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Gas, GaSe and GaTe

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INFRARED AND UV-VISIBLE SPECTRA
OF LAYER SEMICONDUCTORS GaS, GaSe AND GaTe

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Résumé. — On présente les spectres de réflectivité thermomodulée et dérivée du tellurure de
gallium dans la région UV-visible (1-6 eV) et les spectres d’absorption dérivée du sulfure et du
sélénure de gallium dans l’infrarouge (15-80 meV) à température ambiante. Nous avons interprété
les premiers comme dus aux points critiques bidimensionnels ou tridimensionnels et les seconds à
l’absorption d’un ou de deux phonons. On a même utilisé un modèle nouveau pour la constante
diélectrique dans le but d’identifier la nature des structures observées dans l’intervalle des transitions
interbande.

Abstract. — Wavelength derivative and thermomodulated reflectivity spectra of gallium telluride
in the UV-visible range (1.0-6.0 eV), and infrared (15-80 meV) derivative absorption spectra of
gallium sulphide and selenide at room temperature are presented and interpreted as due to three-
dimensional or two-dimensional critical points and one or two phonons absorption respectively
A new model for the complex dielectric constant is used to identify the nature of the observed struc-
tures in the range of the interband transitions.

1. Introduction. — As is well known, gallium sul-
phide, selenide and telluride are semiconducting layer
structure compounds built up from weakly interact-
ing two-dimensional layers. A lot of theoretical and
experimental information [1-13] is available on these
III-VI semiconductors. Recent thermoreflectance [14,
15], electroreflectance [16-18] and wavelength modu-
lation [19] together with normal reflectivity [20] and
absorption [21] measurements have been carried out,
making an interpretation of the main optical behaviour
of these compounds possible. As far as the long-
wavelength region is concerned, polarized and unpo-
larized Raman [22, 23], infrared reflectivity [24] and
absorption [22, 25] studies have been published on
gallium sulphide and selenide concerning the inves-
tigation of their vibrational spectra in order to esti-
mate the force constants of the bonds.

In this paper we wish to present a study of the
infrared and visible-ultraviolet optical properties of
the above mentioned crystals, using modulation spectroscopy. Derivative and thermomodulated
reflectivity spectra of GaTe in the UV-visible range
and the infrared derivative absorption spectra of GaS
and GaSe are separately examined as due to three
dimensional or two-dimensional critical points and
one or two-phonon absorption respectively.

2. Results and discussion. — 2.1 Infrared
Absorption. — A lot of measurements [22-25] have
been carried out in the range from 150 meV to
1 100 meV on gallium sulphide and selenide in order
to evaluate the frequencies of the optically active
modes near the centre of the Brillouin zone. It was
found in these semiconductors that single layers
interact very weakly and the vibrational frequencies
at the centre of the zone are approximately coincident
with those of a single layer.

In figure 1 the logarithmic derivative of the absorp-
tion coefficient of gallium selenide is presented,
showing a sequence of zeros corresponding to peaks labelled from $E_1$ to $E_7$. Starting from lower energies, the first structure $E_1$ at 26.92 meV (217 cm$^{-1}$) corresponds to the main lattice resonance well fitted in terms of a single oscillator model and attributable to an $E_{1u}$ optical mode whose theoretical frequency is 213.9 cm$^{-1}$. Such a frequency is connected to a shear infrared active optical mode given by $[26]$

$$\omega^2 = C_{\kappa,\kappa}'/\mu$$  \hspace{1cm} (1)

