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# Kinetics of radiative recombination in magnesium oxide

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We report time-resolved studies of luminescence excited in nominally pure single-crystal MgO by short pulses of 500-keV electrons at sample temperatures from 10 to 500 K. The principal luminescence bands have peaks at approximately 4.9, 3.3, and 1.7 eV. The decay kinetics and spectral shift of the 4.9-eV luminescence band can be accounted for by the theory of tunneling recombination between randomly distributed hole and electron traps. From prior work, the hole trap has been identified as a magnesium ion vacancy. The electron trap has not been identified, but there is some evidence to suggest that a substitutional $OH^{2-}$ molecular ion could be the neutral donor. The temperature dependence of the luminescence decay has been modeled by including thermal ionization of one trap as a de-excitation channel in parallel with tunneling recombination. Depending on conditions, this thermally-induced hopping of charges can enhance or quench the luminescence.

## I. INTRODUCTION

When nominally pure magnesium-oxide crystals are excited by ionizing radiation, characteristic broad luminescence bands are observed with peaks at approximately 4.9, 3.3, and 1.7 eV. Lee and Crawford recently made a study of the 4.9- and 3.3-eV bands under x-ray excitation and in thermoluminescence for various treatments and dopings of the MgO samples.[1] The 4.9-eV luminescence was found to be correlated with the concentration and thermal stability of $V$ centers, i.e., holes trapped at magnesium ion vacancies. It was proposed that the 4.9-eV luminescence is associated with the recombination of an electron with a hole located on an oxygen ion which is adjacent to a $Mg^{2+}$ vacancy. The term $V$ center will be used generically to denote a hole trapped at a $Mg^{2+}$ vacancy, including those associated with impurities, e.g., $V_{OH}$, $V_{Al}$, as well as the unassociated $V^-$ center. A review of defect centers in simple oxides including a discussion of the $V^-$ center and impurity-associated hole centers is given by Hughes and Henderson.[2] Theoretical studies of the $V^-$ center have been made.[3,4]

A luminescence band at approximately 3.3 eV has been described by Wertz *et al.*[5] and Sibley, Kolopus, and Mallard.[6] This band persists in the steady-state spectrum at higher temperature than the 4.9-eV band. It can usually be observed, though weaker, in crystals lightly doped ($\lesssim$100 ppm) with transition metal ions. Transition metals readily quench the 4.9-eV luminescence, presumably by competing with the $V$ centers as hole traps. The 3.3-eV luminescence exhibits glow peaks in thermoluminescence which are correlated with the release of holes from $V$ centers, and have been suggested to be associated with radiative capture of a hole at an impurity or defect site. It has been suggested,[6] based on correlation of 3.3-eV luminescence with EPR data, that the site for radiative hole capture is $Fe^{2+}$. Yet the data of Lee and Crawford indicate that doping with iron suppresses rather than enhances the 3.3-eV luminescence.[1] Newton and Sibley[7] found that blue thermoluminescence centered spectrally near 2.9 eV is associated with recombination at deformation debris. Thus, identification of the recombination center giving 3.3-eV luminescence remains uncertain.

A structured luminescence band is commonly observed near 1.7 eV in MgO. It has been satisfactorily identified with radiative capture of holes by $Cr^{2+}$ impurity ions.[5,6,8] This band will not be addressed in the present study.

In this work we have measured luminescence excited in MgO by 3-nsec pulses of 500-keV electrons, at temperatures from 10 to 500 K. Decay kinetics and the spectral shift of the 4.9-eV band at low temperature are in good agreement with the donor-acceptor pair model as developed by Thomas, Hopfield, and Augustyniak[9] (and references cited therein). Decay kinetics at higher temperature are described qualitatively in terms of thermal ionization and redistribution of the charges among trapping sites. For the 4.9-eV luminescence, the acceptor is taken to be the

*V*-type center suggested by Lee and Crawford.[1] We propose that the luminescence results from electron tunneling between a donor and the (*V* center) acceptor, rather than direct capture of a conduction electron by the *V* center.

Although the theory of donor-acceptor pair recombination was developed principally in response to observations in semiconductors such as ZnS,[10,11] and GaP,[12–14] it should be noted that similar phenomena have been observed in insulators, particularly alkali halide crystals. Delbecq, Toyozawa, and Yuster[15] reported tunneling recombination of trapped electrons (at $Ag^0$, $Tl^0$) and holes (at $Cl_2^-$) in KCl:AgCl and KCl:TlCl. Delbecq, Dexter and Yuster[16] also describe tunneling recombination between $Ag^0$ and $Ag^{2+}$ in KCl:AgCl, developing a theoretical model which is similar in concept to the semiconductor work.

## II. EXPERIMENT

The high-purity MgO single crystals used for most of this work were cleaved from boules grown at the Oak Ridge National Laboratory by an arc-fusion process. Typical impurity analyses have been published.[17] Samples were mounted on the cold finger of a liquid-helium cryostat. For high-temperature work (to 500 K) the same cryostat was used as a "hot finger" vacuum oven.

The experimental apparatus and techniques for time-resolved spectroscopy have been described previously.[18,19] MgO crystals were excited by a 3-nsec pulse of electrons having 500-keV mean energy. The typical pulse energy density at the sample surface was $5 \times 10^{16}$ eV/cm$^2$ and the electron penetration depth was approximately 0.5 mm. The resulting luminescence pulse was collected by fused quartz optics and dispersed by a grating monochromator with a bandpass of 5 nm. The signal was detected with an Amperex 56*TUVP* photomultiplier having S-20 photocathode response and nominal 2-nsec anode pulse rise time, and was displayed on an oscilloscope. Spectra have been corrected for the response of the photomultiplier and monochromator.

To determine effects of optical ionization of specific traps during or after x-ray excitation, the crystal was irradiated with x-rays (50 kV, 30 mA) and bleached (simultaneously or at a later time) by chopped, monochromatic light from a 200-W xenon arc. Steady-state luminescence spectra excited by x-ray irradiation at temperatures up to 515 K were also recorded.

## III. RESULTS

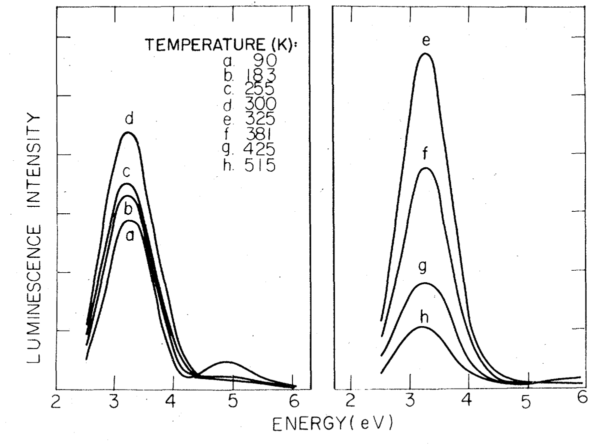

FIG. 1. Spectra of luminescence excited by 30-kV x rays are shown for sample temperatures as indicated.

Luminescence from a MgO crystal excited by 30-kV x rays is shown in Fig. 1 as a function of temperature. The 4.9-eV band can be enhanced by about a factor of 3 by prolonged ionizing irradiation, which acts to build up a concentration of *V* centers.[1] It effectively vanishes from the steady-state spectrum at 180 K. The 3.2-eV band achieves its maximum intensity near 325 K. There is no discernable peak shift and little broadening in the temperature range 90 to 515 K.

