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Transient absorption and luminescence in MgF_2 following electron pulse excitation

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We report time-resolved measurements of optical absorption and emission in pure MgF_2 following excitation by an energetic electron pulse. At low temperature a single asymmetric absorption band having its peak at 275 nm is formed with very high efficiency; approximately one absorber of unit oscillator strength is formed for each electron-hole pair created in the crystal. The absorption band decays with time constants of 6.4 and 0.75 msec at 10 K. A single luminescence band with peak at 385 nm and decay time constants corresponding to those for the absorption is found at low temperature. Thermal quenching of both the absorption and luminescence sets in above 60 K. A second component of transient absorption with a spectrum more nearly resembling the *F* band and with a decay time on the order of milliseconds appears at temperatures above about 170 K. This component grows stronger and decays faster as temperature is raised, but there is no corresponding component of luminescence. At 300 K approximately one absorber of unit oscillator strength is produced per 110 eV deposited by ionizing radiation, and the absorption decays with principal time constants of about 40 and 370 μsec. The low-temperature transient absorption and luminescence is attributed to self-trapped excitons. The high-temperature transient absorption is attributed to the formation of *F* centers and *H* centers which are initially separated by at least several lattice spacings, but which are unstable against nonradiative vacancy-interstitial recombination.

I. INTRODUCTION

In the last ten years, a number of studies of radiation-induced point defects in MgF_2 have been made, spurred both by the extensive use of MgF_2 as an optical coating and ultraviolet window material and by interest in basic defect-production mechanisms in this rutile-structured halide crystal. Following the early work of Duncanson and Stevenson,[1] and Hills and McBride,[2] Blunt and Cohen first identified an absorption band near 260 nm in x-irradiated MgF_2 as being due to *F* centers.[3] The band displays anisotropic linear polarization properties consistent with the C_{2v} point symmetry of the fluorine vacancy, and the band shape is somewhat asymmetric with a shoulder extending into the vacuum ultraviolet. Sibley and Facey, working with electron- and γ-irradiated MgF_2, further substantiated this identification of the 260-nm band and determined that the *F* centers are produced by a photochemical mechanism rather than strictly by momentum-transfer processes.[4] This was especially significant in the context of the Pooley-Hersh model[5] for photochemical defect production since MgF_2 has no long-range focusing directions.

When irradiation of MgF_2 is carried out at a temperature near 150 K, the efficiency for formation of *F* centers is drastically reduced as compared with irradiation at both lower and higher temperatures. This was first noted by Sibley and Facey, who also studied thermal annealing of *F* centers produced at low temperature and concluded that the reduced formation efficiency near 150 K is a result of annealing of close vacancy-interstitial pairs.[4] A model was also suggested[6] to account for reduced probability of correlated *F*-*H* recombination at still higher temperatures than 150 K, thus allowing production of stable well-separated defects. Buckton and Pooley extended the study of defect formation as a function of temperature and proposed a similar model in which radiation creates close pairs of *F* and *H* centers which are stable at low temperature, recombine at intermediate temperatures, and dissociate at high temperature.[7] In further support of this, they also observed that the *F* band which is produced by irradiation at 5 K and measured at 5 K is slightly broader than the *F* band produced by irradiation at room temperature and subsequently measured at 5 K. That is, in a measurement made with polarized light such that only one transition moment of a normal *F* center was excited, they found the width of the *F* band to be, on the average, 0.583 eV in the case of a crystal irradiated and measured at 5 K, but 0.543 eV for the same crystal irradiated at 300 K and measured at 5 K. They measured the energy required to form an *F* center at 5, 50, 250, and 300 K in MgF_2 to be about 4×10^5 eV per *F* center. A value of 2×10^4 eV per *F* center at 300 K was given in Ref. 4.

Luminescence of MgF_2 during x-ray[8] and electron[9] irradiation has been observed, as has the photoluminescence of radiation-damaged MgF_2.[8] According to Bartram and Stoneham, none of the observed photoluminescence can be identified as *F*-center luminescence, and there are theoretical grounds for expecting that excited *F* centers in

MgF_2 decay only nonradiatively.[10] Apparently, most of the photoluminescence in pure radiation-damaged MgF_2 arises from M centers (F-center pairs).[8] The luminescence excited by ionizing radiation includes a broad band centered near 390 nm in all crystals studied so far. Additional bands at 590, 670, and 700 nm have been observed in crystals containing manganese.[8]

Palma has measured the buildup of stable absorption at 180 nm during irradiation by a continuous beam of 1.5-MeV electrons.[11] However, there apparently has been no time-resolved spectroscopy on the scale of electronic-state lifetimes in pulse-irradiated MgF_2. Such time-resolved studies in alkali halides[12,13] and other alkaline-earth fluorides[14] have revealed strong transient absorption bands due to self-trapped excitons and have also proved useful in elucidating defect-production mechanisms. We have, therefore, undertaken time-resolved measurements of absorption and luminescence in MgF_2 following excitation of the crystal by 5-nsec pulses of 500-keV electrons.

