them in order to determine his temperature factors, as did Burley. The problem, however, is that they did not use the same oxygen form factors. When we refined Burley's raw data, using Tokonami's form factor for O^{--} instead of O^{-1},[15] the calculation yielded an R factor of 0.64%, which is very close to our own results. Since we are basically in agreement with Togawa,[9] this indicates that the apparent discrepancy between Togawa's and Burley's results originates in their choice of different oxygen form factors in the processing of the data, and not in the data themselves.

CONCLUSION

In agreement with Togawa's conclusions, we find that the second calculation of Yamashita, which includes the 1*s* and 2*s* wave functions of Watson for O^{--} in the +1 well, gives the closest description of the experimental results. This strongly suggests that improvements of the agreement between theory and experiment, particularly in the case of ionic crystals, can be obtained by calculating the wave functions in the crystalline field.

The error of 4.5% subsisting on the 111 line, which is very sensitive to the outer electron distribution, seems still due to the atomic form factors. A new theoretical investigation of the 2*p* wave functions in O^{--} could improve this situation. Such a new result could still be checked, since the experimental technique seems sensitive enough to do it.

ACKNOWLEDGMENTS

The authors are indebted to J. B. Goodenough, T. A. Kaplan, W. H. Kleiner, D. R. Chipman, and L. D. Jennings for numerous helpful discussions. Also, the care brought to the measurements by C. H. Anderson is very much appreciated.

PHYSICAL REVIEW VOLUME 153, NUMBER 3 15 JANUARY 1967

Irradiation-Induced Color Centers in Magnesium Fluoride*

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(Received 3 August 1966)

Color centers, produced by 50-kV x rays, have been studied in the rutile-structured MgF_2, largely at room temperature. An initial, slightly anisotropic, absorption band near 260 nm is tentatively identified as due to F centers. Subsequent optical bleaching results in the formation of a strong band at 370 nm and several weak bands, including one at 320 nm. Both of these appear only for $\mathbf{E}\perp c$ and are believed to be due to M centers. This choice of models is suggested, in part, by the observation of typical trapped-electron ESR spectra in irradiated samples. Bleaching studies show that the 320-nm band arises from centers lying along the $\langle 110\rangle$ directions, while the 370-nm band seems to be cylindrically symmetric about the c axis. Furthermore, the 320-nm band is reversibly convertible into the 370-nm band. Selection rules have been derived for $(ls)^2 \rightarrow (ls2p)$ transitions in each of the four possible M-center configurations permitted in the rutile structure. It is found that of the two types having F-F bonds in the (001) plane, one identifies rather well with the 370-nm band and the other with the 320-nm band.

INTRODUCTION

Magnesium fluoride is an alkaline-earth halide having the rutile structure. Although color centers in several of the cubic alkaline-earth fluorides have been studied extensively,[1] very little effort has been put on the rutile members of the class. In fact, color centers have been investigated largely on cubic crystals, with the alkali halides receiving the most attention.

Several of the absorption bands discussed in this paper have been observed previously by Duncanson and Stevenson[2] and by Hills and McBride,[3] but were studied in less detail, thus not permitting identification with definite models. Much of the current data was presented earlier,[4] but no attempt at interpretation was made at that time. Hills and McBride[3] did, however, suggest an identification of the bands near 260 nm and 370 nm with the conventional F and M centers, respectively, and we shall attempt to demonstrate in this paper that this identification can be supported.

Our interest in the present investigation arose from several considerations. It was apparent that optical-

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* Research supported by the Advanced Research Projects Agency.

[1] A. Smakula, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 729.

[2] A. Duncanson and R. W. H. Stevenson, Proc. Phys. Soc. (London) **72**, 1001 (1958).

[3] M. E. Hills and W. R. McBride, J. Chem. Phys. **40**, 2053 (1964).

[4] R. F. Blunt and M. I. Cohen, Bull. Am. Phys. Soc. **9**, 643 (1964).

absorption bands were readily produced and that these were thermally stable even at room temperature. Also, only a few bands were observed and these proved to be consistently reproducible from samples from a number of different crystals. For these reasons, it was felt that MgF_2 might be a promising material for color-center studies. It was recognized, of course, that the anisotropy of the crystal could lead to complications of interpretation, yet it was hoped that the lower symmetry might actually be helpful, since the principal spectra are relatively simple.

Experimental work discussed here consists for the most part of optical-absorption and optical-bleaching studies made with polarized light on oriented crystals previously colored with 50-keV x rays. A significant addition was the observation of ESR spectra in the colored crystals that rather clearly arose from trapped electrons. Thus the interpretation presented here is based on the simpler, trapped-electron models. To this end, selection rules were derived for *F*-center and *M*-center absorption, assuming the transitions are $(1s)\rightarrow(2p)$ and $(1s)^2\rightarrow(1s2p)$, respectively. It will be shown that the 260-nm band is consistent with the predicted anisotropy of an *F*-center and that the two other most prominent bands at 370 nm and 320 nm exhibit anisotropy consistent with two of the four possible *M* centers.

