Lattices (Oxford U. P., Oxford, England, 1956), Chap. II.

[23] B. Bendow, Ph.D. thesis (New York University, 1969) (unpublished).

[24] We have omitted, for simplicity, the real energy shift Δ_n, which may be reabsorbed into the previously defined energy levels E_n.

[25] See, for example, R. Loudon, J. Phys. (Paris) 26, 667 (1965); and B. Bendow, Ph.D thesis (New York University, 1969) (unpublished).

[26] Actually, for $\Gamma \rightarrow 0$ the real part of T_C becomes infinite *exactly* at E_g and $E_g + \omega_0$; however, this behavior does not substantially affect any other frequency values, and may be removed by any nonzero choice.

[27] This value for Γ is approximately the one found to best fit reflectivity data in CdS by J. J. Sein [Ph. D. thesis (New York University, 1969) (unpublished)].

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M-Center Fluorescence in NaCl and KI Crystals

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The first excited singlet state Σ_u^+ of the *M* center fluoresces in the near infrared. This fluorescence has been observed at low temperatures and the decay time found to be 41 nsec for NaCl and 60 nsec for KI. In KI, a maximum time (5 nsec) is established for filling the Σ_u^+ state from a higher-excited state Π_u. In addition, the fluorescence spectrum of the *M* center in KI is reported for the first time. At ~10 °K, the fluorescence intensity peaks at 0.818 eV = 1.52 μ and has a half-width of 0.100 eV.

I. INTRODUCTION

The *M* center consists of two *F* centers on adjacent anion sites and is analogous to the hydrogen molecule.[1,2] The analogy arises because this center is composed of two electrons bound to two anion vacancies which act as positive charges. Because of this similarity, the electronic energy states are identified by molecular terminology.[1] The lowest four singlet states are shown in Fig. 1; triplet states do not enter into the present discussion.

The primary purpose of the present experiment is to determine the time constants for fluorescent decay from the excited states shown in Fig. 1. Specifically, the following quantities are sought: the wavelengths and time constants (τ_1) for the $\Sigma_u^+ \rightarrow \Sigma_g^+$ transition in NaCl and KI, and the time (τ_2) for the $\Pi_u \rightarrow \Sigma_u^+$ transition. Previous work has not indicated a higher-energy emission line due to a direct $\Pi_u \rightarrow \Sigma_g^+$ (ground state) deexcitation in other alkali halides.

The above transition times are directly observable since a *Q*-switched ruby laser excites the *M* centers quasi-instantaneously. The ruby photons have an energy of 1.79 eV (6943 Å). This energy falls in the *M* band in NaCl and the M_F band in KI[1,3]; Fig. 1 shows the states involved in these absorption bands. Thus the ruby laser excites the *M* centers to the Σ_u^+ and Π_u states in the respective crystals. The measurement consists of observing the fluorescent intensity due to the $\Sigma_u^+ \rightarrow \Sigma_g^+$ transition as a function of time after the ruby laser flash. The dynamics of filling and emptying the Σ_u^+ state are then determined from the time dependence of this transition.

II. EXPERIMENTAL METHOD

M centers were formed in crystals which had previously been colored[4] so as to have an *F*-center concentration up to 2×10^{17} cm^{-3}. In order to avoid large clusters of *F* centers, the crystals were cooled rapidly from high temperature to 80 °K. The KI crystals were quenched within the optical Dewar; the crystals were first heated to 400 °C

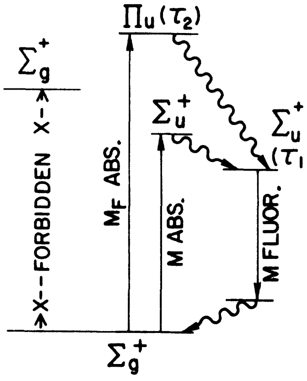

FIG. 1. Energy levels of the *M* center as given by molecular-spectroscopic terms. This is equivalent to considering the *M* center as a hydrogenlike molecule immersed in an isotropic dielectric. It is understood that the right-hand Σ_u^+ level is derived from the upper Σ_u^+ state by the usual rapid Franck-Condon shift (to lower energies on a configuration coordinate diagram); see Fig. 43 of Ref. 1(c). The time constants for deexcitation from the upper levels are given in parentheses.

by a cartridge heater in the coolant chamber, then the chamber was filled with liquid nitrogen. A weak M-center absorption was observed immediately after quenching; however, when needed, additional M centers were produced by a 1-h bleach with F light at room temperature.[1] The final concentration of M centers was ~ 10^{16} cm^{-3} in KI and 2×10^{15} cm^{-3} in NaCl.

