captured by an acceptor is seldom re-emited into the conduction band before recombination. We thus conclude that the main acceptor is not only a capture center, but also a strong recombination center at least for the materials used here.

Electron capture rates by neutral acceptors in silicon have been derived also by Loewenstein and Honig,[6] using double-doped $n$-type silicon crystals. They concluded that the capture rate by neutral boron is temperature independent with the value of $5 \times 10^{-8}$ cm$^3$/sec between 1.1 and 4.2°K. Our measurements, in the meantime, give the values $3 \times 10^{-7}$ cm$^3$/sec at 4.2°K and $2 \times 10^{-5}$ cm$^3$/sec at 1.5°K. One possible reason for the discrepancy might be sought in the method of carrier excitation: Their method is ejection of electrons from the neutral donor sites by monochromatic light, while ours is intrinsic excitation by white light.

A similarly spectacular effect of stress on carrier lifetime has been found also for Si/Ga, but not for other doped crystals tried so far. It seems, therefore, characteristic only of

limited kinds of acceptors both for silicon and for germanium. Temperature effect on the electron capture rate, on the other hand, is still observable in other both singly and doubly doped $p$-type materials. A systematic study is now in progress.

Detailed aspects as well as extensions of this work will be reported in a later paper. The authors are grateful to Professor H. Kawamura for valuable discussions. All the samples used in this work have been supplied by Dr. H. Yonemitsu of the Toshiba Electric Company.

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## ENERGY TRANSFER FROM $F$ TO $M$ CENTERS IN KCl

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The principal $M$-center absorption, the $M$ band, lies on the long-wavelength side of the $F$ band. Nevertheless, excitation in the spectral region of the $F$ band at low temperatures can cause $M$ centers to reorient, to luminesce, and to transform to a metastable triplet state.[1] A question of considerable importance has been whether these processes are initiated through direct absorption in additional $M$-center absorption bands (designated $M_F$) which are known to lie under the $F$ band,[2] or whether they are due to a nonradiative resonant energy transfer from excited $F$ centers to $M$ centers.[3] Recent measurements by Delbecq[4] and by Swank and Brown[5] have strongly supported the former mechanism as the one operative for the luminescence process. This note presents evidence that the energy-transfer mechanism is operative for the process of $M$-center triplet excitation, as suggested by Schneider and Caspari.[6]

The existence of different mechanisms for the luminescence and triplet excitation process-

es is understandable under certain conditions. One such condition is that $M$ centers excited to the triplet state either decay nonradiatively or luminesce in an entirely different spectral region from singlet-excited $M$ centers. This condition would be satisfied if the energy difference between the lowest singlet and lowest triplet states is much smaller than for the singlet luminescence states. Wood and Meyer have shown that this is the case in calculations for LiF and LiCl.[7]

Swank and Brown[5] have demonstrated that the lifetime of $F$-center emission is unchanged in crystals containing $M$ centers. If $F$-center luminescence and energy transfer to $M$ centers were equally important for the dissipation of $F$-center excitation energy, a lifetime reduction of the $F$-center excited state would have been expected. Another condition then, as already suggested by Swank and Brown, is that if $F$ centers in a given crystal both emit and transfer energy to $M$ centers, then those $F$

centers which transfer must do so with very high efficiency. These $F$ centers might be the ones which happened to lie near $M$ centers.

An additively colored crystal of Harshaw KCl was exposed to $F$ light at 0°C to produce $M$ centers and then cooled to 170°K, where it was exposed to intense $[0\bar{1}1]$-polarized $F$ light[8] propagating along the $[100]$ direction. Figure 1 shows its absorption spectra for $[0\bar{1}1]$ and $[001]$ polarized light, measured at 77°K. This treatment evidently produces $M$ centers with axes oriented almost completely along $[0\bar{1}1]$. Delbecq,[4] using a similarly prepared crystal, observed a weak luminescence in the spectral region of the overlapping $F$- and $M$-center emission bands when he excited with $F$-light polarized perpendicular (e.g., $[0\bar{1}1]$) to the $M_F$-transition moments. Energy transfer was ruled out because this excitation was absorbed only by $F$ centers and the emission was unpolarized, characteristic here only of the $F$ center. Instead of looking at luminescence during exposure to $[0\bar{1}1]$ $F$ light at 77°K, the crystal of Fig. 1 was monitored for possible $M$-center triplet absorption bands. After the $F$ light[8] was turned on and saturation was achieved, approximately $\frac{1}{3}$ of the $M$ centers were in triplet states as measured at the maximum of the $M$ band. These measurements were repeated for a similar crystal at 4°K and for a crystal with about an order of magnitude larger initial $F$-center concentration with qualitatively similar results.

Under perfect alignment, the polarization vector of the $F$ light is perpendicular to the $M_F$ transitions and would be expected to excite only $F$ centers. The observed formation of triplets, particularly in such large concentrations, is then a clear indication of energy transfer. In practice, any slight experimental misalignment would introduce a component of the light along an $M_F$ direction, and this could directly lead to some triplets even if $F$ centers were not responsible for the triplet excitation. Assuming that this direct absorption by $M$ centers is responsible for the observed triplets, one would expect that the initial rate of triplet formation would be substantially different for $[011]$ and $[0\bar{1}1]$ $F$ light. These rates were therefore measured directly. The relative values of these were found to be approximately equal even though the rate value did depend on the spectral distribution of the $F$-light excitation. Reorientation of $M$
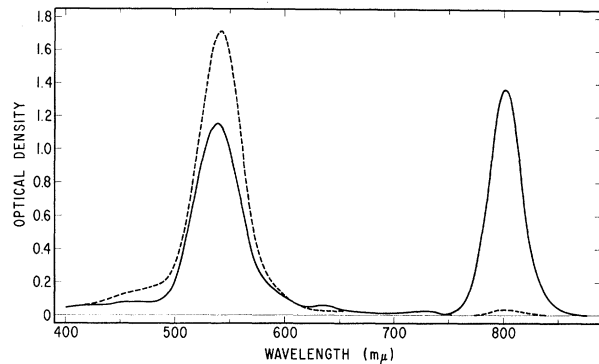