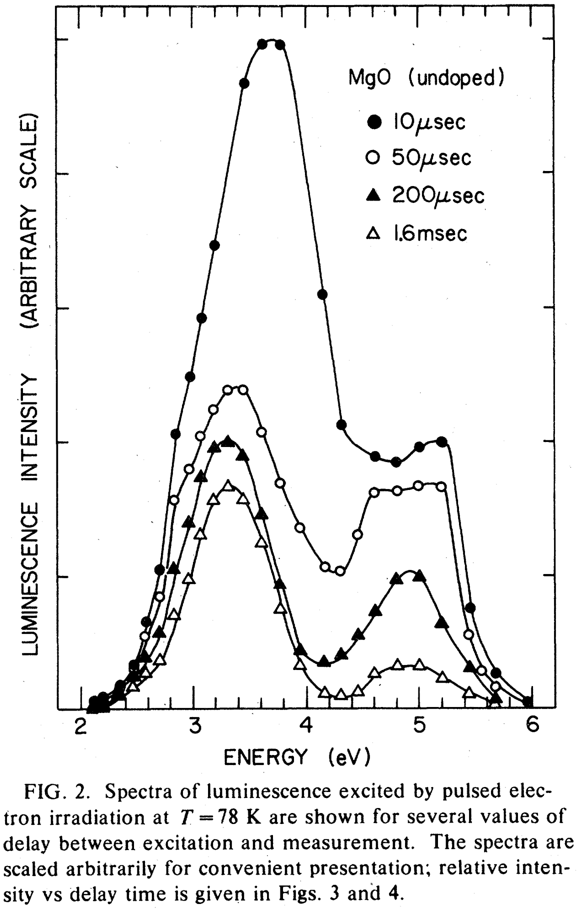

FIG. 2. Spectra of luminescence excited by pulsed electron irradiation at $T = 78$ K are shown for several values of delay between excitation and measurement. The spectra are scaled arbitrarily for convenient presentation; relative intensity vs delay time is given in Figs. 3 and 4.

Similar spectra and temperature-dependent yields have been measured as a function of time after excitation by a short pulse of energetic electrons. Figure 2 shows luminescence spectra for pure MgO at 10, 50, 200, and 1600 $\mu$ sec after pulse excitation, at a temperature of 78 K. The spectra have been scaled by arbitrary factors to facilitate display on the same figure. Thus Fig. 2 shows changes in spectral shape with time, but not the change in relative intensity with time. Data for intensity versus time at specific wavelengths are given in Figs. 3 and 4.

The intensity at 4.9 eV (253 nm) following electron pulse excitation of pure MgO at temperatures from 10 to 453 K is shown in Fig. 3. The decay curves are displaced by arbitrary scale factors to give approximately uniform spacing along the logarithmic intensity axis. Typical curves cover about four decades in time and intensity. Corresponding data for 3.3 eV (376 nm) are given in Fig. 4. Relative intensities as a function of temperature for times of 1 and 500 $\mu$ sec after excitation are shown in Fig. 5, providing scale factors for the decay curves in Figs. 3 and 4.

It is evident that the broad bands in Fig. 2 are composite in nature. At the earliest times, the peaks are at higher energy than the corresponding broadband peaks observed under continuous excitation.

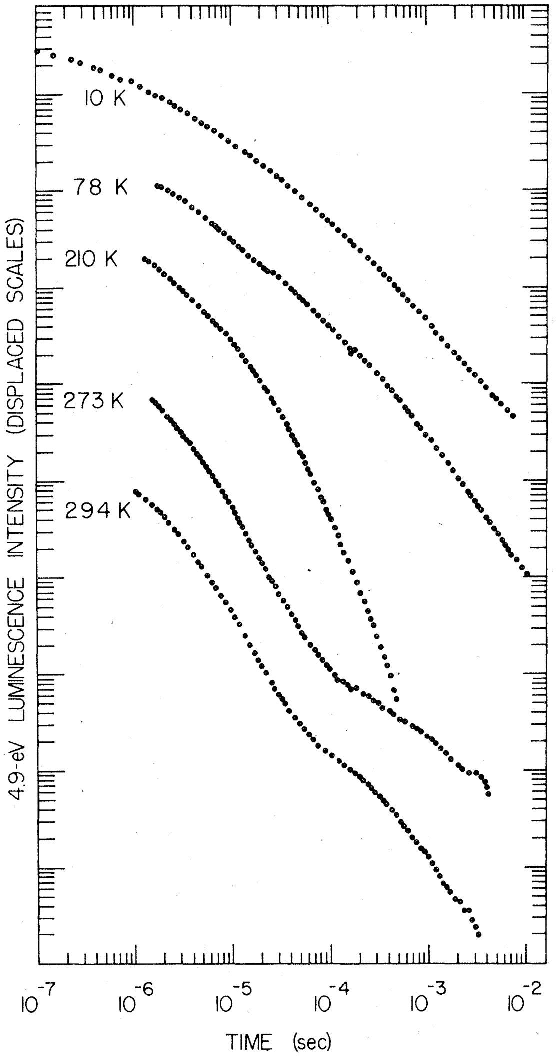

FIG. 3. Luminescence intensity at 4.9 eV is shown as a function of time after electron pulse excitation at the temperatures indicated. Both axes are logarithmic; the data for different temperatures are displaced arbitrarily along the vertical (intensity) axis for convenient graphical presentation. Relative intensity vs temperature is given in Fig. 5.

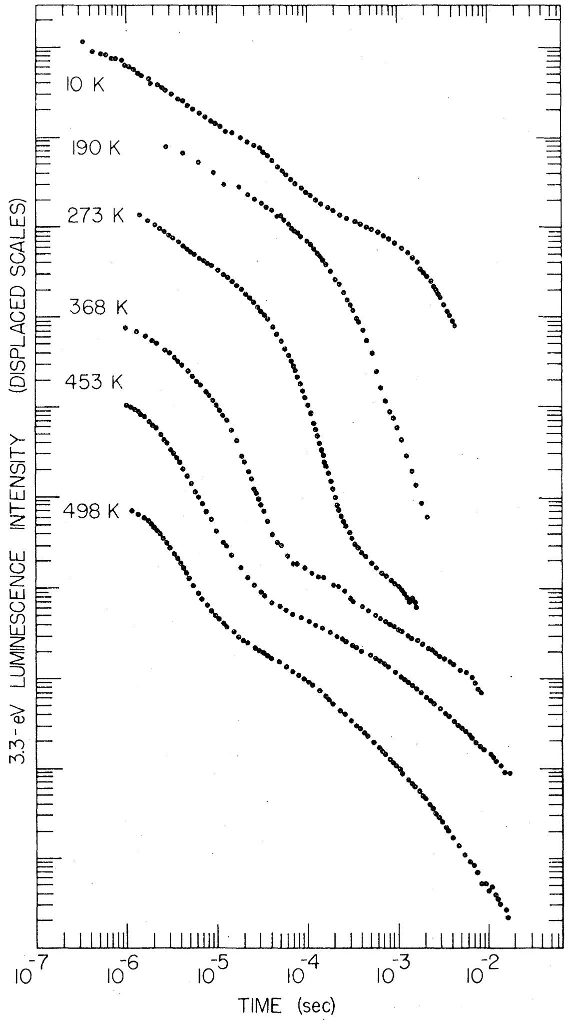

FIG. 4. Luminescence intensity at 3.3 eV is shown as a function of time after electron pulse excitation at the temperatures indicated. Both axes are logarithmic; the data for different temperatures are displaced arbitrarily along the vertical (intensity) axis for convenient graphical presentation. Relative intensity vs temperature is given in Fig. 5.

