Electromodulation spectroscopy of excitons in simple cubic TlCl and TlBr

John Frederick McClelland
*Iowa State University*

David W. Lynch
*Iowa State University, dlynch@iastate.edu*
Electromodulation spectroscopy of excitons in simple cubic TlCl and TlBr

Abstract
Transmission and electromodulated transmission spectra have been measured in the direct Wannier exciton region for TlCl and TlBr. The spectra were obtained at a sample temperature between 5 and 6 K for a range of applied electric fields. The data have been reduced to obtain the electric-field-induced changes in the dielectric function and compared in detail to the calculations of Blossey. The experimental results support the trends predicted by the calculations.

Keywords
Ames Laboratory, Wannier, dielectric function

Disciplines
Atomic, Molecular and Optical Physics | Condensed Matter Physics | Optics | Physics

Comments
Electromodulation spectroscopy of excitons in simple cubic TiCl and TiBr

J. F. McClelland and D. W. Lynch

Ames Laboratory-USDOE and Department of Physics, Iowa State University, Ames, Iowa 50011

(Received: 10 October 1978)

Transmission and electromodulated transmission spectra have been measured in the direct Wannier exciton region for TiCl and TiBr. The spectra were obtained at a sample temperature between 5 and 6 K for a range of applied electric fields. The data have been reduced to obtain the electric-field-induced changes in the dielectric function and compared in detail to the calculations of Blossey. The experimental results support the trends predicted by the calculations.

I. INTRODUCTION

Certain features observed in the optical spectra of some crystalline insulators and semiconductors provided an early indication of inadequacies in simple band theory. The Frenkel exciton model was successful in explaining nonband features which had been observed in alkali halide spectra. Later Wannier excitons were postulated, prior to the experimental work. Subsequently optical measurements on Ge were interpreted on the basis of Wannier excitons in the important work by Elliott. Much of the electronic structure not encompassed by band theory has now been clarified for high dielectric constant solids by adding energy levels associated with Wannier exciton states and altering nearby band states. However, efforts to make detailed quantitative comparisons between the results of calculations based on the Wannier model and experimental measurements often have been difficult because the hydrogenic energy levels of the ideal Wannier exciton are nearly always significantly perturbed by interactions with the crystal. This results in a shifting and broadening of exciton energy levels and often additional states which are outside the scope of the simple Wannier model.

Modulation spectroscopic techniques can be used for quantitative studies of both exciton states and band structures. They provide sharper derivative spectra, usually as a function of an external perturbation applied to the sample. The sharper spectra may allow a more quantitative test of the exciton model than would be afforded by the unmodulated spectra; however, one is then testing the exciton model's ability to predict spectral changes as a function of an applied perturbation rather than directly testing the unperturbed model.

Electric and magnetic field modulation are most appropriate for Wannier exciton studies because they cause a direct perturbation to the exciton Hamiltonian. The most detailed calculations for comparison with experimental results have been done for electric field modulation and a number of experimental comparisons have been made. Definitive comparisons between experiment and theory have been difficult due to a scarcity of solids having ideal Wannier exciton states with low broadening, difficulties with both sample preparation and modulation, and the complexity of data reduction to enable comparison with theory in terms of the field-induced changes in the complex dielectric function.

Progress is reported in this work toward a more quantitative comparison of experimental results with the detailed electroabsorption calculations of Blossey. Section II of this paper will include a discussion of the thallium halide samples used in the investigation and a description of the experimental measurement system. Data-reduction methods are covered in Sec. III. Results of the measurements are presented in Sec. IV, followed by the comparison of results to Blossey's calculations in Sec. V. Finally, a conclusion is given in Sec. IV.

II. SAMPLES AND EXPERIMENTAL APPARATUS

Thin-film simple-cubic samples of TiCl and TiBr were prepared for the exciton electromodulation studies in the region of the lowest-energy direct interband transition at the X point in the Brillouin zone. The electrotransmission measurements were not extended to the indirect band-gap region because the excitons associated with this region do not fit the assumptions of Blossey's theory and substantially thicker samples would have been required than are appropriate for the direct-transition region. The influence of the indirect transitions was, however, present in the direct exciton electromodulation measurements through photocarriers associated in part with the indirect transitions which complicated establishing the electric field modulation in the sample.
This aspect will be addressed in more detail in Sec. IV.

