Dependence of exciton reflectance on field and other surface characteristics: The case of InP

F. Evangelisti*
Istituto di Fisica, Università di Roma, Rome, Italy

J. U. Fischbach
Physikalisches Institut der Universität, Stuttgart, Germany

A. Frova*
Istituto di Fisica, Università di Roma, Rome, Italy†

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Reflectance spectra at 2 °K for the fundamental exciton of pure InP are reported. Both "free" surface and biased Schottky barriers are investigated. It is shown that interference effects, due to various mechanisms of interaction with the surface, have a dominant role in changing the line shape of the excitonic structure, much in the same way as done by electric fields in the Schottky-barrier case. The importance of taking into account the strong spatial inhomogeneity of the surface layer, even in the absence of surface fields, is discussed for both cases of "classical" and spatial dispersion. It is found that, owing to the above features, spatial-dispersion effects may be severely obscured. From the analysis of the measured spectra, a value of 1.4185 eV is derived for the transverse exciton energy and of 4.9 meV for the effective-Rydberg energy.

I. INTRODUCTION

Reflectivity measurements in the energy region immediately below the fundamental gap of solids are used to determine the basic parameters of the exciton bound states. For III-V compound semiconductors, good quality epitaxial materials have now become available and this has stirred renewed interest in this type of experiments and in the understanding of the boundary mechanisms affecting the spectral line shape. Information deduced from reflectance is often useful in the analysis of the luminescence spectra, a field which has also received great attention in recent years. GaAs has been thoroughly investigated by all optical techniques, while InP is still in a rather developmental stage. Reflectance spectra in the former material exhibit strong deviations from the usual line shape of classical oscillators. This behavior was attributed to spatial-dispersion effects (i.e., k dependence of the optical constants) and to the related additional boundary conditions. In this paper we discuss, on the basis of new results obtained for InP and of earlier data for GaAs reported by other workers, the dominant effect of interference across a surface layer, where the exciton properties are greatly distorted owing to interaction with the boundary. We shall also propose that the nonhomogeneity of this region is so important, that approximations in terms of a layer of uniform behavior cannot be made without running into a serious loss of resolving power as to the basic details of the dispersion mechanism involved and of the actual boundary conditions to be used.

In Sec. II we will try to give a general feeling for the various aspects of the surface boundary problem, referring to earlier work in the field to point out the state of the art; this will be followed in Sec. III by a description of the experimental procedure, including preparation and characterization of samples for both "free surface" and Schottky-barrier-controlled reflectance measurements. Finally, the experimental results and a discussion will be presented in Sec. IV, at the end of which we shall summarize our conclusions, with the hope that we have at least succeeded in promoting some new theoretical interest in a problem which presents itself as a rather stimulating but complex task.

II. EXCITONS AT THE SURFACE BOUNDARY

The authors have recently reported the observation of interference effects in the low-temperature reflectance of GaAs around the $n=1$ state of the fundamental exciton.[1] Similar results have been found earlier in CdS by Tyagai *et al.*[2] at room temperature (the binding energy being in that case much larger). The interference effect is attributed to the existence of a surface layer where bound exciton states are quenched due to the presence of an electric field, as discussed for instance by Blossey.[3] The GaAs experiment[1] was performed by means of a Schottky barrier, which allowed, in first place, application of fields high enough to produce ionization of the $n=1$ bound state over a sizeable distance below the surface, and also precise control of the interference conditions by acting upon the depth of the space-charge region. As a result, it was demonstrated that the spectrum of the exciton reflectance could be made to change with continuity through a variety of line shapes.

Now, even in the absence of an electric field, i.e., when dealing with a "free" no-contact surface at temperatures where carrier freeze-out takes place (as is the case for instance of absolute reflectance measurements in GaAs at 2 °K by Sell *et al.*[4]), other surface mechanisms should be capable of affecting the exciton behavior over appreciable distances, giving rise to interference in a way similar to the field-induced-quenching effect discussed above. Therefore, deviations from "normal" line shape are always to be expected, no matter whether one is in the presence of spatial dispersion effects,[5,6] or whether the "classical" limit (i.e., no dispersion) is used. When dealing with a spatially dispersive medium the various authors[5-7] had to resort to additional boundary conditions to derive an expression for the reflectivity: This implies particular physical mechanisms at the surface, different from the bulk behavior. The presence of an "image-force barrier" was postulated, for instance, by Hopfield and Thomas.[5] This originates from the repulsive interaction of the exciton with its electrical image, when the former approaches the surface. The repulsive potential becomes infinite at the boundary, where the local polarization of the exciton oscillator is zero. Deeper into the crystal, one should have a gradual change in the exciton parameters towards the bulk equilibrium conditions.

