Effect of a Uniform Electric Field upon the Optical Absorption of Semi-Insulating Gallium Arsenide*

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The electric-field-induced effect upon the optical transmission of semi-insulating gallium arsenide has been measured for photon energies 1.4–2.0 eV. Electric fields up to 10^5 V/cm were applied to samples ranging from 3.36 to 37 μ in thickness at both 25 and 90°K. In conjunction with zero-field optical-absorption-coefficient measurements, the effect of electric field upon optical-absorption coefficient has been measured. As the photon energy decreases below the experimentally observed edge (1.496 eV at 90°K, 1.503 eV at 25°K), the absorption falls almost exponentially. Above the edge, one or two large field-dependent oscillations are observed which correlate with the $E^{2/3}$-dependent structure predicted separately by Callaway, by Tharmalingam, and more recently by Aspnes. Above 1.55 eV no conclusive evidence of a field-induced optical transmission effect was observed. At values of the electric field near 10^5 V/cm, structure of an oscillatory nature was observed well below the absorption edge. The periodicity of the structure appears to be proportional to the applied electric field, but larger than the Wannier level structure predicted by Callaway.

I. INTRODUCTION

THIS paper reports an investigation of the effect induced upon the optical-absorption coefficient of semi-insulating gallium arsenide by the application of a uniform external electric field. Measurements were performed by observation of the optical transmission at 25 and 90°K using electric-field values up to 10^5 V/cm. Specimens of both ⟨111⟩ and ⟨100⟩ orientations were utilized in the measurements. With the thinnest ⟨100⟩ specimen (3.36 μ), the electric-field-induced optical-absorption effect was observed well above the absorption edge. The energy range 1.4–2.0 eV was scanned repeatedly for evidence of electroabsorption. Conclusive evidence of electric-field-induced absorption was found only within 0.05 eV above and below the edge in this experiment.

Previous measurements of the effect of electric field upon optical absorption in gallium arsenide have been performed by various workers.[1–6] Also, very strikingly similar results have been recently reported for the direct band edge in germanium.[7,8]

Comparison with the various theories of electroabsorption requires that the absorption coefficient be measured in a uniform electric field. This is necessary because these theories predict field-dependent structure in the optical-absorption coefficient. Callaway[9] and Tharmalingam[10] independently worked out the theory of electric-field optical absorption for semiconductors with effective-mass bands. The theory of Callaway replaces the density-of-states expression with a summation over closely spaced discrete energy states arising from the interaction of both a uniform electric field and a periodic lattice potential upon the electrons in the crystal. In the theory of Callaway, steps or discontinuities are predicted in the electric-field optical absorption when the electric field is directed along a reciprocal lattice vector of the absorbing material.

The absorption coefficient predicted by Callaway is given by

$$\alpha=\frac{4\pi^2K\mu\beta^{2/3}}{\omega\kappa}\sum_{j=j_0}^{\infty}A_i^2\left(\frac{2\pi j\beta^{1/3}}{\kappa}-\chi\right),$$

where $K=2e^2|\boldsymbol{\epsilon}\cdot\mathbf{p}_{nn'}|^2/\pi\hbar m^2 n\epsilon_0 c$, $\chi=\kappa^2/12\beta^{2/3}$, $\beta=2\mu F/\hbar^2$, Ai(x) is the Airy function of argument

$$x=\frac{1}{\pi}\int_0^{\infty}\cos(sx+\tfrac{1}{3}s^3)ds,$$

ω is the incident-photon angular frequency, κ is the width of Brillouin zone along principal lattice direction in which the field is applied, $F=eE$ is the electric-field force, μ is the reduced effective mass$=m_vm_c/(m_v+m_c)$, $\mathbf{p}_{nn'}$ is the interband-momentum matrix element, $\boldsymbol{\epsilon}$ is the unit vector in the photon propagation direction, n is the index of refraction, and ϵ_0 is the vacuum dielectric constant.

The lower limit in the summation is given by j_0. The quantity j_0 is dependent upon the photon energy, so that in a graph of α versus energy at any fixed value of

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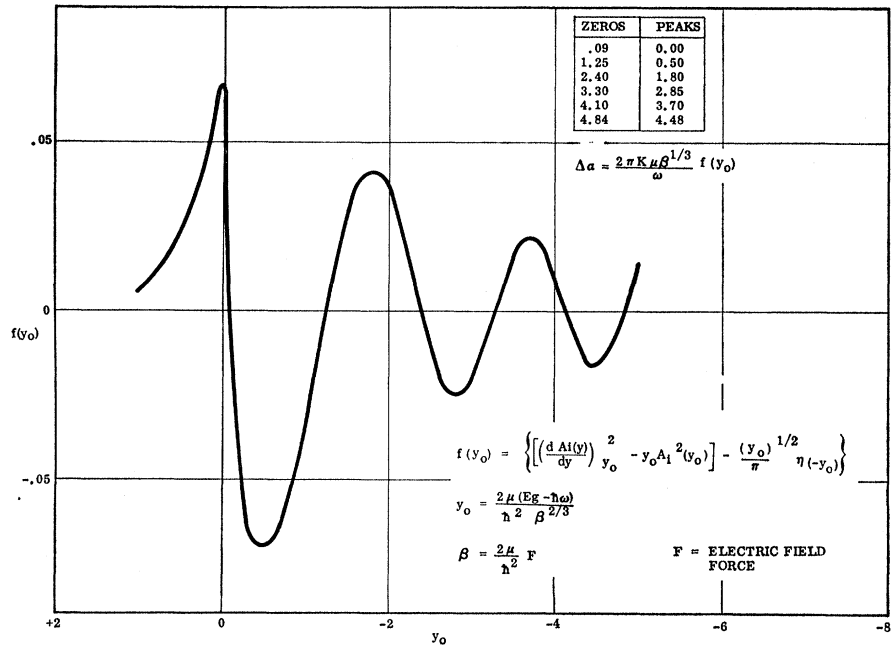

FIG. 1. Graph of electric-field absorption-shift function.

