dipolar forces cause an electron-phonon interaction which allows the longitudinal optic phonon to produce intravalley scattering. The long-wavelength acoustic phonons can also cause intravalley scattering for small but finite phonon wave vectors. In this case the electron-phonon interaction is proportional to the strain produced by the phonon. The possible strains are $\Gamma_1$=pure dilatation and $\Gamma_{12}$ and $\Gamma_{15}$ which are both shears. Which of these strains cause scattering, in each valley, is given by the selection rules summarized in (2). Thus intravalley scattering is allowed for all three transitions in Eq. (2).

The two most fruitful III–V semiconductors for observation of the Gunn effect are GaAs and InP. Both have lowest conduction-band minima at $\Gamma$ and next higher minima at $X$. For GaAs, the $\Gamma_1 \rightarrow X_1$ and $X_1 \rightarrow X_1$ electron transitions proceed by interaction with the LO phonon. For InP it is the LA phonon which produces the intervalley scattering.

If the higher valleys are not exactly at the points $X$ in the Brillouin zone, but lie on the line $\Delta$ which runs

from $\Gamma$ to $X$, the selection rules become less restrictive. For any relative size of the atomic masses, both longitudinal phonons can cause scattering from $\Gamma_1$ to $\Delta_1$. For scattering between adjacent valleys $\Delta_1$, e.g., from $(k,0,0)$ to $(0,k,0)$, the allowed phonon symmetry is $\Sigma_1$; one of the transverse optic phonons, the LO and LA phonons, and one of the transverse acoustic phonons all have this symmetry. For transitions across the zone, e.g., from $\Delta_1(k,0,0)$ to $\Delta_1(-k, 0, 0)$, both the longitudinal phonons can cause scattering.

The full-space-group and subgroup methods predict the same selection rules for all the processes considered in this paper. Karavaev[15] has recently put forward the view that the subgroup methods may sometimes fail to provide the full selection rules for scattering processes in crystals. Our work shows that the subgroup methods do not suffer from any such deficiency as far as intervalley scattering in III–V semiconductors is concerned.

[15] G. F. Karavaev, Fiz. Tverd. Tela **6**, 3676 (1964) [English transl.: Soviet Phys.—Solid State **6**, 2943 (1965)].

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# Evidence for $L$ Bands in NaCl†

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NaCl crystals are investigated in the spectral range 200–800 m$\mu$ by means of photostimulated thermoluminescence and differential-absorption-spectrum measurements. Four weak bands are found on the high-energy side of the $F$ band, which have the properties of $L$ bands: weak absorption coefficient, high and temperature-independent ionization efficiency, ionization intensity roughly proportional to the concentration of $F$ centers. Moreover, it is found that thermoluminescence is stimulated only by light absorbed by electron centers ($R$, $F$, $K$, $L$ bands), not by $V$ centers.

## 1. INTRODUCTION

SOME years ago, $L$ bands were observed by Lüty in potassium and rubidium halides[1,2]; recently Klick gave some evidence on the presence of $L$ bands in LiCl.[3] Although no detailed theoretical model had hitherto been worked out, there is convincing evidence now that the $L$ bands are due to $F$-center transitions: (a) There is a good proportionality between the $L$ and

$F$ band intensities; on the other hand, no relation is found between $L$ bands and crystal purity. (b) The quantum efficiency of $F \rightarrow F'$ conversion under $L$ light is $\sim 2$ (as under $F$ light).[4] (c) By depopulating the $F$-center ground state with intense chopped $F$ light, the $L$-band absorption also decreases, showing that the $L$ bands are caused by transitions starting from the fundamental state of the $F$ centers.[5] (d) Photoconductivity measurements[6,7] show that the quantum efficiency of the $L$ bands is unity, indicating that they

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[2] F. Lüty, Halbleiterprobleme **4**, 238 (1961).
[3] C. C. Klick, Phys. Rev. **137**, A1814 (1965).