TICl and TIBr are good candidates for Wannier exciton studies because they have very high dielectric constants, specifically 37.6 and 35.1, respectively. The exciton Bohr radius to lattice constant ratios for TICl and TIBr are 20 and 15, while the exciton binding energies are 11.7 and 9.8 meV, respectively. The direct excitons have a number of associated energy states which are outside the scope of the simple Wannier exciton model. These states have been attributed to inter- and intravalley scattering of excitons\textsuperscript{17} and to phonon sidebands.\textsuperscript{15,16} These “extra” states, however, have not caused serious interference to observations of the hydrogenic exciton levels as demonstrated in remarkable detail by spectroscopic measurements\textsuperscript{18} using a perturbing magnetic field.

The magnetic field measurements were made possible by a sample preparation method\textsuperscript{15,18} which allowed thin-film samples to be cooled to helium temperature to reduce thermal broadening without inducing strain in the film due to the usual thermal expansion mismatch between a thin film and its substrate. Samples prepared by this method consist of a thin film evaporated on a very thin methacrylate membrane. The membrane is supported by a frame cut from a single crystal of the compound being evaporated, thus providing a close match in thermal expansion coefficients between the film and substrate. This method was initially tried for the electromodulation measurements conducted in this study but proved impractical due to a coupling effect, which does not occur with a magnetic field, between the membrane-supported thin-film sample and the modulating electric field.\textsuperscript{13} The coupling was due to spatially inhomogeneous regions in the electric field which drew the dielectric film toward higher-field regions, thereby inducing a strain modulation in the sample. This resulted in a modulated transmission spectrum containing components due to both electric and strain modulation which could not easily be separated for comparison to theory.

To control the strain modulation problem, samples\textsuperscript{13} were evaporated on methacrylate-membrane-covered solid CsI substrates which have an expansion coefficient close to those of the thallium halides\textsuperscript{10} being studied. The membrane prevented diffusion between the film and substrate and provided a slip plane to relieve strain in the film. The strain relief was, however, not complete and these samples had a higher level of static strain than was associated with the frame-supported membrane configuration.

The substrates were mounted between Teflon-insulated plates which formed a capacitor sample mount\textsuperscript{13} attached to the cold finger of a cryostat. The Teflon prevented injection luminescence and provided padding during cool down. The evaporation was done \textit{in situ} at a rate of 4.0–6.0 nm/min in a vacuum in the low 10\textsuperscript{-6}– to high 10\textsuperscript{-7}-Torr range with the substrate at room temperature. The quartz evaporation boat was charged with single-crystal chips of TICl or TIBr from the Harshaw Chemical Company. The boat could be translated in vacuum between a position adjacent to a quartz crystal thickness monitor, where the evaporation rate was established, and a position in front of the substrate. Film thicknesses were in the 50–70-nm range and were checked by interferometric measurements on films deposited simultaneously on a glass slide mounted adjacent to the sample substrate. The low thickness limit was imposed by a thin-film disorder problem often found in simple-cubic thallium halide films below 50-nm thickness. The upper limit was set, as a result of experience, to reduce photocarrier effects which interfere with the electric field modulation.\textsuperscript{13}

The experimental measurement system\textsuperscript{13} enabled the determination of the transmission $T$ and the electromodulated transmission $\Delta T/T$ spectra of samples near helium temperature. Figure 1 shows a block diagram of the system as operated for transmission measurements. The light beam originates at a quartz halogen lamp, in the upper left-hand corner of Fig. 1, and is focused on the entrance slit of a McPherson model 218 monochromator after being chopped for synchronous detection. After passing through the monochromator the beam has a bandpass of 0.08–0.16 nm or approximately 0.7–1.4 meV, and is focused on the sample after a small fraction has been reflected.

![Block diagram of the experimental measurement system as operated for transmission measurements.](image-url)
to a monitoring photomultiplier. This detector is part of a feedback loop which maintains an approximately constant beam intensity on the sample by automatically adjusting the lamp power during wavelength scans. The photomultiplier, positioned after the sample, provides a signal proportional to the transmitted light intensity which is processed by a lock-in amplifier and plotted by a recorder synchronized to the wavelength scan by an encoder. Scans were also taken with the sample removed from the beam to provide a correction curve for the servo system due to small differences in the optical paths and detector responses. The wavelength was calibrated with Osram line source lamps.