electric field, the effect of the discrete change in the lower limit of the summation is seen as a step. The spacing of the steps is controlled by the condition that j_0 be the next integer larger than q_0, where

$$2\pi q_0 F/\kappa - \hbar^2\kappa^2/24\mu = Eg - \hbar\omega .$$

Thus, to increase the value q_0 by one (drop off a step) it is necessary to decrease photon energy $\hbar\omega$ by

$$\Delta\hbar\omega = 2\pi F/\kappa .$$

The energy separation of the steps is proportional to the applied electric field. In the limit of very small fields, the theories of Callaway and Tharmalingam predict identical results. The small-field-limit expression for the change in optical absorption due to a uniform electric field is given by

$$\Delta\alpha = \frac{2\pi K\mu\beta^{1/3}}{\omega}\left\{\left[\left(\frac{d\,\mathrm{Ai}(y)}{dy}\right)^2_{y_0} - y_0\,\mathrm{Ai}^2(y_0)\right] - \frac{(-y_0)^{1/2}}{\pi}\eta(-y_0)\right\},$$

where

$$y_0 = (2\mu/\hbar)^{1/3}(Eg - \hbar\omega)/F^{2/3},$$

and $\eta(-y_0)$ is the unit step function which turns on for $\hbar\omega > Eg$, and is shown in Fig. 1. This is a valid prediction for nondegenerate effective-mass bands when the electron-hole interaction is neglected.

This theory has been presented in more detailed form in a recent series of papers in which more general applications to band structures are considered.[11–13] In the low-field limit for direct transitions at an M_0 critical point, these results are identical with the one-electron effective-mass band result described here. This more recent theory also ascribes to the Stark or Wannier levels the same periodicity in proportion to an electric field applied along a principal axis.

The electron-hole interaction has also been considered theoretically. The absorption of an exciton has been calculated recently by Ralph,[14] in which an effective-mass equation is solved numerically and used to compute the optical absorption for various values of a field parameter. Comparison of this result with theory is difficult, because the optical absorption of GaAs at low temperature is quite unlike the predicted zero-field absorption of the model. Only the lowest energy line can be resolved in GaAs and it is not sharp even under zero-field conditions at liquid-helium temperature. Thus, experimental electroabsorption data cannot be directly compared with the theory of Ralph. One consistent result is that, in the limit of small electric fields and energies far below the absorption edge, all of these theories predict the same exponential field dependence.

II. EXPERIMENTAL

A. Apparatus

The electric-field effect upon optical absorption was experimentally investigated by observation of field-induced modulation of the optical transmission in plane slabs of semi-insulating GaAs. Using a Cary 14R spectrophotometer, energy resolution of 1 meV was obtained. Measurement of the optical-transmission shift was performed with the system shown schematically in Fig. 2. The optical-transmission shift was induced

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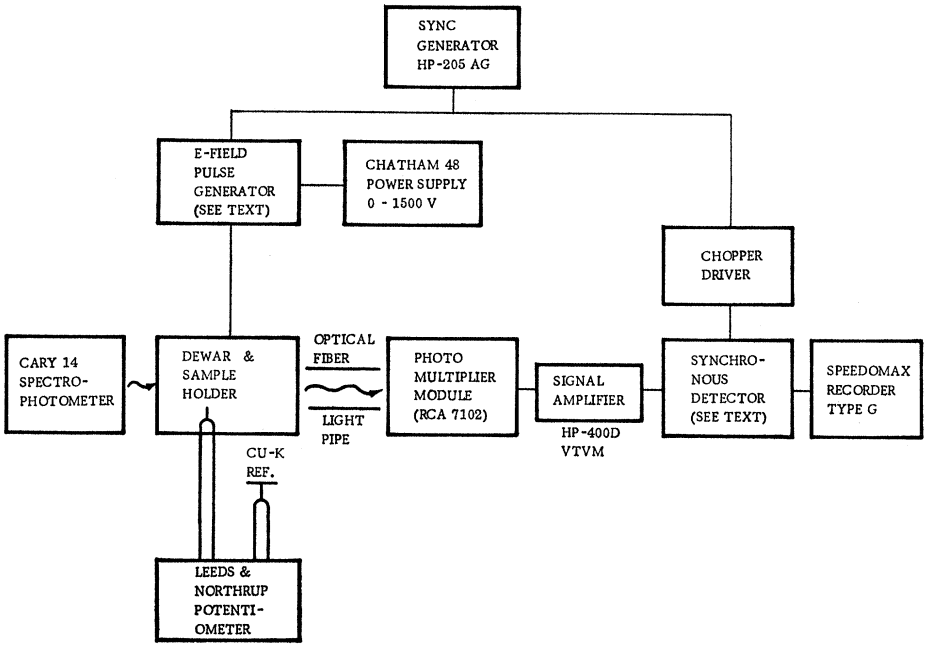

FIG. 2. Schematic diagram of experimental apparatus for observation of effect of electric field on optical transmission.

by the application of alternating rectangular high-voltage pulses from the synchronized pulse generator. A rectangular pulsed optical signal component was formed by the modulation of the optical transmission due to the electric-field-absorption shift. This signal propagated from the sample, through a fiber-optic light pipe, to the photomultiplier, where it generated an analogous signal current. The signal current was next processed by a synchronous detector to improve the signal-to-noise ratio and was recorded.

Wafers of semi-insulating GaAs were obtained from Bell & Howell Research Laboratories. They were taken from ingot No. 470B–10^7 Ω cm. The dopant causing the semi-insulating properties has been identified as chromium.

