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Temperature Dependence of the Wavelength Modulation Spectra of GaAs*

by

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ABSTRACT

Wavelength modulation spectroscopy is used to obtain the temperature dependence of the reflectivity spectrum for GaAs. Results are given in the regions of the E_1 doublet and the major E_2 peak at 5, 80, 150, 225, and 300°K. The theoretical temperature dependence in these regions is obtained through using Debye-Waller factors and thermal expansion coefficients in an empirical pseudopotential calculation of the $(\Lambda_3-\Lambda_1)$ and $(\Sigma_2-\Sigma_1)$ energy splittings.

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We have measured the derivative of the reflectivity for GaAs using a wavelength modulation technique. Results are given in the vicinity of the E_1 and E_2 reflectivity peaks at 5, 80, 150, 225, and 300°K. (Figure 1). This is the first report of a derivative spectrum which has been accurately measured over a wide temperature range, and of a successful theoretical calculation of the temperature dependence of the reflectivity structure at and above the fundmental gap.

Wavelength modulation is achieved through the vibration of a mirror in the optical path inside the spectrometer. A two-beam method with appropriate electronics is used to eliminate the background noise and to yield a derivative reflectivity spectrum $R'(\lambda)/R(\lambda)$ of the sample. This output is converted to the functional form $R'(\omega)/R(\omega)$. The sample is a single crystal of n-type GaAs with a carrier concentration of 10^{16} cm^{-3}. After the sample is freshly polished and etched, it is mounted within an optical dewar, in which the temperature can be varied continuously from 4°K to 300°K, with an accuracy of ±1°K. The detailed construction of our wavelength modulation spectrometer and associated experimental equipment is described elsewhere.(1)

The wavelength modulation spectra for the five temperatures in the regions of the E_1 doublet peak and the E_2 major peak are shown in Fig. 1. The positions of the peaks and valleys of the reflectivity are given by the zeroes of the modulated spectra. The temperature shifts of the E_1 and E_2 peaks are plotted in Figure 2.

To calculate the theoretical temperature dependence of the GaAs spectrum, it is necessary to know the electronic band structure, the transitions which cause the reflectivity peaks, the thermal expansion

function, and the phonon spectrum of the crystals. The band structure of GaAs is obtained by the empirical pseudopotential method,[2] with spin-orbit effects included.[3] The pseudopotential form factors used are $V^S(G^2=3) = -0.2460$, $V^S(8) = -0.0008$, $V^S(11) = 0.0737$, $V^A(3) = 0.583$, $V^A(4) = 0.0509$, and $V^A(11) = 0.0011$ Ry.[4] The form factors for $G^2 > 11$ are constrained equal to zero. The spin-orbit parameter is adjusted so that the spin-orbit splitting at Γ is 0.35 eV. The E_1 doublet is caused by $\Lambda(4-5)$ and $\Lambda(3-5)$ transitions, and the E_2 peak is caused by $\Sigma(4-5)$ transitions.[4,5] The theoretically calculated peaks occur at the same energies as the $\Lambda(4-5)$ and $\Lambda(3-5)$ transitions, and the positions of these peaks, in turn, agree with the experimentally determined positions. For the E_2 peak the agreement is not as good; the theoretically calculated E_2 peak is 0.17 eV below the corresponding experimental peak. In addition, the Σ critical point is 0.06 eV below the theoretical E_2 peak. Consequently, the theoretically calculated Σ critical point lies 0.23 eV below the experimental E_2 peak. We have therefore introduced a corresponding shift in Figure 2, since it is the temperature dependence of the Σ critical point that is actually calculated.

The principal factors governing the temperature dependence of the reflectivity spectrum are the thermal expansion of the crystal and the thermal vibrations of the nuclei (the Debye-Waller effect). Since an expanded lattice reduces the average potential seen by an electron, the energy splittings between the bands are generally smaller[6] at higher temperatures and the positions of the reflectivity peaks shift to lower energies. The temperature dependence of the lattice constant is obtained from the thermal expansion function for GaAs.[7] The lattice constants used at 5, 80, 150, 225, and 300°K are 5.640, 5.640, 5.641, 5.643, and 5.645 Å, respectively. Since both the volume of the unit cell and the values of the reciprocal lattice vectors change

slightly with variations in the lattice constant, we must necessarily scale the pseudopotential form factors, the criterion being that the actual atomic potentials remain unchanged.

