratio is $3\Gamma^2/(8 \ln 2)$. The measured ratio from our $b(E)$ function is smaller than this, if we assume the absorption to be Gaussian with the width $\Gamma = 0.48$ eV; in fact it is rather precisely one-half the rigid-shift value, to within the accuracy of the data. In relation (A25) of Ref. 9,

$$\langle E_\pm^3\rangle/\langle E_\pm^3\rangle_{\mathrm{RS}} = (1+\tfrac{1}{2}x)/(1+x),$$

we conclude that the left-hand side of this relation is approximately 0.5, so that x is very large. Here x is the ratio between the contribution of noncubic lattice modes to the F-band width to that from cubic modes. On the face of it this result argues that the width of the band is almost entirely due to noncubic modes. If this feature is borne out by other types of data, perhaps by direct circular dichroism measurements (which may be more accurate), it will have interesting theoretical implications for the structure of the MgO F center.

B. Additively Colored Crystals

Hensley and his co-workers have recently succeeded in producing good samples of additively colored MgO, using magnesium vapor at relatively elevated temperature and pressure.[10] An astonishing thing about these crystals is that although they appear to show the familiar 4.9-eV absorption band, with intensity increasing monotonically with coloration (Mg vapor pressure), there is no correlating density of F centers as gauged by ESR.[11] In other words, the correlation found in neutron-irradiated crystals appears to fail in these crystals. This observation for a time cast some doubt on the identity of the 4.95-eV band. Subsequently, careful analysis of the absorption line shape under a variety of conditions[12] has resulted in the hypothesis that the band seen in these samples is composite, and that a part (even a large part) of the absorption is due to another species, which is quite probably the F' center: The F and F' bands would thus happen to be almost exactly coincident in MgO. This circumstance, though not an impossible one, would certainly be surprising. Magneto-optic observations on these crystals then had an obvious interest. (Being presumably diamagnetic, F' centers should produce no strong Faraday rotation at liquid-helium temperatures.)

Two samples of MgO:Mg were kindly furnished us by Hensley. From application of Dexter's formula to the 4.9-eV band, with the assumption $f \simeq 1$ and without regard to a possible composite nature of the band, these samples had approximate densities differing by a factor

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[7] B. Henderson, R. D. King, and A. M. Stoneham, J. Phys. B [Proc. Phys. Soc. (London)] 1, 586 (1968).

[8] It is logical to use "per sample" quantities, i.e., rotation θ, (naperian) absorbance a, and circular dichroism b, rather than per unit thickness quantities θ/t, α, and β, since the thickness t does not really enter the computation here. Thus the A we use refers to the F-band area in the sample absorbance curve, and is t times the zeroth moment A of Ref. 9. Note, too, that our circular dichroism $\beta = b/t$ is *twice* the quantity $\alpha_+ - \alpha$ of Ref. 9, as noted in Ref. 3.

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

[10] E. B. Hensley and R. L. Kroes, Bull. Am. Phys. Soc. 13, 420 (1968).

[11] Y. Chen, W. A. Sibley, F. D. Srygley, W. A. Weeks, E. B. Hensley, and R. L. Kroes, J. Phys. Chem. Solids 29, 863 (1968).

[12] L. Kappers and E. B. Hensley (unpublished).

of ten, namely about $1\times10^{17}/\text{cm}^3$ and $1\times10^{18}/\text{cm}^3$, respectively, of centers responsible for the band. The *F*-center densities from ESR, measured at room temperature, on the other hand, were both about the same, about $1\times10^{17}/\text{cm}^3$ for each—exemplifying the lack of correlation.

The MgO:Mg samples were subjected to FR-ESR measurement as in III(A) above, and a clear FR-ESR spectrum was recorded, with the same shape and location as in Fig. 2. This was obtained using the sample with optically determined density $10^{18}/\text{cm}^2$. (Unfortunately, the other sample was of such a size that the expected Faraday rotation was close to our instrument noise level.)