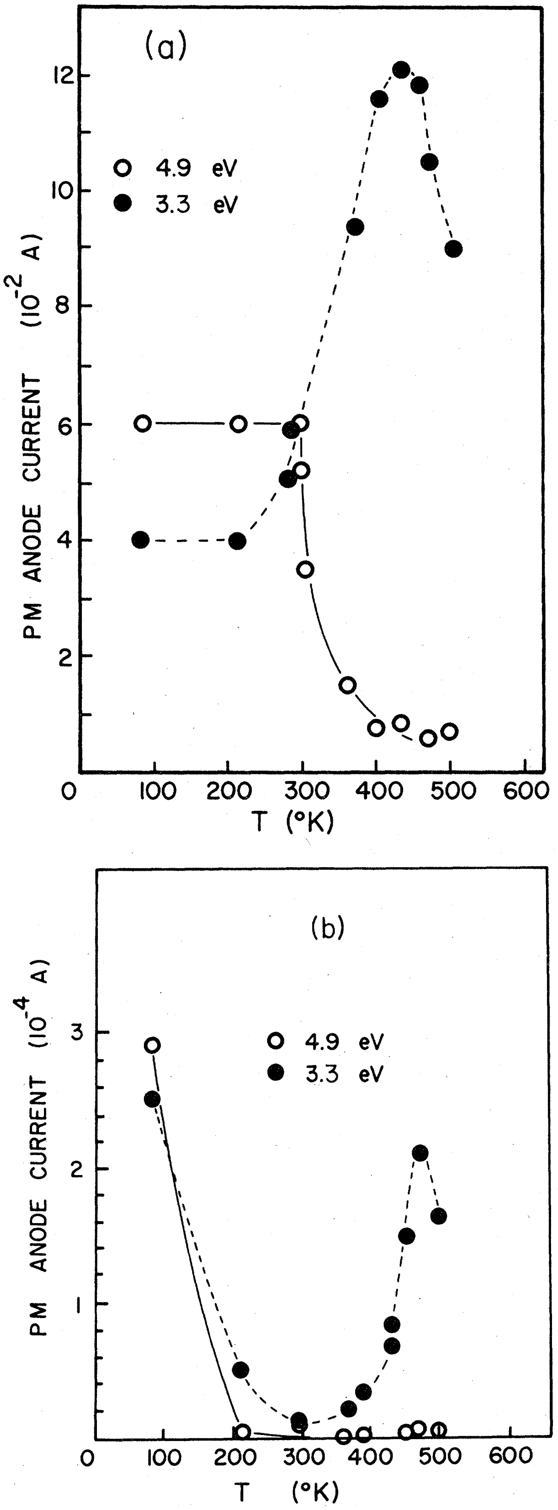

FIG. 5. Instantaneous luminescence intensity (proportional to photomultiplier anode current) is plotted as a function of temperature for the 4.9- and 3.3-eV bands. The measurements were made 1 $\mu$sec (a) and 500 $\mu$sec (b) following electron pulse excitation.

The spectra in Fig. 2 at longer times agree more closely with the steady-state results, which represent time-integrated data. By assuming that the low-energy band is symmetric, we can make an approximate separation of the two broad bands. The "average energy" of each band, corresponding approximately to the first moment, can be defined by

$$\bar{E}=\frac{\int EI(E)dE}{\int I(E)dE}\ , \qquad (1)$$

where $E$ is photon energy and $I(E)$ is the spectrum of luminescence intensity in a given band. It is found that both composite bands shift about 0.25 eV to lower energy within 50 $\mu$ sec after excitation.

We attempted to correlate measured transient absorption in the $V$ band with luminescence decay times. At low temperature the absorption induced by an electron pulse is mostly stable on the time scale of our observation. However, a substantial transient component of optical absorption was observed at temperatures above 300 K. The decay times of 3.3-eV emission and 2.3-eV absorption are roughly comparable, but no quantitative correspondence has been established. The difficulty is that there is also substantial absorption which is stable on the 10 msec scale at all temperatures up to 500 K, so that the transient absorption can be followed only over a limited range.

An indication of the role of mobile holes was obtained from photoluminescence experiments in which we excited $V$ centers with chopped 2.3-eV light while the crystal was x-ray irradiated at 78 K. The spectra of total luminescence and of modulated luminescence in phase with the optical excitation were recorded. Similar modulated spectra with temperature-dependent decay times were obtained when the crystal was bleached with chopped $V$-band light after x-ray irradiation had ceased. It is known that the $V$-type centers can be bleached by optical excitation near 2.3 eV, apparently by thermal ionization out of the relaxed excited state. The photoluminescence data indicate that holes optically released into the valence band from $V$ centers enhance the 3.3-eV luminescence but have no siginificant effect on the 4.9-eV luminescence. These data support the conclusions of prior thermoluminescence studies.[1,6]

## IV. DISCUSSION

### A. 4.9-eV band at low temperature: donor-acceptor pair recombination

The luminescence decay curve for $T=10$ K in Fig. 3 cannot be fit as a power law nor as a simple exponential decay. An attempt to fit the data over the full four decades with a sum of exponentials requires at least four components (i.e., eight adjustable parameters). The form of the experimental decay curve is strongly suggestive of curves for recombination among randomly distributed donors and acceptors in semiconductors, as calculated by Thomas, Hopfield, and Augustyniak.[9] The model is based on an assumption that the rate of radiative recombination of an electron trapped on a donor with a hole bound to an acceptor is

$$W(r) = W_{\max} \exp(-r/R) \;, \tag{2}$$

where $r$ is the distance between the donor and acceptor. $R$ is half the donor (or acceptor) Bohr radius, with the acceptor (or donor) radius considered to be much smaller. $W_{\max}$ is a constant related to the transition rate of the closest pair. It was shown by Thomas *et al.*[9] that for donors or acceptors in excess, with $N$ being the concentration of the majority constituent, the total intensity of light emitted at time $t$ is

$$I(t) = -\frac{d}{dt}\langle Q(t)\rangle \;, \tag{3}$$

where

$$\langle Q(t)\rangle = \exp\left[4\pi N \int_0^\infty \{\exp[-W(r)t] - 1\} r^2\, dr\right]$$

is the probability that an electron initially on a donor surrounded by randomly distributed acceptors remains on the donor at time $t$.

If $R$ is taken as the unit of length, it may be effectively eliminated from Eqs. (2) and (3) for purposes of curve fitting. Thus, defining $\rho = r/R$ yields

$$w(\rho) = W_{\max} e^{-\rho} \tag{4}$$

and

$$I(t) = \left(4\pi n \int_0^\infty w(\rho) \exp[-w(\rho)t] \rho^2\, d\rho\right) \exp\left(4\pi n \int_0^\infty \{\exp[-w(\rho)t] - 1\} \rho^2\, d\rho\right) \;, \tag{5}$$

where $n = NR^3$. The full curve which is fit to the 4.9 eV, 10 K data in Fig. 6 is completely specified within the above donor-acceptor model by *three parameters:* $n (= NR^3)$ determining the curvature, $W_{\max}$ determining the time scale, and an intensity scale factor which slides the curve vertically. In the case of Fig. 6, $W_{\max} = 1.4 \times 10^7$ sec$^{-1}$ and $n = 2 \times 10^{-4}$. The concentration of magnesium ion vacancies in the sample can be estimated from $V$-band optical absorption to be $N_V = 1.3 \times 10^{18}$ cm$^{-3}$. Then $R \approx (n/N_V)^{1/3} \approx 5.4$ Å, which is not unreasonable for a shallow electron trap in MgO.

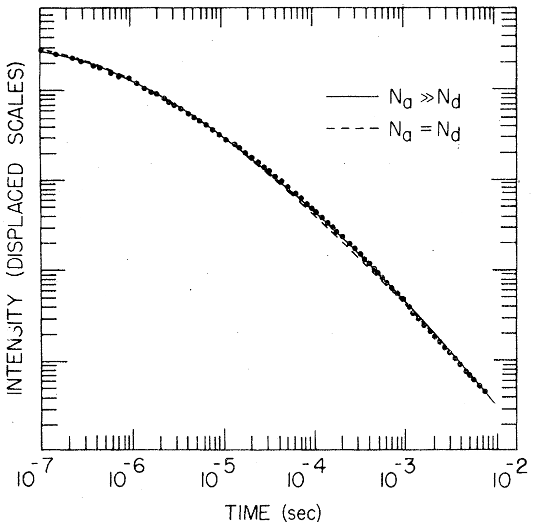

FIG. 6. Calculated decay curves corresponding to tunneling recombination of electrons and holes are superimposed on experimental data for 4.9-eV luminescence measured at $T = 10$ K. The full-line curve corresponds to acceptors (or donors) in excess ($N_a >> N_d$). The dashed curve was calculated for $N_a = N_d$ using the Hartree approximation. The fitting parameters are $NR^3 = 2 \times 10^{-4}$, $W_{\max} = 1.4 \times 10^7$ sec$^{-1}$, and an arbitrary vertical scale factor.

