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Luminescence from oxygen vacancies in MgO crystals thermochemically reduced at high temperatures

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Experimental measurements and theoretical calculations are reported which may resolve some of the remaining difficulties associated with photoemission from anion vacancies in thermochemically reduced MgO crystals. The intensities of the 2.3- and 3.2-eV luminescence bands are found to be strongly influenced by both the concentrations of H^- ions and anion vacancies present, and also by the intensity of the ~ 5.0-eV exciting light. Theoretical calculations predict that for a ${}^1A_{1g}$ relaxation of the surrounding ions the ${}^1T_{1u}$ and ${}^3T_{1u}$ electronic states of the F center are almost degenerate and ~ 0.05 eV above the ${}^3A_{1g}$ state. The ${}^1T_{1u} \rightarrow {}^1A_{1g}$ and the ${}^3T_{1u} \rightarrow {}^1A_{1g}$ transition energies are predicted to be 2.2 and 2.9 eV, respectively.

I. INTRODUCTION

The true nature of the luminescence from anion vacancies in thermochemically reduced MgO (MgO:Mg) crystals continues to be the subject of debate after more than a decade of experimental and theoretical investigations.[1–5] This state of affairs may be compared to the situation for thermochemically reduced crystals of CaO for which the experimental results are well established[1,6,7] and where the theoretical interpretation is generally quite satisfactory.[8,9] One of the difficulties in MgO is that the main optical absorption of the two-electron and one-electron oxygen vacancies (i.e., the F and F^+ centers, respectively) occur at the same energy, ~ 5.0 eV. In addition, the controlled thermochemical reduction of MgO is relatively difficult to achieve, whereas thermochemically reduced CaO crystals can be grown and therefore rapid experimental progress could be made.

In this paper, we present new experimental and theoretical results which may help resolve some of the existing difficulties associated with anion-vacancy luminescence in MgO. We also suggest simple physical models to explain the luminescence behavior observed.

The absorption of 5.0-eV light by MgO:Mg crystals produces two main emission bands, at 3.2 and 2.3 eV. The intensity of either emission band can be altered by proper choice of the initial sample and the reducing conditions. Absorption of the F^+ center has been attributed to a transition from the ${}^2A_{1g}$ ground state to the ${}^2T_{1u}$ excited state.[1] The 3.2-eV band, which decays rapidly once the excitation light is removed, results from electronic decay of the F^+ center back to the ground state following relaxation of the surrounding ions. Attribution of the 2.3-eV band to a transition of the F center has been tenuous, however, because several experimental results[4,10] were in conflict with theoretical predictions,[5] based on an extension of the results for CaO. These arguments suggested that the main emission of the F center in MgO would be from a ${}^3T_{1u}$ excited state which was only loosely coupled to the lattice vibrations. Such a system, in analogy with the F center in CaO, might be expected to show vibronic structure on the emission band and to have an emission lifetime of the order of milliseconds. Neither of these effects is observed for the 2.3-eV band. Furthermore, optically detected magnetic resonance (ODMR) experiments indicate that the emitting state is not predominantly an orbital triplet.[4,10] The lifetime of the 2.3-eV emission is particularly unusual since it is sample dependent and ranges from a fraction of a second to many seconds over the temperature range from 6 K to above room temperature. Recent results[11] have shown that the cause of the long lifetime near room temperature are H^- ions, which serve as metastable traps for electrons excited out of F centers. The slow release of these trapped electrons and their subsequent capture by F^+ centers, thereby forming excited F centers, leads to the 2.3-eV phosphorescence. The effect of the presence of the H^- ions on the emission spectrum of anion vacancies in MgO over the temperature range 6–675 K is described here.

Calculations of the electronic structure of the F center in MgO, until now, have been less satisfactory than in CaO because of the greater difference in the relative sizes and polarizabilities of the Mg^{2+} and O^{2-} ions in MgO compared to those of the Ca^{2+} and O^{2-} ions in CaO.[5] These differences lead to much larger polarization effects in the emission states, which appear to be primarily responsible for the larger Stokes shift observed in MgO than in CaO (2.7 eV as compared with 1.1 eV). The inherent difficulty in treating the polarizability of the O^{2-} ion in the model is therefore magnified in the case of MgO. In the earlier calculations[5] for MgO, therefore, it was necessary to adjust some of the emission parameters in order to obtain reasonable agreement with the observed Stokes shift. In the present calculations, the electronic polarization has been treated more precisely and it is no longer necessary to adjust these parameters from their preset, perfect-crystal values. The new calculations predict that the 2.3-eV emission results mainly from a $^1T_{1u} \rightarrow {}^1A_{1g}$ transition of the F center.

The experimental measurements described here were made on several samples of thermochemically reduced MgO and were made over the temperature range 6–675 K. The results include details of the excitation spectrum of the F-center emission, the dependence of the emission spectrum on the excitation-light intensity, the temperature dependence of the emission intensity and lifetime, and the thermoluminescence spectrum.