$\mu$ being the reduced effective mass defined as $M_{Ga} M_{Se}/(M_{Ga} + M_{Se})$, where $M_{Ga}$ and $M_{Se}$ are the gallium and selenium atomic masses. $C_{\kappa,\kappa}'$ is the shear force constant involved in the interaction Ga-Se. From our experimental value of the frequency, it is possible to evaluate such an intra-layer force constant and this has a value of $1.033 \times 10^5$ dyn./cm, in good agreement with the results of reference $[26]$. The presence of the weak shoulder $E'_1$ in the derivative spectrum at 29.1 meV (234 cm$^{-1}$) has enabled us to estimate also the $C_{\kappa,\kappa}'$ compressional force constant connected to an $A_{2u}$ infrared active normal mode theoretically expected at 237 cm$^{-1}$. By means of the expression (1) one can easily calculate

$$C_{\kappa,\kappa}' = 1.207 \times 10^5 \text{ dyn./cm}$$

slightly higher than $C_{\kappa,\kappa}'$. The $E_3$ absorption maximum at 55.52 meV (445 cm$^{-1}$) may be tentatively ascribed to a combination mode formed by a shear $E_{1u}$ (213.9 cm$^{-1}$) and a compressional $A_{2u}$ (237 cm$^{-1}$) infrared active optical modes. The remaining structures $E_2$ (418 cm$^{-1}$), $E_4$ (492 cm$^{-1}$), $E_6$ (537 cm$^{-1}$) and $E_7$ (627 cm$^{-1}$) may well be interpreted as two-phonons absorption, as also shown in reference $[26]$, and belonging to the $E_{1u}$ species.

The derivative absorption spectrum of gallium sulphide is shown in figure 2. There is a long series of zeros, labelled from $E_1$ to $E_{14}$, each corresponding to a relative maximum in absorption coefficient. The first peak $E_1$ at 26.63 meV (215 cm$^{-1}$) is likely to be due to an $E_{2u}$ normal mode already observed in absorption measurements $[22]$ at 210 cm$^{-1}$. At higher energies, centred at 315 cm$^{-1}$, there is a region in which the derivative values are almost zero. This feature corresponds to the main broad resonance in the gallium sulphide lattice connected to the doubly degenerate TO mode of vibration within a layer at the $\Gamma$ point of the Brillouin zone. In table I we show the positions of all the structures observed in our wavelength-derivative absorption spectra together with the results obtained by other authors.

### TABLE I

<table>
<thead>
<tr>
<th>Peak positions (cm$^{-1}$)</th>
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<tr>
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<td>215</td>
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<tr>
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</tr>
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<td>696</td>
</tr>
<tr>
<td>759</td>
</tr>
<tr>
<td>818</td>
</tr>
</tbody>
</table>

### FIG. 2.

Wavelength modulated absorption spectrum of gallium sulphide.

### TABLE II

<p>| Exciton parameters in gallium selenide and telluride at different temperatures |
|-------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Ref.</th>
<th>$T$ (K)</th>
<th>$R_0^*$ (meV)</th>
<th>GaSe $\Gamma$ (meV)</th>
<th>$E_g$ (eV)</th>
<th>GaSe $R_0^*$ (meV)</th>
<th>GaSe $\Gamma$ (meV)</th>
<th>$E_g$ (eV)</th>
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</thead>
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</tr>
<tr>
<td>[7]</td>
<td>280.5</td>
<td>14.3</td>
<td>9.1</td>
<td>2.025</td>
<td>14.0</td>
<td>12.7</td>
<td>1.695</td>
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<tr>
<td>[1]</td>
<td>78.0</td>
<td>37.0</td>
<td>—</td>
<td>2.139</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[14]</td>
<td>78.0</td>
<td>—</td>
<td>41.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[21]</td>
<td>77.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>25.0</td>
<td>1.797</td>
</tr>
<tr>
<td>[15]</td>
<td>77.0</td>
<td>—</td>
<td>41.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[21]</td>
<td>300.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>25.0</td>
<td>1.700</td>
</tr>
<tr>
<td>[29]</td>
<td>300.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>44.0</td>
<td>1.694</td>
</tr>
</tbody>
</table>
2.2 THE ABSORPTION EDGE. — The absorption curves at RT and LNT of GaS, GaSe and GaTe have been extensively studied and show clearly the presence of excitons, formed by the Coulomb interaction of the electron and the hole produced in the optical transition near the band edge [7, 19, 21]. Furthermore absorption and reflectivity [20] data suggest that the fundamental edges are due to direct transitions in GaSe and GaTe, and to an indirect one in GaS. Above the edge a continuum must be expected with an absorption that increases at increasing photon energy. GaSe and GaTe behave similarly and show at 77 K their first and second excitonic lines at 2.102 and 2.130 eV (selenide) and 1.772 and 1.791 eV (telluride). In the case of gallium selenide, its absorption coefficient shows an exciton at 3.026 eV at 77 K. Absorption, reflectivity, thermomodulation, and electroreflectance measurements have been carried out in the edge spectral region of these gallium compounds and their principal results are summarized in table II.