It was evident that the *F* center exists in the MgO:Mg samples, with the same Faraday rotation pattern and therefore the same *F*-band location as in neutron-irradiated MgO. The ***amplitude***, however, of the rotation pattern turned out to be quite anomalous, at least at first sight. With regard to the disparity between the ESR- and optically-determined *F*-center densities, one would predict that the FR-ESR amplitude would follow the ESR-measured density, i.e., $1\times10^{17}/\text{cm}^3$. Remarkably, the signals had approximately the full strength corresponding to the total absorption band intensity, i.e., $10^{18}/\text{cm}^3$. [We, of course, assumed that the same magneto-optic (spin-orbit) coupling obtains as measured in the neutron-irradiated samples.]

This confusing result for the apparent *F*-center density has a logical explanation in the process of *F*-*F′* conversion, analogous to the process observed in CaO:Ca.[13] In the MgO:Mg samples, Kappers and Hensley have been able to detect small changes in the 4.9 eV band shape, upon light stimulation or other treatment[12]; related light-induced changes in the *F*-center ESR intensity are seen, at low temperatures,[14] reminiscent of the photoreaction in CaO:Ca. Specifically, uv light (over a broad band inclusive of the 4.9-eV region) increases the *F*-center density, i.e., promotes $F'\rightarrow F$. At least at helium temperatures the conversion is metastable. The measuring light used in the FR-ESR experiments was of necessity as strong as is available (500-watt xenon lamp, via a monochromator[3]) and is apparently sufficient to induce complete conversion to *F* centers: One has thus a logical explanation of the anomalously strong rotation recorded. Unfortunately, we are not able to monitor the ESR spectrum directly in our FR-ESR apparatus, at least not with the thin samples used in the present experiments.[5,15]

From analysis of the small changes in the optical band shape, and with use of the same general reasoning as in CaO:Ca, it has been suggested that the unresolved *F* and *F′* band maxima in MgO:Mg are at 4.94 and 5.05 eV, respectively,[12] meaning a separation of 50 Å. The resolution of the FR-ESR pattern in Fig. 2 is adequate to discriminate qualitatively between these two values, and clearly substantiates the *F*-band value.

IV. CONCLUSION

The primary aim of this investigation was the further isolation of the *F* band in MgO. We feel the peak location at 4.95±0.03 eV is now at least as well established as are the positions of the *F* bands in the alkali halides. Certain doubts about this assignment which arose from the curious situation in additively colored MgO are now relieved. The explanation for that situation, the apparent excess absorbance in the 4.9-eV band, must now be sought in terms of near coincidence of a second band (presumably the *F′* band); or conceivably in terms of some more obscure cause, such as a severe broadening of some discrete fraction of the *F*-center spins, as from a nearby paramagnetic species.

A second aim was to elucidate the magneto-optic properties of the MgO *F* center, e.g., to measure the spin-orbit parameter with fair accuracy. The near symmetry of the rotation spectrum tends to verify the Gaussian absorption-band shape, consistent with the apparently large Huang-Rhys factor.[7] The interesting result that the primary broadening is from noncubic modes is subject only to the following qualification: This conclusion is based on the use of the observed absorption-band width, actually on the slightly reduced width of a Gaussian represented in a numerical resolution of the spectrum.[7] Conceivably the true *F*-band width is still smaller, and overlap from other bands may not have been adequately allowed for. Independent evidence for the predominant noncubic broadening, as from spectroscopy with applied stress, would be desirable.

ACKNOWLEDGMENTS

The considerable encouragement we received from Professor J. E. Wertz and from W. A. Sibley and Y. Chen, during the course of this work, is gratefully acknowledged. Also we thank Professor E. B. Hensley for providing the MgO:Mg crystals, and Brian Henderson for some lengthy discussions.

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[13] J. C. Kemp, W. M. Ziniker, and E. B. Hensley, Phys. Letters **25A**, 43 (1967).

[14] J. C. Cheng and J. C. Kemp (unpublished).

[15] We have considered studying the light-induced *F*-center density changes by FR-ESR, by monitoring the FR-ESR signal while irradiating the crystal from the side with a second light source. Apart from the complexity of such an experiment, we doubt if anything new would be learned. One would merely be verifying the changes in the *F*-center spin density, which are more readily detected using a standard ESR spectrometer with provision for sample illumination.