F^+ and F' Centers in Magnesium Oxide*

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Single crystals of MgO have been additively colored by heating them in Mg vapor at temperatures from 1600 to 1800°C and pressures up to 4000 Torr. The F^+ and F' optical absorption bands (due to anion vacancies containing one and two electrons, respectively) were observed to be extremely similar but distinguishable, and were observed at liquid-nitrogen temperature to peak at 4.96 and 5.03 eV, respectively. The oscillator strength for the F' center is estimated to be 0.70 ± 0.05. A photoconversion process $F^+ \leftrightarrow F'$ was studied. The luminescence bands for these centers were observed at 3.1 and 2.4 eV, respectively. The density of F' centers $N_{F'}$ produced by the additive coloring process was observed to be related to the density of atoms in the vapor N_{Mg} by the equation $N_{F'}=1270N_{\mathrm{Mg}}\,e^{-Q/kT}$, where $Q=1.53$ eV. The temperature dependence of these two bands was measured and is discussed.

I. INTRODUCTION

THE search for the F^+ and F' centers[1] in MgO, that is, the oxygen ion vacancies containing one and two electrons, respectively, has had a long and frustrating history. The ESR spectrum of the F^+ center was first identified by Wertz *et al.*[2] in neutron-irradiated MgO. This resonance was later correlated with the optical absorption band at 5.0 eV in neutron-irradiated crystals.[3,4] Further confirmation that the 5.0-eV absorption band is due to the F^+ center has been obtained by combined ESR and Faraday rotation studies.[5,6]

Weber[7] attempted to additively color MgO by heating crystals at 1150°C in Mg vapor. Although he achieved partial success, from the present investigation it is now known that the temperature he used was far too low to achieve equilibrium. Techniques which we have previously reported,[8] and which were successful in producing F' centers in CaO[9] and SrO,[10] have been used to produce F' centers in MgO, and their density has been determined as a function of the coloring temperature and Mg vapor pressure.[11] The absorption band for this center also peaked at about 5.0 eV and was almost indistinguishable from the F^+ band observed in the neutron-irradiated crystals. This remarkable similarity of the F^+ and F' bands led to an initial uncertainty regarding the correctness of the identifications.[12] In this paper we will show that the two absorption bands are indeed quite similar although distinguishable and that for low additive coloring densities, an $F^+ \leftrightarrow F'$ photoconversion process exists. The luminescence bands for these centers were observed to be well separated.

II. EXPERIMENTAL DETAILS

The crystals used in this investigation were produced by W. & C. Spicer, Ltd., St. Mary's Winchcombe, England. Spectroscopic analysis of these crystals showed an impurity content of about 10 ppm Ca and Al and 1 ppm Si, Fe, and Cu. The crystals used were about 4 mm square and from 0.1 to 1 mm thick. Prior to coloring, all crystals were annealed in vacuum at 1500°C for several hours. After polishing, using 0.3-μ Alpha Micropolish, the optical density of each crystal was measured. This was subtracted from the optical density of the colored crystals before calculating the optical absorption constant. Although this procedure partially corrects for the reflectivity of the samples, it is recognized that this is not entirely satisfactory since multiple reflections may be present in the uncolored crystals but not in the colored crystals.

Crystals were additively colored by heating them at temperatures from 1600°C to slightly over 1800°C in Mg vapor at pressures up to 4000 Torr. The procedures used have been described in a previous publication.[8] The pressure of the Mg vapor was determined from the temperature of the Mg metal in the bottom of the coloring bomb using vapor pressure data assembled by Nesmeyanov.[13] The density of atoms in the vapor at the temperature of the crystal was then calculated using the ideal gas law.

Crystals were neutron irradiated in the UMC Research Reactor. They were enclosed in a quartz ampoule

