

REORIENTATION OF M CENTERS IN KCl

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(Received 27 March 1970)

The dependence of the M -center reorientation efficiency on M^+ concentration indicates that at low temperatures, M centers reorient indirectly by absorbing light, forming M^+ centers which then absorb and rotate. Reoriented M centers are produced only after reoriented M^+ centers capture electrons. We further show that M^+ centers reorient with high efficiency during the radiationless transition, $2p\pi_u \rightarrow 2p\sigma_u$.

We report here the results of an investigation in which we show that an M center reorients during de-excitation from an M^+ state,¹ after it ionizes, rather than from a state of the M center, as is commonly assumed.² A reoriented M center appears only after the reoriented M^+ center has captured an electron.

The M center consists of two nearest-neighbor F centers along a $\langle 110 \rangle$ lattice direction.² At low temperatures, it can be aligned most efficiently with polarized light at around 500 nm.¹ The M -center ground singlet³ and lowest triplet states^{4,5} and the M^+ -center ground state⁶ all have absorptions which peak near this wavelength. Since all are normally present during reorientation, it is by no means obvious which state is most directly involved.⁷

The procedure used here to make the identification involved correlating changes in the M -center reorientation efficiency with changes in the M^+ concentration. The latter was varied during reorientation by bleaching F' centers with an auxiliary light source. This proved effective for the samples used⁸ since the M -center electrons were captured mostly by F centers forming F' . Furthermore, the F' light had little effect on the concentration of M centers since the number of M^+ centers was always very small compared with that of the M (less than 2%) and since the spectral range chosen for excitation (wavelengths greater than 850 nm) did not include M absorptions.^{3,4}

The M -center reorientation efficiency was determined at 77°K by first aligning M centers along a $\langle 110 \rangle$ direction and then reorienting about 10% of them under simultaneous unpolarized F' excitation.⁹ After each measurement, the procedure was repeated changing only the intensity of the F' light. The M^+ -center concentration was determined during reorientation from the magnitude of its emission band at 605 nm.^{6,10} Figure 1 shows that the efficiency decreases with decreasing M^+ concentration and practically van-

ishes at the smallest values. These results demonstrate that reorientation occurs only in the presence of M^+ and F' centers and clearly favor a mechanism involving reorientation during de-excitation between M^+ states. For this mechanism, the same 500-nm excitation would be responsible for first producing M^+ centers through absorption in higher states of the M center, then causing reorientation through absorption in higher states of the M^+ center, and finally converting reoriented M^+ centers to M through absorption by F' centers.

The M^+ center has absorption bands at 500 and 1400 nm corresponding, respectively, to the transitions $1s\sigma_g \rightarrow 2p\pi_u$ and $1s\sigma_g \rightarrow 2p\sigma_u$ (see inset of Fig. 2).^{6,11} At 4°K, absorption at 500 nm gives rise to an emission band at 605 nm and absorption at 1400 nm, to an emission band at 1670 nm.

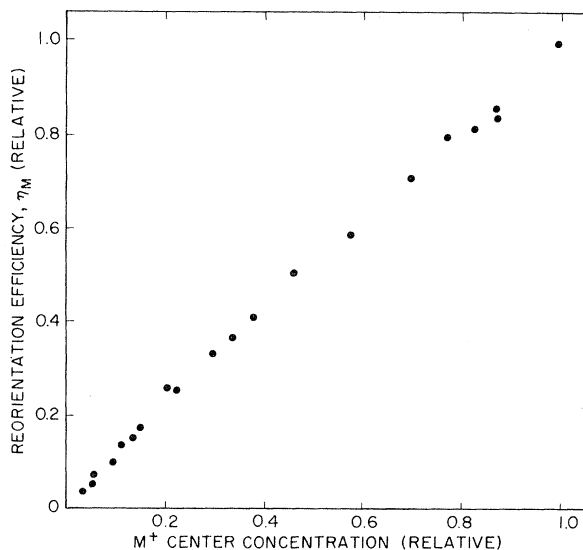


FIG. 1. The M -center reorientation efficiency at 77°K as a function of the photostationary M^+ -center concentration measured during reorientation. In the normalization, η_M and N_{M^+} had estimated maximum values of 5×10^{-2} and $3 \times 10^{-13} \text{ cm}^{-3}$, respectively ($N_{F_0} = 1.1 \times 10^{17} \text{ cm}^{-3}$, $\alpha_{F'}/\alpha_M \approx 5.9$).