The thermal vibrations of the nuclei reduce the effective atomic potentials by the Debye-Waller factor e^{-W}.[8] Like the thermal expansion effect, the Debye-Waller effect reduces the energy splittings and causes the reflectivity peaks to shift to lower energies. The Debye-Waller factor can be calculated from the experimental phonon spectrum, and since this calculation is greatly simplified for a monatomic crystal, we have used the phonon spectrum of germanium instead of GaAs. This is a reasonable approximation because the GaAs phonon spectrum is nearly identical to that of germanium, and the average density of GaAs is the same as that of germanium to within 0.5%. Accordingly, we use an expression given by Blackman[9] for a monatomic crystal:

$$W = \frac{hG^2}{8\pi^2 m} \frac{\int \rho(\nu)\nu^{-1}[\frac{1}{2} + \frac{1}{e^x - 1}]d\nu}{\int \rho(\nu)d\nu} , \qquad (1)$$

where $x = h\nu/kT$, $\rho(\nu)$ is the density of phonon modes for Ge,[10] G is a reciprocal lattice vector, and m is the mass of the nucleus. The values of (W/G^2) we obtain by using Eq. (1) at 5, 80, 150, 225, and 300°K are 0.0010, 0.0015, 0.0024, 0.0034, and 0.0044, respectively.[11] Using X-ray measurements on germanium, Batterman and Chipman[12] obtain a value of $(W/G^2) = 0.0043$ at 300°K.

The Debye-Waller and lattice expansion effects are incorporated in a pseudopotential calculation of the band structure to give the temperature shifts of selected transitions in the Brillouin zone. In Table I, the result-

ing theoretical temperature dependence at Γ (the fundamental gap) is compared to the experimental temperature dependence obtained by Oswald[13] and by Sturge.[14] The calculated result at Γ agrees closely with that of Oswald. The Debye-Waller and lattice expansion effects can be calculated separately to show that the major part of the energy shift is caused by Debye-Waller effect, with only a small fraction caused by lattice expansion. At Γ the total calculated energy change between 5° and 300°K is -0.158 eV, of which -0.020 eV is caused by lattice expansion, or about 13% of the total.

An additional check on the accuracy of theoretical calculations using this pseudopotential band structure is provided by a calculation of the variation of the fundamental gap with respect to a slight change in the lattice constant. This calculation gives a value of $V(\frac{\partial E}{\partial V})_T = -7$ eV, a result which agrees exactly with the experimentally measured value.[15]

The theoretical temperature dependence of the $\Lambda(4-5)$, $\Lambda(3-5)$, and $\Sigma(4-5)$ transitions is shown in Figure 2. The comparison between theory and experiment for the E_2 peak is good, and for the E_1 doublet the comparison is excellent.

The temperature shifts of the reflectivity peaks in GaSb, InAs, and InSb are found to be approximately of the same magnitude as in GaAs.[1] We expect that similar theoretical calculations of the temperature dependence in these crystals would also yield good results.

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5. The notation refers to critical point transitions in the Brillouin zone. The bands are numbered consecutively, the fourth band is the highest valence band, and the fifth band is the lowest conduction band.
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Captions

Table I: Fundamental gap of GaAs as function of temperature. Experiment 1 is due to F. Oswald (Ref. 13). Experiment 2 is due to M. D. Sturge (Ref. 14).

Figure 1: Plots of $R'(\omega)/R(\omega)$ in the regions of the E_1 doublet peak and the E_2 major peak. Plots 1 through 5 refer to temperatures of 5°, 80°, 150°, 225°, and $300^\circ K$, respectively.

Figure 2: Plots of the explicit temperature dependence of the experimental E_1 and E_2 reflectivity peaks and of the corresponding theoretically calculated $\Lambda(4\text{-}5)$, $\Lambda(3\text{-}5)$, and $\Sigma(4\text{-}5)$ transitions.