Segments of the wafers were prepared for optical-transmission measurement by optical polishing, and were mounted upon especially prepared glass substrates containing conducting tin-oxide electrodes. The specimens were firmly bonded to the substrate with Eastman 910 before the last polishing step. After polishing, the specimens were mounted in the Dewar sample holder in a "sandwich" between the substrate electrode and another similar electrode turned at right angles in a manner previously described by Williams.[15] An insulat-

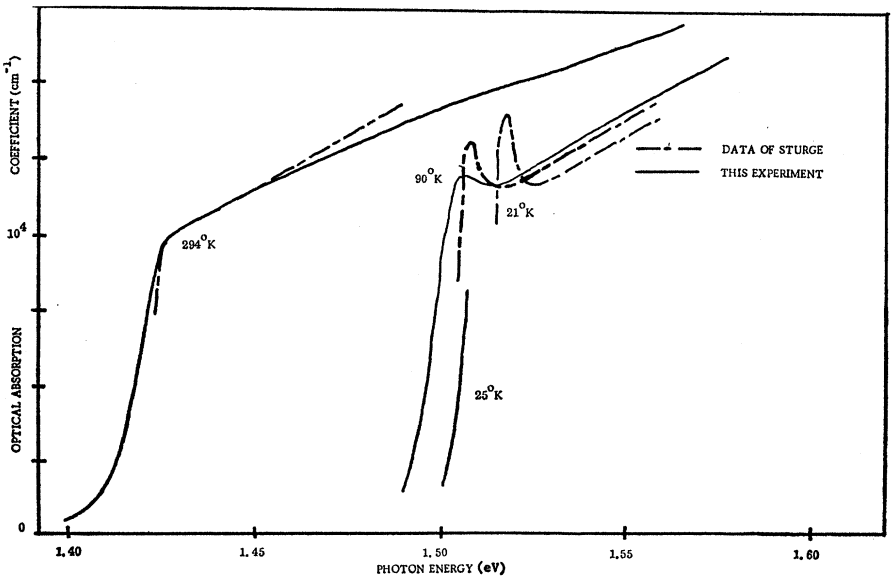

FIG. 3. Zero-field absorption of semi-insulating gallium arsenide.

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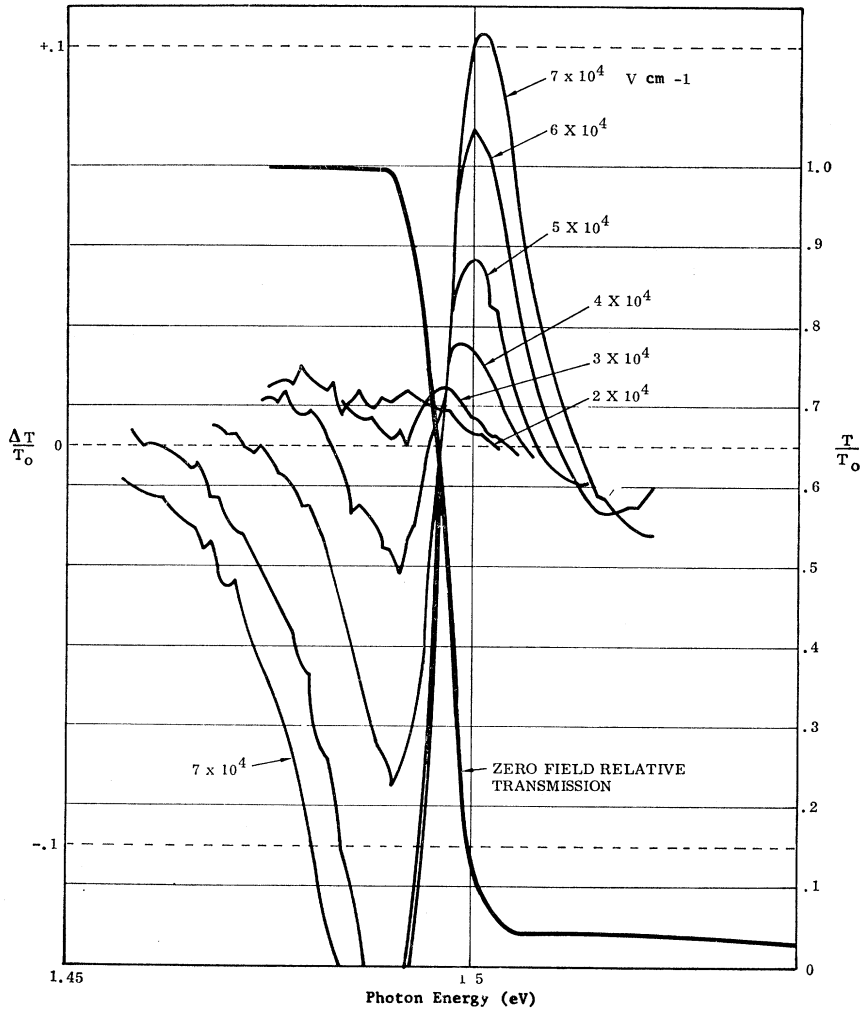

FIG. 4. Transmission-shift data for various values of applied field at 77°K (3.36-μ specimen).

ing layer of Mylar of 6-μ thickness separated the specimen and the opposite electrode.

After cooling to the desired low temperature, electric-field pulses were applied at a nominal 500-pulse/sec rate. Field-pulse duration was initially varied over a wide range. It was noted that for pulse lengths greater than 50 μsec, the photomultiplier output signal deviated from the required rectangularity and developed an exponential tail due to the relaxation of carriers trapped at the specimen surfaces as a result of internal photon-stimulated current flow during the field pulse. The pulse tail was more pronounced at high values of the electric field. At field values greater than 1.3×10^5 V/cm, the specimens exhibited a breakdown attributed to avalanche multiplication and abetted by the tendency of the avalanche-multiplied photocurrent to increase the electric field at the specimen boundaries. The negative differential conductivity of GaAs at high fields did not contribute significantly to field nonuniformity by the growth of instabilities, since the pulse duration times employed were very much less than the dielectric relaxation time of the material. Optically generated carriers were responsible for the bulk of the conductivity at low temperatures. Thus a combination of low optical signal level, small duty cycle rectangular alternating voltage pulses, and precise physical alignment permitted the establishment of very nearly uniform electric fields in the samples. Optical coupling through the light pipe allowed for cooling of the RCA 7102 photomultiplier in order to reduce noise, and also permitted isolation of the photomultiplier from induced electromagnetic signals caused by the application of high-voltage pulses to the sample.