An optical Dewar held the samples during the fluorescence measurements. The samples were mounted on the vacuum side of a copper plate which was in contact with the coolant, usually liquid helium. Two special features were incorporated into the present Dewar design. First, no liquid-nitrogen jacket shielded the helium chamber; instead the cold gas from the helium cooled an aluminum radiation shield by conduction. The resultant heat leak was sufficiently small that $\frac{1}{2}$ liter of liquid helium lasted 1 h. Cold glass windows originally shielded the sample and helium chamber from room-temperature radiant heat. The windows did not alter the behavior of the sample nor the helium evaporation rate, so they were subsequently removed. The second special feature was the cartridge heater for raising the sample to 400 °C, as mentioned above.

A Leiss double-glass-prism monochrometer plus glass filters provided the wavelength selection and rejected the ruby excitation light.

A Philco No. 4520 germanium photodiode detected the fluorescence. The fluorescent intensity results were corrected for the wavelength dependence of the photodiode sensitivity. The response time of the photodiode and oscilloscope together was normally 5 nsec; however, the response time for light near 1.7 μ increased to ~ 100 nsec. This slow response at long wavelengths arises from atypically great light penetration into the germanium crystal when the photon energy approaches the band-gap energy of germanium.

The M centers were usually excited by a Q-switched ruby laser. The laser emitted 0.05 J into 0.12 cm^2; i.e., 1.5×10^{18} photons/cm^2. The ruby flash had a width at half-maximum of 35 nsec and an observed fall time of 17 nsec. The laser pulse was commonly attenuated to ~ 10^{16} photons/cm^2, so that the long fall time would not result in continued excitation of M centers.

In the initial investigation of M-center fluorescence in KI, filtered light from a xenon flashlamp excited the M centers. The filtering limited the light to the vicinity of the M band, that is 97% of the energy lay in the region 0.85–1.12 μ. The following two conditions meant that the slow response of the photodiode near 1.7 μ was not troublesome when flashlamp excitation was utilized: The flashlamp pulse lasted about 10 μsec, and the output of the photodiode was integrated in order to obtain the total fluorescence output at each wavelength.

III. *M* CENTER IN NaCl

The time constant obtained from the M-center fluorescence is the time τ_1 for the $\Sigma_u^+\to\Sigma_g^+$ deexcitation. The fluorescence is peaked at 1.07 μ. The Π_u state does not enter into the present considerations since laser excitation is directly into the Σ_u^+ state via the M absorption band. The fluorescence decayed exponentially (over $1\frac{1}{2}$ decades) with a time constant τ_1 of 41 ± 3 nsec. [Time dependences are given by the usual exponential expression

$$I(t)=I_0e^{-t/\tau} \quad , \tag{1}$$

where $I(t)$ is the observed intensity, I_0 is the initial fluorescent intensity, t is the time, and τ is the time constant.] The 41-nsec time constant is quite reasonable in view of previous results with M centers in other alkali halide crystals; in particular $\tau_1=60$ nsec was reported[5] for KCl and $\tau_1=11$ nsec for NaF.[6]

The present pulse excitation facilitates an accurate determination of the fluorescent spectrum, besides establishing the decay time. The advantage of pulse excitation is that a spurious fluorescence is readily rejected because of its different time constant. (The term "spurious fluorescence" refers to light which arises from centers other than the M center. A presently occurring example of this is weak F light which is emitted even though excitation is in the M band. The F-light emission possibly arises from anion vacancies trapping a free electron.) The result is that the present M-center fluorescence appears narrower than previously reported. As shown in Fig. 2, the width at half-maximum is 0.14 ± 0.01 eV; the previous result[7] was 0.17 eV. The peak appears essentially unchanged in position, 1.155 eV as compared to the previous[7] 1.16 eV.

