Plasmon and interband transitions in $Ti_{1-x}Hf_xSe_2$ systems

A. Borghesi, M. Geddo, G. Guizzetti, E. Reguzzoni, and A. Stella
Dipartimento di Fisica "A. Volta" dell'Università degli Studi di Pavia, I-27100 Pavia, Italy
and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, I-27100 Pavia, Italy

F. Lévy
Institut de Physique Appliquée, Ecole Polytechnique Federale de Lausanne, CH-1007 Lausanne, Switzerland
(Received 5 July 1983)

Thermoreflectance measurements in the infrared were performed to study plasmon and low-energy interband transitions both below and above T_c in $Ti_{1-x}Hf_xSe_2$ crystals. We found that the main effect of the introduction of Hf into $TiSe_2$ is to broaden the plasmon structure. Furthermore, through a detailed analysis of a low-energy interband transition, we followed the progressive uncrossing of the bands and estimated the value of the gap opened by the phase transition.

I. INTRODUCTION

In the last years a large number of papers has been published on the structural, electrical, and optical properties of layered group-V and group-IV transition-metal dichalcogenides[1] (TMD's). In particular, group-V TMD's are metals and some of them (such as $2H$-$TaSe_2$, $2H$-$NbSe_2$, $1T$-TaS_2 $1T$-VSe_2 etc.) exhibit phase transitions which are characterized by charge-density waves (CDW's) induced by electronic instabilities. On the other hand, group-IV TMD's are generally semiconductors with the exception of $TiSe_2$ which is a semimetal due to a partial overlapping (≈ 0.2 eV) between p valence band at Γ and d conduction band at L in the Brillouin zone[2] (BZ). $TiSe_2$ undergoes a structural phase transition around 200 K, with the appearance of a $2\times2\times2$ superlattice and a peak in the resistivity versus temperature curve.[3] As it will be stressed later, several possible mechanisms have been proposed for such a transition (excitonic insulator, electron-hole coupling by electron-phonon interaction, phonon-driven antiferroelectric transition, Jahn-Teller–type mechanism), and the point is still debated in view of a definite assessment.

A recent trend in the field consists in adding known amounts of chemically defined impurities to these crystals. The impurities are usually transition-metal atoms, leading to the formation of mixed systems such as $Ti_{1-x}Ta_xSe_2$, $Ti_{1-x}Nb_xS_2$, $Ti_{1-x}V_xSe_2$, and $Ti_{1-x}Hf_xSe_2$. Of these systems, the first three are influenced by disorder and Anderson localization of free carriers rather than by the increased number of free electrons.[4] The last one is particularly interesting since $HfSe_2$ is a semiconductor with an indirect band gap of 1.13 eV.[5] In other words, if one starts from $TiSe_2$ and increases x, one reaches the uncrossing of the conduction and valence bands for a given intermediate stoichiometry. In principle, this fact may be competitive with others (such as, for instance, disorder) in destroying the low-temperature phase coupled to the $2\times2\times2$ superlattice. According to a recent work by Taguchi,[6] this takes place near $x\simeq0.3$, where the uncrossing of the bands has taken place, as electrical data suggest.

We concentrate our attention on the behavior of plasmon and low-energy interband transitions of $Ti_{1-x}Hf_xSe_2$ crystals with several values of x. The technique used is thermoreflectance (TR), which has proved to be very powerful in detecting peculiarities[7] in the temperature dependence of phase transitions. While electrical properties have been studied in some detail by Taguchi,[6] optical properties are the object of this work.

II. EXPERIMENTAL APPARATUS

The experimental apparatus is briefly described here. In order to minimize spurious effects due to blackbody emission, the samples were mounted before the monochromator. The incident beam was nearly normal to the sample surface. We used samples ≈3 mm$\times3$ mm wide and with different thicknesses, cleaved from crystals grown by iodine vapor transport with excess Se. Attention was devoted to use good and fresh surfaces by cleaving the samples shortly before the beginning of the measurements.