The situation is obviously not dissimilar from the one we have discussed for the Schottky-barrier configuration, apart from the detailed profile of the field, which is no longer triangular. The region of graded behavior should have an extension which is proportional to the volume occupied by the exciton wavefunctions, thus we expect that its influence on the line shape be particularly strong for Wannier excitons, which extend spatially over many lattice constants. In the spatial dispersion treatment by Hopfield and Thomas, the inhomogeneous region characterized by the image-force barrier is not treated as such, being replaced by a uniform film, devoid of excitons, of thickness approximately equal to twice the radius of the first Bohr orbit of the exciton. This layer affects the reflectance line shape to a far larger extent than any spatial-dispersion or lifetime-broadening effect one may wish to introduce. This can be deduced from the CdS spectra of Hopfield and Thomas[5] and the GaAs results by Sell *et al.*[8] In fact, even in the no-dispersion framework, where additional boundary conditions are not needed, the physical mechanisms arising from the presence of the surface have to be taken into account. Biellman *et al.*[9] have recently come to the conclusion that, also for PbI_2, any dispersion model without a finite surface layer of anomalous refractive index behavior cannot give account of certain features of the excitonic spectra. Conversely they show that, provided such layer is included, any type of dispersion (classical or not) gives at least qualitative agreement with the observed spectra. An experimental confirmation of the occurrence of forces repelling the exciton away from the surface into the bulk can be inferred from experiments in thin films of the layer compound MoS_2.[10] An increase in energy of the exciton levels is observed when the crystal thickness approaches the size of the corresponding orbit. It has been shown theoretically[11] that this effect stems from the exciton distortion associated with the spatial confinement. In thick crystals this is still true for excitons approaching the surface to a distance of the order of the effective Bohr radius: The energy of the level would then tend to increase and the exciton therefore experiences a repulsive force.

In any case, in doing reflectance measurements, one has to do with a stratification of media, i.e., free space, transition surface layer, and normal bulk substrate. The principal difficulty sits in the inhomogeneity of the thin intermediate layer, where the variation of the optical parameters is too fast to permit use of the WKB approximation valid in electroreflectance of semiconductors above the gap.[12] It can be verified, starting from the data of Ref. 4, that in GaAs the peak contributions of the $n = 1$ exciton oscillator to the real and imaginary parts of the dielectric function are respectively equal to 6 and 12, against background values of 12.6 and 0.[13] The entire exciton terms are rapidly washed out, approaching the surface, over a distance which should not exceed an effective Bohr diameter, i.e., about 250 Å in GaAs and InP. For Schottky barriers, instead, this distance is determined by the particular profile of the field. It is because of this dramatic variation that we are led to expect a major dependence of the line shape on interference effects, even though precise details can only be predicted if the nonuniformity of the surface layer is duly taken into account.

The role of the broadening parameter Γ is also rather important. First of all, for Γ (in the bulk) larger than the transverse-longitudinal exciton splitting, spatial dispersion effects are probably masked.[5] In GaAs the splitting is estimated to be ~0.1 meV[4] and in InP it is approximately 0.14 meV.[14] These values can hardly be larger, even at 2 °K, than the width of the line associated with phonon interaction, sample inhomogeneity, strain, etc. Moreover, the possible enhancement of the collision processes approaching the surface, works in the direction to make spatial dispersion effects unimportant at least in the inhomogeneous region.

In what follows, we shall report experimental measurements of reflectance in InP "free" surfaces as well as in Au-contact Schottky barriers. This semiconductor has not been given so far as much attention as its companion material GaAs, mainly because of the relatively recent acquisition of good quality epitaxial samples. As a consequence, little is known about its excitonic structure near the fundamental gap, apart from that found in early transmission measurements, indeed quite good, done by Turner *et al.*[14] on bulk samples having carrier concentration equal to $\approx 5\times 10^{15}$ cm^{-3}. An experimental reflectance curve has been reported by White *et al.*[15] but no discussion of its features was attempted. Our results on "free" surfaces will be in agreement with the latter experiment, showing reproducible differences from the behavior observed in GaAs. Such differences will be satisfactorily accounted for in terms of the surface interference effect. The Schottky-barrier samples will be used to confirm our earlier observation[1] in GaAs of field interference, to show that the effect is of general significance and that it can be readily detected by looking at absolute reflectance, without a need for modulation-spectroscopy techniques.

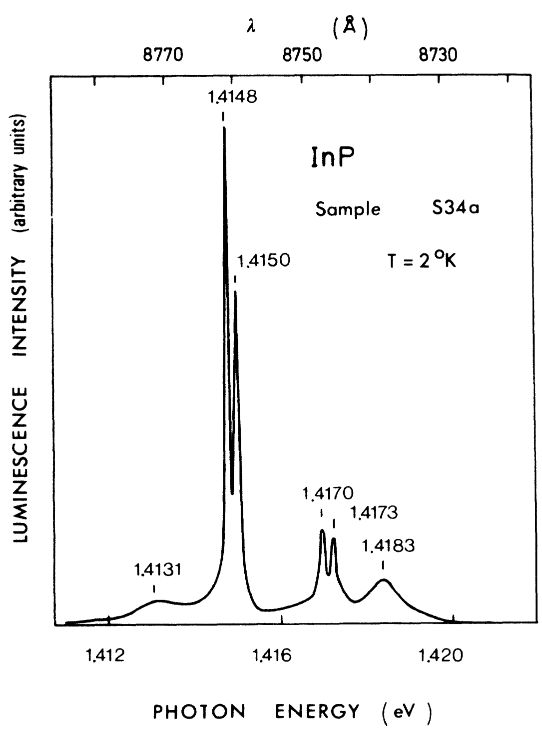

FIG. 1. Photoluminescence of the epitaxial InP sample used to measure the reflectance curve of Fig. 3, testifying to the good degree of purity of the material.