* Work supported by the U. S. Office of Naval Research and the National Science Foundation.
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[1] In a review paper of defects in the alkaline-earth oxides, B. Henderson and J. E. Wertz [Advan. Phys. **17**, 749 (1968)] suggest using F^+ and F centers to designate vacancies containing one and two electrons, respectively. In most of the previous literature these centers were designated F and F' centers, respectively. To avoid the resulting ambiguity of F center, we use F^+ and F', respectively, for these two centers.
[2] J. Wertz, P. Auzius, R. Weeks, and E. Silsbee, Phys. Rev. **107**, 1535 (1957).
[3] J. Wertz, G. Saville, L. Hall, and P. Auzius, Proc. Brit. Ceram. Soc. **1**, 59 (1964).
[4] B. Henderson and R. D. King, Phil. Mag. **13**, 1149 (1966).
[5] J. C. Kemp, W. M. Ziniker, and J. A. Glaze, Phys. Letters **22**, 37 (1966).
[6] J. C. Kemp, J. C. Cheng, E. H. Izen, and F. A. Modine, Phys. Rev. **179**, 818 (1969).
[7] H. Weber, Z. Physik **130**, 392 (1951).
[8] E. B. Hensley, W. C. Ward, B. P. Johnson, and R. L. Kroes, Phys. Rev. **175**, 1227 (1968).
[9] W. C. Ward and E. B. Hensley, Phys. Rev. **175**, 1230 (1968).
[10] B. P. Johnson and E. B. Hensley, Phys. Rev. **180**, 931 (1969).
[11] E. B. Hensley and R. L. Kroes, Bull. Am. Phys. Soc. **13**, 420 (1968).
[12] Y. Chen, W. A. Sibley, F. D. Srygley, R. A. Weeks, E. B. Hensley, and R. L. Kroes, J. Phys. Chem. Solids **29**, 863 (1968).
[13] An. N. Nesmeyanov, *Vapor Pressure of the Elements* (Academic, New York, 1963).

which was in turn enclosed in an aluminum can. The irradiation was in the reflector region of the core where the high-energy flux (>1 MeV) was about 3×10^{12} neutrons cm^{-2} sec^{-1}.

Luminescence measurements were carried out with the crystal mounted in a special Dewar. The outer wall of the Dewar was a 49-mm quartz tube and the inner wall was a 19-mm stainless-steel tube. The crystal was mounted on a copper block on the bottom end of the inner tube. The crystal was irradiated perpendicular to its face through the quartz wall of the Dewar using a Bausch and Lomb Model No. 33-86-25-01 grating monochrometer with a Model No. 33-86-35-01 deuterium light source. The luminescence was measured along a line parallel to the face of the crystal. The light was passed through a Perkin Elmer Model No. 83 quartz monochromater and was detected by an EMI 558 photomultiplier tube cooled to dry ice and acetone temperature. The detection system was calibrated using an Electro Optics Associates type L 101 Spectra Irradiance Standard.

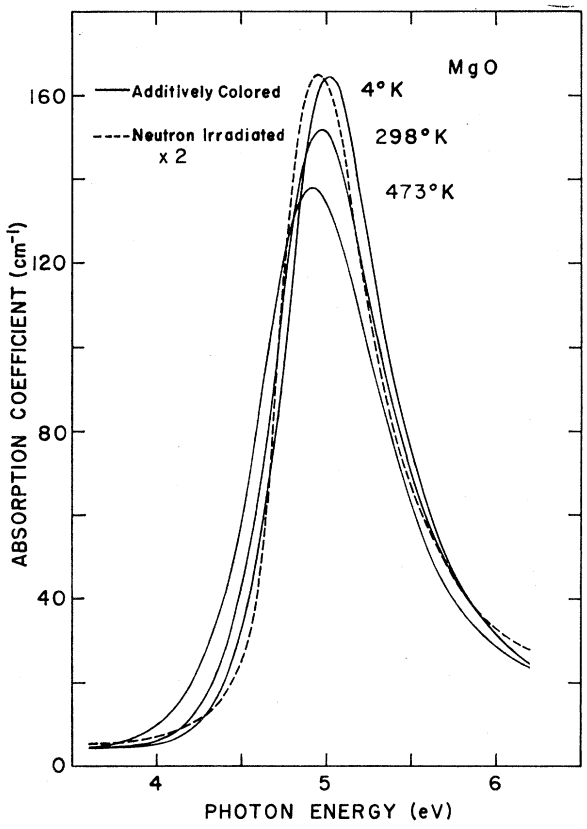

FIG. 1. Induced optical absorption spectra of an additively colored MgO crystal measured at three different temperatures. The crystal was additively colored in Mg vapor at 1800°C at a pressure of 1300 Torr for 1 h. The band is attributed to absorption by F' centers. For comparison the dashed curve is the 4°K curve from Fig. 7 of a neutron-irradiated crystal which is attributed to absorption by F^+ centers.

III. ADDITIVE COLORATION

In Fig. 1 is shown the optical absorption induced in an MgO crystal additively colored in Mg vapor. As discussed in Sec. IV, this absorption band is attributed to F' centers.

