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Optical phonons in bulk $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ mixed crystals in the whole composition range

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Résumé. — Les fréquences des modes optiques des solutions solides $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ sont déduites des mesures de réflectivité infrarouge dans tout le domaine de composition pour la première fois. Ces résultats confirment ceux déjà obtenus sur des cristaux massifs pour $x < 0,5$ mais sont différents de ceux présentés par des couches épitaxiées. Cette différence est expliquée par une plus grande ionicité des liaisons Cd-Te dans les couches épitaxiées provenant vraisemblablement d'une relaxation non totale du réseau pendant leur croissance.

Abstract. — Optical vibration mode frequencies of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ solid solutions have been deduced from infrared reflectivity measurements in all the composition range for the first time. These results are in agreement with those already obtained for bulk crystals with $x < 0.5$ but are different from those displayed by epitaxial layers. This difference is explained by a higher ionicity of the Cd-Te bond in epilayers coming probably from an incomplete relaxation of the lattice during their growth.

1. Introduction.

Cadmium zinc telluride solid solutions $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ (CZTx) have become technological materials as their lattice parameters can be matched to that of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ [1] or other II-VI semiconductors when adjusting x . So they are used as substrate materials [2] or buffer layers [3] for epitaxial growth. They are also widely used as barrier compounds in II-VI heterostructures [4]. Besides lattice matching, Zn substitution to Cd lowers defect densities [5, 6], the crystal lattice improvement has been attributed to a decrease in bond ionicity [7]. Moreover, electrical measurement results have been interpreted by Weil *et al.* as being due to a ferroelectric transition [8]. This result can be explained through the strong bimodal distribution

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of near neighbour distances [9] which expresses the Cd-Te bond strengthening by Zn substitution but can also induce a trigonal distortion in the lattice which allows the existence of the wurtzite structure in addition to the usual sphalerite one [10] and is consistent with recent diffraction results [11].

First results on optical phonons were deduced from infrared reflectivity on polycrystalline CZT samples [12, 13]. They evidenced a two mode behaviour in contrast to the Chang and Mitra criterion [14] with similar linear variations of the transverse frequency for the Cd-Te like mode ν_{TC} and the Zn-Te like mode ν_{TZ} . The longitudinal frequency of the Cd-Te like mode ν_{LC} decreases with x , on the opposite the Zn-Te like mode ν_{LZ} increases with x . New results were obtained on CZT epitaxial layers [14] probed by Raman spectroscopy, the ω_{LZ} frequency has a strong nonlinear variation with x when ω_{LC} remains almost constant.

More recent results of infrared reflectivity and Raman scattering on bulk samples grown by the Bridgman-Stockbarger method give mode frequencies variations with x [15] which are different from those reported in [14]. These differences appear beyond the experimental uncertainties and should reflect the different behaviours of bulk CZT's as compared to epitaxial ones although the layers used in [14] are greatly relaxed.

We report here on values of ν_L and ν_T for both modes in CZT deduced from infrared reflectivity measurements on bulk samples. For the first time results for $x > 0.6$ are given, this allows a more precise determination of $\nu_{LC}(x)$ and $\nu_{TC}(x)$ and of the local mode frequency of Cd in ZnTe.

The next section describes experimental details, the third one reflectivity data analysis and a comparison of the ν_L and ν_T with those already reported. The last section is devoted to a brief discussion.

2. Crystal growth, infrared measurements and reflectivity results.

CZT ingots of graded composition and 15 mm of diameter have been grown by the travelling heater method (T.H.M.) in a single pass using tellurium as solvent. Starting polycrystalline ingots of CdTe and ZnTe are cut with a variable cross section area to obtain a graded composition of the grown ingots. The details of the growth technique are presented in [16].

Slices are cut in the ingots ; composition x is measured with a microprobe [17] on about twenty points per slice. x variations remain lower than 0.02 ; their mean value, calculated from all measurements, gives the sample composition. Samples comprise several crystallites of mean size 5 mm usually of statistical orientation.

Reflectivity measurements are performed with a Fourier spectrometer Beckman FS720 associated with a home built data acquisition system. Reflectivity is measured at room temperature, 180 K and 80 K under nearly normal incidence conditions by comparison with a freshly polished copper sample.

Reflectivity values are monitored between 10 cm^{-1} and 300 cm^{-1} with a precision of 2×10^{-2} , that on frequency is better than 1 cm^{-1} . Reflectivity appears independent of the light polarization direction on monocrystalline samples.

