

Luminescence decay and electron traps in thermochemically reduced MgO

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We report an analysis of the decay curves for 2.3-eV F -center luminescence in several samples of thermochemically reduced MgO. Previous measurements have shown that the concentration of H^- ions in a sample determines the lifetime of the luminescence at 260 K. We show here that the decay tends to become approximately second order in a characteristic time τ , which depends on the concentrations of traps in the crystal, especially H^- ions. At room temperature τ is smallest for the sample containing the largest relative H^- -ion concentration, whereas at 40 K the converse is found to be the case. These results are explained semiquantitatively in terms of a general theoretical model involving two kinds of electron traps with different thermal activation energies.

I. INTRODUCTION

Luminescence from anion vacancies in thermochemically reduced MgO has been studied for some time and a considerable amount of data has been collected, from which information about the electronic structure of F centers and F^+ centers has been deduced.¹ Substantial theoretical progress has also been made concerning the vibronic properties of these defects.^{2,3} The F^+ - and F -center absorption bands in MgO both peak near 5.0 eV (250 nm) (Ref. 4), the latter being due to a ${}^1A_{1g} \rightarrow {}^1T_{1u}$ transition. Theoretical calculations indicate that the 2.3-eV F -center luminescence is mainly due to a ${}^1T_{1u} \rightarrow {}^1A_{1g}$ transition, although the ${}^3A_{1g}$ excited state is predicted to be slightly lower in energy than the ${}^1T_{1u}$ state and therefore to become important at very low temperatures, in agreement with experiment.⁵

Although it has long been known that charge traps in the crystals affect the luminescence from anion vacancies, it is only recently that significant progress has been made in identifying these traps. In particular it has now been shown that the concentration of substitutional H^- ions in a sample determines both the lifetime of F -center luminescence near room temperature⁶ and the relative luminescence intensity from F and F^+ centers over a large temperature range.³ The suggested mechanism is that optical irradiation excites electrons from F centers into the conduction band from which they are trapped at the net positive charge at H^- ion sites, thereby forming H^{2-} ions. H^{2-} ions become unstable near room temperature and electrons are released into the conduction band. These electrons can be retrapped many times at other H^- ions before finally being retrapped at F^+ centers, which leads to 2.3-eV luminescence. Below ~ 240 K, H^{2-} ions are stable. Low-temperature electron paramagnetic resonance (EPR) signals from H^{2-} ions have recently been detected in optically illuminated samples,⁷ which tends to confirm this model. However, these and other EPR and optical results^{8,9} indicate that additional impurity ions such as Cr^{2+} and Fe^{2+} are also important as charge traps, but in ways which are not yet clear. When the excitation is removed, the 2.3-eV luminescence decays in a

non-first-order manner at all temperatures down to 4 K (Ref. 3). We have reported previously, however, that there is a tendency towards second-order behavior at room temperature, and this effect is the main subject here.

Information about electron traps and the temperature ranges over which they affect the luminescence has also been obtained from thermoluminescence (TL) glow curves. In thermochemically reduced MgO there are two main temperature regions below 350 K where electron traps become thermally unstable.³ These are at ~ 260 and ~ 40 K, and in each case the luminescence is at 2.3 eV. The TL intensity in the higher temperature peak is correlated with the concentration of H^- ions present, whereas for the lower temperature peak no such direct correlation has been found.

For several reasons, then, it is known that F -center luminescence decay at room temperature in MgO is strongly influenced by the concentration of H^- ions in the sample. At lower temperatures the decay is also influenced by another unidentified trap(s). In this paper we describe F -center luminescence decay in detail in both the high- and the low-temperature regions. A model is then developed which accounts for the difference in the shapes of the observed decay curves.

