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Gallium Phosphide: Observation of the Γ-L Indirect Transition by Electroabsorption

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The phonon structure of the 2.67-eV indirect transition in GaP has been resolved in a transverse electroabsorption measurement. The transition is shown to be from Γ_{15} to L_1, contrary to previous assignments.

In their band-structure calculations, Cohen and Bergstresser[1] predicted a conduction-band X_1-X_3 heteropolar splitting in GaP of about 300 meV. Spitzer *et al.*[2] observed an infrared absorption band in degenerate material which they attributed to the X_1-X_3 transition. The Γ_{15}-X_1 transition has been observed by many workers[3] and confirmed by observation of the phonon structure. Dean, Kaminsky, and Zetterstrom[4] observed an unresolved indirect transition at 2.67 eV, or 290 meV above the Γ_{15}-X_1 transition, which they attributed to Γ_{15}-X_3. In this Letter we report transverse-electroabsorption experiments in which the phonon structure of this transition is resolved and is seen to be appropriate to a Γ_{15}-L_1 transition at 2.637 ± 0.010 eV (78 K).

A simple signal to noise ratio analysis indicates the optimum sample thickness in a modulated absorption experiment to be $t \sim 2/\alpha$, where the absorption coefficient is about 500 cm^{-1}. Accordingly, samples were prepared from a boule of chrome-compensated GaP ($\rho > 10^7$ Ω cm) and thinned to 40–100 μm by mechanical polishing. Experimental broadening effects are thought to be small because of the extreme narrowness of an impurity peak just below the Γ_{15}-X_1 edge (about 2-meV peak to peak in the modulation spectrum at 78 K).

Because of the transparency of GaP at energies lower than 2.4 eV, stray light is a severe problem in a transmission experiment at 2.67 eV. We use two Corning glass filters (5-57 and 4-96) and an interference filter (International Light type WB400; pass, 300 to 500 nm). It is estimated that stray light is less than 20% at the highest energies discussed herein. Because of fluorescence, it is necessary that filtering be done between the sample and the detector.

The sample holder used is similar to one described previously.[5] The sample is mechanically clamped between insulating electrodes of 1-mm spacing. Electric fields up to 6 kV/mm were used. No effect in the modulation due to optical polarization or field orientation was observed, other than a small ($\sim 5 \times 10^{-4}$) uniform background change with polarization. The structure is quadratic in applied field, with the terms odd in field less than 5% of the even part.

The modulation of the transmitted beam was detected and normalized to the dc transmitted beam by servoing the photomultiplier-tube gain. The convention which we use is that a positive value reported is a positive $\Delta\alpha$. The quoted values for $\Delta\alpha$ are accurate only to $\pm 50\%$ because of uncertainties in sample thickness and stray light.

The electroabsorption spectrum is shown in Fig. 1. The major up-down structure near 2.67 is similar, except for width, to the resolved phonon structure in the 2.3-eV Γ_{15}-X_1 electroabsorption spectrum (Fig. 2).[6] The peak above 2.77 eV is thought not to be a part of the 2.67-eV structure, but relates to a higher transition—the Γ_{15}-X_3 transition or possibly the direct edge at 2.86 eV. (All energies refer to 78 K.) Furthermore, this peak is artificial; that is, the high-energy cutoff of the modulation is due to the dominance of stray light at higher energies as the sample becomes increasingly opaque.

The remaining spectrum shows a strong negative peak at 2.677, a weak shoulder at 2.691,

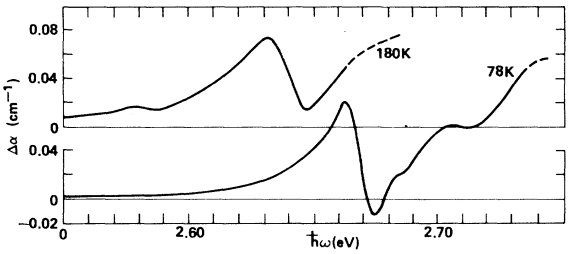

FIG. 1. Electroabsorption spectra of gallium phosphide near 2.67 eV. These spectra were taken at a temperature of 180 K (upper) and 78K (lower), and at 6 kV/mm. Spectral resolution is 6 Å (~3 meV).

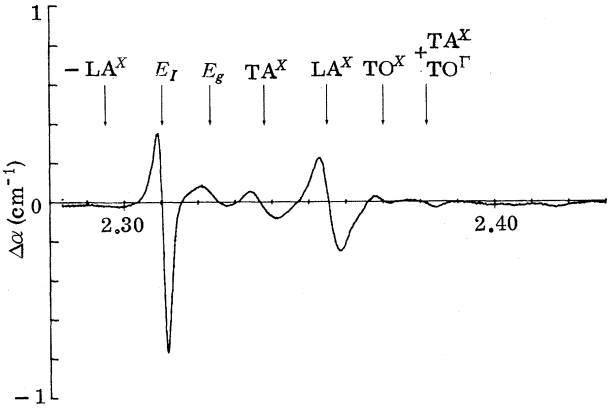

FIG. 2. Electroreflectance spectrum of gallium phosphide near 2.32 eV at 85 K and 5 kV/mm. The indirect gap (E_g) was determined from the LA emission and absorption structures. Phonon energies indicated are from Dean and Thomas, Ref. 3. The structure E_I is an impurity peak which masks the TA emission structure.

and a just-resolved peak at 2.720 eV. (We use the negative peak as the easiest to resolve; no particular fit to the actual transition energy is implied.) The spectrum was observed at temperatures from 65 to 220 K. The average temperature dependence of energy is -190 ± 20 μeV/K from 65 to 100 K and -320 ± 15 μeV/K from 120 to 180 K.