In Fig. 2, the densities of the F' centers versus the density of atoms in the Mg vapor are shown for several crystals colored at 1612 and at 1813°C. The densities of the F' centers were obtained from the absorption maximum and width at half-maximum, using the Gaussian form of Smakula's formula.[14] The index of refraction used was 1.85, and the oscillator strength was assumed to be 0.7. It will be noted that for a given density of atoms in the vapor, the density of F' centers increases with higher temperatures and also that the density of F' centers is lower than the density of

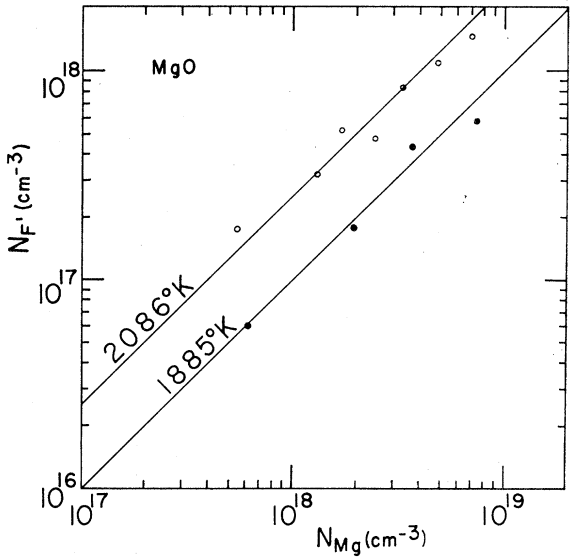

FIG. 2. Equilibrium density of F' centers $N_{F'}$ plotted as a function of the density of atoms in the vapor N_{Mg} for two different temperatures.

atoms in the vapor. Both of these are the reverse of the situation for SrO.[10] As a consequence, much higher temperatures and pressures were required to color MgO than was the case for any of the other oxides.

For thermal equilibrium, the density of F' centers $N_{F'}$ in the crystal should be related to the density of atoms in the vapor N_{Mg} by the equation[15]

$$N_{F'}/N_{Mg}=Ce^{-Q/kT},$$

where C is a slowly varying function of the temperature which will be treated as a constant, k is Boltzmann's constant, and Q is the energy of formation of the color centers. In Fig. 3, the ratio of the densities $N_{F'}/N_{Mg}$ for

[14] D. L. Dexter, Phys. Rev. **101**, 48 (1956).

[15] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystal* (Clarendon Press, Oxford, England, 1940), p. 144.

the data in Fig. 2 has been plotted as a function of the reciprocal of the temperature on a semilog graph. The two open points represent the ratios depicted by the straight lines in Fig. 2. Also data for one additional crystal colored at an intermediate temperature are shown. From the slope of the straight line in Fig. 3 the energy for F'-center formation is found to be $Q=+1.53$ eV. Thus the reaction for MgO is observed to be endothermic where as for SrO it was observed to be exothermic.[10]

IV. IDENTIFICATION OF F^+ AND F' BANDS

At the time we were performing the measurements on the F' band we were aware that others had identified an

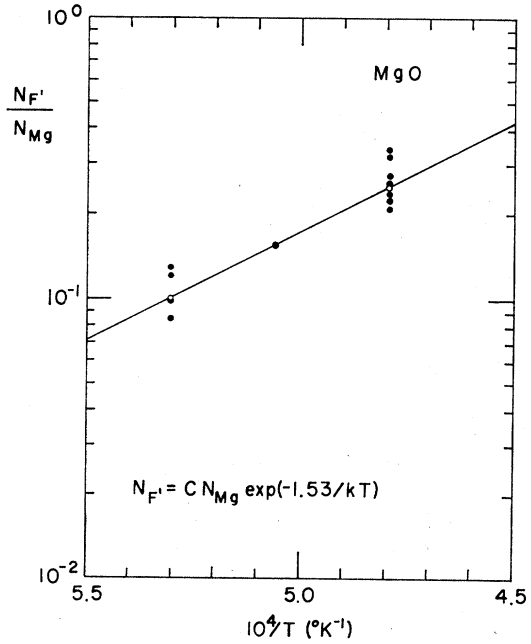

FIG. 3. Ratio of the equilibrium density of F' centers $N_{F'}$ to the density of atoms in the vapor N_{Mg} plotted as a function of the reciprocal temperature. The two open points represent the ratios depicted by the straight lines in Fig. 2.

absorption band that appeared to be identical to our F' band as being the F^+ band.[2–6] It was found that when the band was produced by neutron irradiation, the density of F^+ centers as determined by ESR was in excellent agreement with the density of centers determined from the optical data. On the other hand, essentially no F^+ centers were detected by ESR using additively colored crystals. Electron irradiation produced an intermediate result.[12] Although it was with great reluctance, we were finally forced to conclude that the F^+ and F' optical absorption bands were nearly identical in position and shape.