I. EXPERIMENTAL

Oriented single-crystal samples were cut from larger crystals obtained from a number of sources. Most of the work described here was done on commercial crystals[5] (which we designate as *SE*1, *SE*2, etc.). Boules pulled from the melt by two different groups at the National Bureau of Standards were also employed.[6] One additional crystal was also used briefly.[7]

The samples used appeared to be of excellent quality. Before coloring with irradiation, they exhibited scant evidence of absorption down to below 200 nm (the lowest limit available in this laboratory). Spectrochemical analysis on a piece of boule *B*1 shows Al and Cu in the 0.001–0.01 mole % range with no other metallic impurity above 0.001%. A piece of *SE*1 gave similar results except for a trace of Ti in place of the Cu. The significance of oxygen as an impurity in alkaline-earth fluorides has been emphasized by Guggenheim.[8] However, the measurement of the amount of oxygen in such crystals by chemical means is very difficult. No such measurements were attempted. On the other hand, the infrared spectrum on a typical colored sample was measured and weak bands were found near 3, 6, and 7 μ. These could very well be due to oxygen (or OH^-) and could even involve surface water. However, they are considered to be too weak to be of any significance.

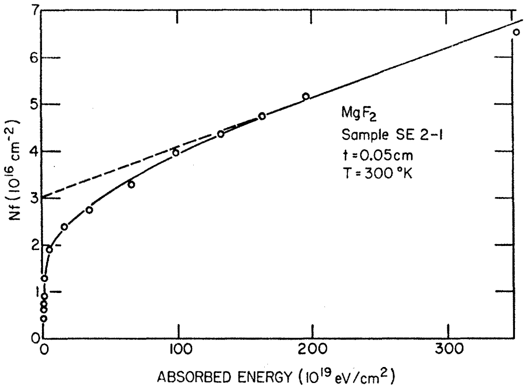

FIG. 1. x-ray saturation curve for an MgF_2 crystal. Nf is plotted as a function of absorbed energy in eV per cm^2, where N is the concentration of centers per cm^3 and f is the oscillator strength. The sample was 0.05-cm thick.

Simple thermal-bleaching experiments on the colored samples were done in which it was found that a brief heating to 500°C removed all observed color centers. It was assumed, then, that a sample so treated is returned to its initial condition prior to irradiation. Finally, it was observed that both of the large bands at 260 and 370 nm show marked thermal stability at room temperature, remaining unchanged, even for months, if kept in the dark. Because of this, room temperature is clearly a useful as well as convenient temperature for the studies which are described here.

A. Irradiation of Samples

Nearly all of the irradiation was done with a 50-keV Be-window tungsten-target tube, and the samples were mounted so as to permit dosages of up to 10^7 R/h. However, a few preliminary experiments were done prior to the use of this arrangement.

A number of slices were prepared from boule *B*1, each about 0.5 mm thick. Some of the these were irradiated with known dosages of x rays in the High Voltage Laboratory of the National Bureau of Standards. They were each given about 0.5×10^6 R irradiation at voltages of 50, 140, and 250 keV. All yielded pronounced absorption bands near 260 nm and weaker bands at 370 nm. The observed spectra were sufficiently similar between samples to preclude definitive conclusions about relative efficiency of color-center production by different radiations. One slice from boule *B*1 was also irradiated with 250-kV electrons. The irradiation was visually observed by means of a fluorescent screen to be largely, though not completely, absorbed in the sample. The accepted conversion factor between electron and x-ray dosage indicated a dosage equivalent to about 2×10^6 R. The resulting color-center

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[5] Obtained from Semi-Elements, Inc., Saxonburg, Pennsylvania.

[6] Crystals designated as *B*1 and *B*2 were grown by the Crystal Growth Section, while those labeled *DER*1, *DER*2, etc. were grown by the Solid State Physics Section.

[7] Obtained from Koch-Light Laboratories Ltd., Colnbrook, England.

[8] H. Guggenheim, J. Appl. Phys. 34, 2482 (1963).

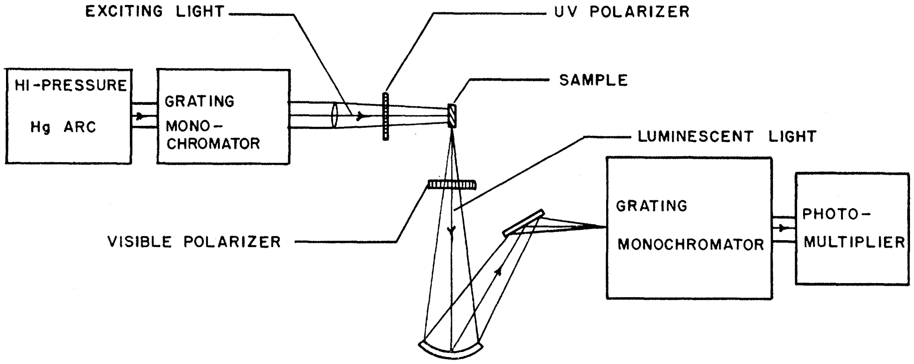

FIG. 2. Diagram of apparatus used for optical bleaching and for observing luminescence.

bands were a very large 260-nm band and a quite definite, now no longer small, 370-nm band. We also found that, in the samples irradiated in our laboratory, the 370-nm band was invariably small, even negligibly so. The reason for this difference is clearly due to the considerably lower sample temperature ($\leq 300°$K) during irradiation in our own facility.