Table I

Temperature (^{o}K)	Theory (eV)	Experiment 1 (eV)	Experiment 2 (eV)
5	1.52	1.53	1.52
80	1.50	1.49	1.51
150	1.46	1.45	1.49
225	1.41	1.42	1.46
300	1.36	1.38	1.43

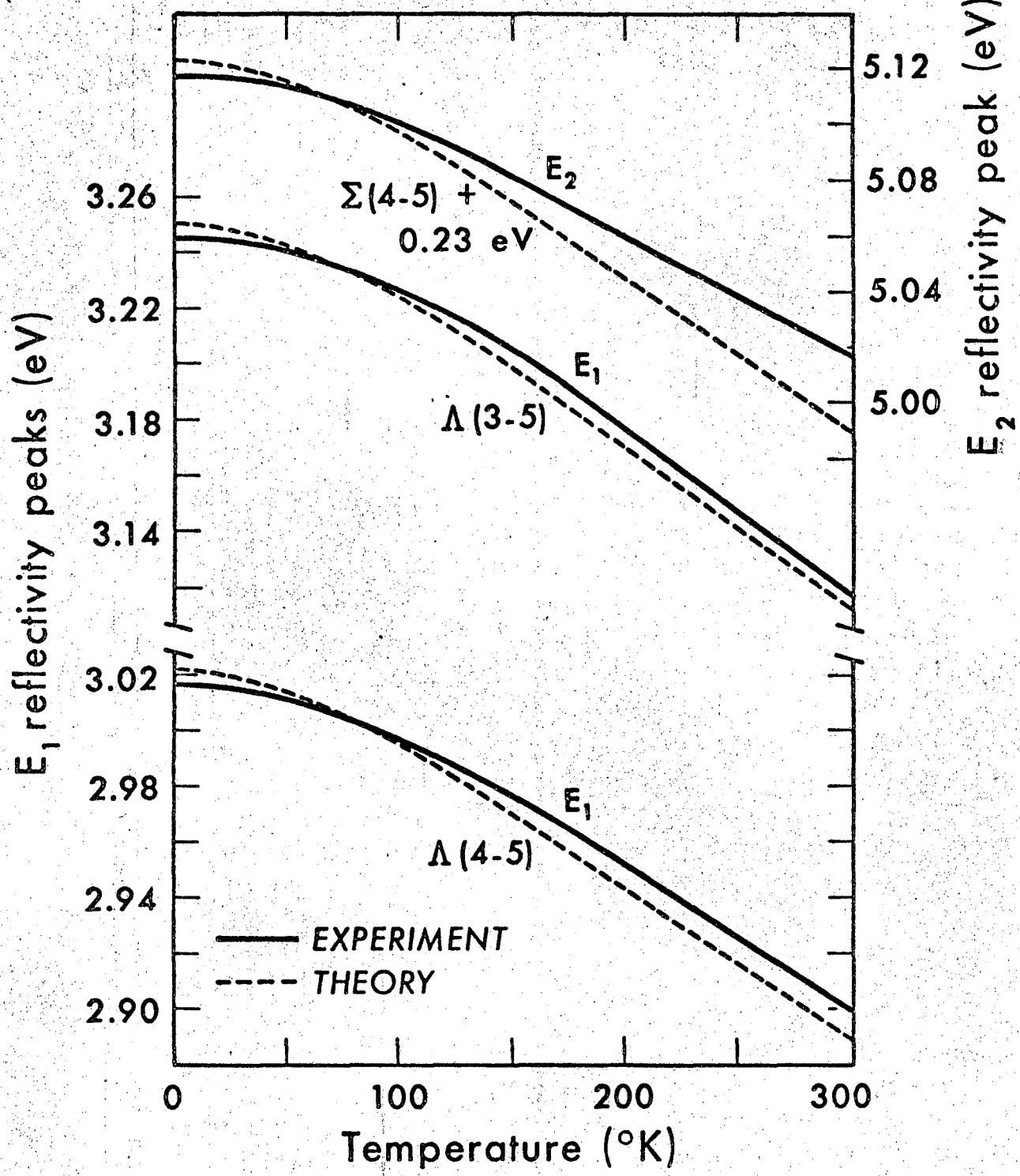
E1 reflectivity peaks (eV)
3.26
3.22
3.18
3.14
3.02
2.98
2.94
2.90
E2 reflectivity peak (eV)
5.12
5.08
5.04
5.00
E2
Σ(4-5) +
0.23 eV
E1
Λ(3-5)
E1
Λ(4-5)
EXPERIMENT
THEORY
0
100
200
300
Temperature (°K)