In an effort to observe directly any differences between the F^+ and F' absorption bands, we decided to attempt to observe an $F' \rightarrow F^+$ photoconversion process

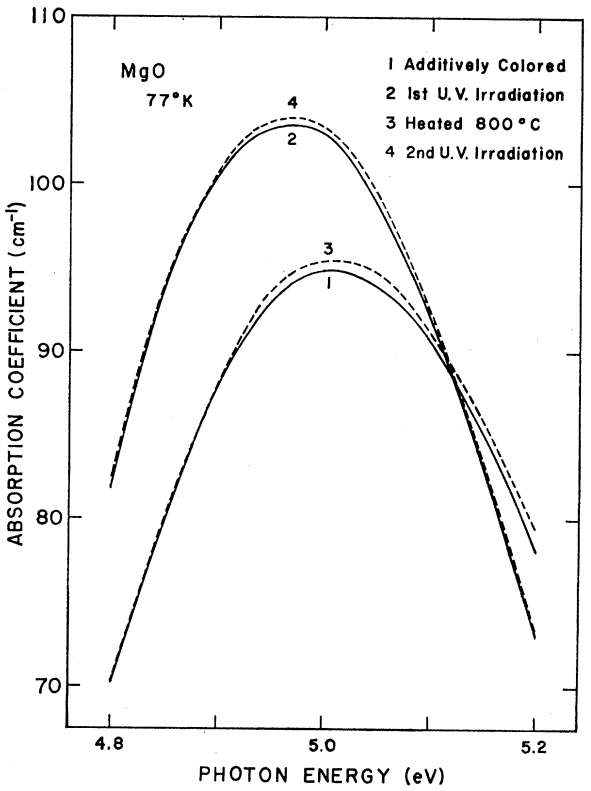

FIG. 4. Absorption spectra illustrating the reproducibility of the $F' \rightarrow F^+$ photoconversion process. Curve 1 shows the upper portion of the F' band of the initial additively colored crystal. Curve 2 shows the shift in the absorption spectra as a result of irradiation with 250-nm light. Heating to 800°C restores the spectra to its original state as shown by curve 3. The result of a second ultraviolet irradiation is shown by curve 4.

similar to that we had observed in CaO.[16] As we now understand that process[17] most of the color centers are in the F' state when the crystal is in thermal equilibrium. Irradiation with light in the F' band results in electrons being released to the conduction band from which some of them become trapped in impurity centers. This results in a decrease in the F' band and the growth of the F^+ band. The effect saturates when all of the impurity sites are filled. Irradiation at longer wavelengths or even more effective, heating the crystal results in the restoration of the F' band and the decrease or disappearance of the F^+ band.

The existence of a similar photoconversion process in MgO is illustrated in Fig. 4. Curve 1 shows the peak of the optical absorption after additive coloration. Curve 2 shows the absorption after the crystal had been irradiated for about 10 min with a Bausch and Lomb deuterium light source. Heating the crystal to 800°C resulted in a blue thermoluminescence. After this luminescence had ceased, the optical absorption was

[16] J. C. Kemp, W. M. Ziniker, and E. B. Hensley, Phys. Letters **25A**, 43 (1967).
[17] D. L. Packwood and E. B. Hensley (unpublished).

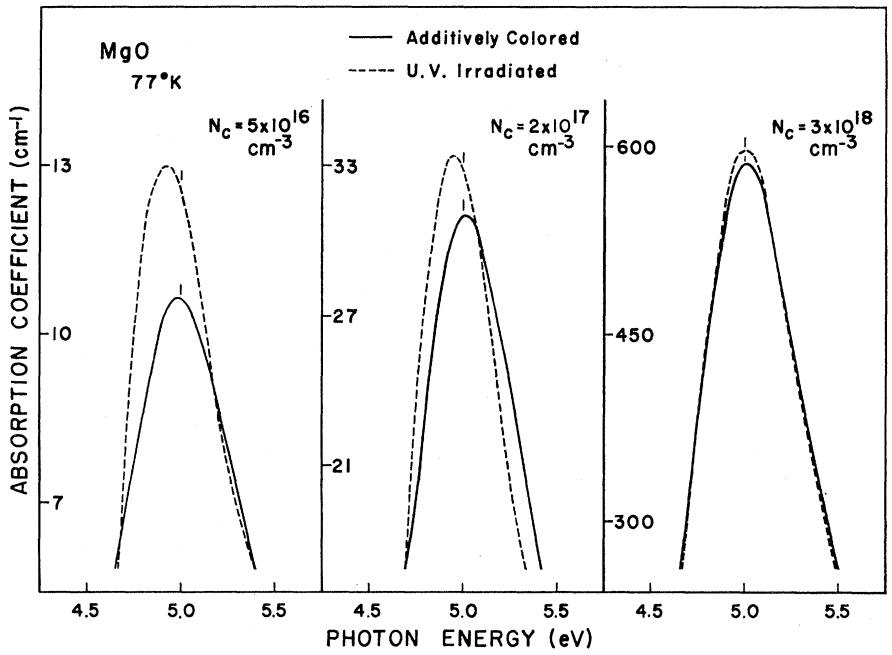

FIG. 5. Photoconversion process as observed in three crystals with different densities of F' centers. The solid curves represent the spectra in the initial F' state. The dashed curves show the result of 250-nm irradiation.