IV. *M* CENTER IN KI

The first step in fluorescence measurements is to determine the photon energies emitted during the $\Sigma_u^+\to\Sigma_g^+$ transition in KI. Apparently the M-center fluorescence has not been previously reported for KI crystals.[3] In order to avoid exciting F centers during these initial experiments, flashlamp excitation was utilized with the results shown in Fig. 3. The peak positions and half-widths are tabulated in Table I. A Mollwo-Ivey plot, Fig. 4, shows that the peak position agrees with an extrapolation from M centers in other alkali halides. The width of the present fluorescence peak is one-half the F-center width; the same ratio is found for M- to F-center fluorescence peaks in KCl and

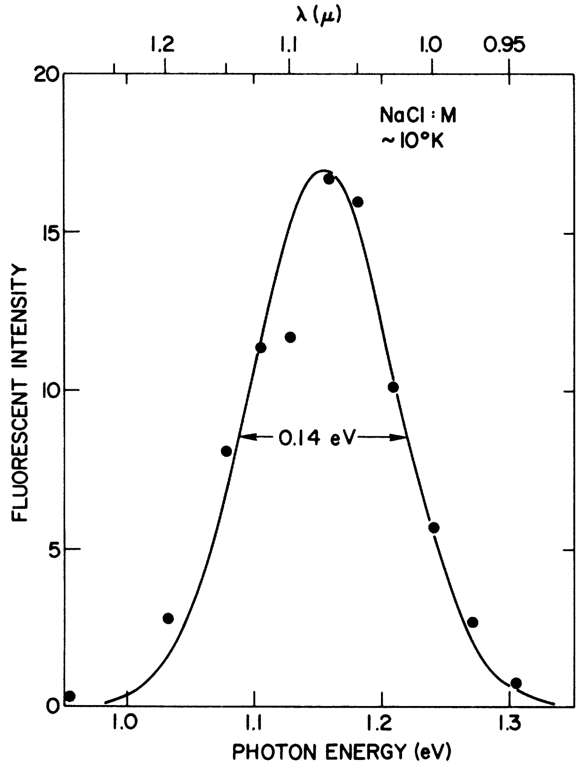

FIG. 2. Fluorescent intensity vs photon energy for *M* centers in a NaCl crystal. The points are fitted to a Gaussian curve which peaks at 1.155 eV and has a 0.14-eV half-width. Excitation was with a ruby laser, whose wavelength lies in the *M* band.

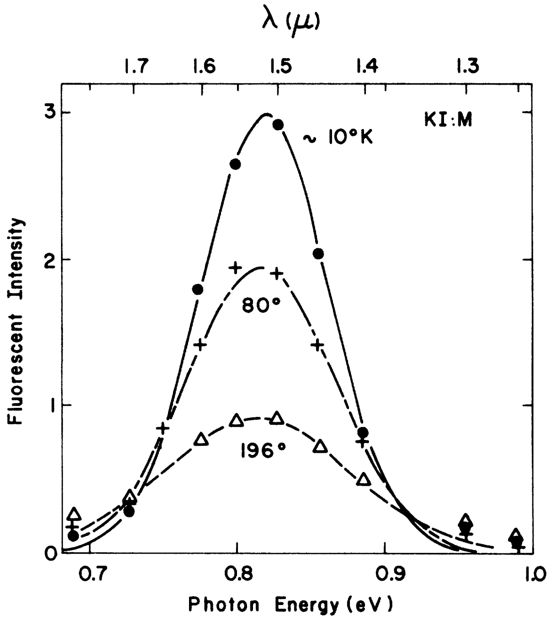

FIG. 3. Fluorescent intensity of *M* centers in KI which have been (flashlamp) excited via the *M* band. The spectra are shown for three temperatures; other experimental conditions were the same for the three curves. The peak energies and half-widths for the three (Gaussian) curves are given in Table I.

KBr crystals.[3,8] The half-width merits careful consideration, because in straightforward (i.e., neglecting time resolution or temperature variations) fluorescence measurements the half-width is the only parameter which separates *M*- from *F*-center fluorescence. The two centers give fluorescence peaks at the same wavelength. In view of the peak energy, half-width, and excitation wavelength, it is reasonably concluded that the *M* center is the origin of the fluorescence spectra in Fig. 3.

The next step involves exciting the *M* centers with ruby laser light in order to observe the time constants associated with the transitions. The ruby light is in the M_F absorption band and consequently produces the $\Sigma_g^+ \to \Pi_u$ transition. Two transitions are involved in returning to the ground

TABLE I. $\Sigma_u^+ \to \Sigma_g^+$ fluorescence spectra.