Simple "saturation" experiments were done on samples cut from several boules including *B*2 and *SE*2. Irradiation was performed at room temperature with unfiltered 50-keV tungsten x rays at dose rates up to 10^7 R/h, and produced negligible 370-nm bands. The irradiation was periodically interrupted for measurement of the unbleached 260-nm band. In all cases, a very early apparent "saturation" was obtained, at dosages of the order of 10^6 R. Little increase in the band was noted with increased irradiation. When the Smakula equation was applied to the 260-nm band and an oscillator strength of ~ 1.0 assumed, saturation values of 5×10^{17} and 1×10^{18} centers per cm^3 were obtained, respectively, for *SE*2 and *B*2 samples.

A more extensive saturation experiment was also performed on a 0.05-cm slice of *SE*2. The dosage used was carried out to about 10^8 R. Calibrated glass dosimeters were used to enable reasonable estimates of the irradiation absorbed by the sample as well as the dosage used. The results are shown in Fig. 1. The initial, fast-rising part of such curves is sometimes attributed to the ionization of imperfections initially present, including vacancies and chemical impurities. If that were the case here, then the extrapolation of the subsequent slow-rising "linear" part back to zero would give the concentration of the impurities. As can be seen in Fig. 1, a value of Nf of 3×10^{16}/cm^2 is obtained, or an average value of about 5×10^{17} centers per cm^3 (if $f=1$ is assumed). If one assumes that the slow-rising portion of the curve results from intrinsic damage to the crystal,[9] then the slope is indicative of the energy required to produce the 260-nm center. An energy of 90 000 eV per center is obtained.

The results discussed in this paper were obtained on samples carried well into the saturation region. Aside from the greater strength of bands obtained thereby, spectra essentially the same in appearance as obtained for smaller dosages resulted. We shall assume, therefore, that we are dealing with centers that are intrinsic to the crystal and not related directly to imperfections initially present. In this case, then, the initial imperfections are simply serving as electron traps (or hole traps) such as to facilitate the initial radiation damage, and do not give rise to the bands studied here.

In addition to the irradiation of uncooled samples, several samples that were thoroughly bleached optically were reirradiated. It was found that the 260-nm band was restored to the original value for only a small fraction of the dosage originally required. Also, the bands such as the 320- and 370-nm bands produced by optical bleaching were completely removed.

Although most of the work reported here was done at room temperature, one liquid-nitrogen-cooled sample was irradiated with 50-keV x rays. A rather weak 260-nm band was produced for a dosage that would have given a strong band at room temperature.

B. Optical Absorption and Bleaching

The absorption measurements were made with a commercial double-beam spectrophotometer.[10] When polarized light was required, matched sheet polarizers were inserted in both the sample beam and the reference beam. The loss in transmission and polarizing efficiency of these polarizers is significant only well below 300 nm and permitted absorption spectra to be measured down to 210 nm. Optical bleaching was done with a small grating monochromator equipped with a 200-W high-pressure mercury arc source which provided considerable energy at the wavelengths of the bands studied. This bleaching source is used as the excitation source for the luminescence experiments (Fig. 2) described later. In the bleaching experiments, the same polarizers were used as in the optical-absorption measurements.

Irradiation produces, at room temperature, a strong, slightly anisotropic band near 260 nm. Two components

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[9] P. W. Levy, Phys. Rev. **123**, 1226 (1961).

[10] Cary, Model 14R.

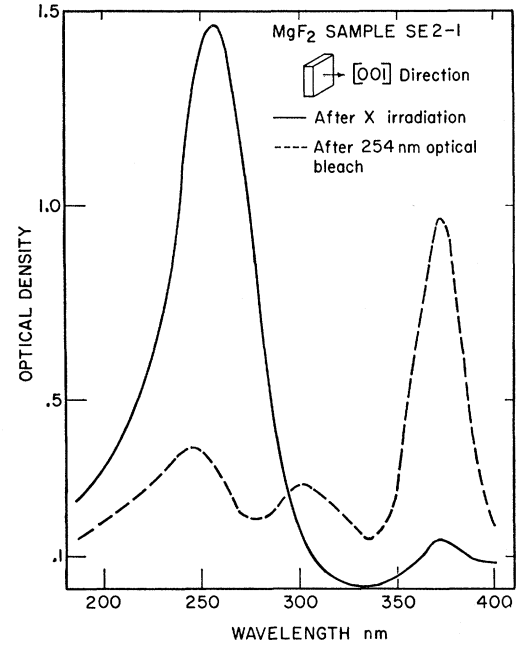

FIG. 3. The optical-absorption spectra of an MgF$_2$ crystal (0.05-cm thick) just after irradiation and just after a subsequent 254-nm optical bleach.