II. EXPERIMENTAL DETAILS

The samples of MgO used in this work were grown and thermochemically reduced at Oak Ridge National Laboratory by Y. Chen. These samples were the same ones used for our previous measurements.^{3,6,10} The concentrations of anion vacancies in the samples were determined from the absorption coefficients at the peak of the 5.0-eV band. Similarly the concentrations of H^- ions were determined from the peak absorption of the local-mode oscillations¹¹ at 1053, 1032, and 1024 cm^{-1} . The details of these measurements have been given previously.³ For convenience the characteristics of the samples used here are summarized in Table I, in which the previous nomenclature has been used. Since we presently have no direct way of calculating the concentration of traps responsible for the 40-K TL peak, we give the relative intensity of the peak in

TABLE I. Characteristics of thermochemically reduced MgO samples.

| Sample | n_F (cm ⁻³) | n_H (cm ⁻³) | Relative intensity of 40-K TL peak |
|---------|---------------------------|---------------------------|------------------------------------|
| MgO-I | 1.6×10^{18} | 3.0×10^{18} | 2.5 |
| MgO-III | 5.5×10^{17} | 5.4×10^{16} | 1.0 |
| MgO-IV | 3.7×10^{18} | 1.6×10^{17} | 6.0 |

each sample as a way of estimating the relative concentration of these traps. Table I shows that although the concentration of anion vacancies and the apparent concentration of "low-temperature" traps in the samples varies by only a factor of ~ 6 , the concentration of H^- ions varies by a factor of ~ 55 .

F -center luminescence was excited with a 60-W deuterium lamp which was used in conjunction with a 230-nm thin-film interference filter. The luminescence was detected by an EMI Gencom, Inc. model No. 9813 B photomultiplier tube and stray light was reduced by using suitable glass filters. The samples were illuminated for several minutes before the decay was monitored. Intensity-time curves were recorded on a chart recorder, from which the data were obtained.

III. EXPERIMENTAL RESULTS

It has been reported earlier that there is a tendency once the excitation is removed for the F -center luminescence intensity I to decay following approximately second-order kinetics.¹⁰ It is convenient, therefore, to present the results in a form in which this property becomes immediately apparent. The data will be plotted as $I^{-1/2}$ versus time t . For a second-order decay such a plot would be a straight line.¹² This will be discussed further in Sec. IV.

Figure 1 shows the luminescence decay curves for three

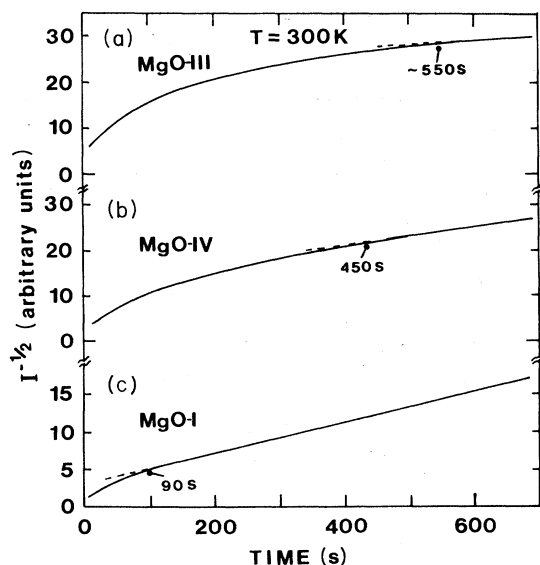


FIG. 1. 2.3-eV F -center luminescence decay in three samples of thermochemically reduced MgO at $T=300$ K. A characteristic time at which approximately second-order behavior becomes apparent is indicated for each curve (see text).

samples MgO-I, MgO-III, and MgO-IV at room temperature. The important difference between these curves is that the $I^{-1/2}$ -versus- t curve for MgO-I, which contains the highest H^- -ion concentration, becomes nearly straight after an initial transient period of only ~ 90 s, whereas for MgO-III, which contains a concentration of H^- ions ~ 55 times smaller, the curved transient period lasts ~ 550 s.