The $\Delta T/T$ operating mode is shown in the block diagram in Fig. 2. In this mode the beam intensity was neither chopped nor served prior to reaching the sample. A unipolar 50% duty-cycle square-wave voltage of up to 10 kV was applied to 200 Hz to the sample by capacitor plates with a spacing of 1.8 mm. The electric field modulation resulted in a transmission modulation at wavelengths where field-sensitive exciton features exist. In these regions there was a corresponding ac component added to the dc transmission signal from the photomultiplier. The ac photomultiplier signal was approximately proportional to $\Delta T/T$ when a servo system, as shown in Fig. 2, automatically maintained the dc photomultiplier signal at a constant value by adjusting the voltage applied across the photomultiplier. A lock-in amplifier processed the ac signal which was plotted with the dc signal on a chart recorder.

FIG. 2. Block diagram of the experimental measurement system as operated for electromodulated transmission measurements.

III. DATA REDUCTION METHODS

The $T(hv, \delta)$ and $\Delta T/T(hv, \delta)$ spectra were reduced to the electric-field-induced changes in the real and imaginary parts of the dielectric function, $\Delta \varepsilon_1(hv, \delta)$ and $\Delta \varepsilon_2(hv, \delta)$, respectively. The symbols $hv$ and $\delta$ represent the photon energy and applied electric field amplitude, respectively. Data reduction to obtain $\Delta \varepsilon_1$ and $\Delta \varepsilon_2$ spectra required solving simultaneous equations given by

$$\frac{\Delta T}{T}(hv, \delta) = \frac{1}{T} \frac{\partial T}{\partial n} \Delta n(hv, \delta) + \frac{1}{T} \frac{\partial T}{\partial k} \Delta k(hv, \delta)$$

and

$$\Delta \varepsilon(hv, \delta) = \frac{\partial \varepsilon}{\partial n} \Delta n(hv, \delta) + \frac{\partial \varepsilon}{\partial k} \Delta k(hv, \delta)$$

for $\Delta n$ and $\Delta k$, the field-induced changes in the real and imaginary parts of the index of refraction, respectively. $\Delta T/T$ and $1/T$ were provided by the experimental measurements. $\Delta \varepsilon$, the electric-field-induced change in the transmission phase shift, was calculated with the Kramers-Kronig expression,

$$\Delta \varepsilon(hv, \delta) = \frac{hv}{\pi} \int_{hv_d}^{\infty} \ln\left[1 + \frac{\Delta T/T(hv, \delta)}{(hv)^2 - (hv_d)^2}\right] \frac{d(hv_d)}{(hv_d)^2 - (hv)^2}.$$  

The limits of integration spanned the direct bandgap exciton region since contributions from other regions are expected to be negligible. Equation (3) was derived from the Kramers-Kronig phase shift formula and the integration was performed by computer. The partial derivative expressions were derived from standard thin-film formulas.

The $\Delta \varepsilon_1$ and $\Delta \varepsilon_2$ spectra were calculated from

$$\Delta \varepsilon_1 = 2n \Delta n - 2k \Delta k$$

and

$$\Delta \varepsilon_2 = 2k \Delta n + 2n \Delta k,$$

which are derived from the usual expressions relating the index of refraction and dielectric function. Both these equations and the partial derivative expressions require spectra of $n$ and $k$ for the thallium halides, the methacrylate membrane, and CsI. The latter two were obtained from a measurement and the literature, respectively. The $n$ and $k$ data used for the thallium halides were values measured by Bachrach which were adjusted to account for a higher level of static strain in the samples used in this study. The adjusted values were obtained by programming a computer to search over ranges near the literature values to locate $n$ and $k$ values which produced a calculated transmission within a specified tolerance of
the experimental measurement. This procedure resulted in multiple solutions and final values of \( n \) and \( k \) were determined by starting at low photon energy where \( k = 0 \) and \( n \) is known, and working graphically to higher photon energy, using requirements of continuity of \( n \) and \( k \) pairs, the known general functional form for \( n \) and \( k \) in this region, and calculations to check the agreement between calculated and measured transmission. The values of \( n \) and \( k \) finally obtained gave calculated transmission spectra which reproduced the experimental spectra for both TlCl and TlBr.