In performing the numerical integration in Eq. (5), the upper limit has been taken to be $\rho_0 = 100$ (e.g., $r_0 = 500$ Å when $R = 5$ Å). Increasing the limit beyond 100 produced no significant change in the curves over the time range of interest. The effect of varying $n (= NR^3)$ when $W_{\max}$ is constant is illustrated in Fig. 7. The effect of varying $W_{\max}$ is to translate the curves along a diagonal of the log-log plot.[9]

The model decay curve is independent of temperature as long as the donors or acceptors are not thermally ionized within the measurement time. In Fig. 3 the luminescence decay curves for $T = 10$ and 78 K are very similar. If it were supposed that the long luminescence decay time arises from a model in which carriers are thermally released from a distribution of traps of different depths to recombine directly, then even a small change in temperature should have a large effect on the decay curve. The observed insensitivity to temperature at low temperature is more consistent with the model presently considered, where thermal untrapping is not a prerequisite for radiative recombination. Thermal ionization of the donor will be treated in Sec. IV B, as a process competing with radiative recombination.

The energy of $D$-$A$ pair emission can be written

$$E(r) = E_{\text{gap}} - E_d - E_a + \frac{e^2}{\epsilon r} \;, \tag{6}$$

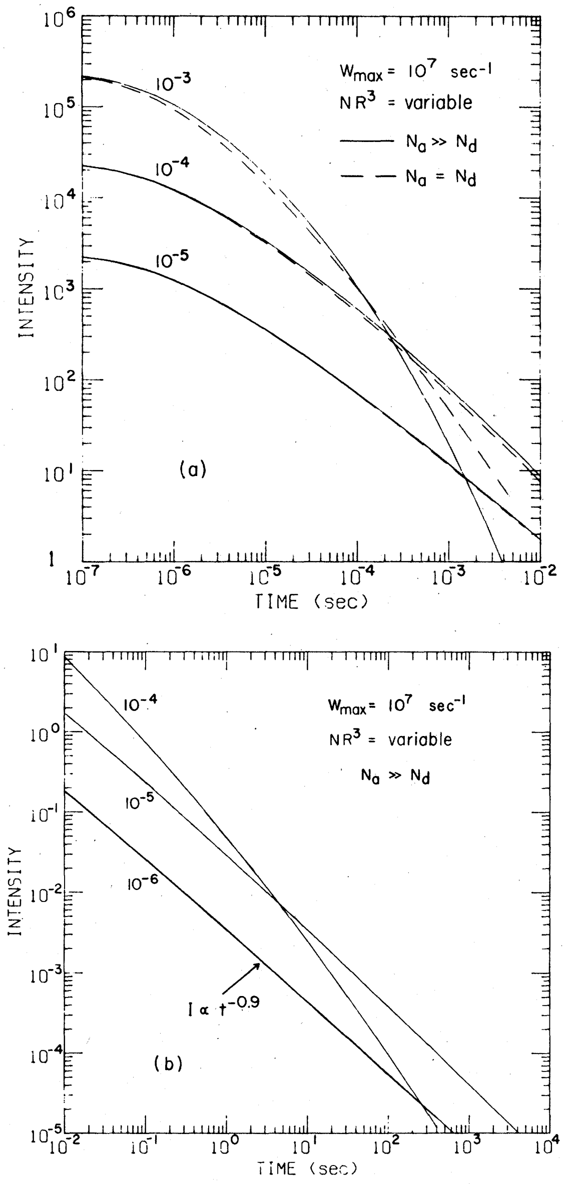

FIG. 7. Effect of varying $NR^3$ in the donor-acceptor pair recombination model of Ref. 9 is illustrated for the time range $10^{-7}$ to $10^{-2}$ sec (a), and $10^{-2}$ to $10^4$ sec (b). At long times and relatively low values of $NR^3$, the curves are in agreement with the $t^{-0.9}$ dependence found in Ref. 16.

where $E_{gap}$ is the band-gap energy, $E_d$ and $E_a$ are the donor and acceptor binding energies, $\epsilon$ is the low-frequency dielectric constant, and $r$ is the donor-acceptor separation.[9] We hypothesize that in MgO, sums of such transitions constitute the 4.9-eV emission band. In semiconductors having the zinc-blende structure, discrete lines are typically observed corresponding to the closest *D-A* pairs, merging into a broad envelope of lines from many *D-A* pairs at larger separation. Such discrete lines have not yet been observed in MgO, probably because of the strong interaction with phonons. Equation (6) serves as an adequate description of the energy of a discrete (weak-coupling) phonon-assisted *D-A* emission line if the phonon energy is taken into account. Its application to the peak energy of a band which is broadened by strong phonon coupling is more complex, as discussed in Sec. IV D. We make the assumption here that at constant temperature, the strong phonon coupling contributes a constant Stokes shift that would appear on the right side of Eq. (6) when applied to a broad band peak.

Since the pairs characterized by small $r$ experience a higher rate of radiative recombination than distant pairs, it is expected on the basis of Eq. (6) that the emission should shift to lower energy at later times. This shift is observed in both luminescence bands of MgO between 10 and 50 $\mu$sec. By equating the observed energy shift of about 0.25 eV to $e^2/\epsilon r$, we obtain a value of $r$ which should correspond approximately to the separation of the closest donor-acceptor pair. Taking $\epsilon = 9.8$ yields $r \approx 6$ Å for the distance between closest donor and acceptor. The lattice constant of MgO is 4.2 Å.

In the work of Delbecq, Dexter, and Yuster[16] the transition rate for tunneling recombination between $Ag^{2+}$ and $Ag^0$ at relative separation $r_i$ was written

$$W(r_i) \propto \left[ \frac{x_i^2 - y_i^2}{r_i^2} \right]^2 e^{-Kr_i} . \tag{7}$$

This is analogous to Eq. (2) [which is Eq. (6) in Ref. 9] except that the angular dependence of the 4*d* hole wave function on the $Ag^{2+}$ ion is included in Eq. (7), whereas an *s*-like wave function is assumed in Eq. (2). The anisotropy of the 4d orbital is important in the KCl:AgCl system because the $AgCl_4^{2-}$ molecular-ion complex (denoted $Ag^{2+}$) retains a definite orientation at low temperature, leading to polarized luminescence and a tunneling recombination glow peak upon thermal reorientation.[16]

In contrast, the hole on the $V^-$ center in MgO hops among 2*p* orbitals of the oxygen ions neighboring the $Mg^{2+}$ vacancy, even at low temperature. The hopping rate has been estimated[2] to lie between $10^7$ sec$^{-1}$ and about 1 sec$^{-1}$. Thus there exists the possibility that hopping of the hole among oxygen ions neighboring the magnesium vacancy may affect the tunneling kinetics in MgO on some time scale between $10^{-7}$ and 1 sec. However, presently there is no compelling evidence for including such effects in analysis of data from our work on MgO. The simple isotropic transition rate in Eq. (2) seems justified for the $V^-$ center and a hydrogen-like donor in MgO.