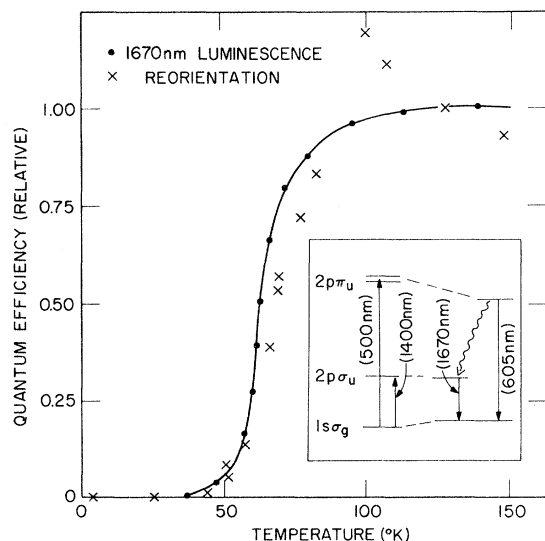


FIG. 2. The quantum efficiency of the M -center reorientation and of the 1670-nm luminescence as a function of temperature ($N_{F_0} = 1.1 \times 10^{17} \text{ cm}^{-3}$, $\alpha_F/\alpha_{M_1} \approx 7.1$).

Aegerter and Lüty have recently shown that at 100°K or above, the 605 nm emission is fully quenched and replaced by a radiationless transition to the $2p\sigma_u$ state followed by emission at 1670 nm (see Fig. 2).¹² We have now found that M^+ centers reorient near or above 100°K and will do so only if the exciting light falls within the 500-nm band. This implies that reorientation must occur during the radiationless transition, but prior to relaxing in the $2p\sigma_u$ state.

We have also determined the polarization of the 1670-nm emission at 77°K for an aligned system of M^+ centers. In these measurements, the emission was viewed perpendicular to the excitation through Polaroids oriented along $\langle 100 \rangle$.¹³ To within experimental error, the emission was fully polarized for excitation with 1400-nm light showing that emission from the relaxed $2p\sigma_u$ state is highly anisotropic. This being the case, the fact that the emission was unpolarized for excitation with 500-nm light strongly indicates that the reorientation efficiency is extremely high.

Figure 2 shows that the M -center reorientation efficiency¹⁴ increases substantially above 40°K, reaches a maximum value at around 100°K, and then decreases. The similarity between this curve and that for the efficiency of luminescence of 1670 nm evidently reflects the onset and predominance of the nonradiative $2p\pi_u \rightarrow 2p\sigma_u$ process above 40°K. The discrepancy between the two above 40°K is partly due to a variation of the

M -center ionization efficiency with temperature. Above 100°K, it is also partly due to an increase in the production of M' centers.¹⁵ This behavior also rules out the possibility that reorientation occurs during de-excitation from an M' state.

The reorientation efficiency of M centers has been found to depend also on sample purity¹⁶ and on the state of aggregation. With regard to the latter, reorientation is less easily accomplished when F centers are replaced by R centers. This investigation provides a new basis for understanding and predicting variations of this sort since it shows that it is the M^+ concentration which is of key importance. Its value in turn is determined largely by the electron trapping and optical bleaching behavior of other defects present in the material, such as F and R centers.

The author is indebted to Dr. Milton N. Kabler, Dr. Herbert D. Rosenstock, and Dr. Clifford C. Klick for their many useful suggestions.

¹The possibility of such a mechanism was recently suggested by Y. Haven, T. J. Turner, and W. R. Warren, in *Proceedings of an International Symposium on Color Centers in Alkali Halides, Rome, Italy, September 1968* (Consiglio Nazionale delle Ricerche, Rome, 1968).

²C. Z. van Doorn and Y. Haven, *Phys. Rev.* **100**, 753 (1955). Also see the review article by W. D. Compton and H. Rabin, *Solid State Phys.* **16**, 121 (1964).

³F. Okamoto, *Phys. Rev.* **124**, 1090 (1961).

⁴I. Schneider and M. E. Caspari, *Phys. Rev.* **133**, A1193 (1964).

⁵H. Seidel, *Phys. Letters* **7**, 27 (1963).

⁶M. Aegerter and F. Luty, in *Proceedings of an International Symposium on Color Centers in Alkali Halides, Rome, Italy, September 1968* (Consiglio Nazionale delle Ricerche, Rome, 1968).

⁷An M' -center mechanism was excluded from consideration because the M' center has no reported absorption at 500 nm and because the number formed at 77°K in the samples used was too small to be detected, even through emission measurements. It will be noted from the data of Fig. 2 that an M' mechanism appears unlikely even under more favorable circumstances.