A Leiss double monochromator and a Golay detector were used. The temperature of the sample was indirectly modulated by means of a heater, which was a Ge crystal of suitable resistivity, fastened to the cold finger of a Cryotip refrigerator from Air Products and Chemicals, Inc. The sample was pressed on the Ge heater by two springs. The temperature modulation, obtained by applying current pulses at 1.5 Hz to the heater, was 1 K in all of the reported measurements.

The ac output of the detector was synchronously detected by the lock in, whose output voltage (proportional to ΔR) was integrated. The ratio between this signal and the one obtained by chopping the beam reflected from the sample (proportional to R) yields the ratio $\Delta R/R$.

III. INTERBAND TRANSITIONS

A semimetallic band structure with a band overlap of ≈0.2 eV has been reported by Zunger and Freeman in the case of $TiSe_2$,[2] while $HfSe_2$ is known to be a semiconductor with an indirect gap of 1.13 eV.[5] Low-energy struc-

tures corresponding to interband transitions have been observed by several people[8–12] and higher-energy transitions, up to ≈ 4 eV, have been studied in a previous TR work.[11]

In this section we examine the lowest-energy structure due to interband transitions, which has been observed to be particularly prominent at low temperature in absorption calculated from reflectivity,[8] transmission,[9] and TR in the energy range 0.2—0.5 eV.[11] It is worth noting that TR gives experimental evidence which allows one to study features and details on a finer scale with respect to other techniques. In particular, shifts versus x at a given temperature and presence of the structure also above the transition temperature T_c can be extracted from our data.

Figures 1(a) and 1(b) show in that energy range and for a given stoichiometry the existence of a negative dip, located at energies which are ≈ 0.2 eV lower at 200 K with respect to 100 K. Negative dips in TR are indicative of peaks in reflectivity characterized by negligible temperature-shift coefficients and predominant broadening effects caused by temperature increases. Such TR dips may become largely asymmetric if the spectral feature of reflectivity, which broadens with temperature, differs from a peak. Several optical transitions in TMD have evidenced such a behavior.[13,14] Figure 1(a) shows that the dip, centered at 0.4 eV at 100 K for the smallest Hf concentration, shifts toward the lower energies with increasing x, the amount of the shift being 0.1 eV up to $x=0.1$ and 0.2 eV with $x=0.3$, where significant line-shape changes, however, start to take place.