B. Zero-Field Measurements

Zero-field optical absorption was measured for each specimen of semi-insulating GaAs to provide quantitative data for calculation of absorption shift from the electric-field transmission-shift data. Optical transmission was scanned from 0.6 eV to the absorption edge with the Cary 14 spectrophotometer in order to obtain an optical interference-fringe spectrum for determination of specimen thickness. On the thinnest specimens where absorption above the edge could be measured,

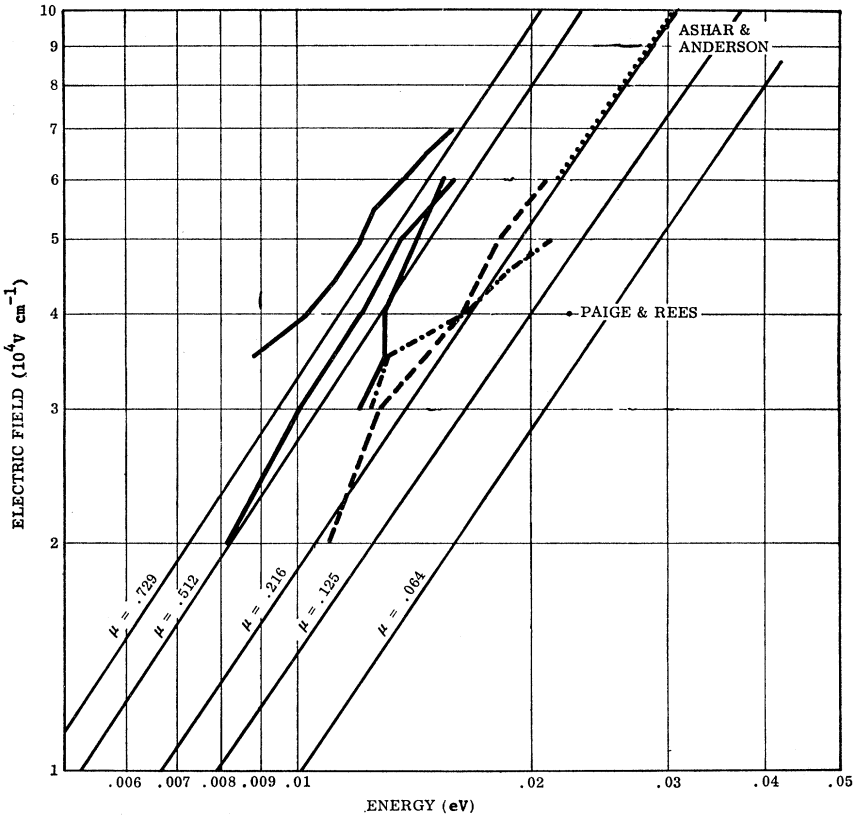

FIG. 5. Graph of spacing of first (solid lines) and second (dashed lines) zeros as a function of applied field at 77°K.

thickness was calculated by scaling the observed absorption against the data of Sturge[16] (as shown in Fig. 3). A profile of the specimens was also measured by means of a Taylor-Hobson surface indicator in order to determine the uniformity of thickness and the thickness of the bonding layer of Eastman 910.

At low temperatures, the absorption coefficient of semi-insulating GaAs exhibits a broad but well-defined exciton peak. After cooling 24 h at liquid-nitrogen temperature, the position of the observed edge was 0.008 eV below the edge energy calculated by Sturge. This shift was attributed to the effects of dilatational strains induced in the samples by the optical-polishing process. Strain-induced splitting of the exciton line should also accompany this shift. Sturge observed significant splitting of the exciton in glass-mounted ⟨111⟩ specimens. The thinnest specimen used in the work described here was ⟨100⟩ oriented for which the strain-induced forbidden bandwidth shift is estimated to be an order of magnitude smaller than the ⟨111⟩ shift.[17,18] It was therefore reasonable that no splitting of the exciton could be discerned during these measurements. At liquid-helium temperature, some limited measurements of zero-field optical absorption were made by monitoring optical-transmission measurements. The edge observed in this manner is also shown in Fig. 3. It differs from the liquid-nitrogen temperature edge in that it is located 0.009 eV higher in energy, and its characteristic exponential slope has increased from 288 eV^{-1} at liquid-nitrogen temperature to $\simeq$330 eV^{-1}. This is consistent with the recent observations by Redfield using uncompensated GaAs.[19]

C. Measurement of the Effect of Uniform Electric Field on Optical Absorption

After evaluation of the zero-field optical-absorption characteristics, each specimen was subjected to synchronized electric-field pulses of various magnitudes, in order to evaluate the effect of the electric field upon optical transmission. A representative sample of the data obtained is shown in Fig. 4. Each curve shows the variation in optical transmission as a function of wavelength for a particular value of applied electric field. This value of field is calculated using the appropriate dimensions and constants of the specimen-holder configuration. Below the common crossover or zero point (1.496 eV at 90°K for this specimen), the field effect upon transmission is negative with an extremum near the crossover which decreases with increasing field. Above this crossover point, oscillations about the zero