II. EXPERIMENTAL CONSIDERATIONS

The MgO samples were grown by the arc-fusion method using high-purity—grade powder obtained from the Kanto Chemical Company, Tokyo, Japan. The samples were subsequently reduced by heating to a high temperature (2100–2400 K) under a high pressure of Mg or Ca vapor (4–7 atm) in a tantalum bomb. This procedure produced samples with an optical absorption at 5.0 eV from which the concentration of vacancies could be estimated. The absorption coefficients ranged from ~ 50 to $\sim 800\ \text{cm}^{-1}$. Infrared-absorption lines at 1053, 1032, and 1024 cm^{-1} were also measured, which are due to H^- ions.[12] The absorption coefficients of the 1053-cm^{-1} line ranged from <0.1 to $\sim 11\ \text{cm}^{-1}$.

Low-temperature emission spectra were taken with two systems. In one a Sulfrian liquid-helium cryostat was used to hold the sample. The detection system consisted of a 1-m Jarrell-Ash grating monochromator directed to an EMI 9658 or RCA 31034 photomultiplier tube cooled to dry-ice temperature. The wavelength response of the system had a calibration traceable to the National Bureau of Standards. The other system used an Oxford Instruments continuous-helium-flow cryostat to support the sample. Emitted light was dispersed by a McPherson 0.3-m monochromator and detected with a thermoelectrically cooled RCA 31034 photomultiplier tube. Optical excitation was induced with a high-pressure mercury lamp, a xenon lamp, or a deuterium lamp, employing either a monochromator or an interference filter to select the incident energy. The excitation energy was selected to be either 5.0 or 5.4 eV, depending on the experiment.

III. EXPERIMENTAL RESULTS

A. Photoluminescence

Our results show that the spectral dependence of the luminescence emitted by MgO:Mg is determined primarily by the concentrations of anion vacancies and H^- ions present. Both the relative and the absolute concentrations are important. In one sample the emission varied from a green color (2.3 eV) on the surface to a blue color (3.2 eV) in the interior of the sample when cleaved. There was definite evidence that the presence of hydrogen favors the green emission. For example, when a "hydrogen-free" crystal and "hydrogen-doped" crystal were reduced in the same tantalum bomb, the hydrogen-free crystal yielded primarily blue luminescence, whereas the hydrogen-doped sample yielded primarily green luminescence. There is no direct correlation between the lifetime of the 2.3-eV band and the concentration of F centers, nor between the absorption coefficient at 5.0 eV and the color of the luminescence. Thus, a range of luminescence behavior is exhibited when different samples are measured. In order to illustrate the types of behavior observed we describe below the results obtained from four different samples, which we label MgO I–IV. Details on these samples are given in Table I. Samples MgO I–III were the same as those used in our earlier measurements.[11]

Figure 1 shows the emission spectrum excited by 5.4-eV light in sample MgO II in which the anion-vacancy and H^--ion concentrations are 4.1×10^{18} and $1.3\times 10^{17}\ \text{cm}^{-3}$, respectively. The low intensity of the 3.2-eV band enables the characteristics of the 2.3-eV band to be clearly observed at all temperatures. The 2.3-eV band is slightly asymmetric with a halfwidth of 0.68 eV at 5 K, which increases to

TABLE I. Characteristics of thermochemically reduced MgO samples.

Sample	Anion vacancies α_F (cm^{-1})[a]	n_F (cm^{-3})[b]	H$^-$ ions α_H (cm^{-1})[c]	n_H (cm^{-3})[d]
MgO I	330	(1.6×10^{18})	11.0	(3.0×10^{18})
MgO II	820	(4.1×10^{18})	0.50	(1.3×10^{17})
MgO III	110	(5.5×10^{17})	0.20	(5.4×10^{16})
MgO IV	750	(3.7×10^{18})	0.60	(1.6×10^{17})

[a] Absorption coefficient at 4.95 eV.

[b] Calculated using the formula given in Ref. 11.

[c] Absorption coefficient at 1053 cm^{-1}.

[d] Calculated using the formula $n(\mathrm{H}^-)=2.7\times10^{17}\alpha(\mathrm{H}^-)$, where $\alpha(\mathrm{H}^-)$ is the absorption coefficient at 1053 cm^{-1}.

0.72 eV at 290 K. The peak position is almost independent of temperature over the range 5—290 K. Figure 1 also shows the excitation spectrum of the 2.3-eV band. To obtain these measurements, detection was made at 2.3 eV while the energy of the excitation light was slowly scanned first in one direction, then the other. The results were then averaged. The peak position of the excitation band is 5.0 eV and the halfwidth 0.90 eV. These results should be compared to those obtained by Chen *et al.*,[2] who found that the *F*-band peaks at 5.01 eV with a halfwidth of 0.77 eV. It is characteristic of samples with low H$^-$-ion concentrations that there is no significant change in the intensity of the 3.2-eV band between 100—300 K. This observation is not apparent in Fig. 1 because the 3.2-eV band is relatively weak, but was more conspicuous in sample MgO III, in which the two bands had comparable intensities.

Figure 2 shows the behavior observed in sample MgO I in which both the anion vacancy and H$^-$-ion concentrations are large and comparable. At low temperatures, the intensity of the 2.3-eV band is small and that of the 3.2-eV band is large. As the temperature increases above ~200 K the 2.3-eV band becomes progressively more intense, while the 3.2-eV band diminishes in intensity. It can be seen that there is approximately a one-to-one correspondence between the intensity increase in the 2.3-eV band and the intensity decrease in the 3.2-eV band over this temperature range.

