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Electric-field-modulated reflectance of the band-gap exciton region of GaTe

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In this paper room-temperature flat-band electroreflectance measurements in the exciton region at the fundamental edge of high-quality GaTe single crystals are reported and discussed. The changes in the real and imaginary parts $\Delta\epsilon_1$ and $\Delta\epsilon_2$ of the dielectric constant have been obtained through a Kramers-Kronig analysis of the experimental $\Delta R/R$ spectrum. A comparison is presented between the experimental $\Delta\epsilon_2$ line shape and that obtained by the excitonic electroabsorption calculations of Blossey.

I. INTRODUCTION

Modulated spectroscopy, particularly electroabsorption or electroreflectance (ER) has generated the possibility to obtain a great deal of information about the band structure of solids.[1] The major task of such an analysis is the assignment of the structures present in differential spectra to band-to-band transitions at critical points of a certain type, and their location in the Brillouin zone. However, for the complete understanding of the optical properties of a solid, the Coulomb electron-hole interaction cannot be neglected and it has been pointed out by several authors that exciton effects are very important and often dominant.

Theoretically, expressions for the change of the optical constants due to external electric fields have been derived for excitonic and interband transitions and provide a basis for a qualitative interpretation of the experimental data. Theories of the optical response of semiconductors in an electric field were based primarily on the one-electron Franz-Keldysh theory until 1965, when Duke and Alferieff[2,3] attempted to include electron-hole scattering, using a model potential. Subsequently, Ralph[4] obtained numerical solutions of the effective-mass equation for an exciton in a uniform electric field. Blossey[5] extended Ralph's theory to include excitonic effects at M_3 as well as M_0 critical points; in addition, he discussed the effects of thermal broadening and calculated differential electroabsorption at the M_0 critical point in lead iodide. The effects of a uniform electric field on the optical response functions of a semiconductor were calculated by Weinstein, Dow, and Lao,[6] who numerically solved the effective-mass equation for a Wannier exciton.

The layer semiconductor GaTe is a III-VI compound which presents a strong anisotropic behavior of its physical properties due to the singularity of the crystal structure. Optical absorption near the edge,[7] photoconductivity,[8] Hall effect and electrical resistivity,[9] thermoreflectance spectra at and well above the fundamental edge,[10,11] photoreflectance at the band gap,[12] have been reported for this material. The energy-band structure of GaTe, on the contrary, has not yet been evaluated because of the complexity of the crystal structure. In this paper, electroreflectance measurements in the exciton region at the fundamental edge carried out with high-quality GaTe single crystals are for the first time reported and discussed.

II. EXPERIMENTAL

The experimental arrangement that has been used for electroreflectance measurements is the standard one in the technique of solid-state modulation spectroscopy. Unpolarized light from a xenon lamp Hanovia 976C-1 is focused on the entrance slit of a Hilger and Watts D-331 double-grating monochromator. The monochromatic light is focused on the samples, reflected at an angle of about 8°, and refocused on a Philips 56-TUVP photomultiplier. The dc portion of the output current from the photomultiplier, proportional to the reflectance of the sample R, is kept constant throughout the experiment by a simple analog-dividing system[13] which varies the high voltage applied to the phototube. The ac component, proportional to the reflectance change ΔR induced by the periodic electric field modulation, is detected by a PAR model 124-A lock-in amplifier, whose reference signal is supplied by the same wave generator that determines the modulation frequency. The frequency used was a compromise between signal strength and noise level and was usually chosen between 100 and 300 Hz. An X-Y recorder simultaneously receives at the Y input the inphase

output of the amplifier and at the X input a voltage linearly varying with wavelength, so that the ratio $\Delta R/R$ versus wavelength is directly obtained. With this experimental apparatus, modulation depths as small as 5×10^{-6} could be measured with a 10-sec time constant.

Single crystals of GaTe were obtained by the Bridgman technique with 99.999% pure Ga and 99.999% pure Te. Crystals were p type, not intentionally doped, with mobility 28 cm^2/V sec, and resistivity 11 Ω cm at room temperature. An electron diffraction investigation was performed to characterize the crystal structure. These electron diffraction patterns were indexed on the basis of a monoclinic cell of gallium monotelluride (space group C_{2h}^3) with lattice constants in fairly good agreement with those previously proposed by Hahn.[14] The crystals were in platelet form and the specimens suitable for reflectivity measurements were readily obtained by cleavage using a razor blade. These surfaces, normal to the c axis, were mirrorlike and no further etching treatment was necessary to improve their optical quality.

The room-temperature ER spectrum of GaTe was obtained by the standard surface-barrier electrolyte technique. The modulation was applied by using a 1-molar solution of KCl in water. The samples were immersed in the solution at the center of a cylindrical quartz cell in such a manner that the incident and the reflected light beams propagated in the radial direction.