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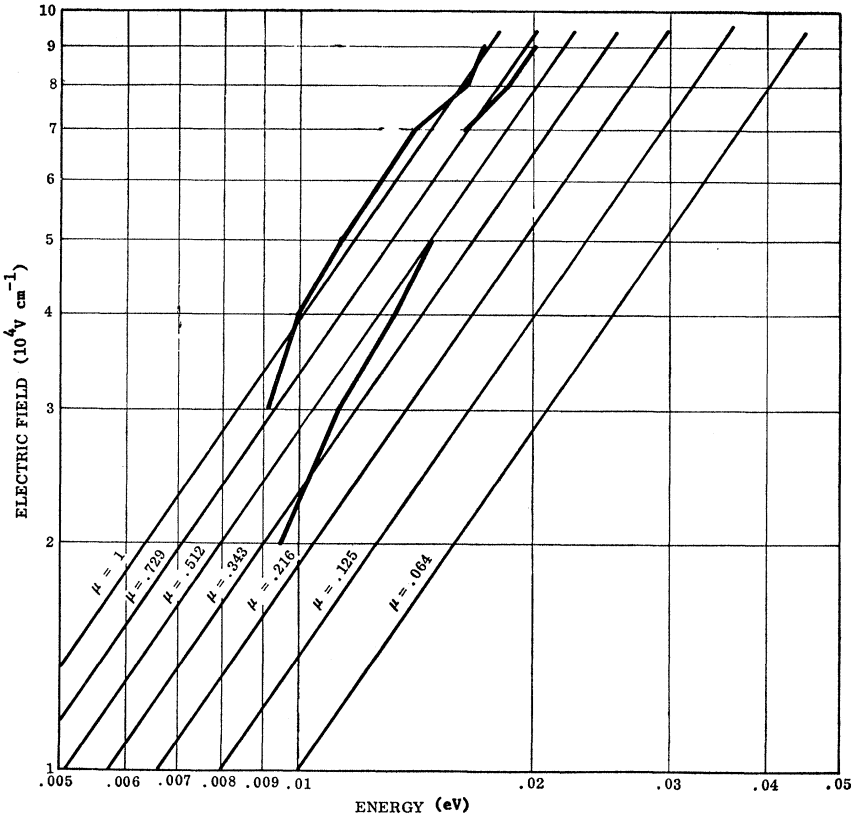

FIG. 6. Graph of first zero spacing as a function of applied electric field at 25°K.

axis can be observed. These oscillations die out rapidly but are seen to increase in energy period as the applied electric field is increased. For the thinnest specimen the absorption-induced transmission change is not large. Thus the small effect of electric field upon the index of refraction of the material can also be seen. This manifests itself as a broad increase in transmission at lower energies. This effect might well be referred to as the electrotransmittance, in contrast to the term "electroreflectance" coined by previous workers.[20] Accurate measurement of electrotransmittance was unfeasible with this apparatus, which was not optimized for detecting electric-field effects of small magnitude and gradual energy variation. Nevertheless, the observed effect resembles the room-temperature data cited by Pollak *et al.* This effect alters the optical transmission of thin specimens in such a manner that absorption shift appears to fall off unduly or become reversed at low energies, and therefore transmission-shift data are unreliable for very thin specimens in this region.

Above 1.55 eV, no conclusive evidence of electric-field-induced transmission shift was obtained. Scans have been made at field values up to 10^5 V/cm with widely opened slits, corresponding to 0.01-eV resolution, without obtaining firm evidence of a field effect. It was desired that the electric-field effect upon the spin-orbit split-off band at 1.88 eV might be observed, but increasing absorption above the edge (3×10^4 cm^{-1} at 1.88 eV) apparently cut off this region from observation even using the thinnest (3.36-μ) specimen. For thicker specimens, the transmission cutoff point was always at or very near the lowest-energy crossover point, so that only the negative transmission shift below the energy gap was observed.

A comparison with the low-field limit of the one-electron theory was made by plotting the observed zero points in the field-induced absorption oscillations as a function of applied electric field. Theory predicts that the energy period of these large oscillations above the edge should increase in proportion to the $\frac{2}{3}$ power of the applied field. The observed separations between the zeros were plotted and appear to be in agreement with a $\frac{2}{3}$-power law.

In Fig. 5, the energy displacements of the first two zero points have been plotted as a function of applied field at 90°K. The apparent energy gap is 1.496 eV. Theory predicts that the energy spacing between these two zeros should be very nearly equal at every value of applied field if the pair of bands can be characterized by a reduced effective mass. Nearly this result was obtained by Paige and Rees[5] using an electric field perpendicular to the incident photons. Their absorption shift is matched to theory by a reduced effective mass of 0.065 m. Ashar and Anderson[6] showed zero-spacing data

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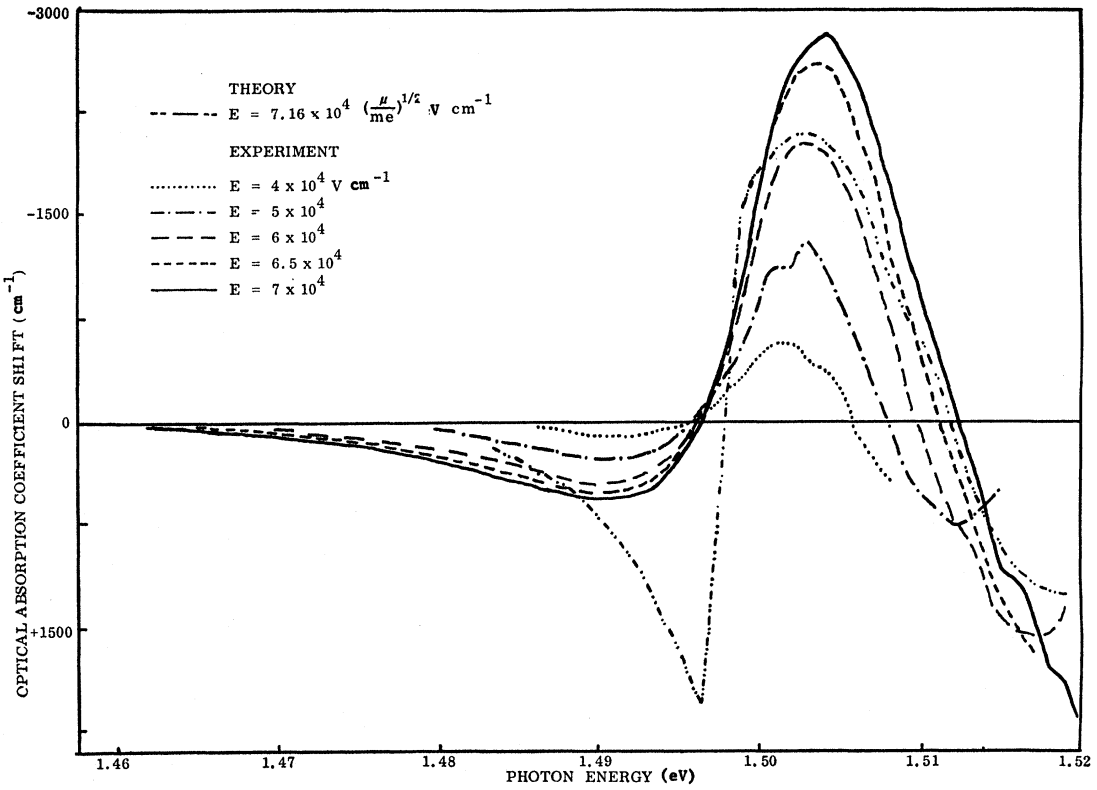