of comparable strength are observed at 255 nm for $\mathbf{E}\perp c$ and at 265 nm for $\mathbf{E}\|c$ on appropriately oriented crystals. The $\mathbf{E}\perp c$ component on an *SE*2 sample is shown in Fig. 3. Although a band is seen at 370 nm, it is quite weak and would have been even weaker had the sample been a few degrees cooler. No other bands have been observed on samples irradiated at room temperature prior to optical bleaching. As mentioned earlier, the 260-nm band is thermally stable at room temperature, but it is readily bleached with the 254-nm mercury light.

Optical bleaching of the 260-nm band produces a strong band at 370 nm and weak bands at 300 and 320 nm. The results of the bleaching are illustrated as the dashed curve in Fig. 3, but the weak bands were not resolved in this particular case. These new bands appear only in $\mathbf{E}\perp c$ spectra, having negligible $\mathbf{E}\|c$ components. Prolonged bleaching does not completely remove the 260-nm band, reducing it to about 10% of its original value. Bleaching in small increments with $\mathbf{E}\|c$ on a sample with polished (110) faces reduced both components apparently proportionately. Similar results were obtained when bleached with $\mathbf{E}\perp c$. This would suggest that the 260-nm band is due to a single center having a slight tetragonal asymmetry relative to the *c* axis, and this center is largely bleached into other centers. The identification of the 260-nm band with an *F* center would require three components rather than the two observed, since the anion has orthorhombic symmetry. This additional splitting could be obscured easily by the large breadth of the components and the over-all tetragonal symmetry of the unit cell.

It was found in subsequent optical-bleaching experiments, that, like the initial 260-nm band, the new 370-nm band also had a high thermal stability at room temperature. The weaker bands at 300 and 320 nm did not, and, in fact, both will decay appreciably in a few hours even when kept in the dark. They are readily bleached optically, and the 300-nm band can be bleached with 300-nm light leaving the 320-nm band. The 300-nm band is completely and irreversibly removed during the course of these bleaching experiments.

We refer again to Fig. 3 in which it is to be noted that results are presented only for $\mathbf{E}\perp c$. The spectra resulting from room-temperature irradiation followed by prolonged bleaching with 254-nm light are shown. Unpolarized 370-nm light was applied and found to enhance appreciably the 300- and 320-nm bands and slightly reduce both the 260- and 370-nm bands. This effect seems to saturate after only a slight reduction in the latter two bands. If unpolarized 313-nm bleaching light is used, the 300- and 320-nm bands are completely removed and the 260- and 370-nm bands are restored to original values. These two effects are reversible and have been so demonstrated a number of times on a single sample without observable loss. Figure 4 shows the two extremes on a *B*2 sample, after the 300-nm band was removed. The symmetry of these centers was further investigated by directional bleaching of the bands.

Preferential-bleaching studies of the 320- and 370-nm bands were done with polarized light on *c*-plane samples (polished faces normal to [001]). Bleaching of the

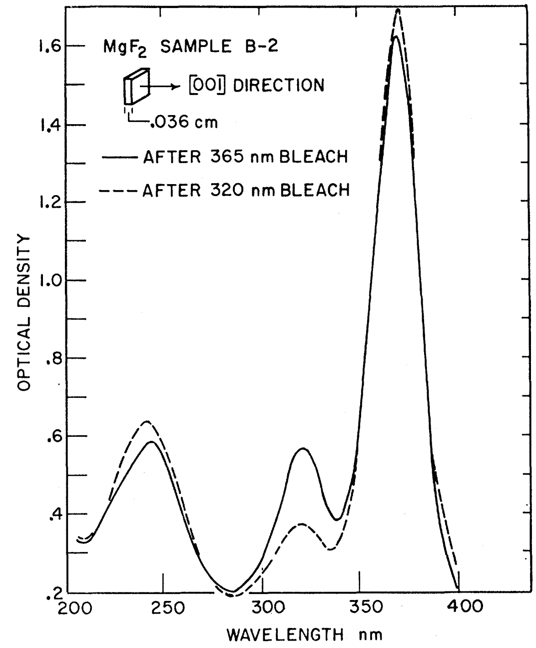

FIG. 4. The optical-absorption spectra of an irradiated and optically bleached MgF$_2$ crystal after successive 365- and 320-nm bleaches.