For gallium telluride, we have measured [27] the wavelength-derivative reflectivity spectrum at RT shown in figure 3. In order to clarify the line-shape behaviour of the measured $\Delta R/R$ spectrum, the variation $\Delta \varepsilon_2$ of the imaginary part of the complex dielectric constant was obtained by means of a Kramers-Kronig transform. The $\Delta \varepsilon_2$ spectrum is also shown in figure 3 together with a best fit obtained by means of the derivative of the sum of two asymmetric lorentzian lines:

$$
\Delta \varepsilon_2(E) = \sum_{i=1}^{2} \times \frac{c_i^2 \delta_i \Gamma_i^2 + 2 \Gamma_i (E_{0i} - E) - 2 \delta_i (E_{0i} - E)^2}{[(E_{0i} E)^2 + \Gamma_i^2]} \Delta E
$$

Where $E_{0i}$, $\Gamma_i$, $\delta_i$, and $c_i$ being the energy positions of the structures, the broadening and asymmetry parameters and constant scale coefficients respectively. As can be seen, the spectral dependence of $\Delta R/R$ shows two significant negative peaks that correspond to maxima in the absorption coefficient. These two structures can be explained in terms of direct exciton formation, representing the ground state and the first excited state respectively. The best fit of $\Delta \varepsilon_2$ spectrum has allowed us to estimate the true energy of the two exciton lines that are at 1.650 eV ($n = 1$) and at 1.680 eV ($n = 2$). The superposition of the two lorentzian curves weighted as $n^{-3}$, fitted the experimental results well enough to make it possible, using the relation $E_g = E_g - R_0^*/n^2$, to deduce that $E_g = 1.694 \text{ eV}$ and $R_0^* = 44 \text{ meV}$. The Rydberg value is somewhat larger than those previously deduced [28].

The validity of the relation used to deduce the values of the energy gap and the exciton Rydberg in gallium telluride seems to suggest that the exciton absorption reflects the effects of a three-dimensional structure. The alternative two-dimensional model reported in reference [29] is not adequate for layer structures which show a very small anisotropy in the exciton spectrum. Our value of $R_0^*$, if we take $\varepsilon_0 = 7.3$ [21], gives an effective reduced mass associated with the conduction and valence bands of $\mu = 0.172$, slightly larger than that reported in reference [21].

2.3 INTERBAND TRANSITION ABOVE THE EDGE. — In figure 4 the reflectivity spectra of gallium sulphide and selenide are reported together with one of gallium telluride which we obtained by means of near normal incidence measurements [20]. As can easily be seen, the three spectra show a similar complex sequence of singularities. It is likely that there is a high density of states along the $k_z$ direction due to the small interlayer interactions, giving rise to this very close experimental resemblance between the three reflectivity curves although the crystal structure of these semiconductors is remarkably different. Two main broad structures characterize the optical spectra of figure 4. In fact it must also be noted that in the case of GaTe,
another higher energy structure in the region of vacuum ultraviolet exists, as found in recent reflectivity measurements (1). Thus, one can hypothesize that these two strong groups of singularities may be attributed to two different groups of interband transitions. In the low energy range (1.0 to 7.0 eV), four structures ($E_1$ to $E_4$) are observed for all the semiconductors, the position of each corresponding peak being different: higher in GaS and lower in GaTe. This is in agreement with the fact that, in a given crystal structure, the energy gaps in semiconductors and insulators decrease as the size of the atoms and the lattice parameters increase. In the spectrum of gallium telluride is included the optical response of the excitonic edge discussed previously. The main features of the reflectivity spectra of GaS, GaSe and GaTe may be interpreted on the basis of the Brillouin zone symmetry. As suggested by Bassani et al. [1], the three-dimensional lattice must be considered because the $z$-direction is a critical line where high values in the joint density of states are likely to occur. The higher valence band and the conduction bands are not as flat as the lower bands in the $k_z$ direction because their wave functions are oriented perpendicularly to the layers. Therefore overlap can exist between the latter.