FIG. 7. Shift of optical absorption as a function of photon energy for various values of electric field in semi-insulating GaAs ⟨100⟩ oriented 3.36-μ-thick specimen at 90°K.

for three maximum-field values from their p-n junction photoresponse experiment. They interpreted their result as a manifestation of accidentally obtaining a uniform electric field due to "freeze out" of carriers at 78°K. Their spacing is also shown in Fig. 5 and is characteristic of an effective mass of 0.21 m. It is not understood why the energy gap observed in their experiment is so large. It may be due in part to the inherent discrimination of their photogeneration experiment against observation of absorption by bound exciton states. This is difficult to verify because no comparative zero-field absorption data are shown for their experiment with which to compare relative strain and temperature related optical-absorption behavior.

In this work, the first zero spacing is always observed to be smaller than the second. Fitting the sets of first zero spacings to theory yields a reduced effective mass of 0.6 m, while the second set of spacings may be characterized by $\mu \simeq 0.25\ m$. Differences between these data and the data of Paige and Rees may be related to the fact that they did not observe an exciton line in their thin-specimen zero-field data. In Fig. 6, the field-dependent spacing of the first interval is shown for the 25°K measurements. The gap energy is shifted 0.009 eV and the reduced effective mass is roughly 0.6 m.

The calculated field-induced absorption-effect data have been plotted for various values of electric field for several specimens. Oscillations in the electroabsorption are seen above the absorption edge only for measurements on the thinnest specimen (3.36 μ). These data are shown in Fig. 7 for liquid-nitrogen temperature. A very noticeable departure from theory in this figure is the round-off of the field-induced increase in optical absorption at energies just below the edge. This suggests that impurity or defect fields may be present to cause a "built-in" Franz-Keldysh effect as predicted by Redfield.[19] Upon application of external field, a signal results which is the difference between the uniform large applied field contribution and the impurity field contribution.

Above the edge at low fields, the height of the first peak depends roughly on the square of the electric field. Above 7×10^4 V/cm, the peak height apparently saturates. This behavior deviates markedly from the theoretically predicted $E^{1/3}$ dependence for an effective-mass band. In combination with the narrowing of the first zero spacing, it may be a result of the electron-hole interaction. Although the sharp exciton line is only vaguely suggested by the observed peak in the zero-field absorption at 90°K, the accompanying absorption is also quite different from that predicted when the electron-hole interaction is neglected. Similar behavior has been observed at the direct band edge in Ge by Hamakawa *et al.*[8] They show zero-spacing growth

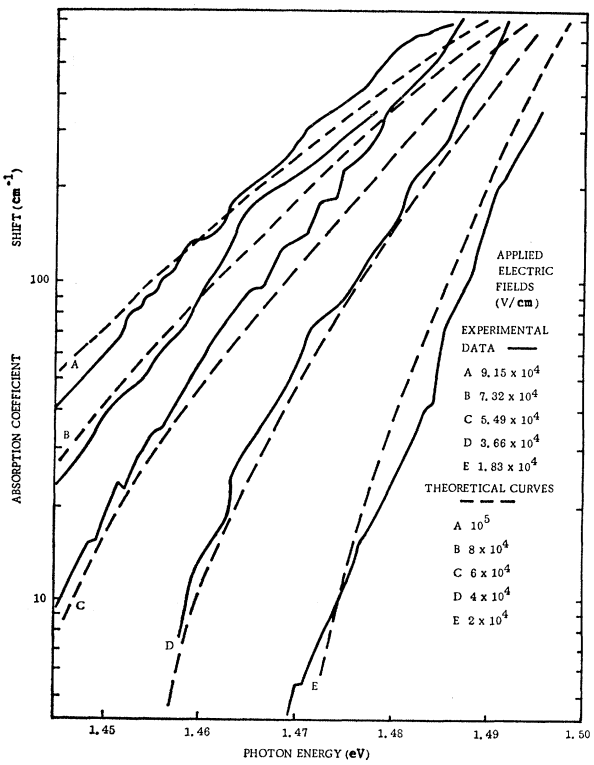

FIG. 8. Electric-field optical-absorption-shift data obtained from 12-μ-thick $\langle 100 \rangle$ specimen at 90°K.

according to $E^{2/3}$ and an enlarged first peak above the edge that exhibits a field dependence not predicted by one-electron theory. They qualitatively equate the large positive peak above the edge and the two neighboring negative peaks with quenching and broadening of the exciton. In this work, similar curves can be drawn which seem to quench the exciton, but scaling difficulties preclude accurate quantitative comparison with this reference and with the theory of Ralph. The decrease in peak height observed by Hamakawa *et al.* at large fields was not observed in this experiment.

Experimental observation of the optical transmission of the thick specimens has yielded detailed information about the optical-absorption shift in the energy region beneath the band edge. In general, the shape of the calculated optical absorption conforms to the theory of Callaway for the case of two reduced-mass bands which was utilized previously by Lambert to explain his data (see Fig. 8). Broad fixed shoulders, which may be due to the Franz-Keldysh effect upon impurity states, are observed using thicker specimens. These shoulders occur in the region around 1.47–1.48 eV at fields in the vicinity of 3×10^4 V/cm and tend to smear out as the field is increased.