Figure 3 shows the temperature dependence of the emission spectrum of sample MgO IV in which the H$^-$ concentration is intermediate between samples MgO I and MgO II (~1.6×10^{17} cm^{-3}). It can be

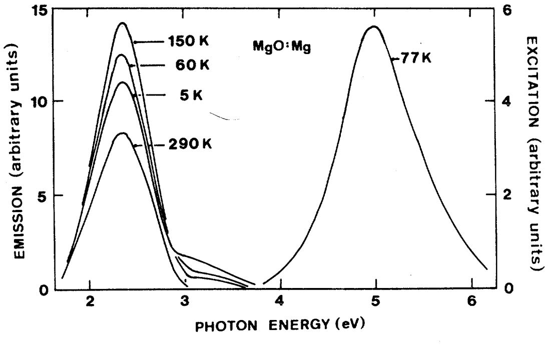

FIG. 1. Temperature dependence of the emission spectrum and the excitation spectrum of the 2.3-eV emission band at 77 K in sample MgO II. This sample contained a large concentration of anion vacancies and a much smaller concentration of H$^-$ ions (see Table I). For the emission spectra, $E_{ex}=5.4$ eV, and for the excitation spectrum, $2.1<E_{em}<2.6$ eV.

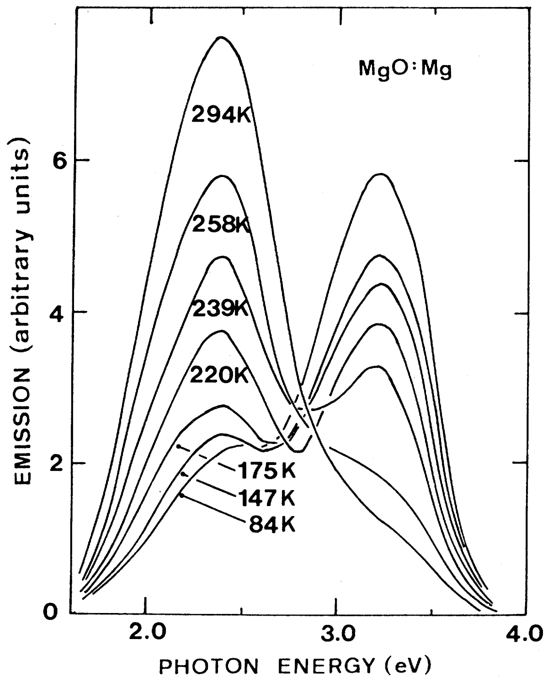

FIG. 2. Temperature dependence of the emission spectrum in sample MgO I. This sample contained a relatively large concentration of both anion vacancies and H$^-$ ions (see Table I). $E_{ex}=5.4$ eV.

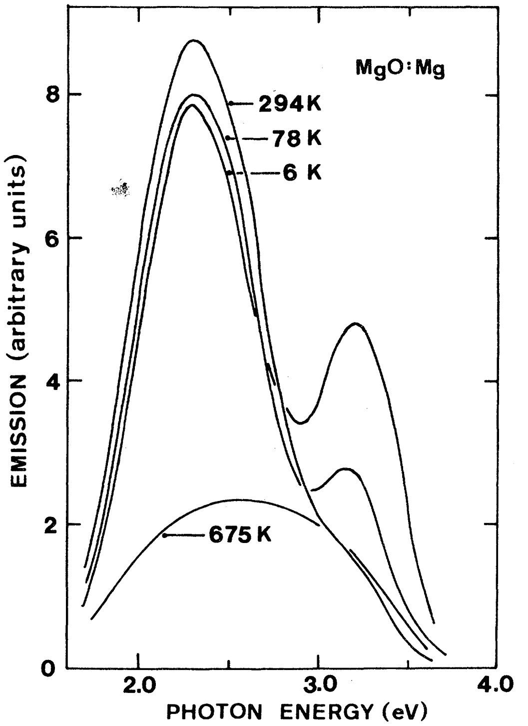

FIG. 3. Temperature dependence of the emission spectrum in sample MgO IV. This sample contained a relatively large concentration of anion vacancies and an intermediate concentration of H^- ions (see Table I). $E_{ex}=5.4$ eV.

seen that the behavior in this case is also intermediate between those shown in Figs. 1 and 2. That is, at 6 K the 3.2- and 2.3-eV bands have comparable intensities. However, the 3.2-eV band rapidly diminishes in intensity as the temperature increases. Meanwhile, there is a small increase in the intensity of the 2.3-eV band over the same temperature range. Above 300 K the peak intensity of the 2.3-eV band decreases monotonically with temperature and is reduced by ~75% at 675 K. As the band diminishes in intensity, it broadens and its peak position shifts toward higher energy, so that at 675 K the peak position is 2.6 eV rather then 2.3 eV. The decrease in the intensity of the band between 300—600 K does not follow any simple kinetic law.

It is apparent from the results described above that the concentration of H^- ions determines the relative intensities of the emission bands. However, the intensity of the exciting beam also affects the relative intensities of the luminescence bands. Figure 4 shows that as the intensity of the 5.0-eV excitation light increases the 3.2-eV emission grows at the expense of the 2.3-eV emission. The intensity of these bands depends logarithmically on the excitation intensity.