III. EXPERIMENTAL APPROACH

In this section the essential features of the experimental apparatus are illustrated and the different methods of sample preparation are described. All reflectance measurements were performed at about 2 °K, using normal incidence from a tungsten source. The energy accuracy was better than 0.1 meV in the wavelength range of interest.

Let us first describe the experimental situation for those experiments involving "free-surface" samples. Measurements were performed using both monochromatic light and white light, in the latter case the wavelength selection occurring after reflection at the crystal surface. It should be mentioned that no difference was apparently seen in the two cases. Various samples were used: (i) n-type bulk material, supplied by Royal Radar Establishment, with doping $N_D - N_A \simeq 4\times 10^{15}$ cm^{-3} at room temperature, which was polished and etched. (ii) n-type epitaxial layers with either degenerate or semi-insulating substrate: For these samples the surface was left as grown. Characterization of these crystals has been done by luminescence. As an illustration, we show in Fig. 1 the near-gap luminescence at low laser-excitation intensities (~100 mW/cm^2). This sample was used for the "free surface" experiment described in Fig. 3. A sharp line structure due to several bound excitons is observed: From comparison of these spectra with luminescence results taken from samples with known carrier concentration,[15] we infer $N_D - N_A \approx 10^{15}$ cm^{-3} at room temperature. The spectrum shows the following features which cannot be observed in material with higher carrier concentration[15,16]: (a) two lines at 1.415 eV (exciton bound to neutral acceptor), (b) two lines and shoulder at 1.417 eV (radiative decay connected with donors), and (c) broader line at 1.4183 eV (probably free-exciton decay). As to reflectivity measurements, we may anticipate here that we were never able, in InP samples, to observe the so-called "spike" on the high-energy side of the exciton structure, reported by Sell *et al.*[4] for GaAs. This was true even for the high-quality epitaxial sample described in Fig. 1; however, we had no difficulty in detecting that spike when using GaAs crystals of comparable quality.

When using the Schottky-barrier configuration, experiments were only done with monochromatic light. The barrier was prepared by evaporation of a thin semitransparent gold layer onto the surface of the crystal. Characterization of the barrier was done by C-V along with I-V and photovoltage measurements, as described in an earlier publication.[13] The field-induced interference effect discussed in Sec. II can be directly observed, at fixed wavelength, as an oscillatory reflectance

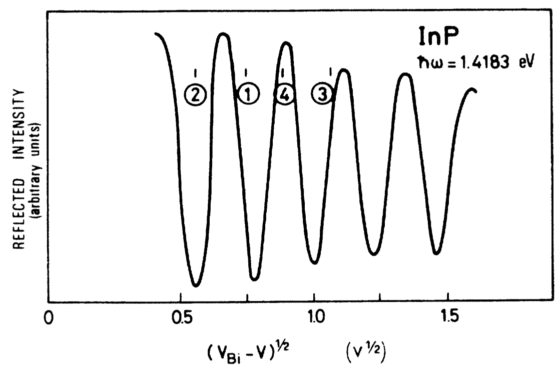

FIG. 2. Oscillatory behavior of the reflectance in Schottky barriers for varying bias. The quantity $(V_{Bi} - V)^{1/2}$ is proportional to the depletion-layer depth w. The photon energy was fixed at $\hbar\omega = 1.4183$ eV (Epitaxial InP.) From the period of the oscillations one computes $N_D - N_A = 4.4 \times 10^{15}$ cm^{-3}. Numbers 1–4 refer to the spectra of Fig. 4.

versus applied voltage across the metal-semiconductor contact. Figure 2 shows absolute reflectance versus $(V_{Bi} - V)^{1/2}$, where V_{Bi} is the built-in barrier, equal to 0.782 V, at a fixed value of the wavelength.

The data shown refer to epitaxial material; the behavior of bulk material is very similar. In the latter case, the carrier concentration could be carefully determined by Hall measurements, thus allowing a precise determination of the proportionality constant between the depletion-layer depth and $(V_{Bi} - V)^{1/2}$. It turns out that the separation between maxima corresponds very well to half a wavelength in the medium, i.e., 1250 Å in our case.

An estimate of the depletion depth at zero bias in bulk InP gives 4800 Å, corresponding to a surface field of 3×10^4 V/cm. Hence, the width of the region where the field is smaller than the exciton ionization value of $\sim 4\times 10^3$ V/cm [for a binding energy of 5 meV (Ref. 17)] is ~650 Å, indicating that in most of the depletion region the only possible absorption is associated with the Franz-Keldysh exponential tail of the edge and, maybe, with transitions involving impurities. Such absorption explains the slow decay of the oscillations observed in Fig. 2. When the depletion-layer boundary is moved deeper into the sample, the interfering light beam, containing the exciton information, travels longer distances and gets increasingly attenuated.