II. EXPERIMENT

The basic apparatus is similar to that used in earlier time-resolved spectroscopic studies.[12,14,15] Electron pulses of 5-nsec duration and 500-keV mean electron energy were used to excite the crystals. Transient optical absorption was measured by reflecting an optical probe beam internally from the irradiated surface of the sample at an angle of about 11°, thus increasing the optical path length in the region of electron penetration. Spectra were recorded point-by-point, with normalization to the electron pulse dosage provided by monitoring luminescence at a fixed wavelength. The response of the monochromator-photomultiplier combination used to record luminescence spectra was calibrated against a standard lamp. The spectra presented in this paper have been smoothed by three-point averaging.

The MgF_2 used in this study was Harshaw ultraviolet-grade single-crystal window material cut to $0.5 \times 0.5 \times 0.1$ in. with the irradiated face and edge surfaces polished. Unpolarized light was used in the time-resolved studies since all of the available probe beam intensity was needed in the 190–250-nm range to obtain a good signal-to-noise ratio. No particular orientation of the crystal axes was chosen. The data displayed in this paper were obtained in a sample whose c axis was oriented at 45° to the electron irradiated face and in the plane of incidence of the probe light beam. For comparison, steady-state absorption was measured in a spectrophotometer with unpolarized light incident from approximately the same direction. As a result, our steady-state F-band spectra are superpositions of the $\vec{E}\parallel\vec{c}$ and $\vec{E}\perp\vec{c}$ spectra, which differ in peak wavelength by 4 nm. It turns out that this smearing of the band is much smaller than the spectral characteristics which are of principal interest in this study.

Spectral and kinetic data were measured at 300, 77, and 10 K with the sample mounted on the cold finger of a simple liquid-helium cryostat. The temperature 10 K, as used in this paper, refers to the estimated temperature of the electron penetration layer shortly after an excitation pulse when liquid helium was in the cryostat. Electron-pulse heating was negligible at 77 K and room temperature. The typical electron pulse energy density incident on the surface of the sample in this work was 2×10^{16} eV cm^{-2}pulse^{-1} as determined by substituting a silver-activated glass dosimeter for the sample.

A variable-temperature cryostat was used for measurements of the decay kinetics of absorption and luminescence over the temperature range 10–300 K. The sample was mounted on a cold finger whose temperature was measured by a thermocouple. The accuracy of determining the sample temperature is estimated to be ±5 K, sufficient for present purposes.

III. RESULTS

In Fig. 1, we show the transient optical absorption spectrum of MgF_2 at $T = 10$ K in the 192–1000-nm range, as measured after delays of 0.1, 6, and 14 msec following irradiation by a pulse of energetic electrons. Permanent absorption produced by

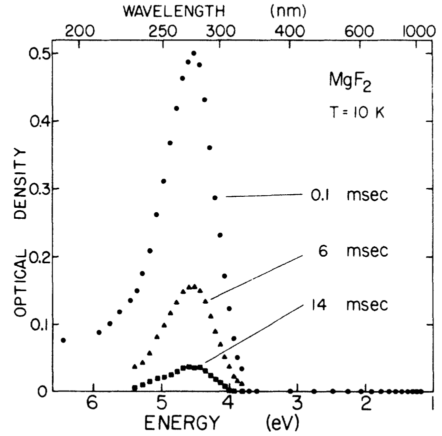

FIG. 1. Optical absorption in pure MgF_2 at 10 K is shown for delays of 0.1, 6, and 14 msec after irradiation by a pulse of energetic electrons. The stable absorption, i.e., that remaining after several minutes, is about 10^4 times lower than the maximum transient absorption shown here.

the same electron pulse at this temperature is not detectable in our experiment, being at least 10^2 times lower than the peak transient absorption by direct measurement. Comparison of transient and stable darkening efficiencies indicates that the stable absorption is in fact about 10^4 times lower in optical density than the peak transient absorption produced by the same pulse of radiation.