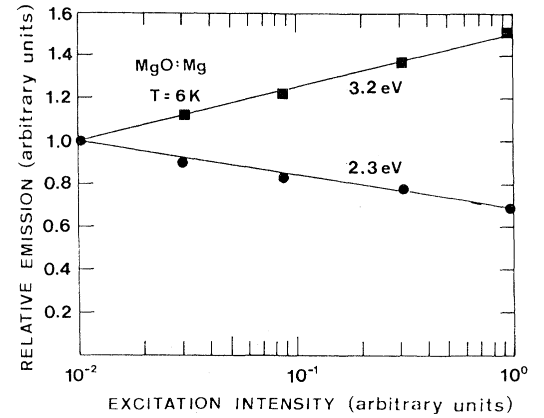

FIG. 4. Dependence of the normalized intensities of the 2.3- and 3.2-eV emission bands on the intensity of the exciting 5.0-eV light beam at 6 K in sample MgO IV.

B. Phosphorescence and thermoluminescence of the 2.3-eV band

The 2.3-eV emission band is long lived at all temperatures down to 6 K. Figure 5 shows a comparison of the spectra of the long-lived phosphorescence with the total photoluminescence in sample MgO IV. The 3.2-eV band is clearly absent in the phosphorescence spectrum. Within the error expected in

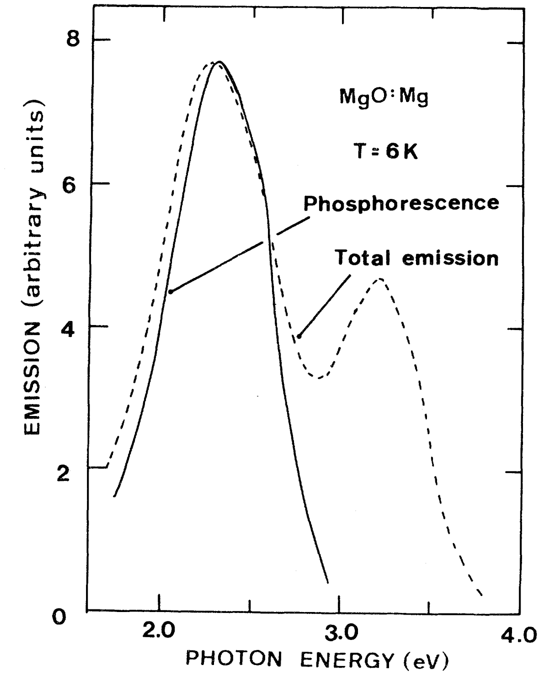

FIG. 5. Comparison of the spectral dependence of the phosphorescence and the total luminescence of sample MgO IV at 6 K. $E_{ex}=5.0$ eV.

measuring a time-dependent spectrum, the phosphorescence has the same peak position and band shape as the 2.3-eV photoluminescence band. The decay of the phosphorescence varies from sample to sample. However, the intensity of the decaying phosphorescence can be temporarily enhanced by illuminating the sample with a short pulse of visible light as can be seen in Fig. 6. In this experiment, which was performed with sample MgO IV, the 2.3-eV band was allowed to decay at 6 K for 250 s. The sample was then illuminated with a 4-s pulse of 2.2-eV light, with the result that the emission was significantly enhanced. When the excitation light was removed, the emission continued to decay slowly.

Figure 7 shows the thermoluminescence glow curves for two samples, one with a high H^- concentration (sample MgO I) and the other with a lower H^--ion concentration (sample MgO III). In both cases the luminescence originated from the same sample volume. The measurements were made over two different temperature ranges and the data normalized at 270 K. In all experiments the sample was cooled to ~ 10 K, then illuminated with ultraviolet light for a few minutes. The heating rate was ~ 5 K/min. The two curves in Fig. 7 are representative of the behavior seen in all samples.[13,14] At 10 K, sample MgO I glowed for many seconds following the removal of the excitation light. When the samples were heated an intensity maximum occurred near 40 K with a much weaker maximum at 220 K (bottom curve). In sample MgO I, peaks occurred at 40 and 265 K (top curve). All the samples studied showed a peak at 470 K, which has been reported previously[3] and attributed to the thermal release of electrons from Fe^+ centers, with subsequent capture by F^+ centers. This suggestion is supported by two observations. Firstly, the spectrum of the thermoluminescence is similar to that of the 2.3-eV photoluminescence band. Secondly, after bleaching with 5.0-eV light, both Fe^+ ions and F^+ centers are observed by electron paramagnetic resonance at 4.2 K. After heating the sample above 480 K, these two paramagnetic resonances could not be observed.

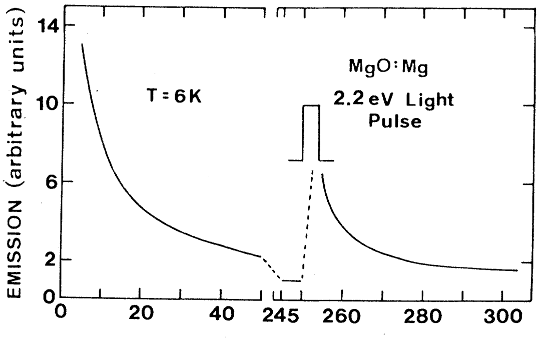

FIG. 6. Time decay of the 2.3-eV emission intensity following excitation with 5.0-eV light at 6 K. After 250 s, the sample was illuminated for 4 s with 2.2-eV light.