Few words remain to be said about the occurrence of a depletion layer at ~2 °K, where complete carrier freeze-out should be taking place. This is due to the presence of the metal-semiconductor contact potential, causing field-ionization of the shallow donor levels. The barrier then sweeps carriers away to a depletion depth w, as in normal room-temperature behavior. It should be pointed out that the interference effect described here lends itself to be used for a characterization of the depletion-layer parameters; in particular, from the spacing of the oscillation, it allows a determination of the sample doping other than by galvanomagnetic measurements.

IV. RESULTS AND DISCUSSION

From our previous arguments, we can say that the surface inhomogeneous layer in the Schottky-barrier configuration is rather different from the one discussed in Sec. II for the "free" surface. In the Schottky case, the exciton behavior is determined by the influence of an electric field of triangular profile, extending over at least 30 effective Bohr radii at zero bias (for the doping used). In contrast, the "free surface" transition behavior is mainly restricted to within a Bohr diameter or so and has a more complex origin. Although we cannot predict the details of the spectra, we foresee some differences in the line shapes for the two cases. The "free surface" spectrum corresponding to the epitaxial sample of Fig. 1 is reported in Fig. 3. This curve agrees very well with that reported in Ref. 15. As previously mentioned, no "spike" on the high energy side is observed, however, the structure is by no means the "normal" reflectance expected for a classical oscillator. Figure 4 illustrates the evolution of reflectance curves mea-

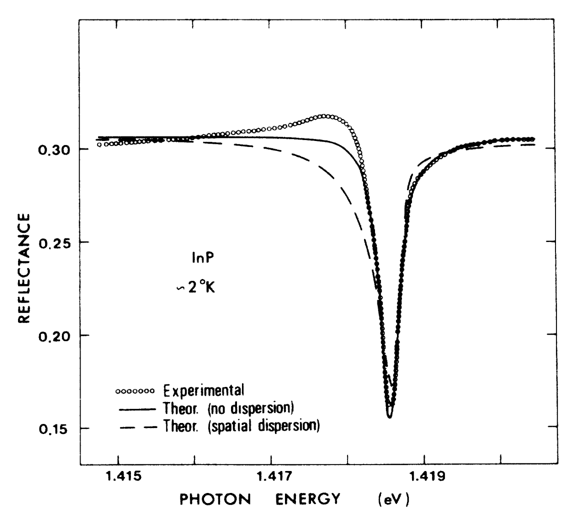

FIG. 3. Absolute reflectance (dots) of "pure" epitaxial InP in the "free surface" configuration. Spectrometer resolution is better than 0.1 meV. Calculated best fits in terms of interference theory with spatial dispersion (dashed line) and no dispersion (solid line) are also shown ("uniform-layer" approximation).

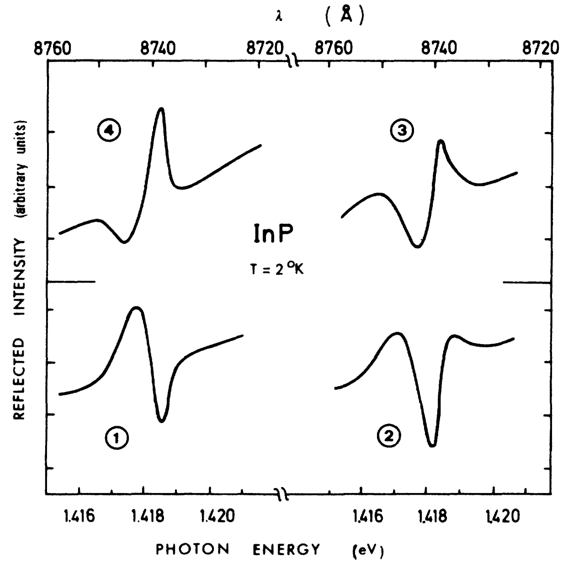

FIG. 4. Set of reflectance curves measured in Schottky barriers made of epitaxial InP and a semitransparent gold layer. Each curve corresponds to a given value of the applied voltage, i.e., of the depletion-layer depth. For curves 1–4, bias is respectively 0.22 V, 0.45 V, −0.35 V, and 0 V (plus sign = forward), as indicated also in Fig. 2.