Reflectivity results for different values of x are presented in figure 1. They display the two band behaviour of these mixed crystals. As samples are always of p type of moderate or low concentration (as grown or after annealing) no plasma contribution appears in the reflectivity spectra down to 30 cm^{-1} . There is no change of reflectivity in the frequency interval of the two main bands after an annealing of the samples at $750 \text{ }^\circ\text{C}$ which is used to modify native defect concentrations. A peak near 80 cm^{-1} is found on about half the compositions and is usually attributed to a cluster mode. The amplitude of this peak decreases strongly after a low temperature treatment ($T < 550 \text{ K}$), and is not recovered on cooling and appears correlated with the irreversible modification on the optical dielectric constant shown by the same samples

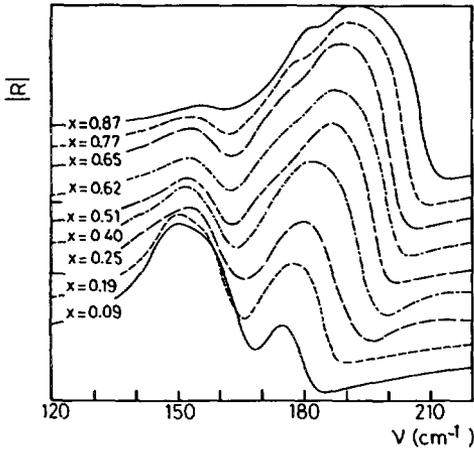


Fig. 1.

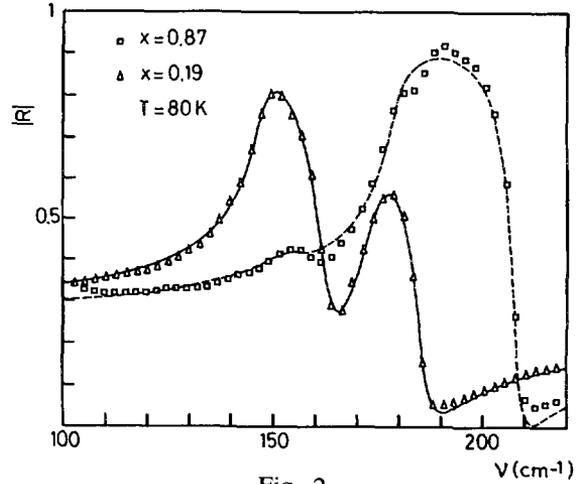


Fig. 2.

Fig. 1. — Reflectivity spectra of Cd_{1-x}Zn_xTe at 80 K, curves are shifted by steps of 1/9 in *R*.

Fig. 2. — Comparison between experimental data (open squares and triangles) and calculated reflectivity with two oscillators (dotted and solid curves).

under this low temperature increase [18]. This part of the reflectivity spectra will not be considered here as the peak amplitude remains small.

Structures appear clearly in the main bands for several compositions, they are associated with clustering in the lattice [15] in contrast to the case of HgCdTe [19] or HgZnTe [20]. The effect of clustering which is seen on the ZnTe band at high *x* and on the CdTe band at low *x* is currently examined but it appears that its effect varies with *x* and reflectivity data have only been fitted by two oscillators associated respectively to Zn-Te and Cd-Te dipole vibrations. We verify that this description gives consistent results and so the corresponding frequencies can be compared with those already published.

3. Reflectivity data analysis and results.

The dielectric function $\epsilon(\nu)$ is usually described by a sum of Lorentzian contributions each corresponding to one oscillator with characteristic frequency ν_T [15, 19, 20]. The longitudinal frequencies are then deduced from the zeros of the fitted $\epsilon(\nu)$.

The more general form of the linear susceptibility response has been chosen to fit reflectivity data. $\epsilon(\nu)$ is expressed as the ratio of polynomials containing the transverse and longitudinal frequencies [21]: for a two-band system the dielectric function reads:

$$\epsilon(\nu) = \epsilon_{\infty} \frac{\nu_{LZ}^2 - i\nu\gamma_{LZ} - \nu^2}{\nu_{TZ}^2 - i\nu\gamma_{TZ} - \nu^2} \frac{\nu_{LC}^2 - i\nu\gamma_{LC} - \nu^2}{\nu_{TC}^2 - i\nu\gamma_{TC} - \nu^2}$$

Where the γ_s are the damping constants associated with each mode frequency and ϵ_{∞} is the optical dielectric constant.