observed to have returned ot its initial state as shown by curve 3. A second ultraviolet irradiation again put the crystal in its photoconverted state as shown by curve 4. The crystal could be cycled between these two states repeatedly. When the crystal was in the F' state (curves 1 and 3) no F^+ centers could be detected by ESR; however, with the crystal in the photoconverted or F^+ state (curves 2 and 4) a strong F^+-center resonance was observed. It is important to note that prolonged exposure of additively colored crystals to room light can result in the photoconversion of F' to F^+ centers.

According to the above description of the photoconversion process, the effect should be most pronounced for lightly colored crystals. Figure 5 shows the effect of ultraviolet irradiation on three crystals with different levels of coloration. The effect is seen to be most pronounced on the lightly colored crystal with only a slight effect on the heavily colored crystal. The position and shape of the F^+ peak in lightly colored, fully converted crystals are in good agreement with those of the F^+ peak in neutron-irradiated crystals.

V. OSCILLATOR STRENGTH OF THE F' CENTER

From Smakula's formula, the density-of-color centers N times the oscillator strength f is proportional to the maximum absorption α_m times the half-width H. If the photoconversion of a lightly colored crystal completely converts the F' centers to F^+ centers, then the ratio of the oscillator strengths $f_{F'}/f_{F^+}$ will be equal to the corresponding ratio of the $\alpha_m H$ products for the two bands. These ratios were observed to decrease with the decreasing density of coloration and to level off at a value of about 0.87 for $N<10^{17}$ cm^{-3}. Henderson and King[4] estimated the oscillator strength of the F^+ center in MgO to be 0.8. Using this value, we estimate the oscillator strength of the F' center to be 0.70 ± 0.05.

Chen *et al.*[18] recently reported a value of 1.25 ± 0.15 for the oscillator strength of the F' center. This value is consistent with Fig. 1 in their paper which shows α_m decreasing following conversion to the F^+ state. However, we believe this result to be anomalous and are at a loss to explain it. Without exception, we have observed that α_m increases following conversion to the F^+ state as shown in Figs. 4 and 5.

VI. LUMINESCENCE OF F^+ AND F' CENTERS

Figure 6 shows the luminescence spectra observed from neutron-irradiated and additively colored crystals. The luminescence was excited by irradiating with 250-nm light. The curve on the right shows a typical luminescence spectrum for neutron-irradiated crystals. We measured the peak position at 298°K to be at 3.16 eV with a width at half-maximum of 0.66 eV and at 77°K to be at 3.22 eV with a width at half-maximum of 0.59 eV. These results are in good agreement with values obtained by Chen *et al.*[18] who identified this luminescence band as due to F^+ centers. The curve on the left shows the luminescence spectrum for an additively colored crystal. This band was observed to peak at 2.4 eV with a half-width of 0.65 eV. Very little difference was observed between the 298 and 77°K spectra. This band was also observed to be the thermoluminescence band that occurs when an additively

[18] Y. Chen, J. L. Kolopus, and W. A. Sibley, Phys. Rev. 186, 865 (1969).