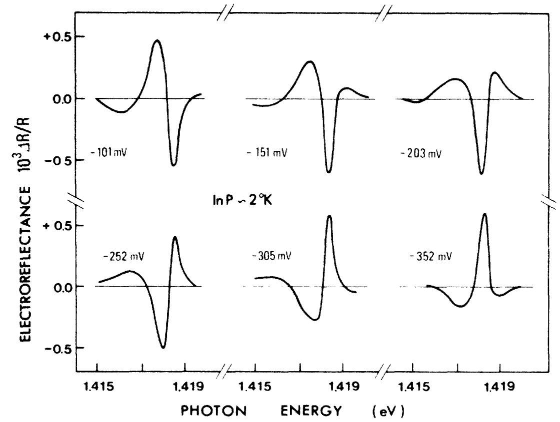

FIG. 5. Schottky-barrier electroreflectance spectra for different values of the dc bias. Bulk material with $N_D - N_A \simeq 4\times10^{15}$ cm^{-3}.

sured in Schottky barriers for different applied voltages. For no value of the depletion depth has it been possible to reproduce the line shape of the "free-surface" spectrum, as we had predicted. The main difference appears in the behavior of the background level, which is probably affected here by the electric field via the Franz-Keldysh effect of the continuum, in the manner which we have discussed in Sec. III. Electroreflectance spectra of the type reported earlier for GaAs [1] have also been measured, as shown in Fig. 5 for a number of values of the dc bias across the barrier. We are in a position now to demonstrate that each electroreflectance spectrum is given by the difference of two absolute reflectance curves. Owing to the periodicity in the mechanism of the line shape evolution, even for modulating voltages much smaller than the dc bias one can obtain modulated signals which are as large as the total exciton contribution to the reflectance. This is illustrated in Fig. 6. These results indicate, however, that there is no particular advantage here in using modulation techniques. In discussing the data, we shall therefore refer to absolute spectra and refrain from comparing the present electroreflectance spectra with those obtained earlier for GaAs. [1]

The Schottky-barrier spectra of Fig. 4 confirm beautifully that the interference effect across the exciton-free surface layer can alter dramatically the reflectance line shape. A similar effect must be responsible, to a large extent, for the anomalies of the "free surface" spectrum of Fig. 3. We shall try to make a theoretical estimate of this effect in the usual approximation of a homogeneous intermediate layer, [5] i.e., assuming that interference occurs across a surface region of thickness l which is totally devoid of excitons. In agreement with our discussion in Sec. II it will become apparent from the results that this assumption is very drastic and casts doubt on all other details of the mechanisms involved. To prove this, we do our calculations for the two different cases when

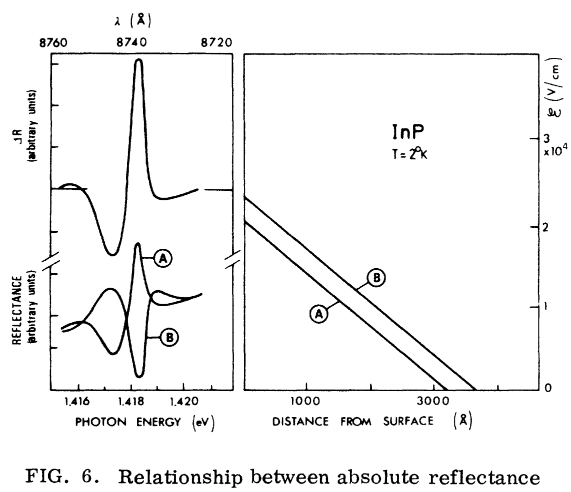

FIG. 6. Relationship between absolute reflectance spectra at two values of the applied forward voltage and corresponding electroreflectance (A → 0.35 V, B → 0.45 V). The right-hand-side of the figure illustrates the field profiles in the depletion layer, for the two cases. Since the main source of signal is the change in interference conditions, electroreflectance here is not a "derivative-type" spectrum. (Epitaxial InP.)

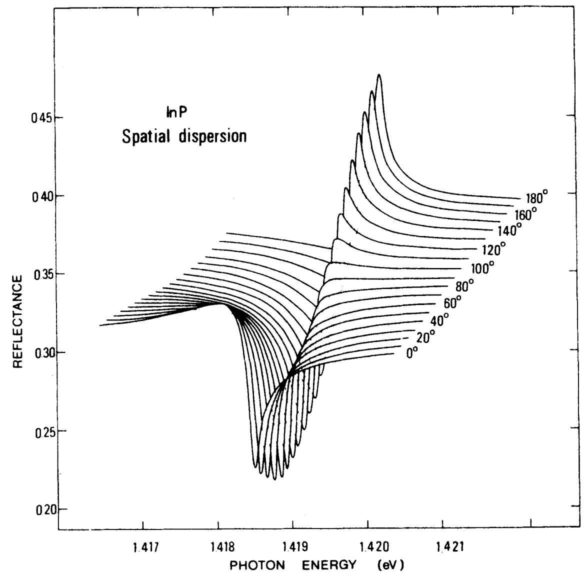

FIG. 7. Calculated evolution of the exciton reflectance line shape ("free" surface) as obtained by the "uniform-layer" approximation. The varying parameter is the interference angle $\theta = 4\pi l/\lambda_m$, where l is the surface-layer thickness. Spatial dispersion is assumed. $\Gamma = 0.05$ meV, $E_{ex} = 1.4185$ eV, $M^* = 0.200 m_0$, $4\pi\alpha = 2.35 \times 10^{-3}$. Curves are progressively shifted in steps of 0.094 meV to the right and 0.00444 upwards.