FIG. 1. Optical absorption measured at 77°K of an additively colored crystal exposed to $F$ light[8] at 0°C for 20 min, cooled to 170°K, and exposed to $[0\bar{1}1]$ $F$ light for 60 min. Solid curve is the absorption of $[0\bar{1}1]$-polarized light; dashed curve, the absorption of $[011]$-polarized light. $(N_{F_0} = 0.72 \times 10^{17}/\mathrm{cc}$, 1.9 mm thick.)

centers with $[011]$ $F$ light was kept to a minimum by carrying out these measurements at 4°K.

It is interesting that the ratio of the number of triplets produced at saturation with $[1\bar{1}0]$ $F$-light exposure to that produced by an equal $[011]$ $F$-light exposure did vary with the wavelength of $F$-light excitation. This ratio at 4°K was approximately 2.8 for 499 m$\mu$, 1.2 for 539 m$\mu$, and 0.75 for 568 m$\mu$.

Different saturation values would be expected simply because the excitation light is absorbed somewhat differently for the two polarizations. However, the general features of this wavelength variation may be understood by taking into account the fact that certain $M$-center triplet absorptions can also be excited by the incident $F$ light. It is known that excitation in the triplet 685-m$\mu$ band leads to a substantial reduction in the lifetime of the triplet state.[8,9] From former studies, the moment of the 505-m$\mu$ triplet absorption is perpendicular to that of the $M$ band while that for a weaker absorption at about 580 m$\mu$ is parallel to it.[10,11] Thus, $[011]$ light at around 505 m$\mu$ or $[0\bar{1}1]$ light at around 580 m$\mu$ for the crystal of Fig. 1 is also absorbed by triplet $M$ centers. To interpret the wavelength variation one simply assumes that absorption by higher triplet absorptions when it occurs also leads to a lifetime reduction.

The $F$- and $M$-center concentrations in these crystals are apparently much smaller than those which are generally associated with energy-

transfer processes producing multiplicity changes. Evidence now exists that the $F$-center aggregation process induced by $F$ light in the room-temperature range involves a photoinduced migration[12] which, during its earliest stage, results in the clustering of $F$ centers.[4,13] With further irradiation, $M$ centers begin to form, some probably located in these cluster regions. Thus, aggregation, in effect, locally increases these concentrations.

An $F$ center might behave differently after excitation depending on whether it is isolated or whether it lies in a cluster region, which may or may not also contain $M$ centers. $F$-center luminescence might be expected from the more isolated $F$ centers; energy transfer with triplet formation, for $F$ centers lying in cluster regions containing $M$ centers. The reason why energy transfer produces $M$ centers in the triplet state and does not appear to excite $M$ centers to states within the singlet system is presently not clear.

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# OPTICAL NONLINEARITIES DUE TO MOBILE CARRIERS IN SEMICONDUCTORS

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Optical nonlinearities due to conduction-band electrons have been observed in InAs, InSb, GaAs, and PbTe using 10.6-$\mu$ ($\omega_1$) and 9.6-$\mu$ ($\omega_2$) radiation from a $Q$-switched $CO_2$ laser. Difference frequencies $\omega_3 = 2\omega_1 - \omega_2$ at 11.8 $\mu$ and $\omega_4 = 2\omega_2 - \omega_1$ at 8.7 $\mu$ were measured for a variety of carrier concentrations at several temperatures.

We have observed optical nonlinearities arising from conduction electrons in semiconductors. The 10.6-$\mu$ ($\omega_1$) and the 9.6-$\mu$ ($\omega_2$) radiation from a $Q$-switched $CO_2$ laser focused into samples of single crystal InAs, InSb, GaAs, and PbTe generates difference frequencies at 11.8 $\mu$ ($\omega_3 = 2\omega_1 - \omega_2$) and at 8.7 $\mu$ ($\omega_4 = 2\omega_2 - \omega_1$) from the above nonlinearity. In addition, in InAs and GaAs the sum frequency at 3.53 $\mu$ ($3\omega_1$) was observed. The process we describe is of entirely different origin from the one responsible for most second-harmonic-generation[1] (SHG) and parametric-oscillation[2] experiments hitherto observed. The latter process is due to bound electrons and is often called the "electronic" effect.[3] The optical nonline-

arities studied in our experiments seem to be caused by the nonparabolicity of the conduction band. The interaction we observe, which involves the closely spaced frequencies $\omega_1$, $\omega_2$, $2\omega_1 - \omega_2$, and $2\omega_2 - \omega_1$, permits near phase-matched mixing over significantly long crystals.

The $Q$-switched $CO_2$ lasers used were similar to the one described earlier.[4] The 10.6-$\mu$ radiation ($P$ transitions of the $00^01$-$10^00$ band) and the 9.6-$\mu$ radiation ($P$ transitions of the $00^01$-$02^00$ band) were focused to produce power densities in the range $10^4$-$10^6$ W $cm^{-2}$, and peak electric fields of about $10^3$-$10^4$ V $cm^{-1}$ in the sample. The confocal distance[5] in all samples significantly exceeded the actual crystal length. Power levels were such that changes