The constant $K^{-1}$ in Eq. (7) is comparable to $R$ in Eq. (2). Delbecq *et al.* chose $K^{-1} \approx 1$ Å as a reasonable value for the KCl:AgCl system, noting that moderate changes in this parameter made little difference in the shapes of the model curves.[16] Their study provides an example of a system where the tunneling recombination model is successful even for wave functions of small radial extent. Their data showed that the luminescence intensity decreased approximately as $t^{-0.9}$, where the time $t$ is in the range 1 to $10^3$ minutes. Their model calculation based on Eq. (7), taking the sum over specific lattice sites, produced a comparable slope over the same time range. The curvature which is evident in Fig. 7(a) is not seen in the plots of Delbecq *et al.*[16] because of the different time ranges addressed. For the roughly equivalent time range of $10^{-2}-10^3$ sec shown in Fig. 7(b), the decay curves can be approximately described by a $t^{-0.9}$ dependence if the effective trap density is small ($NR^3 \lesssim 10^{-5}$). The KCl:AgCl crystals used by Delbecq *et al.*[16] contained 0.02 mol% AgCl. If half the silver ions were prepared as $Ag^{2+}$ and half as $Ag^0$, and if the value $R = K^{-1} = 1$ Å is assumed, then $NR^3 \approx 1.5 \times 10^{-6}$. In fact many of the silver ions remain as $Ag^+$, so $NR^3$ will actually be smaller than this, or $R$ can be taken somewhat larger than 1 Å. The lower curve in Fig. 7(b) demonstrates agreement of the computational approaches developed in Refs. 9 and 16.

Equation (3) was obtained by considering the radiative decay of a single neutral donor surrounded by many hole-bearing acceptors (or vice versa), so that the hole concentration was constant throughout the probabilistic decay process being considered. If the concentrations of donors and acceptors are comparable, then some of the hole states available to a given donor electron will be filled by electrons from other nearby donors during the luminescence decay process. The calculation is then more difficult. Donor-acceptor recombination luminescence in the case of exact compensation was addressed by Thomas *et al.*[9] With $N_i$ representing the number of electrons (0 or 1) on donor sites $i$, $M_j$ the number of electrons on acceptor sites $j$, and $W_{ij}$ the separation-dependent transition rate,

$$\frac{d}{dt}\langle N_i\rangle_{\rm av} = -\sum_j W_{ij}\langle N_i(1-M_j)\rangle_{\rm av} \ , \tag{8}$$

where $\langle\ \rangle_{\rm av}$ is the average over random transitions. In the special case of a single electron, single donor, and many acceptors, $\langle N_i M_j\rangle_{\rm av}$ is zero, and Eq. (8) leads to Eq. (3). As an approximate solution to the case of comparable donor and acceptor concentrations, where $N_i M_j$ can depart from zero, Thomas *et al.*[9] introduced a Hartree approximation to Eq. (8), replacing $\langle N_i M_j\rangle_{\rm av}$ by $\langle N_i\rangle_{\rm av}\langle M_j\rangle_{\rm av}$. While neglecting correlations in occupations of specific sites, this approximation takes into account the decrease with time of the average concentration of holes available to each electron.

It was pointed out in Ref. 9 that the Hartree solution is a poor approximation to the case of exact compensation at long times and low concentrations unless the physical system includes the possibility of hopping of electrons and/or holes from one trap to another during the decay process, thus tending to keep the different $\langle M_j\rangle_{\rm av}$ at the same average value throughout the sample. If the hopping is rapid compared to the radiative decay rate, as it must be at sufficiently long time and/or high temperature, the Hartree average should be a good approximation. Note, however, that the approximation as given ignores kinetics of the hopping, and thus contains no explicit temperature dependence. It assumes that the redistribution of carriers among traps occurs instantaneously (on the radiative time scale) at any temperature.

Following Ref. 9, the ensemble average of the probability $Q(t)$ that an electron is on a given donor in the case of exact compensation is found by solving the equation

$$\langle Q(t)\rangle_{\rm comp} = \exp\left\{4\pi N \int_0^\infty \left[\exp\left\{-W(r)\int_0^t \langle Q(t)\rangle_{\rm comp}\,dt\right\} - 1\right] r^2\,dr\right\} \ . \tag{9}$$

With $\langle Q(t)\rangle$ given by Eq. (3), Eq. (9) may be solved using the relations

$$\langle Q(t)\rangle_{\rm comp} = \langle Q(\tau)\rangle \ ,$$

where

$$\tau = \int_0^t \langle Q(t)\rangle_{\rm comp}\,dt \ ,$$

and

$$t = \int_0^\tau \left\langle \frac{dt'}{Q(t')}\right\rangle \ , \tag{10}$$

following Ref. 9. Then

$$I(t)_{\rm comp} = -\frac{d}{dt}\langle Q(t)\rangle_{\rm comp} \ .$$

Figure 7(a) compares $I(t)_{\rm comp}$ (dashed lines) with $I(t)$ (full lines) for several values of $NR^3$ at fixed $W_{\rm max}$. The curves are similar for early times and/or low concentrations. At later times or high concentration the curves for $N_a = N_d$ (Hartree solution) lie above those for $N_a >> N_d$. Comparison of the curves at early, intermediate, and late times has been discussed in Ref. 9. In Fig. 6, the 4.9-eV data for $T = 10$ K have been fit using Eq. (10), as shown by the dashed line. The full line computed from Eq. (5) was discussed in Sec. IV A. The values of $NR^3$ and $W_{\rm max}$ are the same in both cases, and Eq. (5) provides only a slightly better fit for this concentration and time range. Thus it is not clear from the data at

$T = 10$ K alone whether the kinetics of $D$-$A$ luminescence in MgO correspond to unequal or nearly equal concentrations of donors and acceptors.

### B. Temperature dependence

The simple model for $N_a >> N_d$ discussed earlier was specifically a low-temperature theory, with no hopping of charges among the trap sites allowed. The Hartree solution for the case $N_a = N_d$ implied charge redistribution among traps, but contained no explicit temperature dependence. As temperature is increased, the carriers ultimately escape from their traps and perform a random walk among the trap sites. There is a position-dependent tunneling probability, $W(r_j)\tau$, for radiative recombination on each step of duration $\tau$ at site $j$, where $r_j$ is the distance from the donor to the $j$th acceptor. In general it would be necessary to include probabilities of stepping on a deep trap or a nonradiative recombination center as well. Then the ensemble average of transitions involving $N$ such hopping charges having position-dependent radiative recombination probabilities constitutes the observed luminescence.

If all traps are initially occupied, a random walk among the few traps vacant at early times can have little effect. For the case $N_a = N_d$ at later times, more of the traps will have been depleted by prior recombination, and hopping to the vacant sites becomes significant. Since the sites closest to the donors will have been depleted first by the radiative recombination, the effect of hopping is to replenish these sites and thus speed up the recombination process.

A thermally activated ionization of the donor or acceptor with subsequent recombination probability independent of $W(r_j)$ can affect the model for $N_a >> N_d$ as follows. Suppose that there occurs nonradiative thermal ionization of the donor at a rate $W'$ which is independent of the concentration or distribution of acceptors

$$W'(T) = s\exp(-E/kT) \ . \tag{11}$$

Then Eq. (7) of Ref. 9 becomes

$$\frac{dQ}{dt} = -Q\left(\sum_j^{N_0} W(r_j) + W'(T)\right) \ . \tag{12}$$

Here $Q$ is the probability that the electron is on the donor, and $N_0$ is the total number of acceptors in the crystal volume considered. In the present work the relevant crystal volume is the sphere of integration of radius $r_0 = 100$ R. Following through the analysis with this temperature-dependent parallel decay channel, we find in analogy to Eq. (3)

$$\langle Q(t,T)\rangle = \exp[-W'(T)t + 4\pi N \times \int_0^\infty \{\exp[-W(r)t] - 1\} r^2\, dr] \ . \tag{13}$$