Some structure is also observed in these optical-transmission-shift data below the edge which seems to be oscillatory. This structure is repeatable and proportional to the applied electric field. Indications of this structure were obtained using three different specimens in both $\langle 111 \rangle$ and $\langle 100 \rangle$ orientations (see Fig. 9). The strongest evidence was obtained with a $\langle 100 \rangle$ specimen of 12-μ thickness, which was the most uniformly flat and parallel mounted sample of the group. One group of these data is shown in Fig. 10 for electric fields up to nearly 10^5 V/cm at 90°K. Note the apparent growth and shift of the irregularly shaped structure patterns as the electric field is increased. Also note that the extrapolation of sets of pattern growth increments back to zero-field results in an intersection with the experimentally observed energy gap at 1.496 eV. However, since the observed energy spacing is 0.01 eV at 8.54×10^4 V cm^{-1} and the predicted Wannier level spacing for a $\langle 100 \rangle$ direction is $2.82\times10^{-8}E$ or 0.0024 eV for this field value, observed level spacing is not in good agreement with theory.

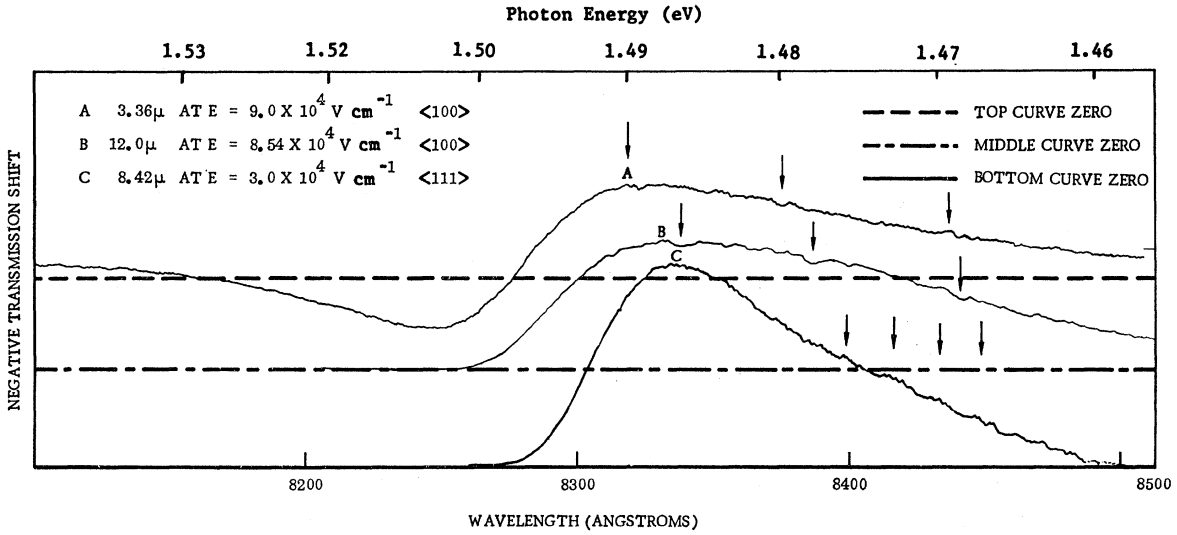

FIG. 9. Comparison of structure in transmission-shift data in three specimens at 90°K.

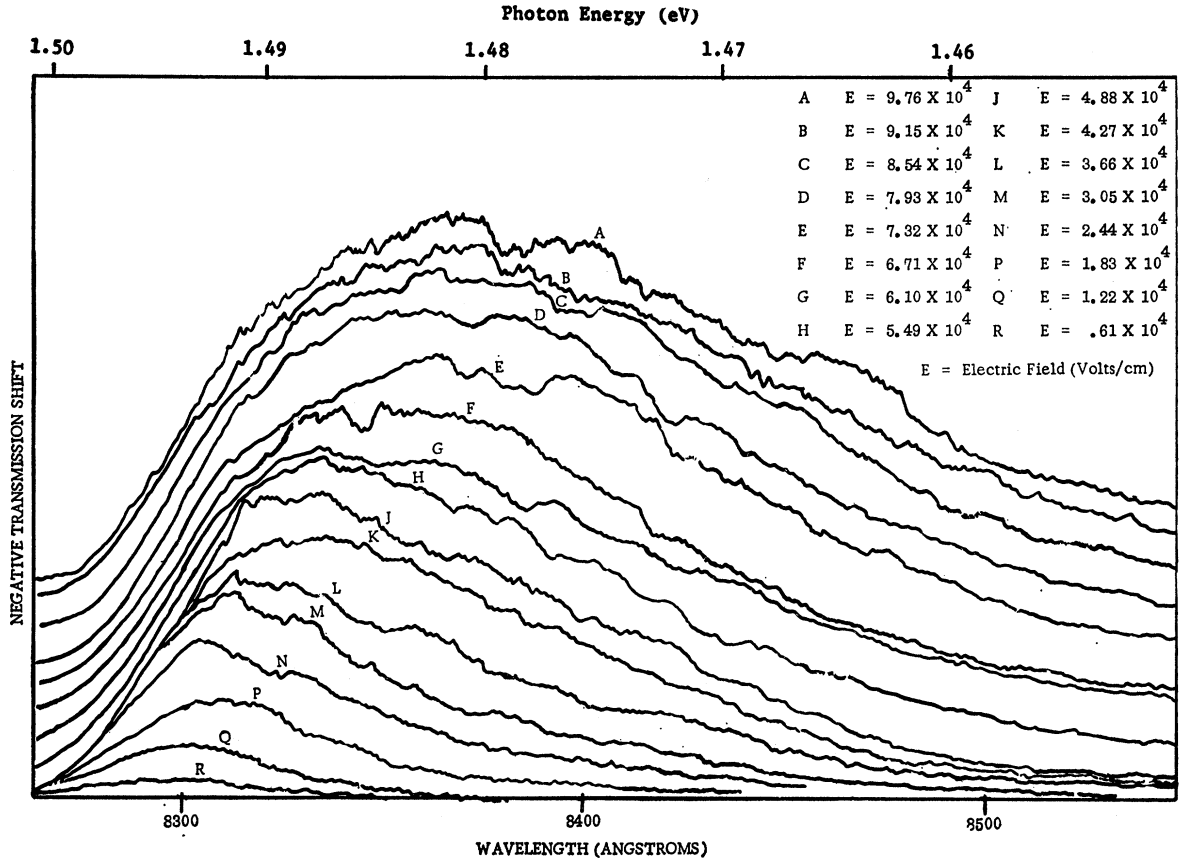

FIG. 10. Optical-transmission-shift data using a 12-μ-thick $\langle 100 \rangle$ oriented specimen of semi-insulating gallium arsenide at 90°K (high-field curves displaced for clarity).