IV. EXPERIMENTAL RESULTS

Spectra of \( \Delta T/T \), \( \Delta \epsilon_1 \), and \( \Delta \epsilon_2 \) are presented in this section at two applied field strengths for TlCl and TlBr. The unmodulated spectra are included in each figure for comparison. The primary features of these spectra and others taken on the same samples at different applied fields are compared to the results of Blosey's calculations in Sec. V.

The \( T \) and \( \Delta T/T \) spectra are shown in Figs. 3 and 4 for TlCl and TlBr, respectively, at sample temperatures between 5 and 6 K. The locations of the \( n = 1, 2, \) and \( \infty \) hydrogenic energy states are marked, with \( \infty \) denoting the series limit at the conduction-band edge. The \( n = 2 \) position was located in Fig. 3 by calculating the energy spacing from the \( n = 1 \) peak using the reported exciton binding energy\(^\text{16}\) and the hydrogenic model, The energies of other expected spectral features were plotted relative to the \( n = 1 \) peak using energy spacings from Ref. 16. The primed features correspond to splittings of the hydrogenic levels caused by the inter- and intravalley scattering perturbation.\(^\text{17}\) The \( \alpha \) and \( \beta \) symbols denote the locations of the phonon sideband features.\(^\text{15,16}\) The spectra for TlBr do not show as much resolved structure due to three factors: the lower exciton binding energy and splitting characteristic of TlBr, the greater thermal broadening caused by a lower Debye temperature, and the higher applied fields.

Figures 5 and 6 show the \( \epsilon_1 \) and \( \Delta \epsilon_1 \) spectra for TlCl and TlBr, respectively, which were calculated from the spectra shown in Figs. 3 and 4. The main effect of the electric field, as seen in the \( \Delta \epsilon_1 \) spectra, is a broadening and attenuation of the major positive and negative \( \epsilon_1 \) peaks below the direct band-gap corresponding to \( n = \infty \) while oscillations appear in the \( \Delta \epsilon_1 \) spectra above the band-gap, as predicted by theory.\(^\text{8-10}\)

The \( \epsilon_2 \) and \( \Delta \epsilon_2 \) spectra are shown in Figs. 7 and 8 for TlCl and TlBr, respectively. The \( \Delta \epsilon_2 \) spec-

---

FIG. 4. TlBr transmission (dashed line) and electromodulated transmission spectra at two applied voltages.

FIG. 3. TlCl transmission (dotted line) and electromodulated transmission spectra at two applied voltages.

FIG. 5. \( \Delta \epsilon_1 \) spectra (solid lines) and \( \epsilon_1 \) spectrum (dotted line) of TlCl. The marked photon energy locations coincide with those in Fig. 3.
tra also show the peak broadening and attenuation effect of the field below $\eta = \infty$ and the higher photon energy oscillations. A small amount of peak shifting of uncertain origin occurs in the $\Delta \epsilon_2$ spectra relative to the $\Delta T/T$ spectra for features associated with the hydrogenic exciton states. In all cases these shifts are small fractions of the linewidths of the unmodulated spectra. The photon energy locations labeled in Figs. 7 and 8 coincide with those in Figs. 3 and 4.

V. COMPARISON OF EXPERIMENTAL RESULTS TO CALCULATIONS

A detailed comparison is made in this section between the measurements and Blossey's calculations for the primary spectral features as a function of the applied electric field modulation amplitude. The primary spectral features, as designated in Ref. 9, are shown in Fig. 9.

A spectral broadening parameter, $\Gamma = 0.2R$, was selected on the basis of a comparison between calculated and measured line shapes for unmodulated spectra. $R$ is the exciton binding energy. This is a larger value than the sample temperature would have indicated due to the broadening of the spectra by strain.