The *F* center in MgF_2 has been shown by combined optical and EPR studies to have an oscillator strength of one.[16] If the transient band we observe at 275 nm is assumed to be due to a center which also has unity oscillator strength, then the total deposited energy required for creation of each center at 10 K is 28 ± 10 eV. This is to be compared with 4×10^5 eV per *stable F* center produced at 5 K, as measured by Buckton and Pooley.[7] To draw another comparison, 28 eV is approximately the average ionizing energy required to create one electron-hole pair in MgF_2 (applying the general rule that the electron-hole pair creation energy is approximately three times the band gap[17]). Then our observations imply not only that nearly all electron-hole pairs created in MgF_2 at low temperature reach the metastable state associated with the 275 nm absorption but also that the oscillator strength of this transition *is* near unity.

The spectrum of luminescence excited by the electron pulse is displayed in Fig. 2, as measured at three delays after the excitation pulse. The complete absence of the manganese impurity band at 590 nm is in agreement with earlier observations on Harshaw MgF_2 by Sibley and Facey.[4] The broad band we observe is quite similar to the x-ray excited 390-nm band they observed in MgF_2 from three different sources. The entire luminescence band is seen to decay at the same rate, except for a slight attenuation of the early luminescence in the high-energy tail. This may be due to absorption of the luminescence by the 275-nm transient band.

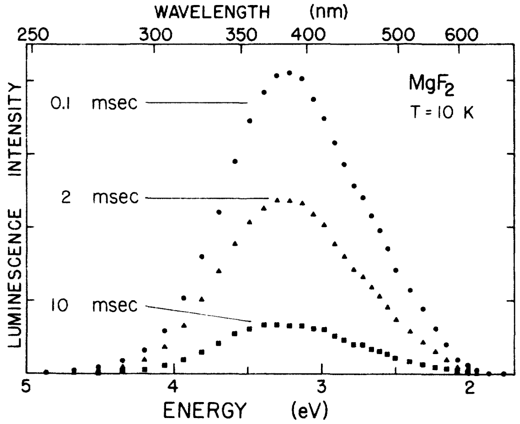

FIG. 2. Luminescence in pure MgF_2 at 10 K is shown for delays of 0.1, 2, and 10 msec after irradiation by a pulse of energetic electrons. The data, shown on an arbitrary scale at constant-energy bandwidth, have been corrected for the spectral response of the photomultiplier-monochromator combination.

The decays of the absorption at 285 nm and the luminescence at 385 nm are plotted in Fig. 3. Except for a small fast component ($\tau = 0.75$ msec), both the absorption and luminescence are accurately described by a single exponential decay with $\tau = 6.4$ msec. Further comparison of decay times at 77 K in Fig. 4 and at a variety of other temperatures to be discussed later demonstrates conclusively that the principal absorption band in Fig. 1 and the luminescence band in Fig. 2 originate in the same excited state.

Transient absorption spectra at 10, 77, and 300 K are shown by the data points in Fig. 5. For comparison, the solid lines show stable *F*-band spectra measured on a spectrophotometer after the same crystal used in the electron-pulse experiments had been irradiated with 50-keV x rays. Whereas the optical probe beam used in the time-resolved spectroscopy made an angle in the crystal of 11° with the irradiated face, the spectrophotometer beam propagated straight through the edge, i.e., at 0° to the irradiated face. However, this small difference in angle of incidence cannot produce spectral shifts even approaching the mag-

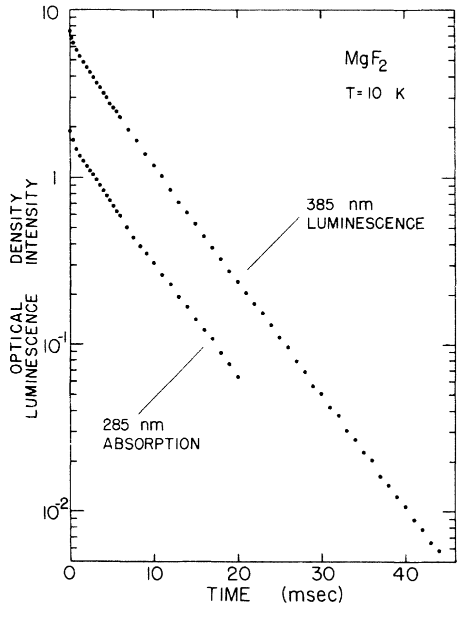

FIG. 3. Decay of optical density at 285 nm and luminescence at 385 nm following electron-pulse irradiation is shown for MgF_2 at 10 K. The initial values are arbitrary.