Direct correlation of these data with the Wannier-level theory of Callaway is extremely difficult for several fundamental reasons. First, the effects of lattice and impurity scattering in this experiment are not well understood. The motion of field-accelerated holes and electrons predicted by theory is probably strongly modified, since in GaAs these carriers readily emit LO phonons due to polar optical scattering. The existence of the Coulombic electron-hole interaction leading to apparent observation of exciton absorption and subsequent quenching by the field also leads to difficulties for a Wannier-level interpretation. The one-electron theory could only apply if the electron-hole interaction can be neglected, that is, in the presence of external electric fields strong enough to quench the exciton absorption. Observation of exciton quenching for fields approaching 10^5 V cm^{-1} may indicate the relative importance of the external field compared with the Coulombic interaction between the electron and hole. Also, for the 12-μ-thick specimen of this experiment, a Laue pattern showed the $\langle 100 \rangle$ lattice orientation vector and the electric-field direction to be misaligned 3.5° in a $\langle 110 \rangle$ direction, which is probably a significant deviation from the desired reciprocal lattice vector direction.

Observations of Stark or Wannier levels by optical-transmission methods have been reported previously in cadmium sulfide. The first observation by Snavely[21] utilized oriented deposited thin films. Subsequently, Vavilov *et al.*[22] observed the theoretically predicted dependence of the discrete levels upon both field magnitude and reciprocal lattice vector in cadmium-sulfide crystals. The structure reported in the present paper is different from that of the data reported for cadmium sulfide and from Wannier-level theory. The present paper clearly indicates field-dependent structure in the optical absorption of GaAs in the energy region below the absorption edge but does not demonstrate the existence of Wannier levels.

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discussions concerning the relationship of the observed data with theory. I wish to express my gratitude to R. R. August of Autonetics for his assistance and direction, and to Mrs. D. A. George and J. Carlson for help in the preparation and mounting of the very thin specimens of gallium arsenide. The partial support of this work by the U. S. Air Force Office of Scientific Research is also gratefully acknowledged.

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Optical Properties and Formation Kinetics of M^+ Centers in NaF

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It is shown that the M^+ center in NaF has an absorption band at 740 mμ and an emission band at 943 mμ. M^+ centers in NaF can be produced by prolonged x irradiation at room temperature, or by irradiation at low temperature followed by annealing to near room temperature. From a study of the production and transformation of the M and M^+ centers it is concluded that the formation of an M center is preceded by the intermediate formation of an M^+ center. It is suggested that M centers in NaF, as in LiF, are formed through the reaction $\alpha+F \rightarrow M^+$, followed by electron capture. The kinetics of aggregation to M^+ centers in NaF and LiF are also studied in the present work.

INTRODUCTION

In recent years, a number of studies have been reported[1–5] on absorption bands associated with ionized F-aggregate centers in several alkali halides. Specifically, the existence of the ionized M and R centers, which will be referred to as M^+ and R^+ centers, respectively, has been established with a reasonable degree of certainty.

In this paper, the absorption and emission bands for the M^+ center in NaF are reported, along with a study of M^+-center formation by a thermally activated process. It was observed that formation of an M center in NaF, as in LiF, is preceded by the intermediate formation of an M^+ center. The kinetics of the aggregation to an M^+ center, apparently through the reaction $\alpha+F \rightarrow M^+$, has been studied in the present work. In general, the formation and transformation behavior of the M^+ and M bands in NaF resemble those reported previously[4,5] for the M^+ and M bands in LiF.

EXPERIMENTAL

Crystals obtained from Harshaw were cleaved into plates of dimensions $1\times10\times10$ mm. Low-temperature irradiations and measurements of absorption spectra, emission spectra, and optical bleaching were carried out with equipment and techniques similar to those described previously.[4,5]

The samples were mounted in a variable-temperature cryostat fitted with a rotatable head. Temperature measurements were made with a copper-constantan thermocouple mounted close to the sample on a copper sample holder. An electrical heating element was used to achieve a controlled rate of warming. A given temperature could be maintained within $\frac{1}{4}$°K. Optical-absorption measurements were made with a Beckman DK-1A spectrophotometer. To obtain greater accuracy, weak absorption bands were recorded in the 90–110 transmittance range of the spectrophotometer.

RESULTS

$M^+ \rightarrow M$ Transformation

An absorption band at 740 mμ, most probably arising from a transition of the M^+ center, is produced together with the stronger F and M bands by prolonged x irradiation at room temperature (RT). Support for this M^+ assignment is provided by the following observations: (a) During F-band illumination at low temperatures, the band at 740 mμ decreases in constant proportion to the growth of the M band; (b) as in LiF, crystals containing M^+ centers can undergo $M^+ \rightarrow M$ conversion under a short reexposure to x rays alone at low temperature. The conversion 740 m$\mu \rightarrow M$ is depicted in Fig. 1. Curve a shows the absorption spectrum of a crystal cooled to liquid-nitrogen temperature (LNT) immediately after the termination of the RT x irradiation. Curve b, taken after a short reirradiation at LNT, shows a decrease in the 740-mμ band and an increase in the M band at 499 mμ. Curves c and d show the spectra after longer reirradiations at LNT. The growth of the M band during the LNT reirradiation is proportional to the decrease in the 740-mμ band. The conversion ratio $|\Delta\alpha_M/\Delta\alpha_{M^+}|$ expressing the change in the absorption coefficients at the peaks of the respective bands is 3.6. From the half-widths of the M band ($W_M=0.105$ eV)

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