Exciton Thermoreflectance of GaTe

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Thermoreflectance spectra in the exciton region were obtained on the layer compound GaTe. The experimental results can be explained by assuming that the only temperature effect is a shift of the whole structure. The spectra were subjected to a Kramers–Kronig analysis and the changes in the real and imaginary parts of the dielectric constant, induced by the temperature change of the samples, were obtained. At a temperature of 284 °K the values of $E_0 = 1.676$ eV and $\Gamma = 23.5$ meV are found for the first energy level and the broadening parameter, respectively.

I. INTRODUCTION

Among the gallium III-VI layer compounds, GaSe and GaS have been especially investigated, while few works have been reported on GaTe. The band structure of GaTe has not yet been well understood because of the complexity of its crystal structure, which has been reported by Pearson.[1] Optical absorption[2-5] and reflectivity,[6-8] in the vicinity of and well above the fundamental edge, photoconductivity,[2,4,8,9] and exciton photoreflectance[10] at the band gap, have been measured in this semiconductor material.

In this paper we report the results obtained by thermally modulating the reflectivity of GaTe near its fundamental edge in the spectral region from 1.6 to 1.8 eV. The thermoreflectance spectra were subjected to a Kramers–Kronig analysis, and the change in the real and imaginary parts of the dielectric constant, induced by the temperature change of the samples, were obtained. A phenomenological interpretation of the observed experimental results is obtained by assuming that the only temperature effect is an energy shift of the whole exciton structure.

II. EXPERIMENTAL

The experimental arrangement which has been used is the standard one in the technique of temperature-modulated solid-state spectroscopy.[11-13] Light from a xenon lamp Hanovia 976C-1 was focused on the entrance slit of a Hilger and Watts D-331 double-grating monochromator. The monochromatic light was focused on the sample, 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 servo mechanism varying the photomultiplier power-supply voltage.[14] The ac component, proportional to the reflectance change ΔR induced by the periodic temperature modulation, is detected by a Tekelec model TE-9000 lock-in amplifier, whose reference signal is supplied by the same wave generator that determines the modulation frequency (3 Hz) and supplies power to heat the sample.

An X-Y recorder simultaneously receives at the Y input the in-phase output of the amplifier and at the X input a voltage linearly varying with the wavelength, so that the ratio $\Delta R/R$ versus wavelength is directly obtained.

The crystals were in platelet form and the specimens suitable for reflectivity measurements were readily obtained by cleavage using a razor blade and not further treated. The samples were bonded with silicone grease to a vacuum-evaporated gold

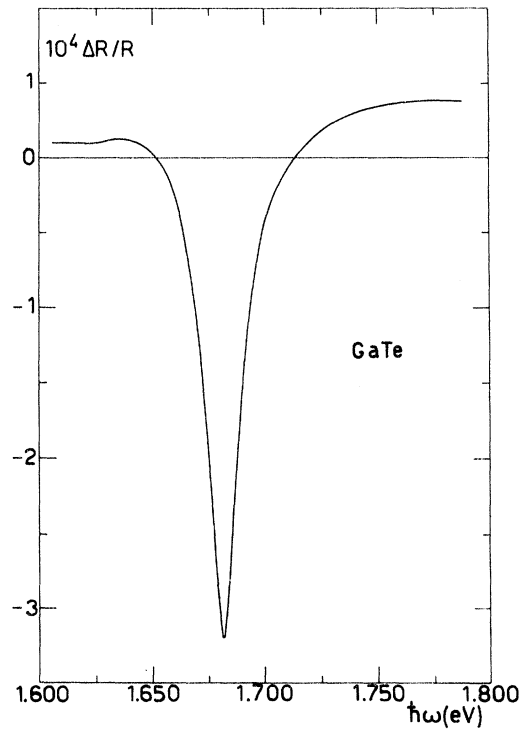

FIG. 1. Thermoreflectance spectrum of GaTe single crystals for $E \perp c$ at 284 °K.