The luminescence intensity $I(t,T)$ at time $t$ and temperature $T$ is found as the term proportional to the radiative transition rate $W(r)$ in the time derivative of $\langle Q(t,T)\rangle$

$$I(t,T) = \left\{4\pi N \int_0^\infty W(r)\exp[-W(r)t] r^2 dr\right\} \times \langle Q(t,T)\rangle \ . \tag{14}$$

In treating the case $N_a = N_d$, it is useful to rewrite Eq. (12) in the form

$$\frac{dQ}{dt} = -Q\sum_j^{N_0} [W(r_j) + N_0^{-1} W'(T)] \ . \tag{15}$$

Performing the ensemble average as in Eqs. (9)–(13) of Ref. 9, but neglecting to factor the term involving $W'(T)$ out of the integrand, yields

$$Q(t,T) = \exp\left[4\pi N \int_0^\infty \{\exp[-\mathcal{W}(r,T)t] - 1\} r^2\, dr\right] , \tag{16}$$

where

$$\mathcal{W}(r,T) = W(r) + N_0^{-1} W'(T) \ .$$

Here $N_0 = \frac{4}{3}\pi N r_0^3$, where $r_0 = 100$ R is the arbitrarily chosen upper limit of integration. Equations (16) and (13) yield identical results in fitting the data. The usefulness of the form given in Eq. (16) is that the Hartree solution for the case $N_a = N_d$ including thermal quenching follows by analogy to Eq. (9) and (10) with $W(r) + N_0^{-1} W'(T)$ replacing $W(r)$. Thus we write an equation for $\langle Q(t,T)\rangle_{\text{comp}}$, the probability that a donor contains an electron at time $t$

$$\langle Q(t,T)\rangle_{\text{comp}} = \exp\left\{4\pi N \int_0^\infty \left[\exp\left(-\mathcal{W}(r,T)\int_0^t \langle Q(t,T)\rangle_{\text{comp}}\, dt\right) - 1\right] r^2\, dr\right\} \ . \tag{17}$$

This may be solved by the method of Thomas *et al.*[9] [see Eq. (10)] with $Q(\tau,T)$ given by Eq. (16).

In Fig. 8, all curves have been computed for $N_a = N_d$ in the Hartree approximation, using only the parameter values $NR^3 = 2\times10^{-4}$ and $W_{\max} = 1.4\times10^7$ sec$^{-1}$ which were determined earlier by fitting the decay curve for $T = 10$ K. The family of curves superimposed on the experimental data for 4.9-eV luminescence is then obtained by varying the single parameter $W'(T)$. Reasonably good agreement with the experimental data at all temperatures is obtained. Agreement is not as good when Eq. (14) corresponding to $N_a >> N_d$ is used. The additional component seen at long times on the higher temperature (273 and 294 K) curves is ignored for purposes of this curve fitting. It may be associated with the overlapping 3.3-eV band rather than the 4.9-eV band.

The thermal ionization rate $W'(T)$ which is deduced from fitting the data of Fig. 8 has been plotted against temperature in Fig. 9. Similar data for the 3.3-eV band discussed in Sec. IV E are also shown.

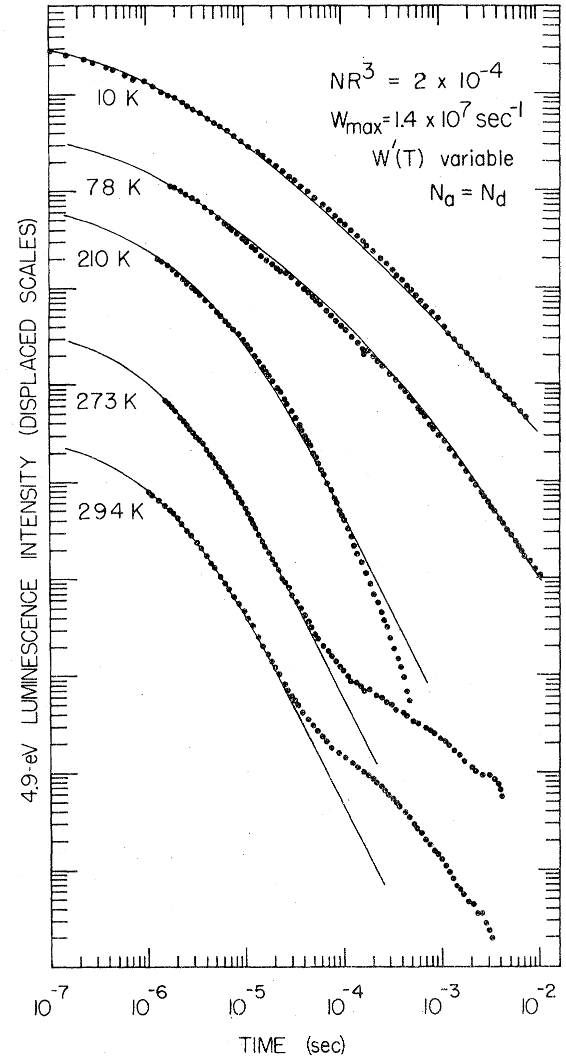

FIG. 8. Model curves calculated from Eq. (17) are plotted, with the parameters $NR^3$ and $W_{\text{max}}$ fixed at the values determined from fitting the data for $T = 10$ K. The single parameter $W'(T)$ is varied to obtain best fits to the superimposed 4.9-eV luminescence data at temperatures between 10 and 294 K. The resulting values of $W'(T)$ are plotted in Fig. 9.

Within the present model, activation energies governing the thermal ionization of the shallow traps can be deduced. The trap whose ionization appears to control the thermal decay of 4.9-eV luminescence is described by an activation energy $E = 0.06$ eV and pre-exponential factor $s = 3.4 \times 10^6 \text{ sec}^{-1}$.

The donor-acceptor model is qualitatively consistent with the available data on thermoluminescence of the 4.9-eV band. When an MgO crystal is excited by ionizing radiation at low temperature, electrons and holes trapped at small separations would undergo tunneling recombination during or shortly after irradiation, leaving only the distant donors and acceptors with trapped carriers. Upon warming the crystal, charges released from the distant traps can repopulate the depleted close *D-A* pairs, thereby producing a glow peak of donor-acceptor luminescence. An interesting analogous phenomenon is the glow peak accompanying thermal reorientation of anisotropic traps as observed by Delbecq *et al.*[15,16] in KCl. The 210 K thermoluminescence peak observed in MgO by Lee and Crawford[1] involves only the 4.9-eV luminescence, not the 3.3-eV band. Since the 3.3-eV band is correlated at higher temperature with release of holes from *V* centers, it was concluded that the 210 K thermoluminescence peak corresponds to release of electrons which subsequently recombine with the holes trapped at *V* centers. Some fraction of the released electrons also find deep traps or nonradi-

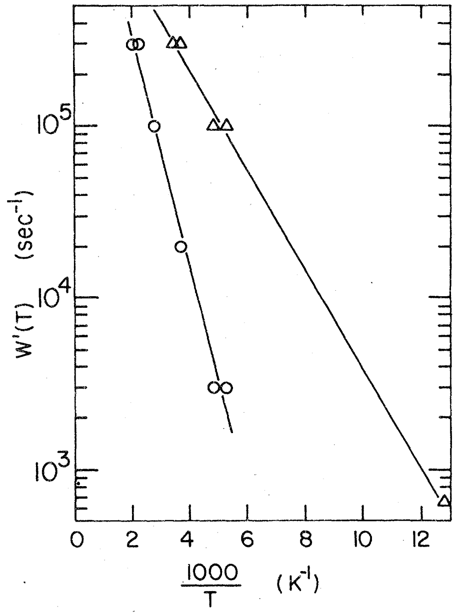

FIG. 9. Values of the parameter $W'(T)$ obtained by fitting the 4.9-eV luminescence decay curves in Fig. 8 (triangles) and the 3.3-eV luminescence decay curves in Fig. 11 (circles) are shown on an Arrhenius plot.

ative recombination centers. Thus thermal ionization of the donors on a time scale faster than radiative recombination can quench the 4.9-eV luminescence, whereas on a slower time scale the effect may be to enhance the 4.9-eV luminescence (glow peak) by redistributing electrons among the available donor sites.