370-nm band with light having $\mathbf{E}\|[110]$ yielded the same absorption spectra for both $\mathbf{E}\|[110]$ and $\mathbf{E}\|[1\bar{1}0]$. Similar results were obtained for bleaching with $\mathbf{E}\|[100]$ light and measuring absorption spectra with $\mathbf{E}\|[100]$ and $\mathbf{E}\|[010]$. Significant preferential bleaching of the 320-nm band did prove to be possible in these samples, however.

When the 320-nm band was bleached with light having $\mathbf{E}\|[110]$, it was found that the $\mathbf{E}\|[110]$ component was reduced with insignificant loss to the $\mathbf{E}\|[1\bar{1}0]$ component. Bleaching for periods longer than 2 or 3 minutes usually resulted in appreciable reduction of both components. Bleaching with $\mathbf{E}\|[100]$ light, on the other hand, always gave equal reduction of both the $\mathbf{E}\|[100]$ and $\|[010]$ components of the band. These facts are taken as evidence that the centers responsible have significant symmetry axes along a $[110]$ axis, in a manner analogous to the *M* centers in alkali halides.[11] The $\mathbf{E}\|[110]$ bleaching reduces the number of the 320-nm band centers having a unique axis along the $[110]$ direction; however, this illumination has little effect on the number of centers whose axes lie along $[1\bar{1}0]$.

A few measurements were made in a liquid-nitrogen-cooled Dewar. Absorption bands, present at room temperature, are somewhat sharpened and shifted toward shorter wavelengths, the 260-nm band shifting about 10 nm. When optical bleaching was attempted at the lower temperature, little or no bleaching of either the 260- or 370-nm bands was produced, and the 320-nm band was bleached only with some difficulty.

C. Luminescence

Ultraviolet-induced luminescence bands have been observed at ~420 and ~560 nm in the colored crystals. Both are excited by all of the broad lines available from the high-pressure mercury arc below the 405-nm line. On the other hand, light of the 405- and 436-nm mercury lines excite only the yellow, 560-nm band. The yellow band appears to be isotropic while the 420-nm band has been shown to be excited principally by light having $E\perp c$. Moreover, this band is very strongly polarized with $E\perp c$, probably cylindrically symmetric about the *c* axis.

The experiments were performed as indicated in Fig. 2, viewing the luminescence in a direction normal to that of the exciting light. A sample having large polished (001) planes, excited along the *c* axis, shows bands essentially independent of the state of polarization of the exciting light. The resulting 420-nm band has a ratio of $\mathbf{E}\perp c$ to $\mathbf{E}\| c$ components of at least 4:1 as measured by the detector. On the other hand, the 560-nm band is essentially isotropic. A typical luminescence spectrum for 365-nm excitation is shown in Fig. 5. Scattered exciting light is seen on the short-wavelength side of the 420-nm band. A photomultiplier with an *S*-1 response was used, and the spectrum shown is not corrected for the spectral efficiency of the detecting system. The polarization inherent in the detecting system was found to be appreciable, but is rather insignificant compared with the results reported here.

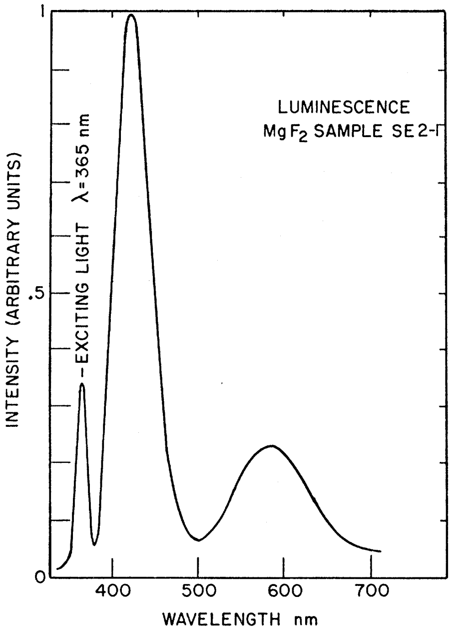

FIG. 5. Luminescence spectra of an MgF_2 crystal showing the 420- and 560-nm bands and scattered exciting 365-nm light. The curve is not corrected for photomultiplier spectral sensitivity.

A sample was also mounted with the *c* axis normal to the plane of Fig. 2 and the exciting light directed along the $[110]$ axis. In this case, it was found that the luminescence for both bands was markedly weaker for exciting light having $E\| c$ than for $E\perp c$, and, as before, the 420-nm band was strongly polarized with $E\perp c$.

It became apparent, during these bleaching experiments, that the strength of the luminescent bands is directly related to the intensity of the absorption bands. Little quantitative data was taken, but it was visually obvious. The luminescence produced by the initial 254-nm bleaching light visibly weakens as the initial 260-nm band is being reduced. The luminescence excited by 365-nm light increases considerably as the 370-nm band builds up during the course of the above bleach. As expected, the luminescence produced during the bleach of the 320-nm band decreased along with the rapid decrease of the absorption band.