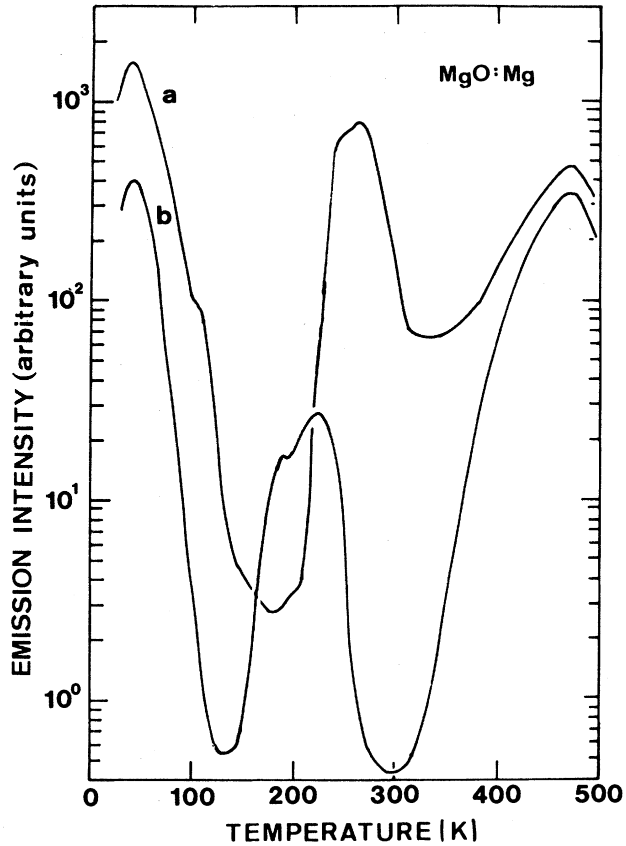

FIG. 7. Thermoluminescence glow curves for sample MgO I [curve (a)] and sample MgO III [curve (b)]. Sample MgO I has a higher concentration of H^- ions than sample MgO III (see Table I). The measurements were made over two ranges and normalized at 270 K.

IV. THEORETICAL RESULTS

The model used in these calculations follows that used in earlier work on the F center in CaO.[9] Near the defect, the electronic structure on the neighboring ions is treated in detail by a Hartree-Fock–type approximation, while in the outer region an effective-mass approximation is used. For the F center, the effective two-electron Hamiltonian including the effects of dielectric polarization, but neglecting lattice relaxation, is expressible in the form

$$H(1,2)=\sum_{i=1}^{2} h(\vec{r}_i)+U_{12}\ , \qquad (1)$$

where the effective one-electron Hamiltonian $h(\vec{r})$ is described in detail in Ref. 9. The two-electron interactions, including additional polarization contributions not found in one-electron centers, are contained in U_{12}.

We approximate the two-electron wave function for this system by the expansion

$$\psi^{\pm}(1,2)=\sum_{k=1}^{n} C_k \psi_k^{\pm}(\vec{r}_1,\vec{r}_2)\chi_{\pm}(\zeta_1,\zeta_2) , \tag{2}$$

in which a plus sign refers to a singlet state of the F center and a minus sign refers to a triplet state. The spin function $\chi_{\pm}(\zeta_1,\zeta_2)$ has the usual form, and the two-electron basis function $\psi_k^{\pm}$ is expressed in terms of one-electron orbitals,

$$\psi_k^{\pm}(\vec{r}_1,\vec{r}_2)=N_k[g_{k1}(\vec{r}_1)g_{k2}(\vec{r}_2)\pm g_{k2}(\vec{r}_1)g_{k1}(\vec{r}_2)] , \tag{3}$$

when N_k is a normalization factor. This notation emphasizes the need to specify two orbitals, i.e., $k\,1$ and $k\,2$, in order to determine the kth two-electron function. In the present calculations, the one-electron orbitals g_{ki} are taken to be Slater-type orbitals (STO's) that have been Schmidt orthogonalized to the one-electron orbitals on the surrounding Mg^{2+} first-nearest-neighbor (1NN) ions. We used six configurations of the type given by Eq. (3) for each state of the F center. The nonlinear STO parameters were optimized for each symmetrized displacement of the 1NN ions.

To obtain configuration-coordinate curves, the lattice-relaxation energy was calculated within the framework of classical ionic theory and added to the electronic energy for the various values of the configuration coordinate. The lattice-relaxation energy was calculated using the classic Born-Mayer model in which second-nearest-neighbor (2NN) contributions to the repulsive energy and the van der Waals terms were included. The values of the parameters used in this calculation are listed in Table II.