⁸Undoped, additively colored samples which had relatively large F -to- M ratios ($>3:1$) were used.

⁹ M centers were aligned and reoriented with light from a tungsten lamp passing through a $\langle 110 \rangle$ -oriented HN Polaroid and 499-nm interference filter. The F' excitation was provided from a second, variable-intensity tungsten lamp and a 7-56 Corning filter.

¹⁰This reached a steady value only after several seconds of exposure. Except at the very highest efficiencies, this interval was short compared with the total reorientation time.

¹¹I. Schneider and H. Rabin, *Phys. Rev. Letters* **13**, 690 (1964).

¹²M. Aegerter and F. Lüty, Bull. Am. Phys. Soc. **14**, 872 (1969), and to be published.

¹³Excitation was maintained for as short a time as possible in order to minimize reorientation for 500-nm excitation or bleaching for infrared excitation.

¹⁴The efficiency is defined here for absorption by M^+

centers. This absorption decreases by about a factor of 2 in going from 100 to 150°K.

¹⁵H. Hirai, M. Ikezawa, and M. Ueta, J. Phys. Soc. Japan **17**, 724 (1962).

¹⁶See, for example, I. Schneider, M. Marrone, and M. N. Kabler, to be published.

OBSERVATION OF ACOUSTICALLY INDUCED PHASE-MATCHED OPTICAL HARMONIC GENERATION IN GaAs

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(Received 8 April 1970)

Radiation near 5.3 μm arising from the collinear phase-matched mixing of a 10.6- μm Q-switched laser beam and a pulsed ultrasonic shear wave has been observed in GaAs. Phase matching occurs when the crystal momentum of the acoustic phonon is adjusted to equal the familiar momentum mismatch observed in conventional second-harmonic generation in cubic GaAs. Three components of the susceptibility governing the four-wave interaction process were measured.

For the first time the nonlinear phase-matched mixing between two infrared waves (angular frequency ω_F) and an acoustic wave (ω_A) to produce an output infrared wave (ω_C) has been observed.¹ Cubic GaAs was used. Since the acoustic frequency (15.7 MHz) was small compared with the optical frequency, the output frequency was extremely close to that of normal optical harmonic generation. The nonlinear four-wave interaction is weak and was observed only under conditions of phase matching. The interaction can be visualized physically as arising from a second-harmonic coefficient induced by the lattice distortion of the acoustic wave. Since the distortion and hence the coefficient will change sign every acoustic half-wavelength, phase matching will occur if the acoustic half-wavelength is made equal to the coherence length l_c of second-harmonic generation (SHG), that is,

$$\lambda_A/2 = l_c \equiv \pi/\Delta k, \quad (1)$$

where $\Delta k \equiv k_H - 2k_F$ and k_H is the wave vector of the second harmonic at $\omega_H = 2\omega_F$. Equation (1) yields the more familiar form of a phase-matching condition,

$$k_C = 2k_F + k_A, \quad (2)$$

since the output wave vector $k_C \cong k_H$. This possibility of using an acoustic phonon to achieve phase matching has also been considered by Har-

ris, Wallace, and Quate.²

Two phase-matched interactions, forward-wave sum mixing (FWSM) and backward-wave difference mixing (BWDM), were observed. They are governed by

$$\begin{aligned} \omega_{C\pm} &= 2\omega_F \pm \omega_{A\pm}, \\ k_{C\pm} &= 2k_F + k_{A\pm}. \end{aligned} \quad (3)$$

The acoustic frequencies $\omega_{A\pm}$ needed for exact phase matching of the two interactions in these experiments differ only by 1.1 kHz. Since the full width at half-maximum of the phase-matching curve is 296 kHz for an interaction length of 1 cm, both FWSM and BWDM can be nearly phase matched simultaneously. In Fig. 1 are

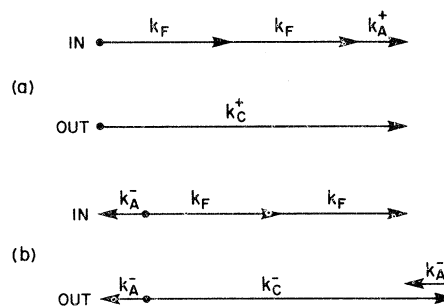


FIG. 1. Wave-vector conservation diagrams for (a) collinear forward-wave sum mixing and (b) backward-wave difference mixing.