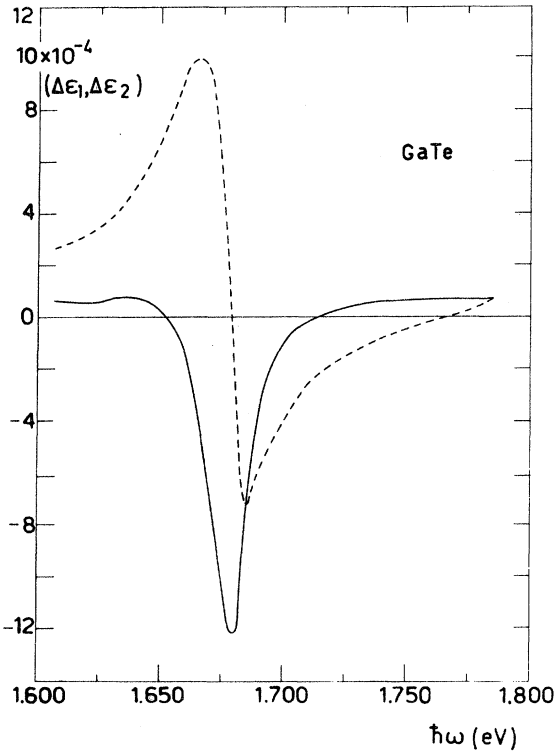

FIG. 2. Relative changes of the real (solid line) and imaginary (dashed line) parts of the dielectric constant of GaTe as derived from the data of Fig. 1 by application of the Kramers–Kronig dispersion relations.

film on a sapphire substrate acting as a heat sink and mounted on the copper cold finger of a metal cryostat fitted with quartz windows. A vacuum of the order of 10^{-6} Torr was kept inside the cryostat while water plus ice was added to the reservoir in order to work at a fixed temperature. The dc temperature rise of the samples was measured by a thermocouple attached to their surfaces, away from the incoming light beam; as a result of the thermal modulation the average temperature was raised to 284 °K, about 10 °K higher than that in absence of modulation.

III. RESULTS AND DISCUSSION

The experimental exciton thermoreflectance spectrum of GaTe at 284 °K is reported in Fig. 1. The extent to which this characteristic pattern can be evaluated in terms of type and location of optical transitions will depend upon a theoretical understanding and a subsequent analysis of the effect. The basis of such an analysis is provided by the relation between the periodic variation of temperature and the corresponding change of the density-of-states function induced in the neighborhood of the exciton line by this variation. To clarify the thermoreflectance line shape, the $\Delta R/R$ spectrum has been transformed into the temperature-induced changes in the real and imaginary parts of the dielectric constant, $\Delta\epsilon_1$ and $\Delta\epsilon_2$, through Kramers–Kronig (K-K) dispersion relations. For the values

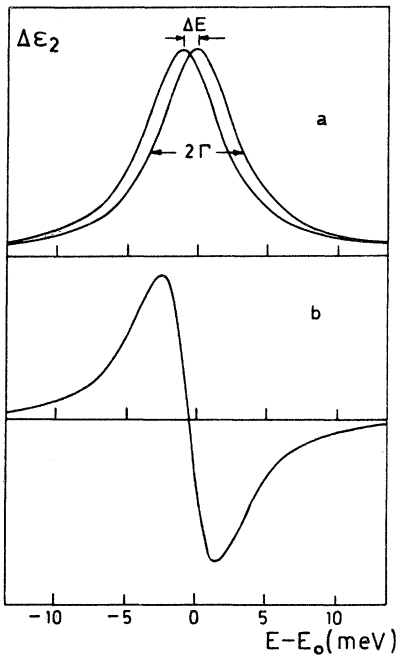

FIG. 3. Shift of a Lorentzian line shape to lower energies without change of shape: (a) unshifted and line shifted by ΔE; (b) resulting shape of $\Delta\epsilon_2$.

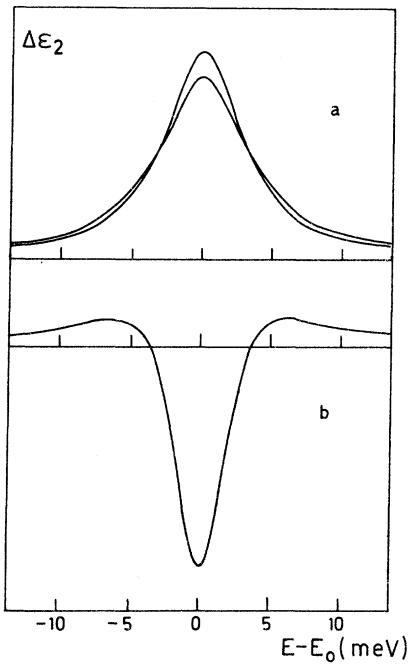

FIG. 4. Broadening of a Lorentzian line shape without change of position: (a) unbroadened and line broadened; (b) resulting shape of $\Delta\epsilon_2$.

of ϵ_1 and ϵ_2 necessary in the process of the K-K transformation, it is assumed that the imaginary part ϵ_2 is neglected as compared with the real one, and that ϵ_1 has the spectral variations near the fundamental edge calculated by Tatsuyama *et al.*[8] by using their experimental reflectivity values. A typical calculated result of $\Delta\epsilon_1$ and $\Delta\epsilon_2$ spectra is shown in Fig. 2.