The electronic structure calculations were made using an improved treatment of the electronic polarization. Here the first-order corrections to the Toyozawa-Haken-Schottky (THS) expressions[15,16] for the interaction between the electron and the hole via the electronic polarization field were included. The THS expression, while having the correct limiting behavior for both large and small electron-hole separations, overestimates the polarization energy for electron-hole separations where $\langle r \rangle \approx 1/\rho_i$ is approximately equal to the lattice constant and i refers to either an electron or a hole. We note that in Mott-Littleton theory $1/\rho_i$ represents the effective radius of a hole or an electron. Shindo[17] and Mahutte *et al.*[18] have shown that for this case the higher-order corrections are significant and should not be neglected. The leading correction to the THS is given by the expression

$$U_{\mathrm{el}}^{1}(r)=-(1-\kappa_{\infty}^{-1})\sum_{i=e,h}\{(\rho_i r)^{-2}-[\tfrac{1}{2}+(\rho_i r)^{-1}+(\rho_i r)^{-2}]\exp(-\rho_i r)\}\frac{\partial}{\partial r} . \tag{4}$$

TABLE II. Input parameters used to calculate the lattice-relaxation energy.

a (Å)	2.102
ρ	0.407[a]
b (eV)	1.531[a]
r_+ (Å)	0.758[a]
r_- (Å)	1.265[a]
c_{+-} (eV Å^6)	3.76[b]
c_{++} (eV Å^6)	0.555[b]
c_{--} (eV Å^6)	41.0[b]
d_{+-} (eV Å^8)	4.01[b]
d_{++} (eV Å^8)	0.227[b]
d_{--} (eV Å^8)	70.7[b]
α_+ (Å^3)	0.094[b]
α_- (Å^3)	1.657[b]
κ_{st}	9.8
κ_{∞}	2.95

[a] M. Catti, Solid State Commun. 29, 243 (1979).

[b] I. M. Boswarva, Phys. Rev. B 1, 1698 (1970).

We have studied the effect of this correction on our results for the luminescence states of the F center in MgO. In this case, the first-order correction $\langle U_{\mathrm{el}}^{1} \rangle$ is large and roughly the same size as the THS contribution $\langle U_{\mathrm{THS}} \rangle$ to the ground-state energy of the F center (see Table III). Here both electrons are in

TABLE III. Polarization contributions to the total energy for the four lowest-lying emission states of the F center. $\rho_{2\mathrm{NN}}$ devotes the integrated charge within the second-nearest-neighbor shell of ions in MgO. Energies are given in electron volts.

State	$\rho_{2\mathrm{NN}}$	$\langle U_{\mathrm{THS}} \rangle$	$\langle U_{\mathrm{el}}^{1} \rangle$
$^1A_{1g}$	1.96	-2.6	$+2.4$
$^3T_{1u}$	1.82	-3.0	$+2.0$
$^3A_{1g}$	1.00	-5.0	$+1.4$
$^1T_{1u}$	0.99	-5.75	$+1.3$

compact a_{1g} orbitals with average radii roughly equal to a lattice constant. The magnitude of this correction drops off rapidly to zero for large electron-hole separations, as in the case for the ${}^1T_{1u}$ state where the t_{1u} orbital is very diffuse and the electron-hole separation is $\sim$4NN distances (Fig. 8). The second electron remains well localized within the vacancy region in an a_{1g} orbital. For this case, the correction has roughly half its value in the ${}^1A_{1g}$ state where both electrons occupy a_{1g} orbitals that are confined within the vacancy region. The rationale underlying the calculation of the electronic and ionic polarization constants ρ_e, ρ_h, v_e, and v_h can be found in Ref. 9. Following the procedures outlined there, we obtain $\rho_e = \rho_h = 0.2702$ a.u.$^{-1}$ and $v_e = v_h = 0.0813$ a.u.$^{-1}$.

The luminescence states of the F center in MgO, shown in Fig. 9, were calculated as a function of the outward A_{1g} relaxation of the 1NN Mg^{2+} ions. The calculations were made using the Hartree-Fock value for the energy of the bottom of the conduction band (ϵ_{HF}) in MgO to be that obtained by Pantelides *et al.*[19] In so doing, we note that the values of all the model parameters used in this calculation correspond to those obtained for the perfect crystal. For this choice of parameters, the calculated absorption energy for the F center is 4.8 eV. Near-perfect agreement could be obtained for both the absorption and emission energies by adjusting the value of ϵ_{HF} as was done in our earlier work on the F center in the alkaline-earth oxides. This was not done in the present work because the calculated and experimental energies are within the relative errors introduced into the calculations through the approximations employed in evaluating the three- and four-center integrals involved. The calculations give energies for the ${}^3T_{1u} \rightarrow {}^1A_{1g}$ and ${}^1T_{1u} \rightarrow {}^1A_{1g}$ transitions of 2.9 and 2.2 eV, respectively, and a halfwidth of 0.60 eV for the ${}^1T_{1u} \rightarrow {}^1A_{1g}$ luminescence band.