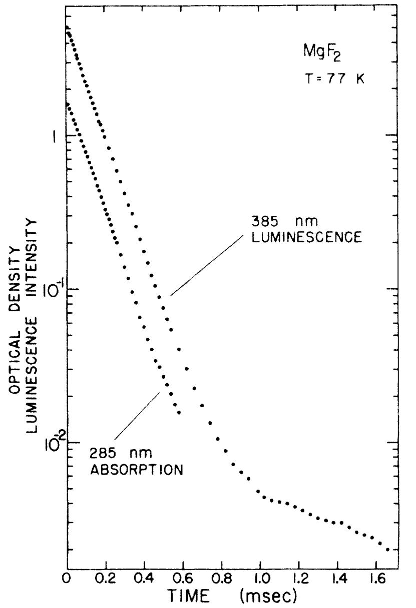

FIG. 4. Decay of optical density at 285 nm and luminescence at 385 nm following electron-pulse irradiation is shown for MgF_2 at 77 K. The initial values are arbitrary.

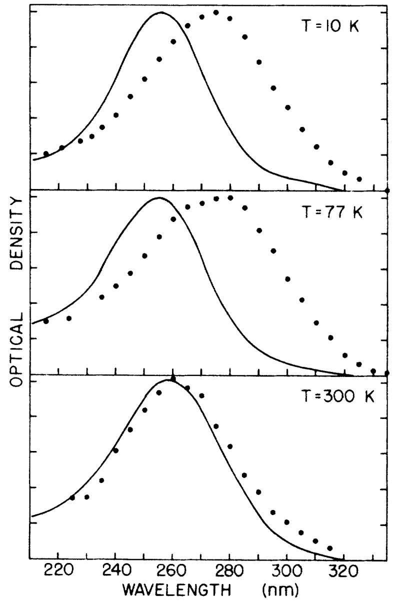

FIG. 5. Data points show transient absorption spectra in MgF_2 following electron-pulse irradiation at 10, 77, and 300 K. The solid lines are steady-state *F*-band spectra measured at the same three temperatures after prolonged x-irradiation of the same crystal. An arbitrary scale of optical density is used in this figure. Peak values of the transient optical density for a given electron-pulse energy density are discussed in the text.

nitude of the effects in Fig. 5, and is essentially negligible for present purposes. Because of the observation by Buckton and Pooley that low-temperature irradiation can produce a slightly broader *F* band than room-temperature irradiation,[7] the *F*-band spectrum (solid line) labeled $T = 10$ K in Fig. 5 was produced and measured at 10 K without warming the crystal. Subsequently, the crystal was warmed to room temperature, x-irradiated again, and measured at 300 and 77 K to produce the other two solid-line spectra shown in Fig. 5. When account is taken of the fact that our measurements are made with unpolarized light, these steady-state *F*-band spectra are in satisfactory agreement with the measurements of other workers. It is readily apparent from the greater breadth and substantially lower peak energy of the transient absorption band observed at low temperature that it is not simply an *F* band. The transient absorption at 300 K, on the other hand, does bear closer spectral resemblance to the *F* band.

The data of Fig. 5 are displayed on an arbitrary normalized optical-density scale. The optical-density values to be assigned to the peaks of the transient bands for the same electron pulse energy density of 2×10^{16} eV/cm^2 are 0.5 at 10 and 77 K, and 0.13 at 300 K. This means that the energy required to produce one transient absorbing center observable after 0.02 msec (prior to significant decay) at 300 K is about 110 eV, again taking an oscillator strength of unity. This value is to be compared with 28 eV required at 10 K.

The relative efficiency of producing transient absorption at various temperatures between 10 and 300 K is shown in Fig. 6. The closed circles represent the optical density at 285 nm produced by an electron pulse having nominal energy density 2×10^{16} eV/cm^2. The open circles represent the corresponding optical density at 255 nm. The actual electron pulse energy fluctuated by up to about a factor of two from shot to shot, and the usual practice of normalizing electron pulse energy by monitoring the sample luminescence was not useful when temperature was being varied. This is the main source of scatter in the data of Fig. 6.