At 40 K the results are quite different from those at room temperature. Figure 2 shows that at 40 K the $I^{-1/2}$ -versus- t plot for the sample with the highest H^- -ion concentration, MgO-I, has a curved region for at least 600 s, whereas the plot for MgO-III, which has the lowest H^- -ion concentration, becomes straight after only ~ 90 s. Figure 2 also shows that the luminescence lifetime at 40 K is largest for MgO-IV, which has the highest TL intensity at 40 K (see Table I). A convenient way to establish a characteristic time τ for second-order behavior to be apparent is the time at which the extrapolated straight-line part of the $I^{-1/2}$ -versus- t curve deviates by more than 2% from the actual decay curve. The values of τ determined in this way are given in Table II and are shown in Figures 1 and 2.

Although we are primarily concerned here with MgO, experiment shows that similar behavior is observed for

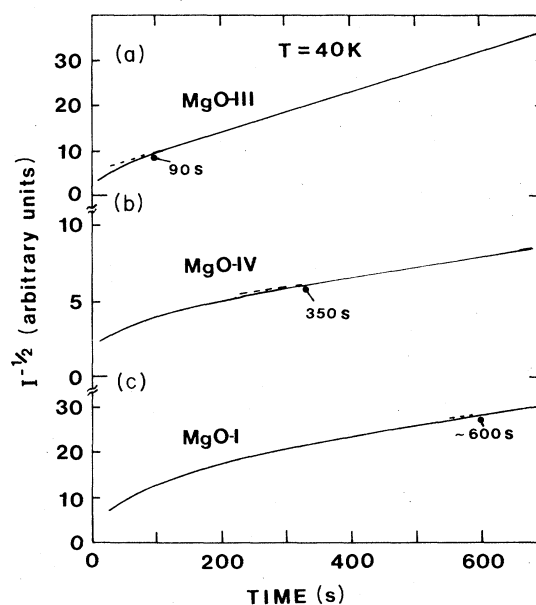


FIG. 2. 2.3-eV F -center luminescence decay in three samples of thermochemically reduced MgO at $T=40$ K. A characteristic time at which approximately second-order behavior becomes apparent is indicated for each curve (see text). These curves should be compared to those shown in Fig. 1.

TABLE II. Characteristic times τ for luminescence decay.

| Sample | τ (s) | |
|---------|------------|------------|
| | 300 K | 40 K |
| MgO-I | 90 | ~ 600 |
| MgO-III | ~ 550 | 90 |
| MgO-IV | 450 | 350 |

thermochemically reduced CaO.¹³ In both cases there is a clear difference of behavior at low and high temperatures, which is correlated with the relative concentrations of deep and shallow electron traps in the samples.

IV. THEORETICAL MODEL AND DISCUSSION

Although the physical processes which lead to the observed 2.3-eV luminescence decay are expected to be quite complex and as yet not completely understood, the general features of the thermoluminescence results strongly suggest that a useful first approximation is to consider the system as comprised of two kinds of electron traps and one kind of luminescent center (i.e., the F center). Figures 1 and 2 show that it is the relative concentrations of these traps and F centers in a sample that determine the luminescence decay kinetics. The trap which becomes thermally unstable near room temperature is the H^{2-} ion which has an activation energy for release of the outermost electron of 0.56 eV (Ref. 13). We estimate from the TL peak temperature that the thermal activation energy for release of an electron from the lower temperature trap is ~ 0.08 eV (Ref. 13). In the following we shall refer to these two kinds of traps as "deep" and "shallow," respectively.

The model we shall consider is shown schematically in Fig. 3, which shows the conditions after the excitation has been removed. In Fig. 3, α_i represents the rate constant for nonradiative transition from the conduction band to the i th trapping level, which is located at an energy E_i into the band gap. γ_i represents the rate constant for the reverse process, i.e., excitation from the trap into the conduction band. β represents the rate constant for 2.3-eV radiative decay of an electron which has been captured by

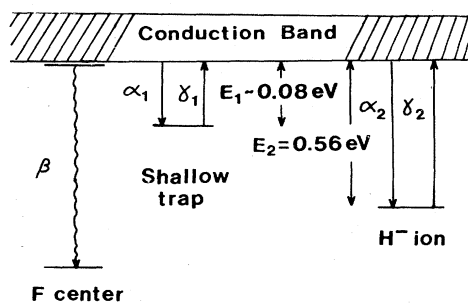


FIG. 3. Schematic energy-level diagram for a system of two electron traps, showing the rate constants considered to influence the F -center luminescence decay.

an F^+ center to form an excited F center.