A sample, whose luminescence had previously been studied at room temperature, was also examined in a liquid-nitrogen-cooled Dewar. The luminescent bands were sharpened a bit, but otherwise no significant change was seen. Consequently, all subsequent work was done at room temperature.

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[11] W. D. Compton and H. Rabin, Solid State Phys. 16, 121 (1965).

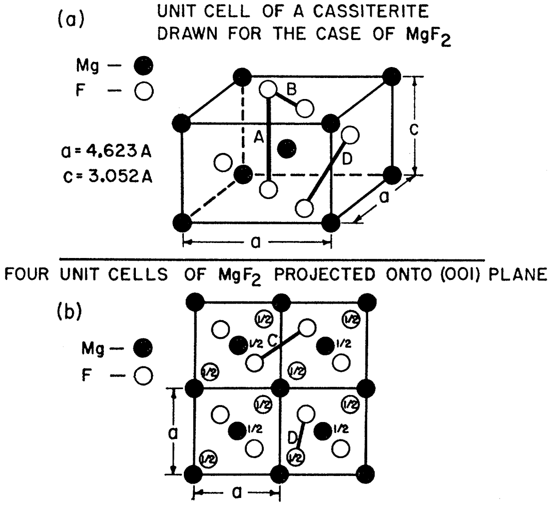

FIG. 6. The cassiterite structure of MgF_2. The F-F bonds for the four possible types of M centers are indicated.

D. Electron-Paramagnetic-Resonance Spectra

Colored samples have been studied at liquid-helium temperature.[12] The spectrum is quite complicated, as would be expected from the crystal symmetry alone, but is quite clearly derived from trapped electrons (g factor ≤ 2.00). Hall has also observed similar spectra in irradiated MgF_2.[13] This very strongly suggests that we are dealing here with trapped-electron color centers, though the correlation of the ESR spectra with the optical bands is by no means proved. We shall assume that trapped-electron centers are responsible for the observed optical bands. Since the principal bands exhibit over-all thermal stability at room temperature, it follows, then, that trapped-electron centers are responsible for all bands.

II. DISCUSSION OF MODELS

In attempting to identify the observations reported here with definite models, a comparison with accepted color-center models in other materials is useful. One obvious comparison is with the cubic (fluorite-structure) alkaline-earth fluorides, such as CaF_2, SrF_2, and BaF_2. Each of these crystals frequently shows two prominent bands. If the positions of these bands are plotted for each crystal as a function of the lattice constant, two smooth curves result. Görlich and Karras[14] give such a plot on which the corresponding smooth curve for the F centers of many alkali halides is also drawn. The rutile structure of MgF_2 precludes any sensible choice of lattice constants to make a comparison possible. Likewise, it is not possible to apply the Ivey[15] relation to aid in the identification of the centers.

The results obtained from the ESR spectra are considered as crucial, however, since they require an interpretation in terms of the trapped-electron models. No effort will be made here to discuss the mechanisms involved in the formation of the centers other than to point out that the results of the saturation experiments suggest the formation of anion vacancy-interstitial pairs by the initial irradiation. These could very well be formed by a mechanism such as that proposed by Klick,[16] for example. Also, no effort be made to discuss the mechanisms involved in the bleaching of one band to form other bands. The luminescence band near 420 nm seems to be associated with the 370-nm absorption band, but the nature of this correlation is not clear at this time. Thus no conclusion can be drawn from this data. The assumption will be made that the three principal absorption bands are due to F centers and the simplest F-aggregate center, namely, the M center consisting of two adjacent F centers.[17] Frequent reference will be made to the survey article of Compton and Rabin[11] on F-aggregate centers in alkali halides in the discussion of the results. Interpretation is based, for the most part, on a comparison of defect symmetries deduced from the polarized-light studies with the F- and M-center symmetries permitted by the crystal structure.

It can be seen from the cassiterite structure of MgF_2, as shown in Fig. 6, that the symmetries of the possible F and M centers are quite different from those for the analogous alkali-halide centers. It is obvious that there are two kinds of equivalent anion sites, each having orthorhombic C_{2v} symmetry. One has the unique C_2 rotation axis along the [110] direction, the other along the $[1\bar{1}0]$ axis. The M-center picture is somewhat more complex. There are four different types of possible M centers, each having different symmetry.

A pair of adjacent anion sites lying along the c axis also has C_{2v} symmetry, and two kinds occur having the single unique C_2 axes along the [110] and $[1\bar{1}0]$ directions, respectively. The M centers formed by two F centers so located can be called the $M(C_{2v})$ center, and the corresponding F-F "bond" is identified by A in Fig. 6. A second type of M center, which will be called a $M(D_{2h})$ center, can be formed from adjacent anion sites lying in the top plane of the unit cell along the [110] axis, and has orthorhombic D_{2h} symmetry. This type is identified by B in the unit cell. Likewise, equivalent $M(D_{2h})$ centers could be formed along the $[1\bar{1}0]$ direction. The three C_2 axes for the $M(D_{2h})$ center lie along [110], $[1\bar{1}0]$, and [001] directions.