Recent thermomodulation experiments [15] on the sulphide and selenide have shown that a good explanation of the optical properties of these semiconductors well above the edge, may be given by invoking the presence of excitons at saddle point singularities. In fact, as pointed out by Toyozawa et al. [30], an exciton at an $M_1$ singularity produces a lineshape for the dielectric constant which is a mixing of the lineshapes for the $M_i$ and $M_{i+1}$ singularities. In particular, the $E_1$ peak was assigned to such a metamorphism of Van Hove singularities built up by the mixing of $M_1$ and an $M_0$ critical point. Also in GaTe, due to the structural similarity of the three gallium compounds the same behaviour for the involved sequence of critical points is to be expected. In fact, exciton effects in GaTe seem to be relevant as demonstrated by our wavelength-modulated reflectivity measurements shown in figure 5. With increasing photon energy, besides the s-shaped sharp structure associated with exciton formation (only the ground state is visible due to the poor resolution compared to the measurements previously presented), four structures are clear resolved at 2.90 ($E_1$), 3.34 ($E_2$), 3.90 ($E_3$) and 4.70 ($E_4$) eV. The energy positions of these interband transitions are in good agreement with those of the normal reflectivity data [20]. From a critical analysis of the experimental behaviour of $\Delta E_1$ and $\Delta E_2$, obtained by processing the $\Delta R/R$ data by means of a Kramers-Kronig transform, it is possible to assign the $E_1$ structure to a

$$\begin{align*}
\text{FIG. 5.} & \ 
\text{Wavelength modulated reflectivity spectrum of gallium telluride at room temperature.}
\end{align*}$$

$$\begin{align*}
\text{FIG. 6.} & \ 
\text{AR/R spectrum of gallium telluride obtained by processing the data of figure 5 (solid), together with a best fit from two-dimensional critical point lineshapes (dotted). The dashed curve is calculated starting from the values of the parameters obtained by the best fit of the thermomodulated AR/R and is presented to check the sensitivity of the theoretical function to variation in the involved parameters.}
\end{align*}$$

taking for the broadening parameters the values \( \Gamma_0 = 863 \text{ meV} \) and \( \Gamma_1 = 61 \text{ meV} \) for the \( M_0 \) and \( M_1 \) respectively, centred at the same energy \( E = 2.922 \text{ eV} \). For the \( M_2 \) lineshape the fit gives \( E = 3.873 \text{ eV} \) and \( \Gamma = 108 \text{ meV} \). In figure 6 the theoretical behaviour of \( \Delta b_2 \) is also reported, taking different values of the broadening parameter in order to show how sensitive the curve shape is to changes in \( \Gamma \). Due to their small size, the \( E_2 \) and \( E_4 \) structures have been neglected in the fitting procedure. It is easy to deduce that the main sequence of singularity types in gallium sulphide, selenide and telluride remains unaltered in these three compounds.