### C. Identifying the traps involved in 4.9-eV luminescence

Lee and Crawford demonstrated that the intensity of 4.9-eV luminescence is correlated with the concentration and thermal stability of $V$-type centers.[1] It was therefore proposed that the 4.9-eV band results from electron capture by a $V$ center with subsequent radiative decay to the ground state of $V^{2-}$ (or $V_M^-$, where $M$ represents a possible charge-compensating impurity adjacent to the vacancy). The $V^-$ center in MgO is a magnesium ion vacancy with one hole trapped on a neighboring oxygen ion, and it has an effective negative charge due to the Madelung potential. Thus the cross section for trapping a conduction electron in an excited state of the $V^-$ center is expected to be very small despite the vacant oxygen $2p$ bound state. Thus one might expect that $V$ centers which are locally charge-compensated (e.g., by $Al^{3+}$ on an adjacent $Mg^{2+}$ site or $OH^-$ on an adjacent $O^{2-}$ site) are the effective recombination centers giving 4.9-eV luminescence. This is possible in principle, but the charge-compensated centers are at best only neutral with correspondingly modest electron-capture cross sections, and such an explanation ignores the evidence for tunneling in the decay kinetics.

If the compensating impurity is close but not immediately adjacent to the $V^-$ center, then a recombining electron will typically be captured at the positive impurity rather than the negative $V^-$ center. The recombination transition to the $V^-$ (oxygen $2p$) hole state could then proceed by tunneling. The transition rate could be effectively enhanced in this way because of the large electron-capture cross section of the positive impurity and its role in holding an electron in the vicinity of the $V^-$ center long enough for tunneling recombination to occur. On the basis of the data on decay kinetics and peak shift presented above, we therefore suggest that the 4.9-eV luminescence results from tunneling recombination of an electron trapped at a charge-compensating donor impurity and a hole trapped at a nearby $V^-$ center.

A second important observation by Lee and Crawford was that the 4.9-eV luminescence is dramatically enhanced by doping with deuterium (or hydrogen), and by prior $\gamma$ irradiation.[1] This has two implications for our suggestion involving $V^-$ centers. Chen *et al.* have shown that in hydrogen-doped MgO, the reaction

$$V_{OH}^- + \text{hole} \rightarrow V^- + H^+$$

proceeds with high efficiency under ionizing radiation.[20,21] The increase of 4.9-eV luminescence in hydrogenated crystals[1] may then occur because the concentration of $V^-$ centers is enhanced through radiation decomposition of $V_{OH}$, or because hydrogen is important in the tunneling recombination, or both. We speculate that at low temperature, the $H^+$ byproduct of $V_{OH}$ decomposition probably remains for a while close to the $V^-$ center which was its source, existing as $OH^-$ substituting on a normal $O^{2-}$ site. In fact, unassociated substitutional $OH^-$ (or interstitial $H^+$) seems not to have been observed in MgO. Its observation might be difficult because it is diamagnetic. The infrared stretching mode of substitutional $OH^-$ not associated with a $V$ center should be observable, but has not been reported. The frequency might be shifted substantially from the $V_{OH}$ mode. Substitutional $OH^{2-}$ or interstitial atomic hydrogen would be paramagnetic. In neutron-irradiated CaO, EPR studies have demonstrated the existence of $OH^{2-}$ ions occupying $O^{2-}$ sites.[22] The paramagnetic centers disappear if the crystals are stored in the dark for a few days, but can be restored by a few minutes exposure to room light or ultraviolet illumination.[22] This suggests that the $OH^{2-}$ charge state may be unstable against loss of an electron by slow thermal untrapping or tunneling recombination. Halliburton *et al.* observed centers produced by x-ray irradiation of SrO at low temperature which were attributed to $OH^{2-}$ (or possibly $OF^{2-}$) molecular ions occupying $O^{2-}$ sites. They also suggested that the radiation-induced decomposition of $V_{OH}$ centers in MgO and other alkaline-earth oxides may produce OH molecules in a variety of local environments and charge states if the temperature is sufficiently low.[23]

The electron binding energy of a substitutional $OH^-$ molecular ion (forming the neutral donor, $OH^{2-}$) may be significantly reduced by proximity of the negatively charged $V^-$ center. Equation (6) giving the energy of donor-acceptor pair luminescence is usually developed for the case where the donor and acceptor are both neutral in the initial state and oppositely charged in the final state—hence the Coulomb term $e^2/\epsilon r$. In the hypothesis we have offered for MgO, the donor is neutral in the initial state but the acceptor ($V^-$ center) has a single negative charge. In the final state the donor is positive and the acceptor (bare $Mg^{2+}$ vacancy) has a double negative charge. The Coulomb contribution to the transition energy still includes the term $e^2/\epsilon r$ as in Eq. (6) since both traps change charge state by one.

### D. Strong coupling to the lattice

The form of Eq. (6) is correct for discrete no-phonon transitions of donor-acceptor pairs. The energies of resolved phonon side bands can also be

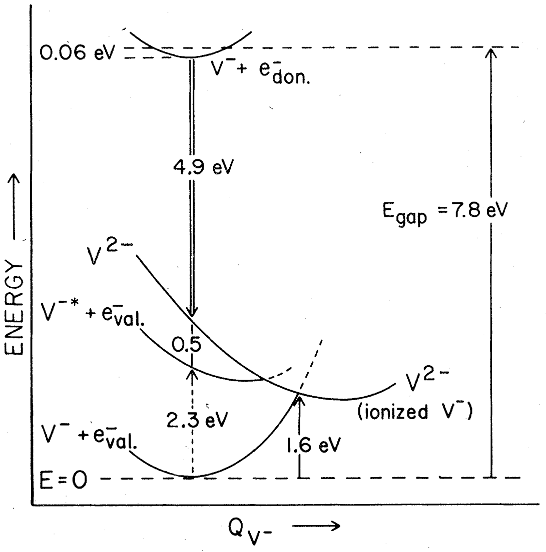

FIG. 10. Combined elastic and electronic energies of the system comprised of a $V^-$ center and a recombining electron are represented hypothetically in this configuration-coordinate diagram. The coordinate $Q_{V^-}$ represents the most important local vibrational mode interacting with the $V^-$ center, typically the breathing mode. Elastic energy of coordinates interacting with the donor is not represented. Optical and thermal ionization of the $V^-$ center and the recombination luminescence transition to $V^{2-}$ are represented.

described by including the phonon energy in Eq. (6). Phonon-broadened luminescence bands, as in the case of MgO, are not quantitatively described by the simple equation, although we found it useful to discuss the peak shift of the broad band in terms of the Coulomb energy in Eq. (6). The trap energies $E_d$ and $E_a$ require careful definition when the lattice coupling is strong.

The configuration-coordinate diagram in Fig. 10 illustrates this. The hypothetical potential curves represent the combined elastic and electronic energies of the system comprised of the $V^-$ center and a recombining electron. For present purposes, the elastic energy of the donor is not considered, since it is removed spatially from the acceptor and interacts with different lattice ions. It could be represented in a multidimensional diagram, however. The local mode coordinate $Q_{V^-}$ represented here is purely schematic, but would typically be the breathing mode of the $V^-$ center.

The zero of energy corresponds to the $V^-$ center in its electronic and vibrational ground state, and an otherwise filled valence band ($V^- + e^-_{\mathrm{val}}$). The initial state for luminescence comprises an electron promoted from the valence band to the donor, with the $V^-$ center as before ($V^- + e^-_{\mathrm{don.}}$). The final state reached in the luminescence transition ($V^{2-}$) corresponds to a magnesium ion vacancy, the empty donor, and a hole remaining in the valence band at a large distance from the $V^{2-}$ center. The minimum of the $V^{2-}$ curve is represented as lying outside the ground-state curve, primarily for convenience. Its actual location has not been established.