The major trends are that the production efficiency remains roughly constant from 10 K up to about 80 K, and then decreases gradually until a temperature of about 160 K is reached. Just above 160 K there is an apparent discontinuity in the data which will be discussed later in connection with Figs. 7 and 8. Following the discontinuity, the production efficiency of observable transient absorption starts from its lowest value near 210 K and increases steadily as room temperature is approached. In this higher temperature range the

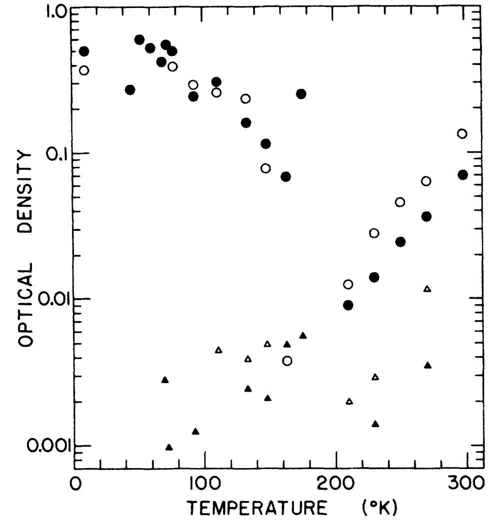

FIG. 6. Optical density immediately following electron-pulse irradiation is plotted for 285-nm (●) and 255-nm (○) absorption as a function of temperature. Long-term absorption ($\tau > 10$ msec) at the same wavelengths is shown with triangular points.

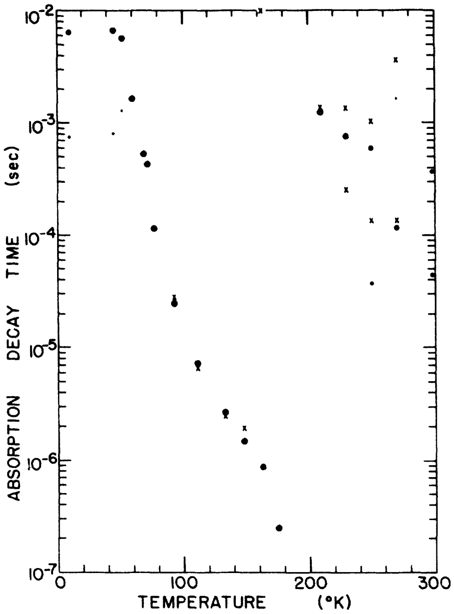

FIG. 7. Decay-time constants of 285-nm absorption (circular points) and 255-nm absorption (crosses) are plotted as functions of temperature. The area of each circular point indicator is proportional to the fractional contribution of the corresponding decay time component to the total 285-nm absorption immediately after excitation.

absorption at 255 nm is consistently greater than the absorption at 285 nm, whereas below 210 K the absorption was roughly comparable at both wavelengths. Consideration of Figs. 5 and 6 together is highly suggestive that the spectral shift evident in the 300 K spectrum in Fig. 5 occurs at the apparent discontinuity in the data of Fig. 6 between the temperatures of 175 and 210 K.

The circular points in Fig. 6 were obtained by fitting the time-dependent data at each temperature to a sum of exponential functions and evaluating the resulting sum at $t = 0$. The sum included a constant term when the data warranted it. The constant term is nominally the stable absorption produced by the electron pulse, though in practice it included any transient absorption with a time constant longer than 10 msec. The magnitude of the constant term is shown as a function of temperature in Fig. 6 by triangles, where again solid points are used for 285-nm data and open points for 255-nm data.

The time constants obtained in fitting the absorption decay data are shown in Fig. 7 as a function of temperature. The circular points refer to time constants for 285-nm absorption, and the *area* of each point is proportional to the appropriate factor A_i in the exponential fitting function:

$$A(t) = \sum_i A_i \exp\left(\frac{-t}{\tau_i}\right), \tag{1}$$

with the imposed normalization $\sum_i A_i = 1$. The constant term ($\tau = \infty$) is not represented in Fig. 7, but its magnitude is shown in Fig. 6 to be generally quite small. The crosses in Fig. 7 represent time constants for 255-nm absorption. No attempt to represent the factors A_i for 255-nm data is made.