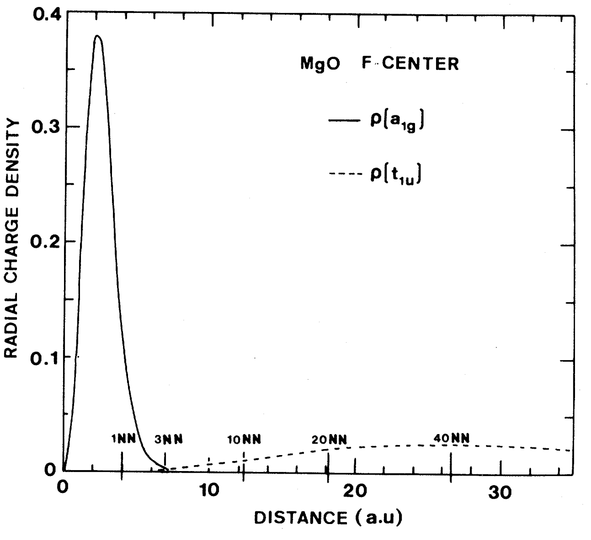

FIG. 8. ${}^1T_{1u}$ radial charge density for an 8% A_{1g} outward relaxation of the F center in MgO.

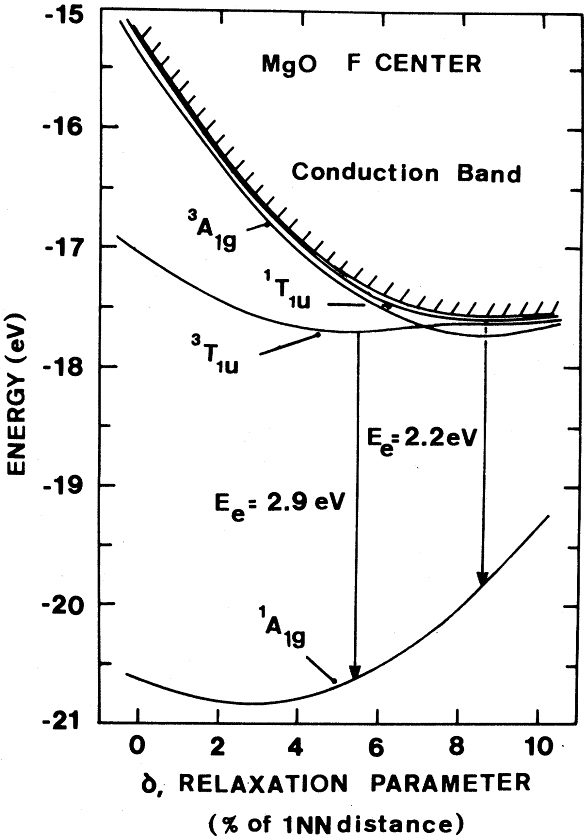

FIG. 9. A_{1g} configuration coordinate curves for F-center emission in MgO.

V. DISCUSSION

The theoretical and experimental results described above allow us to draw several conclusions concerning the nature of the emitting states which produce the 2.3-eV band, and the physical processes which lead to the observed temperature dependence of the emission spectrum and lifetime. As the configuration-coordinate diagram (Fig. 9) shows, the present calculations predict that for an A_{1g} relaxation of the F center the ${}^3A_{1g}$ state has the lowest excited-state energy. This prediction is consistent with the ODMR results of Edel *et al.*[4,10] Our experimental results cannot be explained, however, on the basis that the ${}^3A_{1g}$ state is the only emitting state involved in producing the 2.3-eV band at all temperatures. It is worth noting that a ${}^3A_{1g} \rightarrow {}^1A_{1g}$ transition is both spin and parity forbidden. Figure 9 shows that the ${}^1T_{1u}$ state is calculated to lie only ~0.05 eV above the ${}^3A_{1g}$ state (for an A_{1g} relaxation), and that the ${}^1T_{1u} \rightarrow {}^1A_{1g}$ and ${}^3T_{1u} \rightarrow {}^1A_{1g}$ transition energies are calculated to be 2.2 and 2.9 eV, respectively. It seems likely therefore that the observed 2.3-eV emission band is due largely to the ${}^1T_{1u} \rightarrow {}^1A_{1g}$ transition. However, such a transition is allowed and would be expected to have a relatively short lifetime, i.e., comparable to that for the *F* center in KCl.[20] There is some evidence from our measurements at 6 K that there may be a component in the 2.3-eV emission with a lifetime of ~1 μs. Most of the emission, however, is much longer-lived. We conclude from this result and the temperature dependence of the emission spectra, Figs. 1—3, that a direct emission process involving only the *F* center is unlikely. Instead, when an *F* center is excited with 5.0-eV light, the excited electron must have a high probability of escaping into the conduction band. Additional evidence for this conclusion is (i) the dependence of the intensity of the 2.3-eV band on the intensity of the excitation light (Fig. 4), (ii) the thermoluminescence experiments, which suggest that an electron can be transferred from an *F* center to an H^- ion at ~10 K, and (iii) the theoretical results (Fig. 9). These theoretical results predict that the ${}^1T_{1u}$ excited states lie much closer to the bottom of the conduction band in MgO than in CaO, where the luminescence has been shown to the intrinsic for $T < 100$ K.[21] Furthermore, the t_{1u} radial charge density for the ${}^1T_{1u}$ relaxed excited state is predicted by these calculations to have a much greater radial extent than was found for the *F* center in CaO and the overlap of the a_{1g} and t_{1u} radial charge distributions is also found to be considerably smaller.[22]