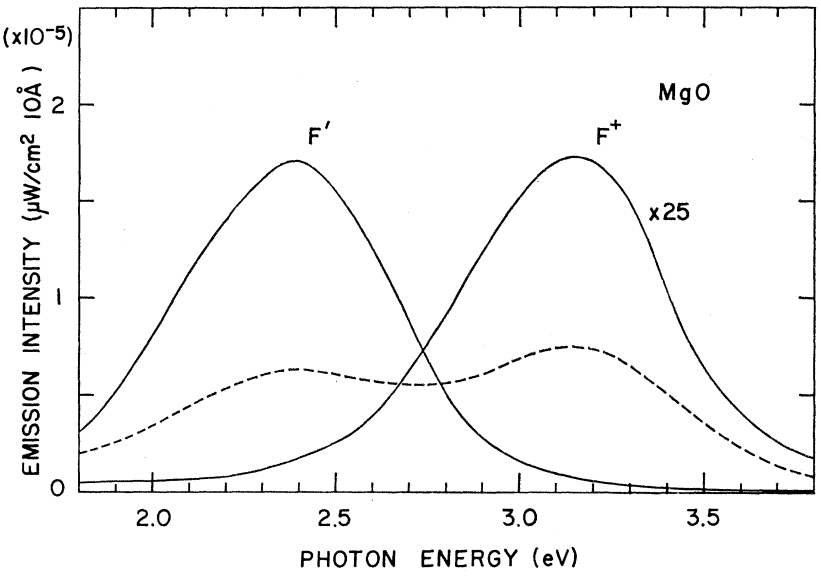

FIG. 6. Luminescence excited by continuous irradiation with 250-nm light. The luminescence spectrum from a crystal previously exposed to a fast-neutron dose of $nvt=1\times10^{18}$ cm^{-2} is shown on the right. The density of F^+ centers in this was estimated to be 6×10^{17} cm^{-3}. The curve on the left shows the luminescence from an additively colored crystal having a density of F' centers of 6×10^{18} cm^{-3}. The dashed curve is the luminescence from an additively colored crystal having a density of F' centers of 8×10^{17} cm^{-3}.

colored crystal which has been photoconverted to the F^+ state is heated. In this process, electrons which have been thermally released from traps are captured by F^+ centers forming F' centers in their excited state. Thus we attribute the 2.4-eV band as being due to F' centers. In order to observe this F' luminescence band in additively colored crystals, the density of coloration must be well in excess of the density of traps, otherwise the centers will be converted to the F^+ state and the F^+ luminescence spectrum will be obtained. By carefully selecting the density of additive coloration, it was possible to observe both bands simultaneously as shown by the dashed curve.

VII. TEMPERATURE DEPENDENCE OF F^+ AND F' BANDS

The temperature dependence of the half-width $H(T)$ and peak position $E(T)$ for both the F^+ and F' bands were measured. The F' band was produced by additively coloring crystals to a moderately heavy density. The optical absorption spectra for three representative temperatures are shown in Fig. 1. A curve for 77°K was not shown as it was almost indistinguishable from the 4°K curve.

The F^+ band was produced by irradiating crystals with neutrons. The optical absorption spectra for three representative temperatures are shown in Fig. 7. Again the 77°K curve was not shown as it was almost identical with the 4°K curve. To facilitate a comparison of the two bands, the 4°K curve from Fig. 7 is also shown as the dotted curve in Fig. 1. The half-widths $H(T)$ and peak positions $E(T)$ versus $T^{1/2}$ for both the F^+ and F' bands are shown in Fig. 8.

An attempt was made to analyze $H(T)$ for both the F^+ and F' bands using the simple theory based on the so-called configuration coordinate model.[19] This theory is based on a single effective vibrational mode and predicts the band shape to be Gaussian. The tempera-

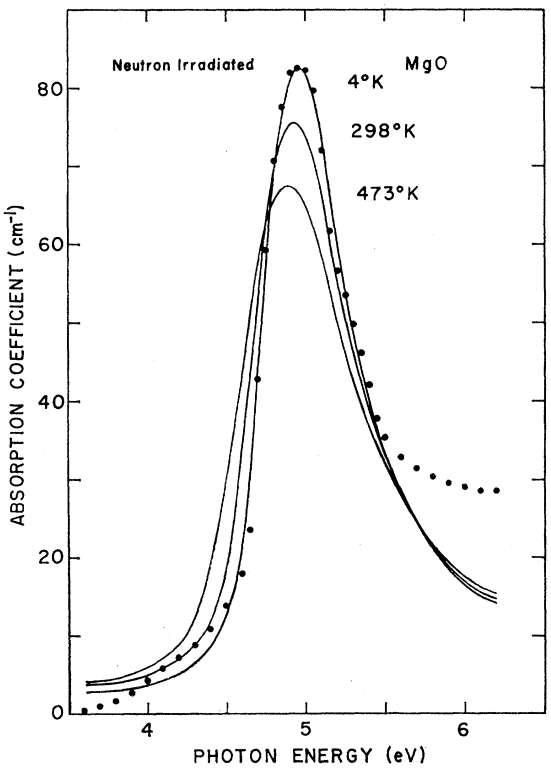

FIG. 7. Induced optical absorption spectra of a neutron-irradiated crystal measured at three different temperatures. The fast neutron dose was 7×10^{17} cm^{-2}. The points represent the 4°K data from Henderson *et al.* (Ref. 21) normalized to the same peak height.

[19] J. J. Markham, *F-Centers in Alkali Halides* (Academic, New York, 1966).