The modulation for the ER measurements was performed by a square wave which could be positioned at any particular dc bias. The flat-band voltage was determined from the zero in the $1/c^2$-vs-V plot, where V was the externally applied voltage. All measurements were obtained with the use of a 1-kHz ac bridge. The knowledge of the flat-band position enabled us to calculate the space-charge electric field at the surface from the equation for a fully depleted space-charge region

$$\mathcal{E} = (2eN_dV/\epsilon_0\epsilon)^{1/2}, \tag{1}$$

where e is the electron charge, N_d is the donor density (assumed equal to free-carrier concentration), $\epsilon_0\epsilon$ is the static dielectric constant, and V is the experimentally determined voltage from flat band. The electric field calculated in this way had a value of 16.8 kV/cm.

In the calculation of the surface field versus applied voltage, any linear-field electro-optic effect,[15] such as that for the first time seen in GaSe by Sasaki *et al.*,[16] was neglected, because all the elements of the third-rank tensor of all crystals belonging to the class C_{2h} are zero, and then the linear electroreflectance is expected to be never observed for any modulation field direction on GaTe.

III. RESULTS AND DISCUSSION

A typical electroreflectance spectrum for a GaTe single crystal is shown in Fig. 1 for unpolarized light at room temperature. The extent to which these characteristic patterns, in which the structure respond to the electric field changes, can be evaluated in terms of type and location of critical points will depend upon a theoretical understanding and a subsequent analysis of the effects. The basis of such an analysis is provided by the relation between the periodic variation of the electric field and the corresponding change of the density-of-states function induced in the neighborhood of the energy gap by these variations.

The measured values of $\Delta R/R$ are related to the variation $\Delta\epsilon_1$, $\Delta\epsilon_2$ of the real and imaginary parts of the complex dielectric constant by the well-known equation

$$\Delta R/R = \alpha(\epsilon_1,\epsilon_2)\Delta\epsilon_1 + \beta(\epsilon_1,\epsilon_2)\Delta\epsilon_2 . \tag{2}$$

On the other hand, the quantities $\Delta\epsilon_1$, and $\Delta\epsilon_2$, whose physical meaning is more direct, may be deduced from the known values of $\Delta R/R$ by means

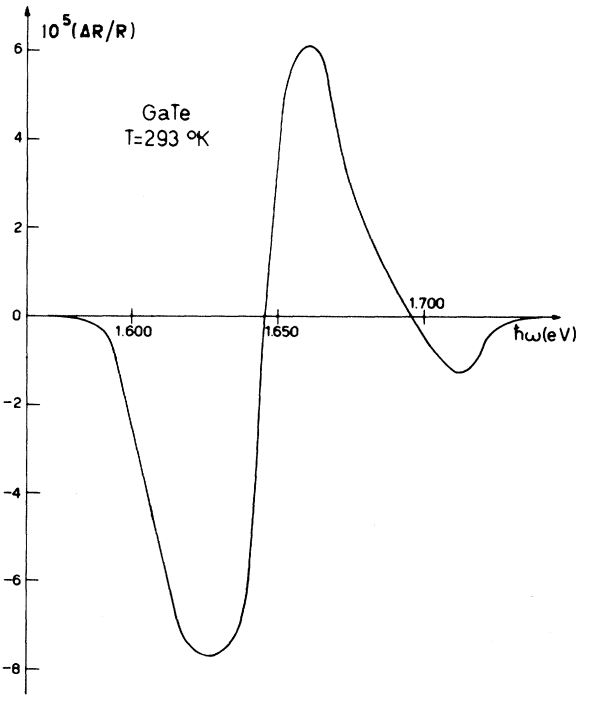

FIG. 1. Electric-field-modulated reflectance spectrum of the band-gap exciton region of GaTe, at room temperature and unpolarized light.

of the Kramers-Kronig dispersion equations. The values of ϵ_1 and ϵ_2 necessary for this computation have been obtained from those experimentally measured by Tatsuyama *et al.*[8] and by Grandolfo *et al.*[7] for the refractive index and absorption coefficient, respectively. Typical calculated results of $\Delta\epsilon_1$ and $\Delta\epsilon_2$ curves are shown in Fig. 2 as derived from the experimental electroreflectance spectrum.