Another possible type, which will be called the $M(C_{2h})$ center, would be formed from the adjacent

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[12] Te-Tse Chang of this laboratory.

[13] T. P. P. Hall (private communication).

[14] P. Görlich and H. Karras, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961) (Academic Press Inc., New York, 1961), p. 703.

[15] H. Ivey, Phys. Rev. **72**, 341 (1947).

[16] C. C. Klick, Phys. Rev. **120**, 760 (1960).

[17] C. Z. van Doorn and Y. Haven, Philips Res. Rept. **11**, 479 (1956).

TABLE I. Selection rules governing possible M-center transitions from a $(\sigma_g 1s)^2$ ground-state configuration to the indicated excited-state configurations. Unless otherwise indicated, the entries give the direction of the dipole moment for the allowed transition.

		Type A	Type B	Type C	Type D
	$F(C_{2v})$[b,c]	$M(C_{2v})$[c]	$M(D_{2h})$[c]	$M(C_{2h})$[d]	$M(C_1)$[e]
		$[F-F]\Vert[001]$	$[F-F]\Vert[110]$	$[F-F]\Vert[110]$	$[F-F]\Vert[011]$
M-center excited-state configuration	$x\Vert[1\bar{1}0]$ $y\Vert[001]$ $z\Vert[110]$	$x\Vert[1\bar{1}0]$ $y\Vert[001]$ $z\Vert[110]$	$x\Vert[1\bar{1}0]$ $y\Vert[001]$ $z\Vert[110]$	$z\Vert[001]$	
$(\sigma_g 1s\sigma_g 2s)$[a]	[110] for 2s excited state	[110]			
$(\sigma_g 1s\sigma_u 2s)$[a]		[001]		$\perp[001]$	all
$(\sigma_g 1s\sigma_g 2p)$		[110]			transitions
$(\sigma_g 1s\pi_u 2p)$	[110] $[1\bar{1}0]$	$[1\bar{1}0]$ [110]	[001] $[1\bar{1}0]$	$\perp[001]$ [001]	allowed
$(\sigma_g 1s\pi_g 2p)$	[001] for $2p$ excited state	[001]			
$(\sigma_g 1s\sigma_u 2p)$		[001]	[110]	$\perp[001]$	

[a] $2s$ final states included for completeness.
[b] F center included for completeness. Molecular orbital classifications do not apply.
[c] Two orientations occur, the second kind with x and z interchanged.
[d] Four orientations occur, one set of two with F-F bonds approximately along [110], the other two approximately along $[1\bar{1}0]$.
[e] Sixteen possible orientations lying along the approximate [011] axes.

pairs of anion sites lying along approximate [110] axes that have monoclinic C_{2h} symmetry. One of these is identified by C in the figure. Without distortion, this bond makes an angle of approximately 11° with the [110] axis. There are four different kinds of $M(C_{2h})$ centers possible, two 11° off the [110] axis but in opposite directions, and two similarly displaced from the $[1\bar{1}0]$ axis. All four have their unique C_2 axes along the c axis of the crystal. The fourth type of M center has the triclinic C_1 symmetry and is called the $M(C_1)$ center; it is identified in the figure by D. The F-F bond lies along approximate [011] axes. There are sixteen kinds of these $M(C_1)$ centers.

In all cases discussed, a distortion of the lattice around the centers can be expected. The reasonable assumption can be made, however, that the symmetry classifications such as C_{2v}, D_{2h}, etc. still apply to any center actually formed independent of the distorted environment.

The general approach used in several efforts made recently at calculating the absorption energies for the M centers has been to draw an analogy between the M center and the hydrogen molecule. Thus the ground state is assumed to have the electronic configuration $(\sigma 1s)^2$, while the lowest two excited states would be $(\sigma 1s\sigma 2p)$ and $(\sigma 1s\pi 2p)$. One example of such calculation is that of Meyer and Wood[18] made on LiF and LiCl, in which case the M center could be expected to have the D_{2h} symmetry. Although not of direct application here, this work did illustrate the direction that could be taken in discussing the symmetries involved here.

We have derived selection rules for electric dipole transitions from the ground state to the various lower excited states indicated in the previous paragraph. This has been done for each of the four types of M centers possible in MgF_2; also included are the $1s \rightarrow 2s$ and $1s \rightarrow 2p$ transitions for the F center. The results are summarized in Table I. The $2s$ cases are included only for completeness, but are not essential to the arguments presented.