In order to achieve a phenomenological interpretation of the observed experimental results we focus our attention initially on the strong dispersionlike shape of $\Delta\epsilon_2$ appearing in correspondence with the strong negative peak in the thermoreflectance spectrum in the vicinity of the gap region. The exciton-phonon interaction practically determines the line shape of the excitonic structures, and leads to a Lorentzian shape of the line, at least for the ground-state exciton line.[15]

The temperature effect can be accounted for by two distinct mechanisms: a shift ΔE of the line without broadening, or a symmetrical broadening $\Delta\Gamma$ without shift. In the former case, differentiation of ϵ_2 with respect to $E=\hbar\omega$ gives the following result:

$$\Delta\epsilon_2 = \frac{(\hbar\omega - E_0 + \frac{1}{2}\Delta E)\,\Gamma}{[(\hbar\omega - E_0 + \Delta E)^2 + \frac{1}{4}\Gamma^2][(\hbar\omega - E_0)^2 + \frac{1}{4}\Gamma^2]}\,\Delta E \tag{1}$$

shown in Fig. 3; while in the latter one we get

$$\Delta\epsilon_2 \equiv \frac{(\hbar\omega - E_0)^2 - \frac{1}{4}\Gamma^2 - \frac{1}{2}\Gamma\Delta\Gamma}{[(\hbar\omega - E_0)^2 + (\frac{1}{2}\Gamma + \Delta\Gamma)^2][(\hbar\omega - E_0)^2 + \frac{1}{4}\Gamma^2]}\,\Delta\Gamma \tag{2}$$

shown in Fig. 4. In Eqs. (1) and (2), E_0 is the energy position of the structure, Γ is the Lorentzian parameter, and ΔE and $\Delta\Gamma$ are their temperature modulations.

An attempt has been made to fit the experimental $\Delta\epsilon_2$ line shape with expressions (1) or (2) or a linear combination of both. The fitting was made by the least-squares method, and the best fit was found using expression (1). In great similarity with the case of GaSe[16] the experimental behavior of the ground-state exciton line of GaTe seems to be accounted for (Fig. 5) in terms of only a nearly rigid shift of the whole structure to lower energies; the agreement with the experiment is rather good taking $E_0 = 1.676$ eV and $\Gamma = 23.5$ meV. A value of -4.7×10^{-4} eV/°K has been obtained from the fitting procedure, consistent with temperature dependence of energy gaps in semiconductors.

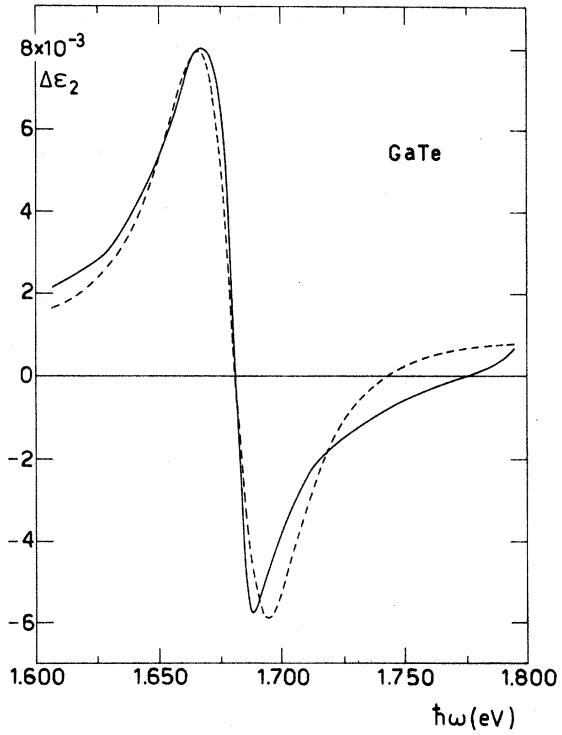

FIG. 5. Comparison of measured (solid) and calculated (dashed) line shapes of $\Delta\epsilon_2$ in the exciton region of GaTe. The best fit has been obtained at 284 °K using Eq. (1) and taking $E_0 = 1.676$ eV and $\Gamma = 23.5$ meV.

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