A detailed study of electric field effects on $\Delta\epsilon_1$ and $\Delta\epsilon_2$ line shapes calculated from experimental spectra obtained in modulation spectroscopy of the exciton absorption region has been recently presented by Blossey,[5] showing in numerical form field effects on both bound and continuous states. In the Wannier exciton theory, the reduced mass of the electron-hole pair along with static dielectric constant ϵ of the material under study combine to define the exciton binding energy R and the exciton radius r, respectively, given by

$$R = \mu e^4/2\hbar^2\epsilon^3 \quad \text{and} \quad r = \hbar^2\epsilon/\mu e^2 . \tag{3}$$

The electric field which is capable of ionizing the exciton must provide at least a potential drop of one effective rydberg across the effective Bohr radius r; from this point of view, the ionization field $\mathcal{E}_I$ is defined as

$$\mathcal{E}_I = R/er . \tag{4}$$

In Table I there is a listing of several useful excitonic electroreflectance parameters for the case of GaTe.

Taking the difference between a properly normalized zero-field spectrum and a finite-field spectrum, Blossey has been able to display the field-induced changes $\Delta\epsilon_1$ and $\Delta\epsilon_2$ as functions of temperature and electric field. In these calculations the density-of-states function is given in the zero-field limit by

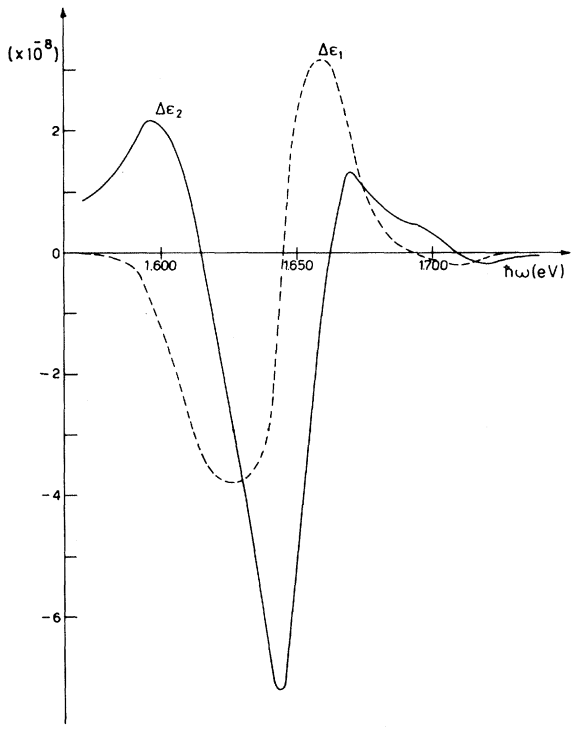

FIG. 2. $\Delta\epsilon_1$ (dashed line) and $\Delta\epsilon_2$ (solid line) for GaTe as obtained from the Kramers-Kronig analysis of the data of Fig. 1.

TABLE I. Several useful excitonic electroreflectance parameters for the case of GaTe.

Quantity	Definition	Values
Energy gap	...	~1.67 eV
Effective rydberg	$\frac{\mu e^4}{2\hbar^2\epsilon^2}$	25 meV
Effective Bohr radius	$\frac{\hbar^2\epsilon}{\mu e^2}$	40 Å
Ionization field	$\frac{\mu^2 e^5}{2\hbar^4\epsilon^3}$	~65 kV/cm
Reduced mass of electron-hole pair	$\frac{m_e m_h}{m_e + m_h}$	$0.098m_0$
Broadening parameter	kT	~25 meV
Electro-optical energy	$\hbar\Theta = R\,(\mathcal{E}/\mathcal{E}_I)^{2/3}$	~10 meV

$$\phi^2(0) = 4\pi \sum_{n=1}^{\infty} n^{-3} \delta\left(\frac{\hbar\omega - E_g + Rn^{-2}}{R}\right), \quad \hbar\omega < E_g , \tag{5a}$$

$$\phi^2(0) = \frac{2\pi}{1 - e^{-2\pi[(\hbar\omega - E_g)/R]^{-1/2}}}, \quad \hbar\omega > E_g . \tag{5b}$$

For a finite field, $\phi^2(0)$ is expressed in terms of parabolic coordinate eigenfunctions which are solutions of a numerically integrable differential equation. In order to obtain a more realistic picture of the optical process and to be able to compare theory with experimental results, a phenomenological lifetime broadening is introduced using convolution with a Lorentzian function.