There are several approximations made in the model. For example, we have not considered the finite probability that an electron captured into the excited state of an F center will be released back to the conduction band.³ Nor have we considered the possibility of nonradiative electron transitions from the traps directly to the ground state of the F center. Welch *et al.*¹⁴ have shown that this latter process seems to occur in thermochemically reduced CaO. Neither of these processes are expected to alter significantly the main conclusions drawn from our model, since we are not directly concerned with temperature-dependent effects. However, the effect of tunneling will be discussed further below. The model is essentially an extension of one proposed initially by Medlin,¹⁵ and Halperin and Braner.¹⁶

The kinetic equations are

$$\frac{dz_i}{dt} = -\frac{dy_i}{dt} = -\gamma_i z_i + \alpha_i n y_i, \quad (1)$$

$$\frac{dx}{dt} = -\beta n x, \quad (2)$$

$$\frac{dn}{dt} = \sum_{i=1}^2 \gamma_i z_i - \sum_{i=1}^2 \alpha_i n y_i - \beta n x. \quad (3)$$

Here, x is the number of empty luminescent centers (i.e., F^+ centers), and y_i and z_i are the numbers of empty and filled traps of the i th kind, respectively. (Here $i=1$ or 2 for the shallow or deep traps, respectively.) Clearly $y_i + z_i = N_i$, where N_i is the total number of traps of the i th kind. n is the number of electrons in the conduction band. In solving Eqs. (1)–(3) we assume that the system is in a quasi-steady-state condition during the slow luminescence decay, so that $dn/dt \approx 0$. Then

$$\frac{dn}{dt} = \frac{dx}{dt} - \sum_{i=1}^2 \frac{dz_i}{dt} \approx 0,$$

i.e., (4)

$$n = \sum_{i=1}^2 \gamma_i z_i / \left[\sum_{i=1}^2 \alpha_i (N_i - z_i) + \beta x \right].$$

It is convenient to define a constant ξ_i , where $\xi_i = \alpha_i / \beta$ is the ratio of the probability of an electron transition at the i th kind of trap to the probability of radiative decay at an F center. Equation (4) can then be written

$$n = \sum_{i=1}^2 \gamma_i z_i / \beta \left[\sum_{i=1}^2 \xi_i (N_i - z_i) + x \right]. \quad (5)$$

The luminescence intensity $I(x)$ is given by the rate of electron transitions at excited F centers, i.e., $I(x) = -dx/dt$. Therefore:

$$I(x) = x \sum_{i=1}^2 \gamma_i z_i / \left[\sum_{i=1}^2 \xi_i (N_i - z_i) + x \right]. \quad (6)$$

Equation (6) defines the general decay rate with two types of traps. In the case of only one kind of trap the result obtained by Medlin is found. We shall use Eq. (6) with the additional condition that the sum of the number

of filled traps is equal to the number of unfilled luminescent centers, i.e., $x = z_1 + z_2$. This condition implies that the number of F centers originally in the crystal is much larger than the number of F^+ centers, which is usually the case for thermochemically reduced samples. Because of the form of the experimental results our purpose in the following analysis is to investigate the conditions under which the luminescence decay curves can be expected to approximate to second order form, i.e., $I^{-1/2} \propto t$. In terms of the number of unfilled luminescent centers, x , at time t , this condition is equivalent to $I(x) \propto x^2$. We shall, therefore, look for this condition. In order to obtain the dependence of I on t , it would be necessary to integrate these equations, which would be difficult, in general, and which would not add significantly to our discussion. We consider below the solution of Eq. (6) for the high-temperature ($T=300$ K) and low-temperature ($T=40$ K) regions separately.