[4] M. Hunger and F. Lüty, Phys. Letters **15**, 114 (1965).
[5] G. Chiarotti and U. M. Grassano, in Symposium on Color Centers, Urbana, October, 1965 (unpublished).
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[7] R. S. Krandall and M. Mikkor, Phys. Rev. **138**, A1247 (1965).
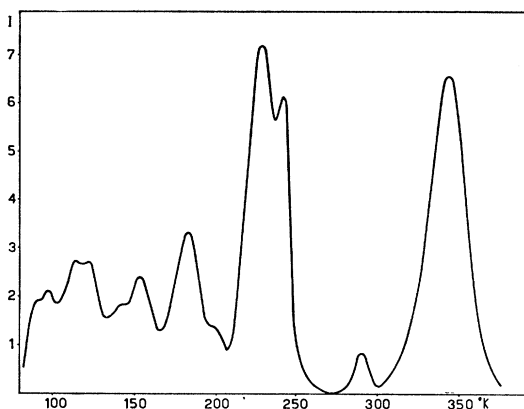
FIG. 1. Thermoluminescence glow curve of a NaCl sample, previously x irradiated at RT and subsequently stimulated at LNT by means of light of $\lambda_s = 450$ m$\mu$ for 2 min (slit width = 0.15 mm); $I$ is in arbitrary units.

are due to transitions to unbound states. Evidence for high-efficiency electronic transitions to the conduction band in KCl corresponding to the $L$-band absorption spectrum comes also from experiments on photostimulated thermoluminescence.[8]

Optical-absorption measurements have not shown the presence of $L$ bands in NaCl single crystals containing $F$ centers; only a weak photoconductivity was detected by Swank[9] in the $L$ region, by irradiating the sample with filtered light. Lüty's measurements show that the oscillator strength of $L$ bands decreases from RbCl to KCl, so that one can expect that in NaCl the $L$ bands are still weaker than in the Rb and K halides, hence difficult to detect by means of absorption measurements. Moreover, in LiCl it is very difficult to resolve the $L$ bands.

The purpose of the present work is to investigate the $L$ spectral region of NaCl by means of photostimulated thermoluminescence (TL)[10] and differential absorption spectrum. Previous experiments[8] have shown that photostimulated TL provides a very sensitive way of detecting photo-ionization of centers, and at the same time of distinguishing whether one is dealing with hole or with electron ionization. Thanks to the high sensitivity of this method, one can employ monochromatic light of narrow bandwidth ($\sim 10$Å) to scan the spectral region of interest.

## 2. EXPERIMENTAL

The crystals used were furnished by Harshaw Chemical Company, by Light, or grown in our laboratory by the Kyropoulos method in dry $N_2$ atmosphere. The crystals, cleaved into platelets approximately $10 \times 6 \times 1$ mm, were colored either electrolytically or by ionizing radiation. The electrolytic coloration was ob-

tained by applying an electric field of 350 V/cm at 680°C; after coloration the crystals were annealed at 680°C for 2 min, and quenched on a copper plate. The apparatus for photostimulated thermoluminescence and the characteristics of this technique are described elsewhere.[8] In the case of NaCl crystals, the x irradiation time at room temperature (RT) is generally 1 h, obtaining a concentration of $F$ centers of about $10^{17}$ cm$^{-3}$. Subsequently, the crystal is cooled to liquid-nitrogen temperature (LNT) and photostimulated at this temperature. Stimulations are performed at intervals of 5 m$\mu$ with bandwidth of 1.2 m$\mu$ (by means of a double monocromator) in the range 200–800 m$\mu$. The illumination time is generally 2 min. Then the crystal is heated at an approximately constant rate (45°K min$^{-1}$) and the total emission is recorded; a typical thermoluminescence glow curve is shown in Fig. 1; the minimum emission we detect corresponds to about $10^5$ photons sec$^{-1}$ emitted by the sample. Notice that the emission intensity is lower by a factor $10^4$ than from crystals x-irradiated 10 min at LNT. At our low illumination doses the heights of the glow peaks vary linearly with the stimulation intensity at a given $\lambda_s$ (Fig. 2) and many cycles of measurements can be carried out on the same crystal before aging effects appear; hence a whole stimulation spectrum can be measured on a single sample.

Optical-absorption measurements were performed with a Cary 14 recording spectrophotometer equipped with a metal cryostat.