At the temperature and electric field values at which the experiment has been performed, corresponding to $\Gamma/R \simeq 1$ and $\mathcal{E}/\mathcal{E}_I \simeq 0.25$, excitons are neither field or thermally ionized. According to the Blossey's calculations, in this case, the first negative oscillations in $\Delta\epsilon_2$ is pinned at $\hbar\omega = E_g - R$, while, at the same energy is pinned the first zero below the edge presented by the $\Delta\epsilon_1$ spectrum. Assuming a value of 0.025 eV for the exciton binding energy, according to the results obtained by Tatsuyama *et al.*,[8] we are led to a room-temperature energy-gap value of $E_g = 1.670 \pm 0.005$ eV, which is in very good agreement with that obtained by thermoreflectance[10] and photoreflectance[12] measurements, evaluated the experimental energy scale resolution. A curve-fitting procedure has been used to compare $\Delta\epsilon_2$ experimental results and those predicted by the excitonic theory. The theoretical curves were generated using the parameters $\Gamma = kT$, $T = 293\,^{\circ}\mathrm{K}$, $\epsilon = 7.3$, $\mu = 0.098 m_0$, and the electric field $\mathcal{E} = 1.68 \times 10^4$ V/cm as evaluated by Eq. (1). The energy-gap value used was 1.67 eV. A fairly good agreement has been obtained, as shown in Fig. 3, with a theoretical curve corresponding to a value of $\mathcal{E}/\mathcal{E}_I = 0.245$, to be compared with the one experimentally obtained, of $\mathcal{E}/\mathcal{E}_I = 0.25$. A disagreement is seen above the edge, where the oscillations are not properly in phase; this is probably due to the over-simplification related to the assumption of the electron-hole interaction as being simply a Coulomb potential, and to the neglection of the possible field inhomogeneity effects.

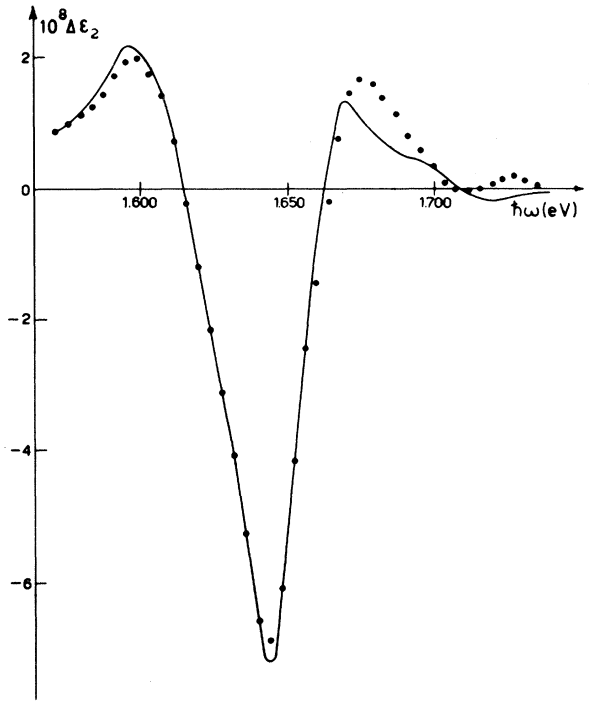

FIG. 3. Comparison between the experimental electric-field induced change in $\Delta\epsilon_2$ for GaTe (solid line) and the change resulting (solid points) from the application of Blossey's theory (Ref. 5).

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[1] M. Cardona, *Modulation Spectroscopy* (Academic, New York, 1969).
[2] C. B. Duke, Phys. Rev. Lett. 15, 625 (1965).
[3] C. B. Duke, and H. E. Alferieff, Phys. Rev. 145, 583 (1966).
[4] H. I. Ralph, J. Phys. C 1, 378 (1968).
[5] D. F. Blossey, Bull. Am. Phys. Soc. 14, 429 (1969); Phys. Rev. B 2, 3976 (1970); 3, 1382 (1970).
[6] F. C. Weinstein, J. D. Dow, and B. Y. Lao, Phys. Rev. B 4, 3502 (1971).
[7] M. Grandolfo, E. Gratton, F. Anfosso Somma, and P. Vecchia, Phys. Status Solidi 48, 729 (1971).
[8] C. Tatsuyama, Y. Watanabe, C. Hamaguchi, and J. Nakai, J. Phys. Soc. Jpn. 29, 150 (1970).
[9] G. B. Abdullaev, E. S. Guseinova, and B. G. Tagiev, Phys. Status Solidi 20, 421 (1967).
[10] D. Gili-Tos, M. Grandolfo, and P. Vecchia, Phys. Rev. B 7, 2565 (1973).

[11]F. Consadori and J. L. Brebner, Solid State Commun. 12, 179 (1973).
[12]E. Burattini, M. Grandolfo, G. Mariutti, and C. Ranghiasci, Surf. Sci. 37, 198 (1973).
[13]C. Felici and C. Ranghiasci, J. Phys. E 6, 1183 (1963).
[14]H. Hahn, Angew. Chemic 65, 538 (1953).
[15]D. S. Kyser and V. Rehn, Solid State Commun. 8, 1437 (1970).
[16]Y. Sasaki, C. Hamaguchi and J. Nakai, Phys. Soc. Jpn. 38, 162 (1975).