The proposed transitions—even in the case of the M center—involve the promotion of only one of the two trapped electrons from the ground state. In the molecular-orbital scheme, then, the symmetry of the various states can be adequately described by considering appropriate s or p orbitals on the sites. In general the p orbitals can be characterized by a σ orbital lying along the F-F bond and two π orbitals normal to it—all three being coincident with appropriately defined coordinate axes; actually each orbital configuration can occur in both even and odd parity, so that there are six $2p$ states as listed in Table I. The ground state will be taken to have the $(\sigma_g 1s)^2$ configuration, counting both electrons.

We consider first the single F center, choosing appropriate axes as listed in Table I. It is easily seen by standard group-theoretical methods that the $2p$-orbital triplet is split into singlets by the C_{2v} environment and that transitions to all three from the s ground state are allowed. Since there are two equivalent kinds of F centers, as previously described, one could expect two bands with $E\perp c$ and one band for $E\Vert c$. We wish to identify the initial band near 260 nm as being an F center. The splitting and linewidths are such as to exhibit slight anisotropy, rather than three bands, as allowed.

One of the two equivalent kinds of $M(C_{2v})$ centers is described in Table I. The lack of inversion symmetry

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[18] A. Meyer and R. F. Wood, Phys. Rev. 133, A1436 (1964).

in the C_{2v} environment eliminates parity as a "good" quantum number. Thus all but one of the six listed $2p$ transitions are allowed. The directions of the dipole moments for the allowed transitions are tabulated. It is to be noted that both σ_u and π_g bonding orbitals allow $\mathbf{E}\|c$ components, and this makes the $M(C_{2v})$ model inconsistent with the observed 320- and 370-nm absorption bands.

One would expect that the σ bonding orbitals would correspond to lower lying states than the π orbitals. As discussed by Compton and Rabin,[11] the π orbitals "point" away from the F-F bond and tend to interact more strongly with an environment not too different from the normal F center. Thus the low-energy M band would be accompanied by one (or more) at higher energies sometimes referred to as the M_F band; often this band is difficult to distinguish from the F band. We wish to identify a low-energy MgF_2 band such as the one at 320 or 370 nm with a σ bond orbital state. The observed 320- and 370-nm bands are inconsistent with the allowed $\mathbf{E}\|[001]$ transition to the σ orbital of the $M(C_{2v})$ center. All models allow both $\mathbf{E}\|c$ and $\mathbf{E}\perp c$ transitions to π orbitals.

The $M(D_{2h})$ center, described in Table I, has an environment with inversion symmetry, and parity is conserved. Only the two π_u and the σ_u final states are allowed. For the aforementioned reasons, we would expect one low-energy dipole transition with $\mathbf{E}\perp c$ for a single center. The weak 320-nm band produced in MgF_2 could thus be identified with this low-lying σ_u state. Both have the same well-defined [110] direction. Since two equivalent kinds of sites exist which have [110] and $[1\bar{1}0]$ axes interchanged, the observed preferential bleaching could be expected. Nothing can be concluded about possible higher states of the 320-nm band owing to the somewhat larger accompanying 260-nm band. On the basis of the above reasoning it is concluded that the 320-nm band stems from the $M(D_{2h})$ center.

Since the $M(C_{2h})$ centers also have inversion symmetry, only odd-parity configurations are allowed for the excited states involved in the transitions. The resulting polarization would be quite different from that of the $M(D_{2h})$ centers. Strictly speaking, the C_{2h} symmetry will not permit the classification of $2p$ molecular orbitals as pure π or pure σ as indicated in Table I. One $(\pi_u 2p)$ orbital can be formed along the c axis. [All four kinds of $M(C_{2h})$ centers have this same unique C_2 rotation axis.] The second $(\pi_u 2p)$ orbital and the $(\sigma_u 2p)$ orbital as ordinarily drawn are permitted to mix, since both have the same irreducible representation in C_{2h} symmetry. Appropriate molecular orbitals could be formed by a slight rotation about the [001] axis of the atomic orbitals from which they are formed. They will still be invariant on reflection with respect to the (001) plane, however. The resulting distorted $(\sigma_u 2p)$ molecular orbital would be expected to lie below the $(\pi_u 2p)$ orbital as before.

As a result of the above distortion, we no longer expect a zero transition probability for $\mathbf{E}$ normal to the F-F bond, in the case of the σ orbital. Further, the four different kinds of $M(C_{2h})$ centers have F-F axes lying 11° off the $\langle 110\rangle$ axes. Thus, it would seem most unlikely that a successful preferential-bleaching experiment could be performed on this center so as to remove apparent cylindrical symmetry; however, the $M(D_{2h})$ center would respond appropriately to such a bleaching procedure. We therefore wish to identify the $M(C_{2h})$ center with the observed band at 370 nm. The 370-nm band arising from the σ bond as described above and the two higher lying π bonds contribute strongly to the residual 260-nm band.

The $M(C_1)$ center can be readily rejected as all transitions are allowed and also because the 16 different orientations permitted offer "pseudo" σ bonds that would have appreciable components along the [001] axis. This situation would simply not permit the anisotropy observed for the 320- and 370-nm bands.