For Franck-Condon transitions, the final-state energy of the electronic recombination is at approximately 2.8 eV ($\approx E_{\mathrm{gap}} - 0.06$ eV $-$ 4.9 eV) relative to the vibrational ground state of $V^- + e^-_{\mathrm{val}}$. The 2.3-eV excited state ($V^{-*} + e^-_{\mathrm{val}}$) and its 17-meV thermal ionization[24] to $V^{2-}$ are represented in the figure. The unrelaxed final state of the radiative recombination is the same as the optically ionized state of the $V^-$ center before relaxation. The 2.8-eV energy of that state as deduced here from the luminescence energy, band gap, and donor energy, is quite reasonable in comparison to the 2.3-eV bound-state transition energy. The thermal trap depth of the $V^-$ center (i.e., the activation energy of the reaction $V^-$ + valence electron $\rightarrow V^{2-}$) is thought to be approximately 1.6 eV.[25] Lower energies of activation, e.g., 0.7 eV,[8] and 1.13 eV,[26] for thermal release of holes are suggested to be characteristic of impurity-associated centers such as $V_{\mathrm{OH}}$ or $V_{\mathrm{Al}}$. The value $E = 1.6$ eV was reported as the activation energy for $V^-$ annealing in high-purity MgO powder.[25]

Because of the nonlocal nature of some of the states represented in Fig. 10 (i.e., including valence-band and donor electron energies in addition to the $V^-$ center), some of the apparent curve crossings require comment. For example, although thermal ionization ($V^- + e^-_{\mathrm{val}} \rightarrow V^{2-}$) of the hole trap is possible by capture of an electron from an adjacent oxygen ion, the reverse process requires the presence of a hole and is unlikely to occur except under conditions of ionizing radiation or thermally released holes. Thus the crossing of the $V^- + e^-_{\mathrm{val}}$ and $V^{2-}$ potential curves will not, as the diagram suggests, lead to rapid depopulation of $V^{2-}$.

### E. 3.3-eV band

The decay of 3.3-eV luminescence at temperatures from 10 to 498 K is shown in Fig. 11 with superimposed curves calculated from Eqs. (13) and (14). The parameters $NR^3$ and $W_{\mathrm{max}}$ which specify the curve superimposed on the 10 K data are the same as those determined for the 4.9-eV band at 10 K. The data can be decomposed approximately into the curve shown and an additional exponential component ($\tau \approx 1.5$ msec) accounting for the hump near $10^{-3}$ sec. At higher temperature, this feature decays faster and becomes less notable relative to the donor-acceptor model curve. Thus above 78 K, the donor-acceptor model curves shown are in moderately good agreement with the early portions of the experimental decay curves. In all cases the parameters $NR^3$ and $W_{\max}$ remain the same as for the data at 10 K. The only variable parameter aside from the vertical scale factor is $W'(T)$. The 3.3-eV data are better fit using Eq. (13) for $N_a >> N_d$ than Eq. (17) for $N_a = N_d$. Resulting values of $W'(T)$ are plotted in Fig. 9.

The long tails of the decay curves at high temperature in Fig. 11 grow in approximate correspondence to the 3.3-eV thermoluminescence reported by Lee and Crawford.[1] Since it is known that $V$ centers anneal by ionization in the same temperature range, it seems likely that the high-temperature features near $10^{-3}$ sec in Fig. 11 are associated with the hole release from $V$ centers. Note the corresponding rise of 3.3-eV luminescence intensity in Figs. 1 and 5.

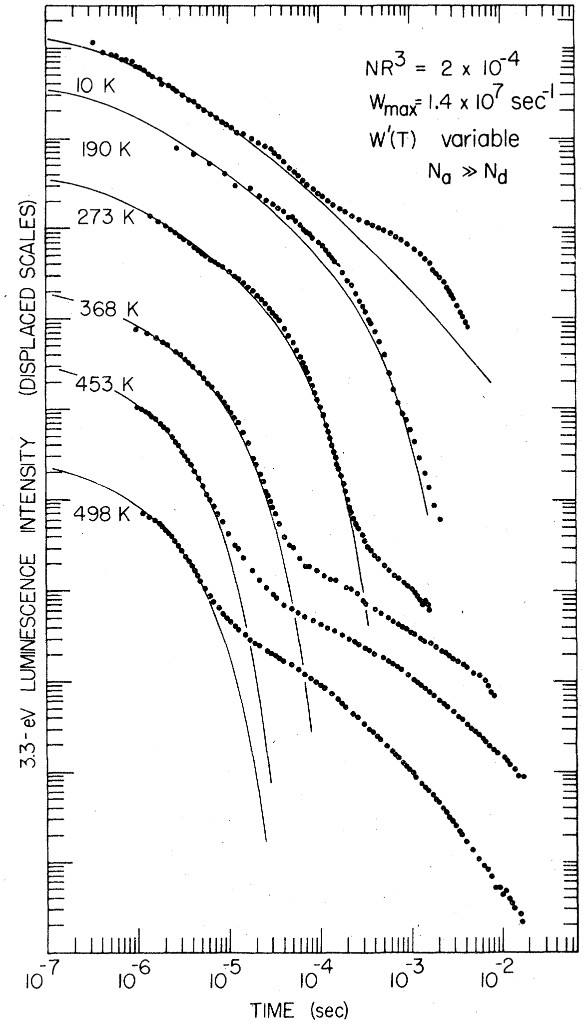

FIG. 11. Model curves calculated from Eq. (13) are plotted, with the parameters $NR^3$ and $W_{\max}$ fixed at the values determined from fitting the data for $T = 10$ K. The single parameter $W'(T)$ is varied to obtain best fits to the superimposed 3.3-eV luminescence data for early times at temperatures between 10 and 498 K. The resulting values of $W'(T)$ are plotted in Fig. 9.

The case for the 3.3-eV luminescence being due to tunneling recombination is much less compelling than for the 4.9-eV band, but the approximate curve fits in Fig. 11 are at least suggestive of such a hypothesis. However, there is presently little evidence to indicate the identities of the traps involved. The temperature dependence of the decay at early times can be interpreted to yield the energy of one of the traps relative to a band edge. From Fig. 9, $E = 0.13$ eV and $s = 5 \times 10^6$ sec$^{-1}$.

## IV. SUMMARY

The decay kinetics and spectral shift of the 4.9-eV luminescence band can be accounted for by the theory of tunneling recombination between randomly distributed hole and electron traps. Utilizing prior work,[1] the hole trap is identified as a magnesium ion vacancy and a possible electron trap is suggested to be the $OH^-$ molecular ion. Further experiments on the role of hydrogen are in order. The magnesium vacancy in MgO retains an overall negative charge even when binding a hole on an adjacent oxygen ion. This would appear to make tunneling the preferred channel for recombination with an electron, and raises interesting questions of partial charge compensation of the donor by the acceptor in the initial state. Unlike most of the semiconductor systems in which donor-acceptor recombination has been studied, the traps in MgO are strongly coupled to phonons.

The temperature dependence of the luminescence decay has been modeled by including thermal ionization of one trap as a de-excitation channel in parallel with tunneling recombination. Under certain conditions this thermally-induced hopping of charges can enhance rather than quench the luminescence. We suggest that this is the mechanism of the thermoluminescence glow peak of the 4.9-eV band, and possibly also the higher-temperature glow peak of the 3.3-eV band.

Experimental data for the 3.3-eV band are presented, but the origin of that band and interpretation of the decay kinetics are rather uncertain. The luminescence is enhanced by release of holes from $V$ centers, and has been suggested in the literature to result from hole capture at $Fe^{2+}$. The decay kinetics are mildly suggestive of donor-acceptor tunneling recombination for this band also.

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