The first comparison of experimental spectral features to theory is shown in a $\Delta \epsilon_2$ plot of the zero-crossing separation $\Delta E_2/R$ vs $\delta/\delta_1$ shown in the upper left-hand corner of Fig. 10. $\Delta E_2/R$ is defined in Fig. 9, $\delta$ is the electric field calculated from the applied voltage and plate separation, and $\delta_1$ is the exciton ionization field $^5$ defined as the exciton binding energy divided by the product of the exciton Bohr radius and the electronic
charge. The $\delta_j$ values were calculated for TICl and TiBr from the exciton parameters given in Ref. 16. The dashed line has been fit to the points calculated by Blossey$^9$ and denoted by squares in Fig. 10. The experimental curves are low in both magnitude and slope until the square-wave voltage amplitude reaches the 6-kV region. The slopes then become approximately equal to those predicted by theory. The most likely cause for the discrepancy between theory and experiment appears to be a lowering of the field sensed by the excitons due to the presence of photocarriers. This cause is suggested both by electroreflection measurements$^{13}$ on TICl and TiBr by other workers and by observations made during the measurements reported here which can be explained on the basis of photocarriers.$^{13,25}$ Since quantitative photocarrier measurements were not possible during this study, no detailed explanation could be definitely established for the role of photocarriers. To provide the most useful comparison of experimental results to theory, effective fields sensed by the exciton were calibrated for each applied voltage by using the experimental $\Delta E_2/R$ values and the theoretical curve in the $\Delta E_2/R$ plot of $\Delta E_2/R$ vs $S/S_1$. The effective field values were read from the abscissa and used for the other plots in Figs. 10 and 11.

Figure 10 shows the other $\Delta \epsilon_1$ and $\Delta \epsilon_2$ zero-crossing separation plots using the effective-field values. The various zero-crossing separations plotted on the ordinates of the graphs are defined in Fig. 9. The plots show reasonably good agreement with theory in the high-field regions where the calculated results are represented by the solid lines. Blossey's results did not extend to the low-field region of the plots. If the calculated lines are extended linearly to the low-field region the experimental points are too low relative to the theoretical extrapolation. This could be due to the effects of photocarriers, inter- and intravalley scattering, and static strain, since these all appear to distort the spectra more at low fields.

---

**FIG. 10.** Experimental zero-crossing separations for the $\Delta \epsilon_1$ and $\Delta \epsilon_2$ spectra plotted as a function of applied effective field, as described in the text. The abscissa labels are defined in Fig. 9. The solid and dashed lines are plotted from Blossey's calculations (Ref. 9).
where the applied field is less dominant.

Figure 11 shows the $\Delta \epsilon_1$ and $\Delta \epsilon_2$ experimental peak heights plotted on the ordinates as a function of the effective field. The various peak heights, denoted by the letter $h$ with different subscripts, are defined in Fig. 9. The calculated $\Delta \epsilon_2$ curve of $h_3$ vs $\delta/\delta_1$ (effective) in the upper left-hand corner of Fig. 11 was used to scale the experimental peak heights. The curve is shown with a dashed region extended with a drafting curve to allow scaling of the lower-field data. The $h_1$ peak heights of both $\Delta \epsilon_1$ and $\Delta \epsilon_2$ are too high relative...
to theory. The other experimental peak heights are reasonably well clustered around the calculated curves.

VI. CONCLUSIONS

This study is the most comprehensive effort reported to date to compare Wannier exciton electromodulation calculations to experimental results in terms of the electric-field-induced changes in the dielectric function. Earlier efforts have generally involved less resolved structure and neglected to obtain results in terms of the dielectric function for comparison to theory.

The measurements reported here are compromised, as most previous investigations have been, by nonintrinsic broadening mechanisms and by difficulties in applying a well-defined electric field modulation, apparently due, in this case, to the presence of photocarriers. The measurements do support the general trends predicted by Blossey's calculations, regardless of these experimental problems. The study also indicates some of the problems which should be addressed in planning improved measurements.

ACKNOWLEDGMENTS

We would like to acknowledge the assistance of Dr. T. Pinter in the computer program coding and Dr. C. Culp in the design of the high-voltage square-wave generator. Thanks are due to Dr. D. Blossey and Dr. R. Bachrach for providing expanded plots of graphs. This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division.

1J. Frenkel, Phys. Rev. 37, 17, 1276 (1931).
2R. Hilsch and R. W. Pohl, Z. Phys. 48, 384 (1928); 58, 145 (1930).