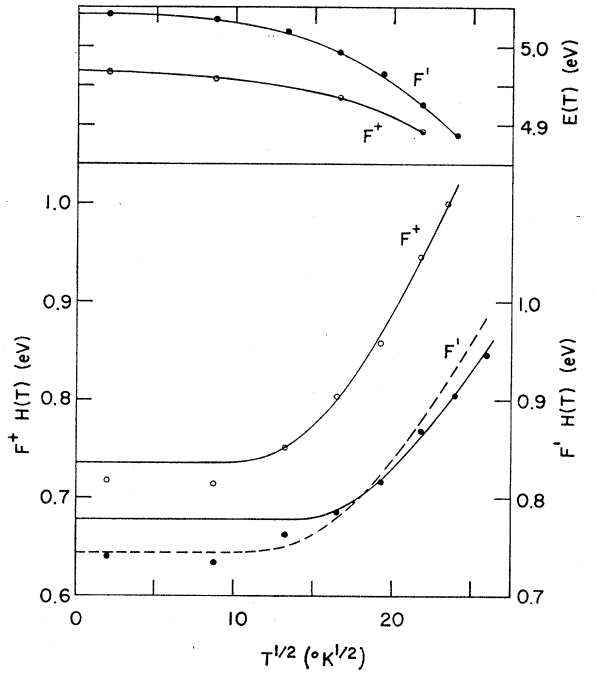

FIG. 8. Half-widths $H(T)$ and positions of peaks $E(T)$ for the F^+ and F' bands in MgO plotted as a function of the square root of the temperature. The smooth curves for $H(T)$ represent attempts to fit Eq. (3) to the data.

ture dependence of the half-width is given by

$$H(T)^2=H(0)^2\coth(h\nu/2kT), \tag{1}$$

where ν is the effective frequency. From $H(0)$ and ν, determined by fitting Eq. (1) to the experimental data, the Huang-Rhys factor S, which in this theory is equal to the average number of phonons emitted when a photon is absorbed, may be determined:

$$S=(1/8\ln 2)[H(0)/h\nu]^2. \tag{2}$$

If it is assumed that the excited state has the same effective frequency ν as the ground state, the energy for the luminescence peak $E_{\rm em}$ will be given by

$$E_{\rm em}=E_{\rm abs}-2Sh\nu, \tag{3}$$

where $E_{\rm abs}$ is the energy of the absorption peak.

The solid lines in Fig. 8 represent the best compromise at fitting Eq. (1) to the data. As can be seen, the fit at high temperatures is very good but at low temperatures the experimental points lie below the theoretical curve. The dotted curve illustrates that forcing the curves to fit at low temperatures makes it impossible to fit the slope of the points at high temperatures. Using the parameters for the solid curves in Fig. 8, the Huang-Rhys factors and the predicted luminescence peaks were calculated from Eqs. (2) and (3). These are shown in Table I together with the experimental values of the luminescence peaks.

TABLE I. Parameters for F^+ and F' bands.

Band	A (77°K)	$H(0)$	ν	S	$E_{\rm em}$ (calc)	$E_{\rm em}$ (expt)
F^+	1.22	0.735	14×10^{12}	29	1.65	3.16
F'	1.16	0.772	22×10^{12}	13	2.65	2.40

It was also observed that if either $2(E_v-E_m)$ or $2(E_m-E_r)$ were used in place of $H=(E_v-E_r)$ to fit Eq. (1), the values obtained for ν were essentially the same as those given in Table I. E_m is the energy at the absorption maximum and E_r and E_v are the energies where the absorption is at half-maximum on the red and violet sides of the band, respectively.

Also shown in Table I is a parameter $A=2(E_v-E_m)/(E_v-E_r)$, which measures the asymmetry of the absorption curves. Thus, for a Gaussian this parameter would be 1.00 and for a Pekarian[20] it seems to be about 1.05.

It is our conclusion that the experimental data for the F^+ and F' bands in MgO deviate significantly from those of the simple coordination coordinate model. First, the observed bands are not Gaussian. Although this departure from being Gaussian is not large, we believe it to be significant (for KCl, $A=1.09$). In this respect it should be noted that for the heavier oxides the asymmetric factors for the F' band have been observed to be even larger: 1.39 for CaO[9] and 1.45 for SrO.[10] Second, Eq. (1) gave a poor fit to the experimental data at low temperatures. We believe this indicates the need to consider more than a single vibrational frequency for the ground state of the center. And finally, although the predicted and observed luminescence for the F' center may be considered acceptably close, the prediction for the F^+ center lies below the F' peak whereas it was observed to occur at an energy above the F' peak. We believe this to be indicative of significant differences in the vibrational frequency for the center between the ground state and the excited state, contrary to the assumption in Eq. (3).