At low temperature there is one major component of absorption with a time constant $\tau = 6.4$ msec, and a weaker component whose time constant is about 0.75 msec. These components were evident in Fig. 3, showing the decay of absorption at 10 K. The two components merge near $T = 60$ K, so that the absorption then decays by a single exponential process as shown in Fig. 4. The decay time constant decreases rapidly above 60 K, and becomes faster than the detection apparatus could readily follow at temperatures above 175 K. Also, near 175 K, we first observe a slowly decaying (10 msec) component of 255-nm absorption. At still higher temperature, this component tends toward shorter time constants in the range of 1 msec, and at some temperatures two time constants differing by roughly an order of magnitude in addition to a component with $\tau = \infty$ are required for the fitting. Recall now that a clear trend of increasing magnitude of absorption was evident in this temperature range in Fig. 6. In addition, the discontinuity mentioned in discussing Fig. 6 is seen to correspond to the disappearance of (or experimental inability to measure) the low-temperature component because of thermal quenching and to a simultaneous increase of the high-temperature absorption. In fact, some of the triangular points in Fig. 6, which were processed as components with $\tau = \infty$, are probably finite-lifetime components representing the onset of the higher-temperature absorption.

Figure 8 shows the temperature dependence of decay time constants for 385-nm luminescence. The format of the presentation is basically the same as in Fig. 7. That is, an exponential fitting function analogous to Eq. (1) was used, and the area of each point indicator is proportional to the integrated light output $A_i\tau_i$ in that component, where the normalization condition is now on $A_i\tau_i$ rather than A_i. It is evident on comparison of Figs. 7 and 8 that the absorption and luminescence share the same decay behavior at temperatures below about 170 K, a consequence of the fact that the absorption and luminescence transitions originate in the same electronic excited state. The luminescence above 170 K is actually 10^4 times weaker than the low-temperature luminescence in terms of integrated intensity $A\tau$, although the points appear large because of the normalization condition. This weak high-temperature luminescence probably arises from extrinsic effects and is presumed to be unrelated to the intrinsic processes under consideration. In any case, there are no luminescence components with decay times matching those of the absorption at temperatures above 170 K.

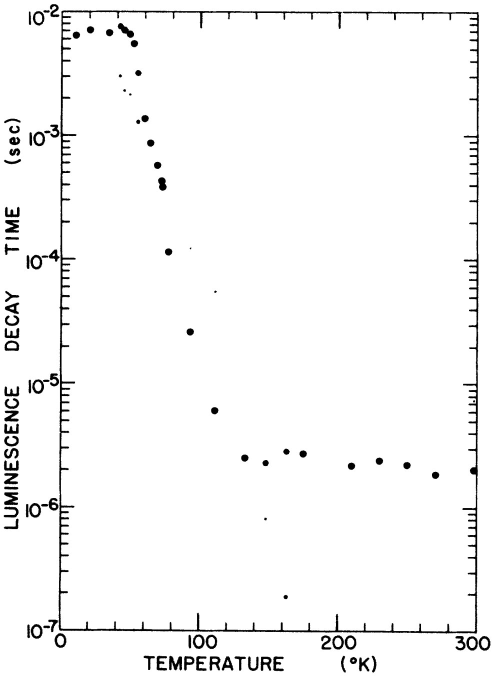

FIG. 8. Decay-time constants of 385-nm luminescence are plotted as functions of temperature. The area of each point indicator is proportional to the time-integrated intensity of the corresponding decay time component, expressed as a fraction of the total light output.

Figures 6–8 together may be interpreted in terms of one principal electronic excited state which is the initial state for both the low-temperature absorption band with peak at 275 nm and the luminescence band with peak at 385 nm. The 0.75 msec component evidently arises from a less-populated state which comes into thermal equilibrium with the principal state near 60 K. At still higher temperature there appears a component of absorption whose decay does not correspond to the decay of 385-nm luminescence, and whose spectrum at 300 K is found (Fig. 5) to be narrowed and shifted relative to the low-temperature spectra.

IV. DISCUSSION

On the basis of the data presented above, it is clear that the transient absorption and luminescence at low temperature originate in an intrinsic localized metastable state of the electron-hole pair. It is reasonable to characterize this state as an electron trapped at a self-trapped hole; that is, as a self-trapped exciton (STE). The MgF_2 data fit well the pattern of behavior exhibited by the STE in fluorites and in alkali halides: the Stokes shift of the recombination luminescence is very large; the decay time is long, suggesting a triplet state; the principal (lowest-energy) transient absorption band lies near but to the low-energy side of the F band; and the efficiency for populating the transient state is high.