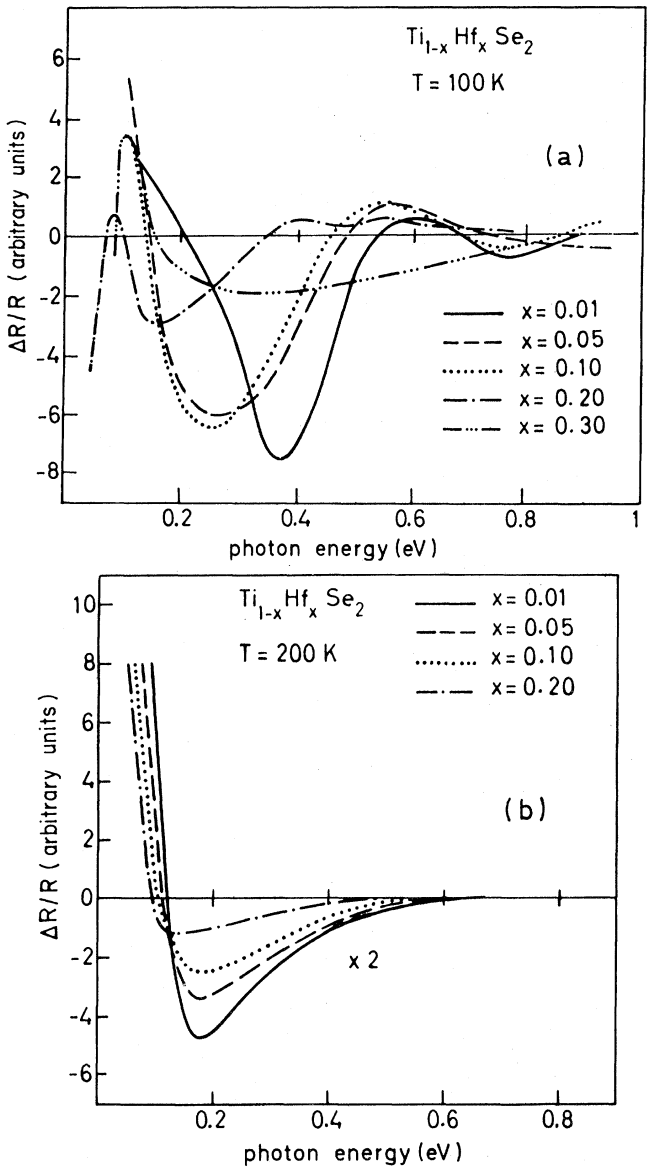

FIG. 1. Low-energy interband TR spectra at (a) 100 K and (b) 200 K. Note that (see Ref. 6) T_c becomes progressively lower than 200 K when x increases. In all of the curves here reported, $\Delta R/R$ is taken as positive if the reflection coefficient increases with increasing temperature. [In (b) the curves are magnified by a factor of 2 in the ordinate scale.]

The values of $\Delta R/R$ for the dip at 200 K are 4 to 6 times smaller than at 100 K. Besides, no appreciable shift of the structure at 200 K as a function of x was observed in the stoichiometry range $0<x\leq 0.1$, whereas the TR curve undergoes substantial changes above these values. Smearing of the density of states around the Fermi level may be the cause of the absence of relatively large shifts at the higher temperatures [Fig. 1(b)], as long as the density-of-states profile is not affected by stoichiometry ($x\leq 0.1$). As for the attribution of the structure, several transitions may take place in the energy range ≤ 0.5 eV (see Fig. 2 and Refs. 2 and 9), particularly below T_c, when the superlattice formation causes a reduction of the size of the BZ and consequent folding back of the bands.

Owing to this, indirect transitions in the $1\times1\times1$ structure may become direct in the $2\times2\times2$ superstructure. This would be the case, for instance, of L_1^+-Γ_3^- or Γ_3^--M_1^+ transitions, which would add to other direct transitions such as Γ_3^--Γ_3^+. In principle, the formation of the superlattice causes two effects on the energy levels: mapping of the bands in the smaller BZ and formation of the gaps around the Fermi level. While in other cases ($2H$-$TaSe_2$) a direct determination of such gaps has been attempted by optical methods,[14–16] the energy position of

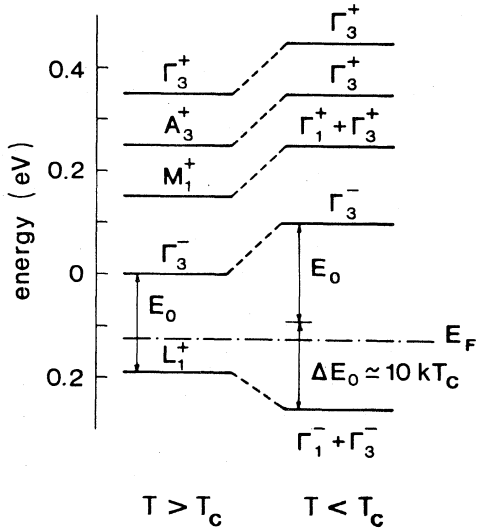

FIG. 2. Band scheme near the Fermi level below and above T_c. The transition L_1^+-Γ_3^- is indirect in the $1\times1\times1$ phase and direct in the $2\times2\times2$ phase. ΔE_0 is the gap opened by the phase transition.

the plasmon and the rich phonon structures have made it very hard to extract a parallel information from reflectivity or TR data in $TiSe_2$.

If we attribute the $\approx$0.2-eV energy difference of the structure position to the gap ΔE_0 which opens with the phase transition, as explained in Fig. 2, we get a value near $10kT_c$, which was considered in Ref. 9 as a reasonable upper limit for the gap.