## 3. RESULTS AND DISCUSSION ON $L$ BANDS

(a) The photostimulated glow curve, as already known, depends strongly on the sample. In each sample, however, the shape of the glow curve does not depend on the stimulating wavelength; the intensity changes but the various glow peaks and the ratio of their intensity remain the same. This means that only one type of carrier is excited by light, and captured by traps in the spectral range 200–800 m$\mu$.
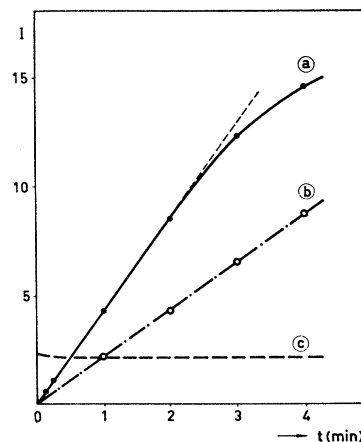


FIG. 2. Maximum intensity of the glow peak at 228°K, as a function of illumination dose of two different stimulations: (a) $\lambda_s$ 450 m$\mu$; slit width 0.2 mm; (b) $\lambda_s$ 410 m$\mu$; slit width 0.2 mm; (c) check curve (slit width 0.15 mm, $F$ light dose: 2 min); ($I$ in arbitrary units).

[8] B. Bosacchi, R. Fieschi, and P. Scaramelli, Phys. Rev. 138, A1760 (1965).
[9] R. K. Swank, thesis, University of Illinois, 1962 (unpublished).
[10] A. E. Stoddard, Phys. Rev. 120, 114 (1960).
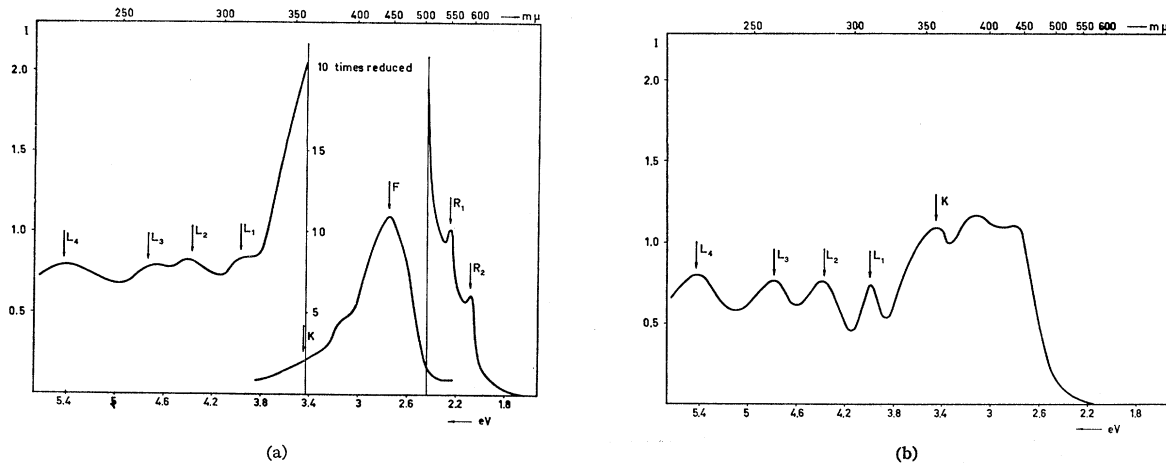
(a)                                             (b)

FIG. 3. (a). Intensity of the glow peak at 228°K, as a function of the stimulation wavelength $\lambda_s$. Optical stimulation is performed at 80°K. The glow intensity is normalized to equal doses of stimulation light. (b). Same arrangement as Fig. 3(a), with optical stimulation performed at 55°K; ($I$ in arbitrary units).