T (°K)	Peak energy (eV)	Half-width (eV)
KI: *M*		
~10	0.818	0.100
80	0.816	0.116
196	0.812	0.150
NaCl: *M*		
~10	1.155	0.14

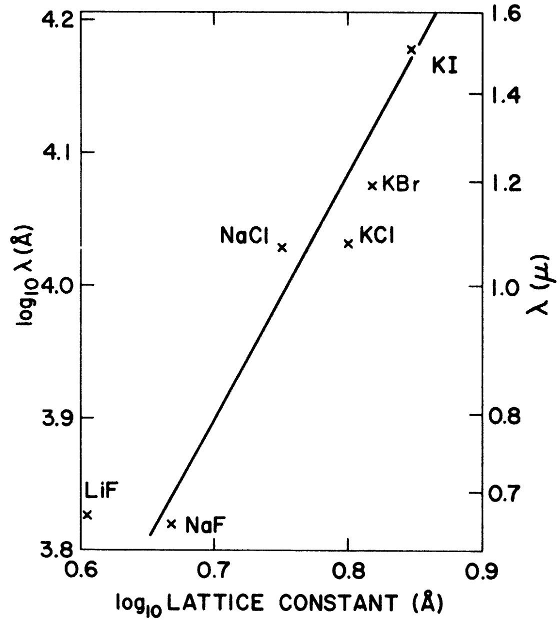

FIG. 4. Mollwo-Ivey plot for the *M*-center fluorescence peaks in various alkali halides. The slope of the line is 1.82, which is similar to the slopes found for other color-center peaks.

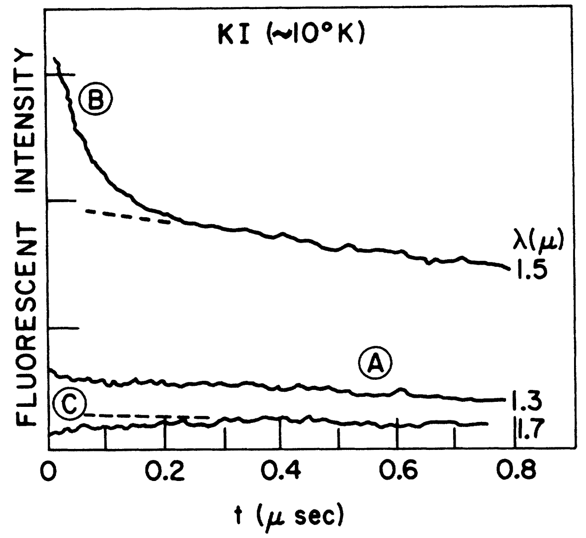

FIG. 5. Fluorescent intensity vs time for three wavelengths. The letters indicate the following regions: A is the slowly decaying (2.1-μsec time constant) fluorescence due to the *F* center; B is the rapidly decaying (60-nsec) fluorescence due to the *M* center; and the part with the positive slope, C, is due to the germanium photodetector, as discussed in the text.

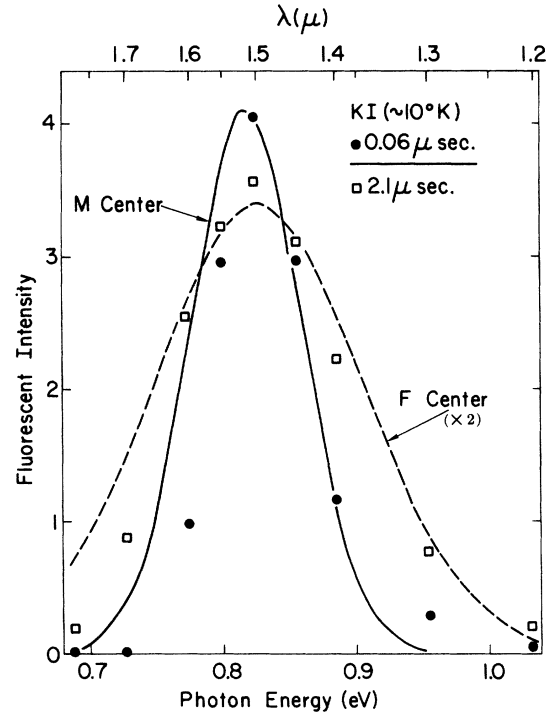

FIG. 6. Fluorescent intensity vs wavelength for a KI crystal. The points are separated according to the time constants for decay. The points from the 0.06-μsec component, ●, are fitted to the *M*-center peak given by Fig. 3. The □ points from the 2.1-μsec component are fitted to the known *F*-center fluorescence (dashed curve); see Ref. 9.

state, the $\Pi_u \rightarrow \Sigma_u^+$ and $\Sigma_u^+ \rightarrow \Sigma_g^+$ transitions. The latter will be considered first since it was just considered for NaCl crystals.