As it is well known, it is possible to show that the main contribution of \( \varepsilon(\omega) \) to its derivatives can be summarized by the universal function :

\[
F(\pm x) = \left[ (x^2 + 1)^{1/2} \pm x \right]^{1/2} / (x^2 + 1)^{1/2}
\]

where the dimensionless variable \( x \) is equal to \( (E - E_0) / \Gamma \), \( E_0 \) is the interband energy gap and \( \Gamma \) the phenomenological broadening parameter introduced to account for the uncertainty in the energy of the states responsible for the investigated optical transition. It is common practice to use such lineshapes to assist the identification of the observed structures when these are due to three-dimensional critical points. We have remarked that three-dimensional effects must be invoked when dealing with layer structures in which interlayer interactions are not negligible, as in the case of the three gallium compounds. Unfortunately, as we pointed out, any attempt to fit the \( \Delta b_2 \) spectrum of GaTe by means of three-dimensional critical points was not successful. In order to clarify such an apparent discrepancy between experimental data and theory we made an attempt to find a more adequate approach to the problem using the dielectric function model suggested by Rabii and Fischer [31, 32]. These two authors found substantial differences between the classical universal function (3) and the results calculated by taking into account two non-resonant terms and the prefactor \( (E + i\Gamma)^{-2} \) contained, on the contrary, in their expression of the dielectric constant :

\[
\varepsilon(\omega) - 1 = - \frac{f(j+1)}{(E + i\Gamma)^2} \times \\
\times 2 \left[ (E - E_0)^{1/2} - (E - E_0 + i\Gamma)^{1/2} - (E - E_0 - i\Gamma)^{1/2} \right]^{1/2}
\]

where \( j \) is the index of any critical point. Using the derivatives of the expression (4) with respect to \( E \), we have fitted our \( \Delta b_2 \) spectrum of GaTe finding very good agreement between experiment and theory as shown in figure 7. No critical points metamorphism must be invoked and the first three structures of the reflectivity spectrum \( E_1 \) to \( E_3 \) can be assigned to a sequence of saddle points positioned at 2.861 (\( M_1 \)), 3.581 (\( M_1 \)) and 3.799 (\( M_2 \)) eV respectively. This is not surprising since such results are in agreement with the conclusions of Kamimura and Nakao and Balzarotti for GaSe. In fact these authors attribute the structures \( E_1 \) to \( E_3 \) in GaSe to interband transitions at saddle points [10]. To obtain further and possibly quantitative information about the nature of the transitions giving rise to the spectral response of GaTe, we also used a temperature modulation technique which is rather simple from the experimental point of view and straightforward in its interpretation. The effect of a temperature variation on the optical properties is simply a shift of energy gaps, which is equivalent to wavelength modulation and a broadening of the involved critical points. Our thermoreflectivity spectrum, quite similar to that reported by Consadori and Brebner [33], shows a marked similarity, in the gap spectral region, with the corresponding wavelength-modulated spectrum, thus excluding any significant contribution of broadening modulation. Therefore, we focused our attention on the main structure of the spectrum corresponding to the \( E_1 \) peak shown in figure 8. Also in this case the experimental \( \Delta b_1 \) and \( \Delta b_2 \) lineshapes, obtained by means of a Kramers-Kronig analysis, are well explained in terms of a set of two three-dimensional saddle points. A best fit of the \( \Delta b_2 \) spectrum was found with the values 359 meV and 306 meV for the broadening parameters for the two singularities centred at 3.207 eV and 3.490 eV respectively. The results have shown that at energies above the gap the broadening term dominates the shift term. In consequence, in this region, our thermoreflectivity spectrum is quite different from the wavelength modulated one as also shown in the data of
When comparing our modulated spectra, it must be taken into account that the temperature acts on the sample as a non-negligible perturbation and the response of the sample is generally altered. This is not the case of wavelength-modulated spectrum that is due only to the optical properties of the semiconductor.