A. $T=300$ K

The activation energy for release of trapped electrons from the shallow traps is ~ 0.08 eV, compared to the deep trap value of 0.56 eV. Since the rate constant for excitation from a trap into the conduction band $\gamma_i \propto \nu_i \exp(-E_i/k_B T)$, where ν_i is the preexponential factor, k_B is Boltzmann's constant and T is the temperature, the rate of emission from the shallow traps at room temperature is expected to be very much larger than the rate for emission from the deeper traps, with all other factors being equal. This means that once the excitation is removed, $z_1 \rightarrow 0$ very rapidly and $x \approx z_2$. In the high-temperature limit, therefore, the system approximates to that for only one trap, for which:

$$I(x) = \gamma_2 x^2 / [\xi_2 N_2 + x(1 - \xi_2)] . \quad (7)$$

As observed by Medlin¹⁵ and others, a second-order decay will then result [i.e., $I(x) \propto x^2$] when $x \ll N_2$. All other things being equal, this condition will occur first for a sample with the largest concentration of traps. In our case this is MgO-I. Figure 1 shows the expected behavior. For MgO-I the characteristic time τ is only ~ 90 s, whereas for MgO-III it is ~ 550 s.

The validity of Eq. (7) can be investigated further by studying the luminescence decay in a particular sample, following excitation with light of varying intensities. Decreasing the excitation intensity has the effect of decreasing the initial value of x , while leaving N_2 unchanged. To test this result we used a fourth sample, MgO-II, for which $n_F = 4.1 \times 10^{18} \text{ cm}^{-3}$ and $n_H = 1.3 \times 10^{17} \text{ cm}^{-3}$. Under normal excitation the characteristic time for second-order behavior in MgO-II was ~ 480 s. As the excitation intensity was progressively reduced by inserting neutral density filters with optical density equal to 0.5, 1, and 1.5, into the light path, the characteristic times fell first to ~ 380 s, then to ~ 270 s and then to ~ 240 s, respectively. As expected, the approximately second-order behavior set in earlier as the initial value of x was reduced.

B. $T=40$ K

At 40 K, $\gamma_2 \rightarrow 0$. The basic equation then takes the form

$$I(x) = x \gamma_1 (x - z_2) / [(\xi_1 N_1 + \xi_2 N_2) + x(1 - \xi_1) + (\xi_1 - \xi_2) z_2] . \quad (8)$$

Since $z_2 < x < (\xi_1 N_1 + \xi_2 N_2)$, we can perform a binomial expansion on the right-hand side of Eq. (8) to find

$$I(x) \approx \frac{\gamma_1 x^2}{\xi_1 N_1 + \xi_2 N_2} \left[1 - \frac{z_2}{x} - \frac{x(1 - \xi_1)}{\xi_1 N_1 + \xi_2 N_2} - \dots \right] . \quad (9)$$

It can be seen that the second and subsequent terms on the right-hand side of Eq. (9) cause the decay to deviate from second order. The criteria for the second-order decay is therefore

$$\frac{z_2}{x} + \frac{1 - \xi_1}{\xi_1 N_1 + \xi_2 N_2} x \leq \epsilon , \quad (10)$$

where ϵ is a constant $\ll 1$. We have taken ϵ to be 0.02 to establish the characteristic times τ .