(b) The stimulation spectrum for illumination at 80°K of the glow peak at 228°K is shown in Fig. 3(a); the plotted glow intensity is normalized to equal doses of stimulation light. From (a) it follows that it is the same also for the other glow peaks of Fig. 1. Comparison with the absorption spectrum of a sample subjected to the same x irradiation establishes that, at wavelength 650 m$\mu \gtrsim \lambda_s \gtrsim$ 360 m$\mu$ the TL stimulation spectrum has the same maxima as the electronic bands of the optical absorption spectrum ($F$ and $R$ bands). Hence optical stimulation excites electrons from color centers to conduction band, from which the carriers are captured by traps. The photostimulated TL in NaCl provides then an indirect but sensitive measure of the electron photo-ionization yield as a function of wavelength.

(c) The weak maxima in Fig. 3 at energy higher than 3.7 eV($\lambda_1$=310 m$\mu$; $\lambda_2$=283 m$\mu$; $\lambda_3$=260 m$\mu$; $\lambda_4$=228 m$\mu$), are also due to electron ionization [see (a)]; since there is no corresponding absorption band (see Fig. 4), they must be due to centers of small
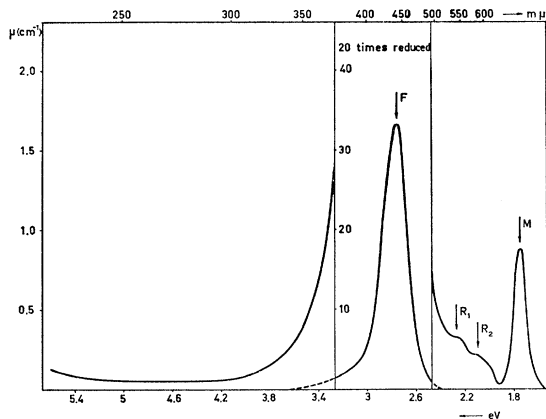


FIG. 4. Absorption spectrum of a sample x irradiated at 293°K (measured at LNT).

oscillator strength and high ionization yield. In this spectral region one expects $L$ bands. Two more facts suggest that these "photoconductivity" bands are in fact $L$ bands: The ratio of the stimulation yield in the $F$ absorption region and in the $L$-band region does not depend on the sample (and hence the impurity content), nor on the mechanism of coloration or the thermal treatment; moreover, this ratio is approximately independent of the $F$-center concentration in the range $5 \times 10^{16}$–$5 \times 10^{17}$ $F$ centers per cm$^3$.

(d) Figure 3(b) shows the stimulation spectrum of the glow peak at 228°K for illumination at 55°K. The intensity of the TL photostimulated by $L$ light is nearly the same as for photostimulation at 80°K; on the other hand, the $F$- and $R$-photostimulated TL drops steeply, and the $K$-band stimulation shows up, centered at $\lambda_s$=360 m$\mu$.

Further measurements on the temperature dependence of the TL intensities in quenched samples in different spectral regions show that, between 55 and 130°K, the TL stimulated by $F$ light increases by about a factor 25, and decreases slightly at higher temperatures; the $F$ behavior hence agrees with the one observed by Pohl on the $F$ photoconductivity[11] and by Pick on optical bleaching.[12] On the other hand, when $F'$ centers have been carefully eliminated, the $L$-photostimulated TL is nearly constant, showing that the $L$ bands are a temperature-independent source of photoelectrons. One should notice that if the sample is not previously quenched, the TL intensity as a function of stimulation temperature has an irregular behavior, close to the one found by Swank[9] for photoconductivity.

(e) As we already said, the absorption spectrum of an additively colored NaCl crystal containing $F$ centers does not show any bands in the region 360–200 m$\mu$.

[11] R. W. Pohl, Proc. Phys. Soc. (London) 49, 16 (1937).
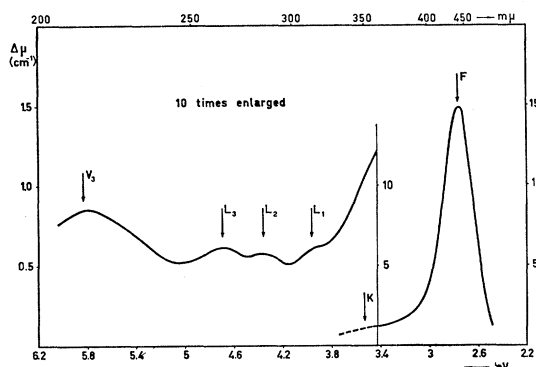[12] H. Pick, Ann. Physik 31, 365 (1938).