The results of Jeffries *et al.*[11] showed that the lifetime of the 2.3-eV emission was determined at 260 K by the concentration of H^- ions. We can explain this result and those described here using the model shown schematically in Fig. 10. Absorption of a photon by an *F* center excites an electron from the ${}^1A_{1g}$ ground state to a ${}^1T_{1u}$ excited state. For the reasons discussed above there is, then, a high probability of the electron escaping into the conduction band, from which it can be trapped elsewhere in the crystal. In particular, it can be trapped at an H^- ion, thus forming an H^{2-} ion and leaving behind an F^+ center [Fig. 10(a)].[23] Above ~240 K, an H^{2-} ion is unstable and the outermost electron is thermally excited into the conduction band with an activation energy of 0.56 eV.[14] As it moves through the conduction band the electron can be retrapped at H^--ion sites or encounter an F^+ center, where it can become trapped permanently by falling to the ground state, with the emission of a 2.3-eV photon [Fig. 10(b)]. The higher the probability of an electron being retrapped, the longer will be the phosphorescence lifetime. Therefore, the larger the H^--ion concentration, the longer it will take an electron to return to an F^+ center, which in turn leads to a longer-lived emission.

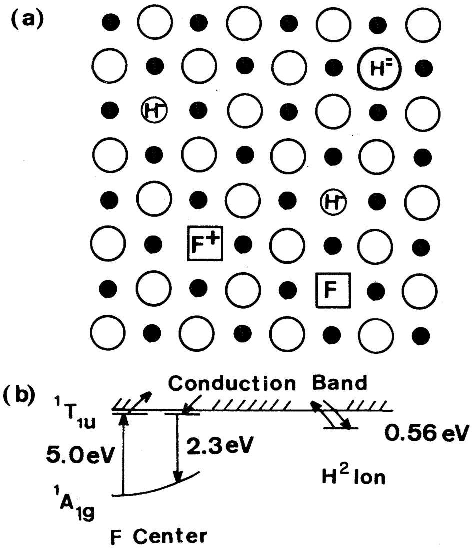

FIG. 10. Schematic representation of the model for the effect of substitutional H^- ions on the 2.3-eV *F*-center emission in MgO:Mg. (a) Schematic MgO lattice containing anion vacancies and hydrogen ions, and (b) schematic energy-level diagram for the *F* center, the H^{2-} ion, and the conduction band. See the text for a complete explanation.

The 2.3-eV luminescence is long lived also at low temperatures where the trap responsible for the 265-K thermoluminescence peak is stable. There are two experimental results which indicate that there is another thermally activated process at low temperatures. The first is the peak in the thermoluminescence curve at ~40 K and the second is the observed decrease of the 3.2-eV band above 40 K (Fig. 3). The cause of this low-temperature phosphorescence is not definitely known, but two possible explanations can be suggested. One possibility is that the low-temperature thermoluminescence peak is due to release of electrons from a different configuration of the H^- ion. As noted above the H^--ion infrared spectrum consists of a three-line series at 1053, 1032, and 1024 cm^{-1}.[12] Although the relative intensities of these lines appear to be the same in different samples, there is now unmistakable evidence that they are not intensity correlated.[24] It has been suggested previously[12] that point-group symmetries lower than O_h may be involved, and that the lower-symmetry configurations may be due to local charge compensation. It is reasonable to expect that the binding energy of electrons to different configurations of the H^- ion would give rise to the 2.3-eV thermoluminescence at different temperatures, such as those at 265 and 40 K. A second possible explanation for the long-lived 2.3-eV luminescence at low temperatures is suggested by the extended nature of the excited-state orbitals of the *F* center and H^{2-} ion. Recent calculations[23] indicate that there is an extended relaxed excited state of the H^{2-} ion which overlaps with the *F*-center excited states for reasonably close *F*-center—H^{2-}-ion pairs. The electron is then able to tunnel to an *F*-center excited state because of the overlap of the extended wave functions (Fig. 8). 2.3-eV emission occurs when the electron falls to the ${}^1A_{1g}$ ground state of the *F* center.

The results shown in Fig. 6 suggest that it is possible to excite an electron from an H^{2-} ion with 2.2-eV light. When the 2.3-eV band has been allowed to decay for 250 s at 6 K, its intensity can be enhanced temporarily by illuminating the sample with a short pulse of 2.2-eV light. We propose that the enhancement is caused by optical excitation of electrons from the more stable configuration of the H^{2-} ion into the conduction band, from which some become retrapped at the less stable H^{2-}-ion configuration. This repopulation of the less stable configuration leads to the observed enhancement of the 2.3-eV emission.

In conclusion, we have shown how the presence of H^- ions strongly influence the luminescence behavior of thermochemically reduced MgO. Models which are consistent with the experimental results have been suggested and new calculations have been described, which explains the differences observed in emission from anion vacancies in MgO and CaO.

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[23] Recent calculations, that were made using a model that is based upon the Hartree-Fock-Roothaan procedure, indicate that the substitutional H^{2-} ion possesses a bound ground state in MgO. Similar calculations of the F^- center (three electrons trapped at an O^{2-} vacancy) indicate that the third electron is not bound and that the stabilizing charge on the proton is necessary to provide a bound ground state. T. M. Wilson, Bull. Am. Phys. Soc. 27, 413 (1982).

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