When the excitation is first removed in an actual experiment, x is relatively large. Approximately second-order behavior will be first apparent when x enters the range $x_- < x < x_+$, where x_{\pm} are the roots of Eq. (10), i.e.,

$$x_{\pm} = \frac{\xi_1 N_1 + \xi_2 N_2}{2(1 - \xi_1)} \left[\epsilon \pm \left[\epsilon^2 - \frac{4(1 - \xi_1) z_2}{\xi_1 N_1 + \xi_2 N_2} \right]^{1/2} \right] . \quad (11)$$

In order for Eq. (11) to have real roots the second term under the square root must be smaller than the first. If we take it that $\xi_1 \sim \xi_2 \sim 1$ and we write $z_2 = f N_2$, where $f < 1$, this condition requires that $N_2 \ll N_1$. Therefore only in samples in which the concentration of shallow traps is much larger than the concentration of H^- ions will second-order behavior be approached. Under these circumstances the characteristic time τ will be first reached when x decreases through x_+ , where x_{\pm} are the roots given by

$$x_{\pm} = \frac{\xi_1 N_1}{2(1 - \xi_1)} \left[\epsilon \pm \left[\epsilon^2 - \frac{4(1 - \xi_1) f N_2}{\xi_1 N_1} \right]^{1/2} \right] . \quad (12)$$

It is apparent from Eq. (12) that $\delta x_+ / \delta N_2 < 0$ and $\delta x_- / \delta N_2 > 0$ for constant N_1 . In all the samples used here the values of N_1 are comparable, while the value of N_2 is small in MgO-III, is larger in MgO-IV, and is largest in MgO-I. Table II shows that the observed values of τ follow the predicted pattern with τ smallest for MgO-III and largest for MgO-I. The results for CaO were also found to follow this trend. An additional prediction which we cannot verify with the available samples is that if the concentration of H^- ions (N_2) is constant in several samples, the second-order behavior should be seen earliest in the sample with the largest concentration of shallow traps because $\delta x_+ / \delta N_1 > 0$. We note in passing that although it is possible to control the concentration of H^-

ions in a sample of MgO by attention to the starting materials and the growth and coloration processes, it has not been possible so far to deliberately affect the intensity of the low-temperature TL peak. This peak seems to be of comparable size in all the samples we have studied, including others not used here.

The second root x_- of Eq. (12) also has an interesting consequence. After a long enough time, the requirement $x_- < x$ will not be met and the decay will no longer show second-order behavior. Although we shall not show it here, $x_- > x$ first in samples for which N_2 is largest. Experimentally this effect is difficult to demonstrate, because at large values of t the luminescence intensity becomes difficult to detect. However, we can conclude from the analysis given above that the general form of a plot of $I^{-1/2}$ -versus- t for a typical sample will be concave towards the t axis for small values of t , will then show a region of approximately linear (second-order) behavior, and will finally turn convex to the t axis for very large values of t . The available data seem to confirm this prediction.

The results of Welch *et al.*¹⁴ for CaO and the theoretical work by Summers *et al.*³ for MgO suggest that direct tunneling by electrons from traps to the luminescent centers is a mechanism that needs to be considered in a complete model. The results of Refs. 3 and 7 suggest, for example, that the wave functions of the outermost electron in an H^{2-} ion and an electron in the T_{1u} state of the F center are very diffuse, so that there is a good chance of significant overlap, especially in samples containing large concentrations of these defects and ions. Possible tunnel-

ing processes can be included to a first approximation in the model discussed above by adding a term $-\delta_i z_i x$ to the right-hand side of Eq. (1) and a term $-x \sum_i \delta_i z_i$ to the right-hand side of Eq. (2). These terms allow for one rate constant for tunneling, δ_i , for each kind of trap. When the resulting equations are solved as in Sec. IV, it is found that the basic conclusions drawn above are not altered. These conclusions are summarized below.

V. SUMMARY

We have shown that 2.3-eV luminescence in thermally reduced MgO shows approximately second-order decay behavior earlier in some samples than in others. At room temperature the second-order behavior is observed after the shortest characteristic time τ in samples which contain the highest concentration of H^- ions. The reverse dependence is found at 40 K, where the sample with the lowest concentration of H^- ions shows second-order kinetics earliest. These results have been explained in terms of a two-trap model, in which the relative concentrations of the two kinds of trap have been shown to determine the observed behavior.

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