In Table III are reported the energy locations of all the reflectivity peaks of the three gallium compounds for comparison. On the basis of the band model of Schluter [11] for gallium selenide, it is possible to explain the reflectivity spectra of GaSe and GaS analogously in terms of transitions at the $\Gamma$ point of the Brillouin zone, whereas the previously mentioned band structure of Kamimura and Nakao is not adequate to explain some features of the optical spectra. One of the main results of Schluter’s calculations is the existence of four groups of conduction and valence bands. The first three valence groups (the nearest to the energy gap) correspond to a bonding orbital between a Ga atom with three Se atoms and another Ga atom, while the last is due to the 4s atomic orbital of the chalcogen atom. Thus the first broad low energy structure may be assigned to transitions from the first valence band group to the first $\Gamma_6 \rightarrow \Gamma_1^*$, to the second $\Gamma_6 \rightarrow \Gamma_1^*$, and to the third conduction band group $\Gamma_6^* \rightarrow \Gamma_6^*$. The second high energy structure is built up by transitions from the third valence band group to the first and the third $\Gamma_6^* \rightarrow \Gamma_6^*$ conduction band group. Nothing, unfortunately, can be said about gallium telluride because of the lack of a band structure calculation. The strong similarity of the optical spectra and of the sequence of Van Hove singularities is probably due to the similar basic structure of the three compounds. In fact such optical behaviour is likely due to the interaction between the nearest neighbour centres. In every layer, each Ga atom is surrounded by one nearest Ga atom and, on the other side, by three S, Se or Te atoms symmetrically placed around the Ga-Ga axis. It is clear that this fundamental structure may play a main role in determining optical spectra: different arrangements of the same Ga-Ga-3 (S, Se, Te) structure are found in GaS and GaSe on the one hand and in GaTe on the other. The interaction between these fundamental structures appears as a small perturbation compared to the main optical behaviour of the three gallium compounds.

In conclusion, our results may give further information about the optical behaviour of layer compounds GaS, GaSe and GaTe due to the sensitivity of the derivative techniques in determining energy position of optical singularities. Infrared absorption spectra of GaS and GaSe have been measured in order to

### Table III

Energy position of the six main peaks observed in the interband transitions region for GaS, GaSe and GaTe. All the energy values followed by an attribution to critical points refer to $\varepsilon_2$ spectrum. The symbols $r$, $t$ and $ex$ stand for derivative reflectivity, thermoreflectivity, and fit of $\varepsilon_2$ by means of eq. (4) respectively.

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<thead>
<tr>
<th>Ref.</th>
<th>$E_1$ (eV)</th>
<th>$E_2$ (eV)</th>
<th>$E_3$ (eV)</th>
<th>$E_4$ (eV)</th>
<th>$E_5$ (eV)</th>
<th>$E_6$ (eV)</th>
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<tr>
<td>GaS</td>
<td>1</td>
<td>3.9</td>
<td>4.75</td>
<td>6.10</td>
<td>6.90</td>
<td>8.05</td>
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<td></td>
<td>15</td>
<td>3.993 (M_0 + M_1 3d)</td>
<td>5.260</td>
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<tr>
<td>GaSe</td>
<td>1</td>
<td>3.63</td>
<td>4.10</td>
<td>4.90</td>
<td>5.90</td>
<td>7.2</td>
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<tr>
<td></td>
<td>15</td>
<td>3.658 (M_0 + M_1 3d)</td>
<td>4.577</td>
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<tr>
<td></td>
<td>20</td>
<td>2.90</td>
<td>3.34</td>
<td>3.90</td>
<td>4.70</td>
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<tr>
<td></td>
<td>28, t</td>
<td>2.90, 2.922 (M_0 + M_1 2d)</td>
<td>3.34</td>
<td>3.873 (M_2 2d)</td>
<td>4.70</td>
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<td>3.207 (M_1 3d)</td>
<td>3.490 (M_1 3d)</td>
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<td>2.661 (M_1 3d)</td>
<td>3.581 (M_1 3d)</td>
<td>3.799 (M_2 3d)</td>
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find more accurate values for peak positions allowing
the calculation of more accurate values for the force
constants associated to the relative displacements of
the atomic layers in these semiconductors. Further-
more the excitonic structure near the gap of GaTe has
been studied in order to obtain exciton parameters at
room temperature. Interband transitions of GaTe in
the visible-U.V. spectral range are finally interpreted
as due to a set of saddle point three-dimensional
singularities, on the basis of a new formulation for the
dielectric constant, without invoking the presence of
singularity metamorphisms or bidimensional critical
points in those cases in which these two interpretations
are not in agreement with the structure of the materials.

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