The actual ionic configuration which characterizes this long-lived STE state in MgF_2 is a matter of conjecture. For the STE in alkali halides, it is known from polarization measurements and from excited-state EPR[18] that the configuration is the same as for the self-trapped hole, that is, the axis of the X_2^- halide molecular ion in which the hole is trapped remains along the close-packed halide lattice row. By contrast, excited-state EPR measurements[19] have shown that in the more loosely packed fluorite lattice the STE rotates its F_2^- axis out of the normal self-trapped hole orientation ⟨100⟩ and into an approximate ⟨111⟩ direction, a configuration equivalent to an unstable, nearest-neighbor, vacancy-interstitial (F-H) pair.[14] This incipient F-H pair is the only STE configuration seen thus far in CaF_2, SrF_2, and BaF_2, and it produces optical spectra which resemble strongly perturbed ($\sim\frac{1}{2}$ eV) replicas of bands due to separated, stable F-H or F-V_k pairs.

Because of the nature of the rutile structure, one might expect MgF_2 to behave more like the fluorites than the alkali halides. There are several plausible configurations for an incipient *F*-*H* pair, and excited state EPR measurements will be necessary to sort out the possibilities. Apparently only one configuration dominates, since only one strong exponential decay component is observed at 10 K. For the present purposes, the designations STE and incipient *F*-*H* pair can be considered equally descriptive of the state which originates the low-temperature transient absorption and luminescence.

Following the interpretation of earlier work on low-temperature production and annealing of "permanent" *F* centers, it is reasonable to attribute the appearance of the new absorption component upon warming past 160 K and the improved agreement of the transient and stable spectra in Fig. 5 at 300 K to the escape of the interstitial farther from the vacancy. Apparently several vacancy-interstitial pair separations may be attained under these conditions, as evidenced by the multiple-exponential (or non-exponential) decay of absorption near 300 K. Above 160 K, the luminescence no longer corresponds to the absorption decay and is in fact much weaker than at low temperature, suggesting that the overlap of electron and hole orbitals in well-separated pairs is simply too small for effective radiative recombination. Nevertheless, the *H* centers are not so far removed at room temperature that *nonradiative F*-*H* recombination cannot occur in a few hundred microseconds in most cases.

Certain of the alkali halides show this same temperature-dependent behavior. For example, in KI under pulsed irradiation at low temperature there are only the strong STE absorptions which correlate with the recombination luminescence, but around 90 K the *F* band begins to appear and the STE absorption decreases correspondingly.[20] One might say that at low temperature, only *F*-*H* pairs at zero separation are produced, but at higher temperatures the interstitials are able to escape and produce characteristic *F* and *H* centers.

The data of Fig. 6 would appear to indicate that the efficiency for producing transient states of any kind goes through a substantial minimum near 200 K. Such is probably not the case; instead, transient absorption components due to STE's with lifetimes shorter than 100 nsec, which would escape detection with the apparatus used for the present work, can be expected to account for at least most of the apparent loss of electron-hole pairs. Thermal broadening also contributes slightly to the apparent loss.

In view of the above, it is reasonable to suppose that a STE or incipient *F*-*H* pair state is the precursor to a separated *F*-*H* pair. This is known to be true for KCl and is probably true for at least most other alkali halides. The general *F*-*H* pair production process and the nature of the precursor state in fluorites and in alkali halides is the subject of a forthcoming paper.[21]

Ueda and co-workers have reported EPR observation of *H* centers in MgF_2 which was neutron-irradiated near liquid helium temperature and measured at 77 K. The *H* center is described as an interstitial fluorine atom which forms an asymmetric ($F^{-0.4}$-$F^{-0.6}$) molecular ion with a lattice fluoride ion.[22] They did not observe *H* centers in MgF_2 which was γ-irradiated and measured at 77 K. However, Norman and Halliburton[23] have recently made EPR measurements on H_A centers (impurity-associated *H* centers) formed by ionizing radiation at 77 K, and on intrinsic *H* centers formed in MgF_2 by ionizing radiation at 35 K. The intrinsic *H* centers are unstable at temperatures above about 60 K. These data indicate that the stable *H* center exists in a split interstitial configuration which is subject to strong impurity perturbations.

An intriguing question encountered not only in the interpretation of the data in this paper, but also in the understanding of earlier steady-state work, relates to the apparent absence of either an *H* band or a V_k band from the optical spectrum. A radiation-produced *F* center must be compensated by a complementary *H* center, or interstitial fluoride ion and V_k center, or interstitial fluoride ion and some other charge compensator. Yet no optical band in the steady-state spectrum of a radiation-damaged MgF_2 crystal has been identified as *H* or V_k, and our transient spectra do not show a distinct feature which can be identified as a hole transition. It is useful to devise an extrapolation procedure to indicate the spectral region where such transitions might be expected to occur.