FIG. 5. Bleaching absorption spectrum of a sample x irradiated at 293°K and optically bleached at 293°K with white light.

In order to be able to detect weak absorption bands it is convenient to perform differential measurements on a colored sample, before and after optical bleaching of F centers.[3] Figure 5 shows the differential spectrum for a sample colored by x irradiation at RT $(2\times10^{17}$ F centers per $cm^3)$ and bleached with white light at RT $(\Delta F \simeq 6\times10^{16}$ $cm^{-3})$. In the uv spectral region one observes, beyond the $V_3$ band, bleached by recombination with the F photoelectrons, three weak bands at the same energies of the bands detected by means of photostimulated TL. This result further supports the assumption that the transitions at 310, 283, and 260 m$\mu$ are L bands, namely, electronic transitions from the F-center ground state to states above the bottom of the conduction band of the crystal.

(f) The energies of the L bands we found in NaCl agree reasonably well with the qualitative "molecular" model proposed by Klick and Kabler[13]; the atomic levels are compressed $\sim$38%, hence more than in KCl but less than in LiCl, as one expects from the effect of the dielectric constant.

## 4. FURTHER OBSERVATIONS

(a) The photostimulated TL spectrum at LNT [Fig. 3(a)] in the region at $\lambda>\lambda_F$ shows two pronounced bands at $\lambda_{R_1}=545$ m$\mu$ and $\lambda_{R_2}=596$ m$\mu$, but no band at $\lambda_M=713$ m$\mu$; the absorption spectrum of the same crystal shows a weak R absorption $(\mu_{R_1}\sim0.328$ $cm^{-1}$; $\mu_{R_2}\sim0.223$ $cm^{-1})$ and a well resolved M band $(\mu_M\sim0.88$

[13] C. C. Klick and M. N. Kabler, Phys. Rev. 131, 1075 (1963).

$cm^{-1})$. This means that, at LNT, the photo-ionization yield of M centers is negligible as in KCl,[14] while for R centers it is high. At lower temperatures [see Fig. 3(b)] the R ionization yield also drops to zero.

(b) At $\lambda_s=394$ m$\mu$ in Fig. 3(a) one notices a band which has no correspondence in the absorption spectrum; at 55°K, where the photo-ionization yield of the F centers is very low, the band is well resolved [Fig. 3(b)]. A closer comparison with the absorption spectrum shows that the photostimulated TL, in the F-band region, is strongly asymmetric. We can only suggest that the F band hides other absorption centers of high photo-ionization yield, which are easily detected by measurements of photostimulated TL. Absorption centers in this spectral region have been detected by other authors.[15,16]

(c) Very strong illumination in the spectral region of the $V_2$ and $V_3$ bands $(\lambda_2=223$ m$\mu$ and $\lambda_1=210$ m$\mu$, respectively) in the range 80–180°K, does not produce any new peak in the glow curve, beyond the ones due to electron traps. This may be due either to the fact that the available $V$ centers do not photo-ionize in the temperature range we explored, or to the absence of the hole traps in the range 55–350°K.

## 5. CONCLUSIONS

(a) As in KCl, the glow peaks are stimulated only by light absorbed by electron centers in the spectral range 200–800 m$\mu$; no $V$-center stimulation is found.

(b) Photostimulated TL and differential absorption spectra show the presence of four weak bands, $\lambda_1=310$, $\lambda_2=283$, $\lambda_3=260$, and $\lambda_4=228$ m$\mu$, which have the properties of the L bands.

(c) The maximum yield for photo-ionization of the K band at 55°K is at 360 m$\mu$.

(d) At 80°K the R bands show a high photo-ionization yield while the M band is not ionized by M light. At lower temperatures, the R ionization yield also drops to zero.

[14] N. Barth, Z. Physik 149, 370 (1957).
[15] D. W. Compton and C. C. Klick, Phys. Rev. 112, 1620 (1958).
[16] P. V. Sastry and K. A. McCarthy, Phys. Status Solidi 10, 585 (1965).