The fluorescent intensity (at three wavelengths) is shown as a function of time in Fig. 5. Near 1.3 and 1.7 μ, the light is primarily emitted with a 2.1-μsec time constant. In Fig. 5, this 2.1-μsec fluorescence predominates in the region marked A. For wavelengths between 1.3 and 1.6 μ, an additional fluorescence appears for $t < 0.2$ μsec. Neglecting the latter fluorescence for the moment, one can obtain the value of I_0 for the 2.1-μsec component at different wavelengths. These values of I_0 are plotted in Fig. 6, and follow the dashed intensity curve, which is drawn on the basis of published[9] *F*-center results. One concludes that this 2.1-μsec fluorescence is due to *F* centers, since this emission reflects lifetime,[5,10] peak energy, and half-width parameters previously correlated with the behavior of *F* centers.

Starting again from data such as Fig. 5, the same parameters are now tabulated for the fast-decaying fluorescence in the region marked B. The intensity exhibits an exponential decay with a time constant of 60 ± 7 nsec. I_0 for the 60 nsec component is also plotted as a function of photon energy and wavelength λ in Fig. 6 and is seen to agree reasonably well with the *M*-center fluorescence spectrum from Fig. 3, also plotted in Fig. 6. The fluorescence in region B of Fig. 5 and the

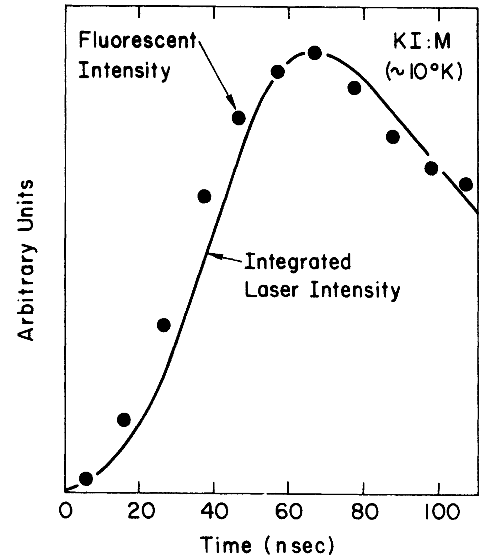

FIG. 7. Rise time of the (primarily) *M*-center fluorescence vs the integrated laser intensity. The sample has been bleached with *F* light at room temperature, so that *F*-center fluorescence contributes less than 10% of the presently observed fluorescence intensity. The integrated intensity is corrected [using Eq. (2)] for the 60-nsec lifetime of the Σ_u^+ state.

0.06-μsec curves of Fig. 6 are thus deduced to arise from the $\Sigma_u^+ \rightarrow \Sigma_g^+$ transition of the M center. The 60-nsec decay time is consequently equated to τ_1 for KI crystals; this result is similar to τ_1 for other halide crystals; see Sec. III.

Some departure from the solid curve in Fig. 6 appears in the vicinity 1.55–1.7 μ. This deviation is due to the previously mentioned slow response of the germanium photodetector at long wavelengths. Thus the short-time (< 0.1-μsec) results for λ near 1.7 μ indicate too low a value of I_0; this accounts for the departure of three points from the previously determined M-center curve.

Until now, the filling of the Σ_u^+ state from the Π_u state has been considered as instantaneous, that is to say, $\tau_1 \gg \tau_2$. Next we examine the time dependence of the M-center fluorescence for very short times, times < 60 nsec, in order to check the validity of the above assumption. If the $\Pi_u \rightarrow \Sigma_u^+$ transition is indeed rapid on the present (nsec) time scale, then the $\Sigma_u^+ \rightarrow \Sigma_g^+$ fluorescence at a time t will be proportional to the laser intensity $I(t')$ integrated from 0 to t. A correction must be incorporated into the integration in order to compensate for τ_1 being comparable to the duration of the laser flash:

$$N(t) \propto \int_0^t I(t') e^{(t'-t)/\tau_1} dt' \quad , \tag{2}$$

where $N(t)$ is the concentration of M centers in the Σ_u^+ state.

The fluorescent intensity at time t is of course proportional to $N(t)$. The comparison of the fluorescent intensity and the integrated laser intensity is made in Fig. 7. The fluorescent intensity points show no delay with respect to the integrated laser intensity. It is thus concluded that $\tau_2 < 5$ nsec; this time represents the resolution of the present electronics. The fact that τ_2 is smaller than most radiative lifetimes, e.g., τ_1, agrees with the difficulty in observing a second emission line due to the direct $\Pi_u \rightarrow \Sigma_g^+$ (ground-state) transition.

ACKNOWLEDGMENTS

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