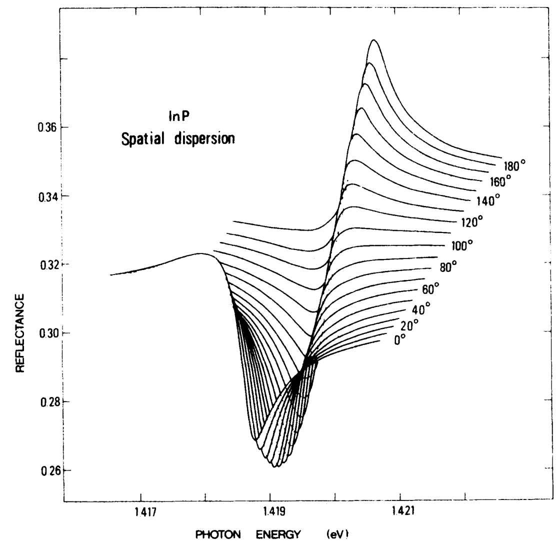

FIG. 8. Same as Fig. 7, i.e., spatial-dispersion case, except $\Gamma = 0.32$ meV. Curves are progressively shifted in steps of 0.094 meV to the right and 0.0086 upwards.

spatial-dispersion effects are included and when they are not, and show that their occurrence, in the experimental results, is hardly detectable. Labeling the free space, the transition layer, and the unperturbed bulk region, with indices 1, 2, and 3, respectively, we have from standard interference formulas

$$R = \tilde{r}\tilde{r}^* , \quad \tilde{r} = \frac{r_{12} + \tilde{r}_{23} e^{2i\theta}}{1 + r_{12}\tilde{r}_{23} e^{2i\theta}} ,$$

with

$$\theta = 2\pi l/\lambda_m ,$$

and

$$r_{12} = (1 - \sqrt{\epsilon_b})/(1 + \sqrt{\epsilon_b}) , \quad \tilde{r}_{23} = (\sqrt{\epsilon_b} - \tilde{n})/(\sqrt{\epsilon_b} + \tilde{n}) ,$$

where λ_m is the wavelength in the medium and ϵ_b is the (real) background dielectric constant, i.e., without exciton contributions. $\tilde{n}$ in the "classical" case, is the refractive index

$$\tilde{n}^2 \equiv \tilde{\epsilon} = \epsilon_b + \frac{4\pi\alpha\omega_0^2}{\omega_0^2 - \omega^2 - i\omega\Gamma} ,$$

and, in the spatial dispersion case, is defined by an effective quantity [5]

$$\tilde{n} = \frac{\tilde{n}_+\tilde{n}_- + \epsilon_b}{\tilde{n}_+ + \tilde{n}_-} ,$$

where

$$\tilde{n}_\pm^2 = \frac{1}{2}\left[\epsilon_b - \left(1 - \frac{\omega^2}{\omega_0^2} - \frac{i\omega\Gamma}{\omega_0^2}\right)\frac{M^*\omega_0 c^2}{\hbar\omega^2}\right] \pm \left\{\frac{1}{4}\left[\epsilon_b + \left(1 - \frac{\omega^2}{\omega_0^2} - \frac{i\omega\Gamma}{\omega_0^2}\right)\frac{M^*\omega_0 c^2}{\hbar\omega^2}\right]^2 + 4\pi\alpha\frac{M^*\omega_0 c^2}{\hbar\omega^2}\right\}^{1/2} ;$$

$\tilde{n}_\pm$ are derived from the k-dependent expression of the dielectric function

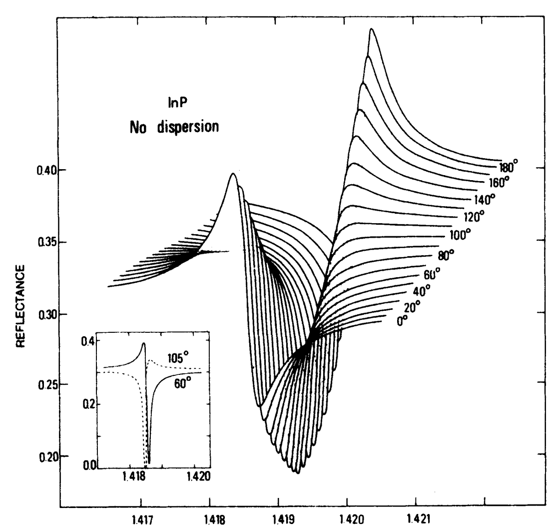

FIG. 9. Same as Fig. 7, except for use of "classical" dispersion ($\Gamma = 0.32$ meV). Curves are progressively shifted in steps of 0.094 meV to the right and 0.00444 upwards. Inset shows two curves for $\Gamma = 0.10$ meV.

$$\tilde{\epsilon}(k,\omega)=\epsilon_b+\frac{4\pi\alpha\omega_0^2}{\omega_0^2-\omega^2+\hbar k^2\omega_0/M^*-i\omega\Gamma}\;.$$

In the above equations, $4\pi\alpha$ is the exciton polarizability, ω_0 is the transverse exciton frequency, M^* is the total exciton mass.