As has been previously noted for STE transitions in alkali halides[12] and alkaline-earth halides,[14] the transient peaks identified with Rydberg states of self-trapped excitons shift to higher energy with decreasing lattice constant. The trend is roughly the same as for *F*-band peak energies in these materials, which for alkali halides has been generalized in the well-known empirical Mollwo-Ivey formula.[24] The simplest rationale for this formula is the particle-in-a-box model for the *F* center. On the other hand, the transient ultraviolet absorption due to the principal STE hole transition as well as the principal transitions of V_k and *H* centers shift very little with lattice constant,[12,14] because of the localized nature of the X_2^- orbitals involved.

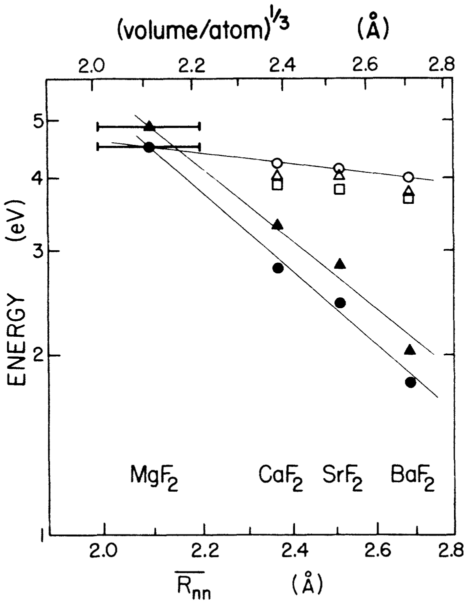

FIG. 9. Peak energies of principal transient absorption bands (●, ○) as well as stable F (▲), H(△), and V_k(□) bands are plotted on logarithmic scales as functions of crystal parameters defined in the text.

In Fig. 9, we have attempted to incorporate MgF$_2$ along with the fluorite-structure crystals in a plot correlating transition energies with lattice parameter. Because two different crystal structures are represented, there is some ambiguity in choosing the parameter to be plotted on the horizontal axis. The scale at the bottom of the figure is the average distance of nearest-neighbor cations around the fluoride ion site. In the fluorite lattice each fluoride ion is surrounded by four equivalent cations situated at the corners of a tetrahedron at a distance $(\frac{3}{16})^{1/2}a_0$. In MgF$_2$, each fluoride ion is surrounded by three nearly equidistant Mg ions, two at a distance of 1.997 Å and one at a distance of 1.981 Å.[25] The average of these distances, $\langle R_{nn}\rangle_{av} = 1.992$ Å, is plotted in Fig. 9 as the lower limit on the horizontal-bar representation of uncertainty for MgF$_2$. The scale at the top of Fig. 9 is (volume/atom)$^{1/3}$, where volume/atom is computed as the volume of a unit cell divided by the number of ions in the unit cell. For the fluorite-structure crystals, this quantity scales with a_0 as does R_{nn}, so that the abscissas of the points for CaF$_2$, SrF$_2$, and BaF$_2$ are in the same ratio on both scales. For MgF$_2$, (volume/atom)$^{1/3}$ is the upper limit on the horizontal-bar uncertainty representation. The point symbols, solid triangles for the stable F-band peak and solid circles for the peak of the lowest-energy transient band, are placed at the centers of the uncertainty bars for MgF$_2$ and at the appropriate (unique) values for CaF$_2$, SrF$_2$, and BaF$_2$. The points representing the F-band peaks are seen to fall more or less on a straight line, as do the points for the low-energy transient band.

The higher energy transient bands for CaF$_2$, SrF$_2$, and BaF$_2$ are represented in Fig. 9 by open circles, and the stable V_k and H bands are represented by open squares and triangles, respectively. The straight line drawn through the points for the high-energy transient bands in the fluorites intersects the point for the single transient band peak observed in MgF$_2$. This strongly suggests that in MgF$_2$ the electron and hole transitions of the self-trapped exciton (or closest F-H pair) in effect coincide. A similar extrapolation of the data for stable F, H, and V_k bands indicates that the H and V_k bands in MgF$_2$ should occur at an energy several tenths of a volt below the F band. However, the limited physical basis for these extrapolations[26] clearly leaves matters uncertain regarding discrepancies of this scale. Thus, since distinct hole transitions have not yet been observed experimentally, it appears a reasonable possibility that for stable as well as transient defects the ultraviolet absorption which has been observed comprises a superposition of hole and electron transitions.

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