As for the specific assignment of the structure, the weakening of the dip favors transitions such as (a) L_1^+-Γ_3^- or (b) Γ_3^--M_1^+, which are indirect above and direct below T_c, although in principle also (c) Γ_3^--Γ_3^+ is possible. The last one, however, is predicted at higher energy[2] and should not particularly weaken or tend to disappear when warming up above T_c. Precursor effects, which are evident way above T_c in several phase transitions in TMD,[17] may actually cause transitions (a) or (b) to start to become direct 20–30 K above the transition temperature. Since this is in line with the experimental observation the structure starts to be visible at those temperatures. Thus, taking also into account angle-resolved photoemission data reported in Ref. 18, we assign the structure to an interband transition L_1^+-Γ_3^-.

The curves of Figs. 1(a) and 1(b) allow us (i) to make a more definite assignment of the spectral feature investigated and observed in previous works by means of different techniques in the energy range 0.2–0.5 eV; (ii) to establish that up to $x=0.1$ there is no appreciable distortion of the line shape (and then of the profile of the density of states); (iii) to clarify that line-shape modifications are relevant at higher values of x, while the structure is completely smeared out for $x=0.3$, where uncrossing of the bands has certainly taken place;[6] (iv) to measure experimentally the overlapping of the p-d bands; (v) to evaluate $\Delta E_0 \approx 10kT_c$.

IV. PLASMON

Phase transitions in layered metallic and semimetallic compounds may affect plasmons in various and sometimes dramatic ways, which are generally located in the infrared. It has been shown that the production of a CDW gap in $2H$-$TaSe_2$ causes a blue shift and an anomalous reduction in width of the plasmon.[16] This effect appears to be negligible in $2H$-$NbSe_2$ where the CDW gap is much smaller.[19] A completely different behavior has been observed in $1T$-$TiSe_2$, where a large red shift takes place with the appearance of the $2\times2\times2$ superstructure.[8–10]

TR was used to analyze plasmons in $Ti_{1-x}V_xSe_2$ and $Ti_{1-x}Nb_xS_2$ systems, where, at a given stoichiometry, line shapes were essentially characterized by the modulation of the broadening parameter Γ. Such a line shape is reported in Fig. 3 (Ref. 20) for TiS_2 as a reference and reproduces very well the typical curves reported by Cardona.[21]

As shown in Ref. 20, the curve in Fig. 3 is amenable to physical cases where Γ modulation is predominant over other mechanisms and is remarkably different from TR curves where parameters, such as e.g., ω_p or ϵ_∞, play a major role in determining the line shape. As for $TiSe_2$, the plasmon structure is located around 0.05 eV at 100 K

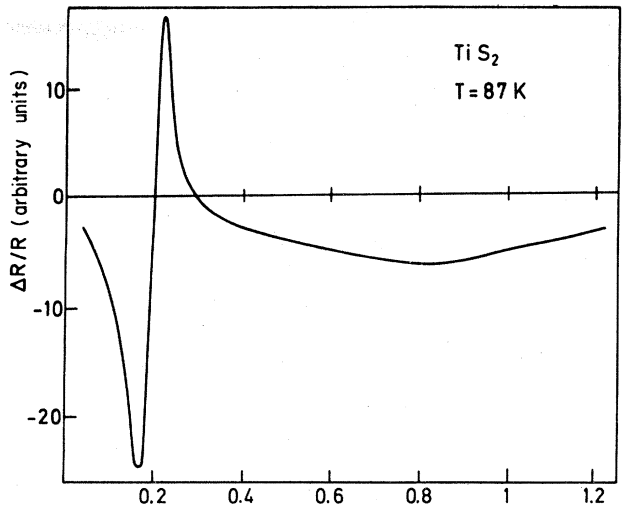

FIG. 3. Plasmon TR structure for a TiS_2 crystal.

(see Fig. 4) and only the high-energy lobe can be picked up completely in the low-temperature curve, at a variance with respect to TiS_2, where the plasmon is entirely visible with our TR apparatus.[22] Since the general behavior of the line shape is substantially conserved at least up to $x=0.1$, by measuring the full width half maximum of the peak one can estimate that the plasmon broadens $\approx$300% when x is increased from 0.01 to 0.1. A remarkable modification of the line shape takes place at higher Hf concentrations.