Figure 1

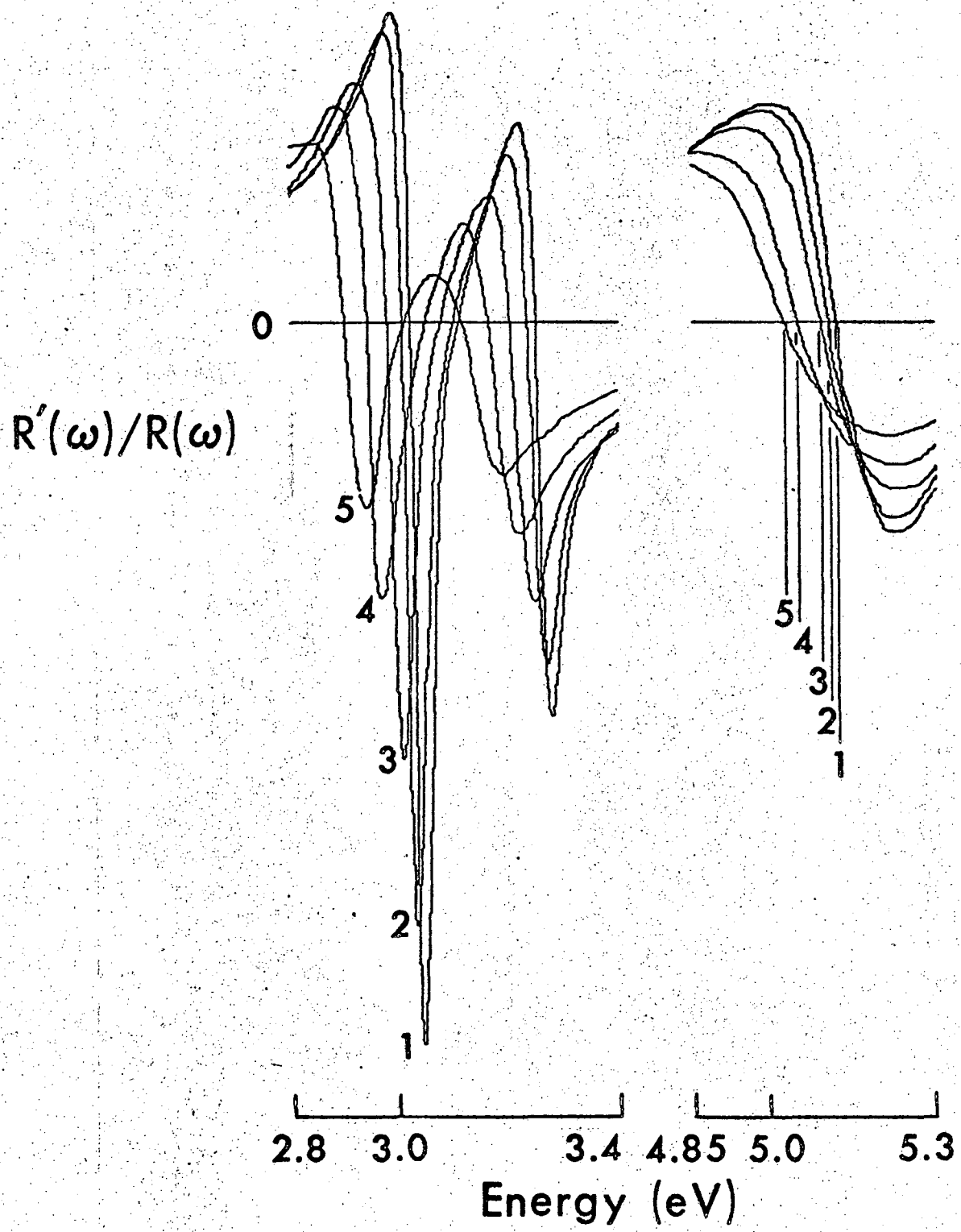

Figure 2

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