Figures 7–9 give the results of our calculation, as obtained for different values of Γ. For varying l, continuous evolution through all possible line shapes is observed both for the "classical" and the spatial-dispersion case. This is qualitatively similar to what is experimentally observed in the voltage-controlled interference of our Schottky barriers. Bearing in mind that the calculation, although made for InP, applies rather well to GaAs also, due to the similarity of all basic parameters, let us examine the figures to deduce the following points.

(a) Neither model gives rise to positive "spikes" on the high-energy side, as observed for GaAs,[8,15] unless the interference angle θ is at least about $\frac{1}{2}\pi$, the exact value of this threshold depending slightly on the model used and on the value of Γ. For higher values of θ, both "classical" and spatial dispersion curves present such a spike, which is merely a result of interference.

(b) For Γ larger than the transverse-longitudinal splitting of the exciton, equal to ~0.14 meV in InP, spatial dispersion effects tend to be masked, as shown by the similarity of the spectra of Figs. 8 and 9 (with suitable readjustment of θ).

(c) For a given material, comparison of the "free surface" spectrum with the calculated curves of Figs. 7–9 should be indicative, within the limits of the uniform-layer approximation made, of the value of the Bohr radius. This will be very clear from the results of the best-fitting procedure done below for InP and GaAs.

(d) It is rather likely that no two semiconductors will have the same type of exciton-reflectance line shape, unless there is at least an accidental coincidence in the values of the interference angle. This is indeed what is found experimentally if one looks through the literature.

(e) Owing to the influence of Γ on the line shape, even in the same material, line shape differences can be brought about by the presence of defects, strains, or by the treatment of the surface. The last one would directly influence the surface scattering mechanism and might therefore affect also the interference conditions.

A more quantitative theoretical fit of our InP "free surface" reflectance, as well as of a representative spectrum of GaAs reported by Sell *et al.*,[8] has been attempted using the CERN $D506$-$D516$ error-minimization program. The parameters which were allowed to vary were the transverse $n=1$ exciton energy E_{ex}, the phenomenological broadening parameter Γ, the interference angle θ and the exciton polarizability $4\pi\alpha$. For

TABLE I. Best-fitting parameters for the calculated curves of Fig. 3 (InP) and for one representative experimental curve of GaAs reported by Sell *et al.*[8] In the fitting procedure of the spatial-dispersion case, an effective total mass of 0.298 m_0 has been used for GaAs,[8] and of 0.200 m_0 for InP, as estimated with the criteria indicated in Ref. 8, using values given in Ref. 17. Comparison is made with data from transmission and luminescence; in the latter case, energies need not correspond exactly to the transverse exciton level.

Material	Source	Transverse exciton energy (eV)	Exciton polarizability $4\pi\alpha$ ($\times 10^3$)	Effective depth l (Å)	Interference angle θ (deg)	Broadening Γ (meV)
InP (~ 2 °K)	Reflectance (present work, no dispersion)	1.4185	2.35	300	86	0.32
	Reflectance (present work, spatial dispersion)	1.4185	3.9	260	74	0.05
	Luminescence (present work)	1.4183				
	Transmission (6 °K) (Ref. 14)	1.4165	2.35			
GaAs (~ 2 °K)	Reflectance (present work, no dispersion)	1.5149	0.69	340	106	0.12
	Reflectance (present work, spatial dispersion)	1.5150	1.58	295	91	0.004
	Luminescence and reflectance (Ref. 4)	1.5149	1.6	290	90	0
	Transmission (Ref. 18)	1.5151				

InP the best fits obtained, with "classical" and spatial dispersion in the uniform-layer approximation, are shown in Fig. 3 and the corresponding values of the adjustable parameters are listed in Table I along with those used for GaAs. It should be mentioned that some discrepancies in the oscillator strength are found for other samples. The table also gives values deduced from other experiments. It can be seen that both models give a reasonably good fit of the data, with a small edge in favor of the classical one for InP. This is a quite surprising result, pointing to a very anomalous dispersion behavior at the surface. In GaAs, spatial dispersion is slightly more evident, as the "classical" curve deviates more markedly from the experimental results (the reader is referred to Ref. 8 for visual presentation of best-fitting curves in terms of spatial dispersion effects in GaAs). The absence of a "spike" in InP is clearly related to the smaller value of the interference angle, as previously discussed. Here again, however, it is found that in the spatial dispersion case, Γ turns out to be unrealistically small. The value of Γ determined in the "classical" treatment is much closer to that obtained by transmission data at the same temperature in GaAs (this result may, however, be purely accidental).

In all cases there is one major point of discrepancy between theory and experiment, and that is the positive bump below the main peak. In the uniform-layer approximation used, this structure can by no means be fitted using physically meaningful parameters. This suggests that the graded, inhomogeneous surface layer may have a very tangible effect on the line shape, actually to the point of making a distinction between the "classical" and spatial dispersion cases rather unclear. Note that in the latter case, not only does such region affect the physical parameters of the excitonic system (e.g., its wave functions, energy levels, broadening, etc.), but also the definition of the boundary conditions applied. In light of the above arguments, we can justify our findings and also similar conclusions by Biellman *et al.*[9] concerning PbI_2, which we have anticipated in Sec. II. In particular, it is not surprising that, to use more realistic values of Γ in the spatial-dispersion model, one would have to resort to a wrong, namely much larger, value of the effective mass.