Since the plasmon frequency ω_p is given by

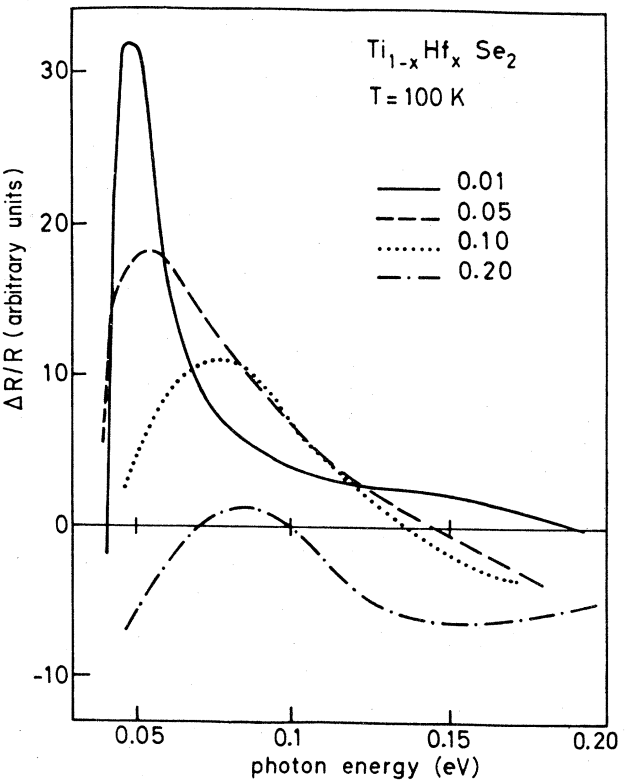

FIG. 4. Plasmon TR line shape at 100 K for $Ti_{1-x}Hf_xSe_2$ crystals with different stoichiometries.

$$\omega_p^2 = \frac{1}{\epsilon_\infty}\frac{4\pi N e^2}{m^*}, \tag{1}$$

one should also take into account changes of ϵ_∞ and N/m^* where N is the free-carrier concentration, m^* is the effective mass, and ϵ_∞ is the high-frequency dielectric constant. While eventual variations of m^* can hardly be evaluated in our case, it is clear that both N and ϵ_∞ must decrease when x increases from 0 to 0.3.[9,10,23] A partial compensation between their variations might actually explain the absence of any substantial shift of ω_p as a function of stoichiometry up to $x=0.1$. However, since no microscopic theory is available to study the modification of ϵ_∞ induced by the introduction of Hf atoms into the $TiSe_2$ lattice, we will not discuss this point any further. As for the variation of the free-carrier concentration, Hall data from Taguchi's work[6] are available.

We confine our attention to a specific argument concerning theoretical estimates of ω_p vs x. Under the assumption of a linear variation of the p-d gap E_g with stoichiometry

$$E_g = -0.2 + 1.33x \tag{2}$$

(E_g expressed in eV), we may write for the free-carrier concentration

$$N \propto E_g^{3/2} \propto (x - x_0)^{3/2}, \quad x \leq x_0 \tag{3}$$

$$N = 0, \quad x > x_0 ,$$

where x_0 stands for the stoichiometry index corresponding to the uncrossing of the bands. The $\frac{3}{2}$ exponent is due to the proportionality between E_g and E_F as long as there is a band overlap. From Eq. (1), neglecting variations of ϵ_∞ and m^* with x, one obtains

$$\omega_p \propto N^{1/2} \propto (x - x_0)^{3/4} \tag{4}$$

which, in the rough approximation used, confirms the expectation that ω_p has no drastic dependence on x for the lower Hf concentrations. Figures 5 and 6 show the modification of the plasmon line shape with temperature for two different stoichiometries: The overall line shape is essentially conserved when warming up above T_c, except for a relevant broadening and smoothing of the curve.