Higher-temperature spectra show a weak structure at 58.4 ± 1.0 meV below the strongest peak, with similar up-down behavior and equal width. This is best observed at about 180 K, where its amplitude is about 16% of the stronger. At lower temperatures the amplitude is smaller, and at higher temperatures the whole structure broadens and suffers from increased noise.

The high-temperature structure is taken to be a phonon-absorption "echo" of the strongest low-temperature structure, which is a phonon-emission transition. Thus, the energy of this phonon is measured independently of edge location or line-shape considerations. The higher-energy phonon energies are then fixed by similar comparison.

The measured phonon energies are shown in the last column of Table I. Also shown are vibration modes and symmetry representations for the corresponding X and L phonons,[7] energy as measured by neutron diffraction,[8] and energy as measured in the 2.3-eV region (Γ_{15}-X_1 transition) by static optical absorption[3] and electroabsorption.[6] The optic phonons have not been resolved in any of the optical spectroscopy.

It is clear from Table I that one cannot make an unambiguous assignment of the final-state symmetry of the 2.7-eV structure from phonon energies alone, and so we consider the selection rules for the process. The energy denominator term[9] for the transition through the Γ_1 conduction-band intermediate state is ~200 times smaller than for other intermediate states; therefore, we expect to see only the effects of this one intermediate state in the spectrum. (This is in marked contrast to the Γ_{15}-X_1 transition.[10]) The vertical transition $\Gamma_{15(v)}\rightarrow\Gamma_{1(c)}$ is allowed; thus, we con-

TABLE I. Phonon symmetry and energies (in meV) in GaP.

Mode	Symmetry[a] X	L	Neutron diffraction[b] X	L	Optical absorption,[c] 2.3 eV	Electro-absorption,[d] 2.3 eV	This work 2.7 eV
TA	X_5	L_3	13.2 ± 0.4	10.6 ± 0.2	12.8 ± 0.5	12.9 ± 1.0	Absent
LA	X_1	L_1	30.9 ± 0.7	26.3 ± 1.0	31.3 ± 0.5	31.3 ± 1.0	29.2 ± 0.5
TO	X_5	L_3	43.8 ± 1.0	44.4 ± 1.0	46.5 ± 1.0	44.5 ± 2.0	43.0 ± 2.0
LO	X_3	L_1	45.4 ± 1.5	46.3 ± 1.0			
Lowest-energy two-phonon					57.0 ± 2.0	55.8 ± 2.0	72.0 ± 2.0

[a]Ref. 7. [b]Ref. 8. [c]Ref. 3. [d]Ref. 6.

centrate on the $\Gamma_{1(c)} \rightarrow X_{3(c)}$ or $L_{1(c)}$ phonon-assisted transition. The phonons allowed to assist are[11]

$\Gamma_1 \rightarrow X_3$, X_3(LO phonons);

$\Gamma_1 \rightarrow L_1$, L_1(LA, LO phonons).

(If the double-group formalism is used—that is, spin effects are considered—additional modes are allowed to participate[11]: X_5 or L_3. This additional allowed transition, however, is expected to be weak[12] and, in fact, is not observed.)

The dominant structure is determined, through its energy, to involve an LA phonon. Since this phonon is not allowed in the Γ_1-X_3 transition, we conclude that the 2.67-eV structure cannot be Γ_{15}-X_3, but Γ_{15}-L_1 fits the observations.

With line-shape analysis by analogy with the 2.3-eV structure,[6] and equating the energy of the major structure with $E(L_1)+E(\mathrm{TA}^L)$, we arrive at an energy of 2.637 ± 0.005 eV at 78 K for the optical transition Γ_{15}-L_1; we estimate an additional 5-meV uncertainty in line-shape analysis. No estimate is offered for the energy of the L indirect exciton.

Auvergne *et al.*[13] point out that the conduction band of a zinc blende semiconductor does not warp with temperature. A direct transition and an indirect transition with the same final valence-band state should therefore have the same temperature coefficient of energy. They also argue (albeit less forcefully) that the Λ_1 conduction band should show little evidence of warping, and thus the E_1 transition should have the same temperature coefficient as the Γ_{15}-L_1 transition. In general, $|dE_1/dT|$ in III-V semiconductors is ~ 100 μeV/K larger than $|dE_0/dT|$. However, in GaP[14] $|dE_1/dT|$ is apparently smaller—about 340 μeV/K. More work on this point is in order, both experimental and theoretical (as suggested in Ref. 13).

Indirect support for this assignment is provided by recent work of Merle and co-workers.[15] They identified the Γ_{15}-L_1 transition as the lowest in GaP-InP alloys of (68–77)% GaP and concluded that in order to have a realistic curve of energy versus composition they should identify the 2.67-eV structure in GaP as the Γ-L transition.

One immediate implication of this work is that the X_1-X_3 splitting is somewhat larger than previously accepted: The smallest value consistent with our spectra is about 410 meV. The possibility remains, of course, that X_3 is below L_1, but that the transition is simply too weak to see. We believe that the L_1 conduction-band minimum is sufficiently well defined to be taken as an input into empirical band-structure calculations.

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