Henderson *et al.*[21] have recently analyzed the temperature dependence of the F^+ band with somewhat different results from those obtained here. The most significant difference in their procedure from ours was that they decomposed the absorption spectra into a series of overlapping Gaussian-shaped bands. In addition to the main F^+ band at 4.95 eV, the Fe^{3+} bands at 4.3 and 5.7 eV and an impurity band at 6.8 eV, they report three new bands at 5.30, 5.58, and 5.95 eV. They state that these "do not appear to be a result of the use of Gaussian line shapes for the bands; it is clear that no simple smooth shape would give the inflections in the absorption due to the bands at 5.30 eV and 5.58 eV." However, in none of our data were we able to detect

[20] J. J. Markham, Rev. Mod. Phys. **31**, 956 (1959).
[21] B. Henderson, R. D. King, and A. M. Stoneham, J. Phys. C 1, 586 (1968).

these inflections (see Fig. 7 for a comparison of their spectra with ours) and thus are forced to conclude that these inflections must be due to the higher-impurity content of the Norton crystals they used compared with the Spicer crystals used in our investigation. We are also convinced that the intrinsic shape of the F^+ band is asymmetric and cannot be meaningfully decomposed into a series of Gaussian bands.

In their paper, Henderson *et al.* showed an excellent fit of their data to Eq. (1) using the parameters $H(0)=0.477$ eV and $\nu=7.8\times10^{12}$ sec^{-1}. This may have been a fortuitous consequence of the above decomposition of the band. To be valid, $\alpha_m H(T)$ (which is proportional to the area under the absorption curve) should be independent of the temperature. However, their data show $H(T)$ increasing by 45% as the temperature increases from 4 to 372°K. This appears to be excessive compared with the observed decreased of α_m. Our analysis shows $H(T)$ increasing by only 20% in this range, while $\alpha_m H(T)$ remains constant to within 2%.

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Significance of the Third-Nearest-Neighbor Divalent Cation K^+ Vacancy Pairs in KCl†

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The identification of the third-nearest-neighbor monoclinic (C_s) site comprised of a Sm^{2+}-K^+ vacancy pair with the vacancy at the (2,1,1) lattice point in KCl has been made through a high-resolution Zeeman anisotropy fluorescence spectroscopic investigation of several prominent transitions between the ^5D and ^7F multiplets. The establishment of the dominant presence of the C_s site in KCl:M^{2+}, which constitutes an important feature of the Maxwell-Boltzmann distribution of the M^{2+}-K^+ vacancy pairs, is of fundamental importance in the understanding of numerous phenomena in polar crystals.

I. INTRODUCTION

THAT the introduction of divalent cations (M^{2+}) into the metal-ion sublattice of an alkali halide creates the phenomenon of vacancy compensation is a well-established fact. The manner in which such charge compensation occurs, however, has been a subject of much debate in recent years.[1] Both of the two prevailing views (which are opposite in nature), that the M^{2+}-vacancy pairs are either associated in complex formation or dissociated according to a law of mass action and that (according to the opposite view) the M^{2+}-vacancy pairs are present only in the nearest-neighbor complex form, have been found to be unrealistic on the basis of a statistical mechanical calculation.[1] In this paper, we wish to report the first observation of the dominant presence of the third-nearest-neighbor M^{2+}-K^+ vacancy pair in the KCl:M^{2+} system, which was predicted by this statistical mechanical calculation.[1]

Earlier, electron paramagnetic resonance (EPR)[2] and Zeeman anisotropy fluorescence (ZAF)[3] spectroscopic investigations have led to the identification of the nearest-neighbor $C_{2v}(1,1,0)$ site and the next-nearest-neighbor $C_{4v}(2,0,0)$ site in alkali halides doped with divalent cations. In the EPR investigations on the KCl:Mn^{2+} system,[2] a large signal was observed in addition to the signals corresponding to the C_{2v} and the C_{4v} sites. The large signal was attributed to cubic sites corresponding to divalent ions in distant compensation beyond the crystalline fields of the associated cation vacancy. In the ZAF experiments,[3] however, no cubic sites were observed. Since the EPR observation of the cubic sites provided apparently irrefutable grounds for the postulation of the dissociation hypothesis,[2] the identification of the sites responsible for the "cubic" EPR signal in terms of the ZAF experiments thus appears crucial to an understanding of the compensated lattice of the KCl:M^{2+} system.

On the basis of existing spectroscopic evidence, we have shown[1] that at low temperatures and high dilution, the canonical ensemble partition function leads to a Maxwell-Boltzmann distribution in the distance of separations of the M^{2+}-vacancy pairs, which can be calculated in terms of the geometric restrictions of the face-centered-cubic lattice. The most predominant pairs at $T<500$ K, in the order of relative importance, are $C_{4v}(2,0,0)$, $C_s(2,1,1)$, $C_{2v}(1,1,0)$, and $C_{2v}(2,2,0)$, of which the first three account for approximately 90% of the M^{2+} ions. If this is true, the so-called cubic sites observed in the EPR experiments must be actually low-symmetry sites beyond the second nearest neighbor, the most important of which are the $C_s(2,1,1)$ sites. In order

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