V. CONCLUSIONS

TR measurements in the infrared are useful in order to obtain a more complete and detailed picture both of the pure $TiSe_2$ crystals and the mixed $Ti_{1-x}Hf_xSe_2$ systems. The main points where new information is obtained are the following: (a) evolution of the plasmon and a low-energy interband transition with the uncrossing of the p and d bands, an estimate of the rate of uncrossing with x and magnitude of the overlap; (b) determination of the magnitude of the gap ΔE_0, which is a topic often discussed in the literature, an upper limit of such a gap being predicted to be $10kT_c$;[9] (c) assignment of a structure due to interband transitions, which are indirect way above T_c and become smoothly (due to precursor effects) (Ref. 17) direct with the progressive onset of the $2\times2\times2$ superstructure; (d) evidence of a perturbation on the density-

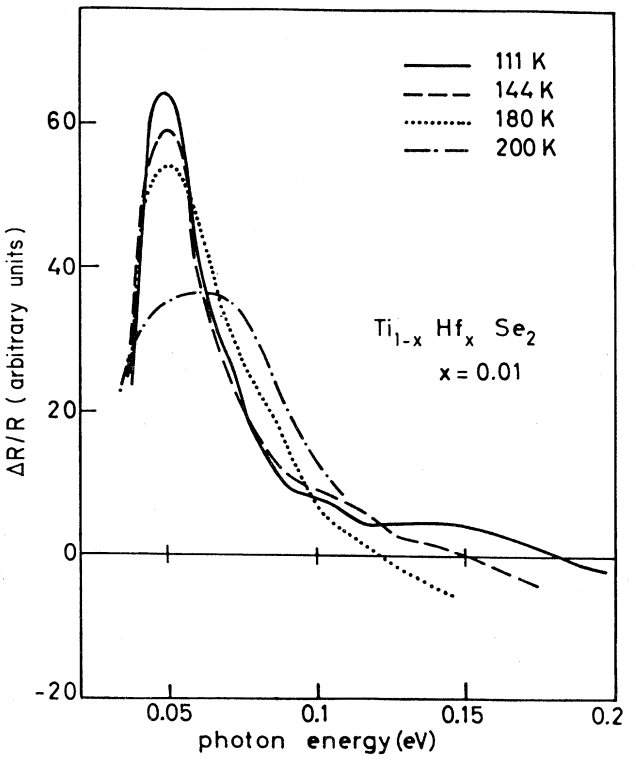

FIG. 5. Plasmon Tr line shape at different temperatures and $x=0.01$.

of-states profile in the valence and conduction bands around the Fermi level, which starts to be appreciable in the TR curves for $x > 0.1$ [see Fig. 1(a)]; (e) pronounced broadening of the plasmon induced by the introduction of Hf atoms.

As for the mechanism responsible for the phase transi-

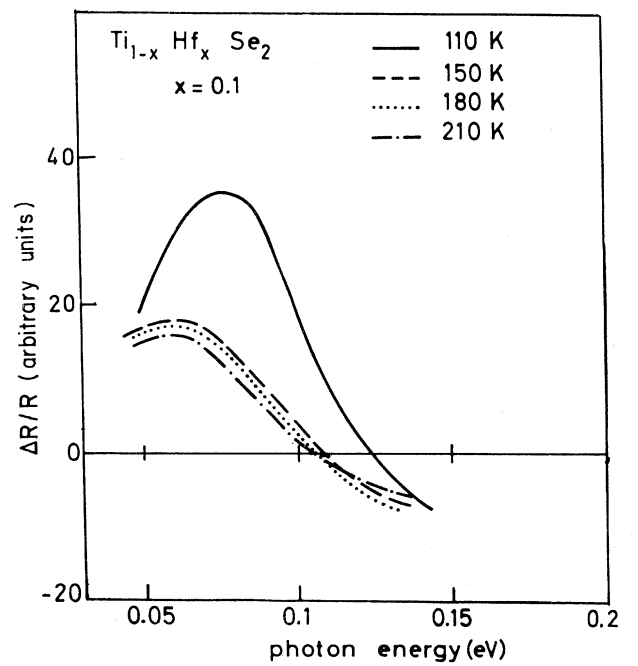

FIG. 6. Plasmon TR line shape at different temperatures and $x=0.1$.

tion, electrical[6] and angle-resolved photoemission data[18] have been interpreted as supporting the excitonic insulator mechanism.[24] Our data do not contradict this interpretation, although it must be stressed that the other mechanisms mentioned in the Introduction cannot be ruled out: As a matter of fact the progressive uncrossing of the bands, which is confirmed in this work, induces not only a decrease of electron and hole concentrations, but also a concomitant decrease of ϵ_∞ which may drive, for instance, an antiferroelectric-type mechanism.[25]

ACKNOWLEDGMENTS

The authors wish to thank Professor E. Tosatti for useful discussions and suggestions.