We conclude therefore by suggesting that reflectance is not a good tool to reveal spatial-dispersion effects in III-V compounds. Detailed knowledge of the effects taking place in the inhomogeneous surface layer is required before we can draw valid conclusions about the mechanisms underlying the anomalous line shape of the exciton oscillator. The only feature which is readily understood is the dominant role of the interference effect across the surface layer, whatever its origin may be, although details of the line shape can depend upon the type of decay of the exciton perturbation away from the surface. These conclusions have been substantiated by looking at the reflectance of Schottky-barrier structures, where it was possible to control the interference effect alone, without altering the spatial dispersion conditions. Our results indicate, in particular, that the exciton-reflectance line shape of semiconductors should be dependent on the value of the exciton binding energy. If we trust that a unique surface scattering mechanism applies to both InP and GaAs, we can infer from the "free-
both InP and GaAs, we can infer from the "free-
surface" experimental data a value of the exciton Rydberg for InP. Using the best effective depths listed in Table I, we can estimate the ratios between the InP and GaAs Bohr radii. We find for both the spatial and the no-dispersion case a value of 0.9. From the constancy of the product $\{(\epsilon) \times (\text{effective Rydberg}) \times (\text{effective Bohr radius})\}$, since the effective Rydberg for GaAs is equal to 4.2 meV from both theory[17] and experiment,[19] we deduce for InP a value of 4.9 meV, in excellent agreement with theoretical predictions.[17]

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*Gruppo Nazionale di Struttura della Materia del C. N. R.

†Authors' names are in alphabetic order.

[1] F. Evangelisti, A. Frova, and J. U. Fischbach, Phys. Rev. Letters 29, 1001 (1972).

[2] V. A. Tyagai, V. N. Bondarenko, and O. V. Snitko, Fiz. Tekh. Poluprovdn. 6, 103 (1971) [Sov. Phys. Semicond. 5, 920 (1971)].

[3] D. F. Blossey, Phys. Rev. B 2, 3976 (1970).

[4] D. D. Sell, R. Dingle, S. E. Stokowski, and J. V. DiLorenzo, Phys. Rev. Lett. 27, 1644 (1971).

[5] J. J. Hopfield and D. G. Thomas, Phys. Rev. 132, 563 (1963); J. J. Hopfield, J. Phys. Soc. Jap Suppl. 21, 77 (1966).

[6] S. Y. Pekar, Zh. Eksp. Teor. Fiz. 33, 1022 (1957) [Sov. Phys.-JETP 6, 785 (1958)]; Zh. Eksp. Teor. Fiz. 34, 1176 (1958) [Sov. Phys.-JETP 7, 813 (1958)].

[7] G. S. Agarwal, D. N. Pattanayak, and E. Wolf, Phys. Rev. Lett. 27, 1022 (1971); Opt. Commun. 4, 255 (1971); Opt. Commun. 4, 260 (1971); J. J. Sein, J. Opt. Soc. Am. 62, 1037 (1972).

[8] D. D. Sell, S. E. Stokowski, R. Dingle, and J. V. DiLorenzo, Phys. Rev. B 7, 4568 (1973).

[9]J. Biellman, M. Grossmann, and S. Nikitine, in *Polaritons*, edited by E. Burstein and F. De Martini (Pergamon, New York, 1974).

[10]B. L. Evans and P. A. Young, Proc. R. Soc. Lond. A284, 402 (1965); Proc. R. Soc. Lond. A 298, 74 (1967); Proc. Phys. Soc. Lond. 91, 475 (1967); Phys. Status Solidi 25, 417 (1968).

[11]P. G. Harper and J. A. Hilder, Phys. Status Solidi 26, 69 (1968); G. Jones and J. L. Brebner, J. Phys. C 4, 723 (1971); B. Bendow, Phys. Rev. B 3, 1999 (1971).

[12]D. E. Aspnes and A. Frova, Solid State Commun. 7, 155 (1969).

[13]F. Evangelisti, A. Frova, and J. U. Fischbach, Surface Sci. 37, 841 (1973).

[14]W. J. Turner, W. E. Reese, and G. D. Pettit, Phys. Rev. 136, A1467 (1964).

[15]A. M. White, P. J. Dean, L. L. Taylor, R. C. Clarke, D. J. Ashen, J. B. Mullin, and P. D. Greene, J. Phys. C 5, 1727 (1972).

[16]J. U. Fischbach, G. Benz, N. Stath, M. H. Pilkuhn, and K. W. Benz, Solid State Commun. 11, 72 (1972).

[17]A. Baldereschi and N. O. Lipari, Phys. Rev. B 3, 439 (1971).

[18]D. E. Hill, Solid State Commun. 11, 1187 (1972).

[19]D. D. Sell, Phys. Rev. B 6, 3750 (1972).