[1]J. A. Wilson and A. D. Yoffe, Adv. Phys. 18, 193 (1969); J. A. Wilson, F. J. DiSalvo, and S. Mahajan , *ibid.* 24, 117 (1975); J. A. Wilson, Phys. Status Solidi B 86, 11 (1978).

[2]A. Zunger and A. J. Freeman, Phys. Rev. B 17, 1839 (1978).

[3]F. J. DiSalvo, D. E. Moncton, and J. V. Waszczak, Phys. Rev. B 14, 4321 (1976); F. J. DiSalvo and J. V. Waszczcak, *ibid.* 17, 3801 (1978).

[4]F. Lévy and Y. Froidevaux, J. Phys. C 12, 473 (1979); F. Lévy, *ibid.* 12, 3725 (1979); 13, 2901 (1980); A. Borghesi, G. Guizzetti, A. Stella, E. Reguzzoni, and F. Lévy, Solid State Commun. 43, 209 (1982).

[5]D. L. Greenway and R. Nitsche, J. Phys. Chem. Solids 26, 1445 (1965).

[6]I. Taguchi, J. Phys. C 14, 3221 (1981).

[7]A. Borghesi, G. Guizzetti, G. Samoggia, and E. Reguzzoni, Phys. Rev. Lett. 47, 538 (1981).

[8]K. Woo and F. C. Brown, Solid State Commun. 28, 341 (1978).

[9]J. A. Wilson, A. S. Barker, Jr., F. J. Di Salvo, and J. A. Ditzenberger, Phys. Rev. B 18, 2866 (1978).

[10]W. Y. Liang, G. Lucovsky, J. C. Mikkelsen, and R. H. Friend, Philos. Mag. B 39, 133 (1979).

[11]A. Borghesi, M. Geddo, D. Maghini, A. Stella, and F. Lévy, Phys. Lett. 83A, 281 (1981).

[12]G. Campagnoli, A. Gustinetti, D. Maghini, A. Stella, and F. Lévy, in *Proceedings of the 14th International Conference on the Physics of Semiconductors, Edinburgh, 1978,* edited by B. L. H. Wilson (IOP, Bristol, 1978), Chap. 25.

[13]G. Campagnoli, A. Gustinetti, and A. Stella, Solid State Commun. 18, 973 (1976).

[14]G. Campagnoli, A. Gustinetti, A. Stella, and E. Tosatti, Phys. Rev. Lett. 38, 95 (1977).

[15]A. S. Barker, J. A. Ditzenberger, and F. J. DiSalvo, Phys. Rev. B 12, 2049 (1975).

[16]G. Campagnoli, A. Gustinetti, A. Stella, and E. Tosatti, Phys. Rev. B 20, 2217 (1979).

[17]W. L. McMillan, Phys. Rev. B 16, 643 (1977).

[18]N. G. Stoffel, F. Lévy, C. M. Bertoni, and G. Margaritondo, Solid State Commun. 41, 53 (1982).

[19]M. Cambiaghi, M. Geddo, A. Gustinetti, and A. Stella, Solid State Commun. 37, 795 (1981).

[20]A. Borghesi, G. Guizzetti, A. Stella, E. Reguzzoni, and F. Lévy, Solid State Commun. 41, 199 (1982).

[21]M. Cardona, *Modulation Spectroscopy* (Academic, New York, 1969).

[22]G. Lucovsky, R. M. White, J. A. Benda, and J. F. Revelli, Phys. Rev. B 7, 3859 (1973).

[23]F. Lévy and H. P. Vaterlaus (unpublished).

[24]B. I. Halperin and T. M. Rice, Rev. Mod. Phys. 40, 775 (1968).

[25]R. M. White and G. Lucovsky, Nuovo Cimento B 38, 280 (1977).