Nine parameters must be adjusted to fit experimental data instead of seven for the additive expression of two Lorentzians however we verify that the fit converges rapidly to a stable solution. The ν_L and ν_T for each of the bands deduced from the fit with one oscillator has been

compared to those obtained with several oscillators (2 to 3). ν_T for one band is the mean of the different transverse frequencies. The same result holds for ν_L but the ν_L 's can have a different ordering as compared to that of the ν_T 's.

Longitudinal and transverse frequencies thus obtained for each sample are presented in figure 3 where the curves have been obtained after a fit with polynomials. Numerical values deduced for equally spaced composition are given in table I together with those obtained in [15]. The differences come mainly from experimental errors and to the fact that frequency values are known only for $x < 0.5$ in [15].

ν_{LC} and ν_{TC} vary non linearly with x and converge towards the local mode frequency of Cd in ZnTe whose value is 153 cm^{-1} . The small difference $\nu_L - \nu_T$ means that the contribution of this Cd-Te type mode to the polarizability is small. The behaviour of the Zn-Te mode is opposite as $\nu_L - \nu_T$ remains large at low x before converging to the local mode frequency of Zn in CdTe of 172 cm^{-1} which is just above the reststrahlen band of CdTe. At 300 K, the shift of all characteristic frequencies towards lower values is almost independent of x . This shift is due to the anharmonicity of the potential and its amplitude is about the same for both binaries as their Grüneisen parameter for optical modes is near 1.8 [23].

Table I. — Numerical values of longitudinal and transverse frequencies in cm^{-1} for the Zn-Te vibration band (ν_{LZ} , ν_{TZ}) and the Cd-Te one (ν_{LC} , ν_{TC}) versus composition x at 80 K : F from [15], G this work after fit and interpolation.

x	ν_{LZ}		ν_{TZ}		ν_{LC}		ν_{TC}	
	G	F	G	F	G	F	G	F
0	172.0	172.0	172.0	172.0	167.5	169.0	143.9	146.7
0.1	182.0	179.0	172.5	173.4	165.2	162.0	145.3	147.8
0.2	186.3	184.5	173.2	174.6	163.1	159.5	146.5	150.7
0.3	190.3	188.5	173.8	179.4	161.2	160.0	147.7	152.5
0.4	193.9	192.5	174.5	177.6	159.4	159.5	148.8	153.4
0.5	197.3	196.0	175.3	178.5	157.8	156.5	149.8	154.7
0.6	200.4		176.1		156.4		150.7	
0.7	203.1		177.0		155.2		151.5	
0.8	205.7		178.0		154.1		152.1	
0.9	207.9		179.0		153.4		152.7	
1.0	209.8	210.0	180.0	182.0	153.0		153.0	

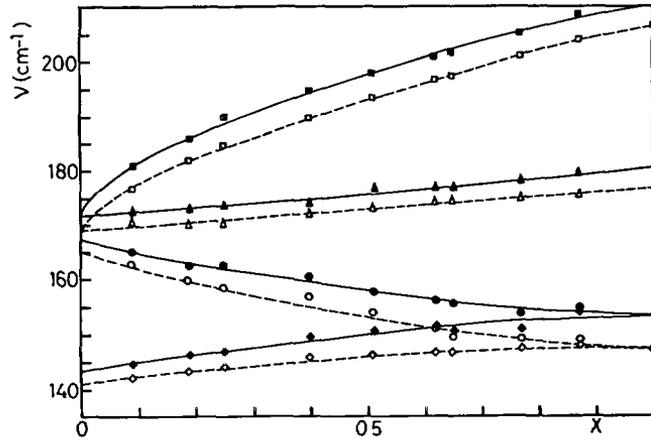


Fig. 3. — Mode frequencies *versus* composition x : (■) ν_{LZ} , (▲) ν_{TZ} , (●) ν_{LC} , (◆) ν_{TC} at 80 K ; (□) ν_{LZ} , (Δ) ν_{TZ} , (○) ν_{LC} , (◇) ν_{TC} at 293 K.

Damping coefficient values are shown in figure 4. In spite of a scattering of the values which can be assigned to the effect of lattice defects the γ_s decreases nearly linearly with the concentration (x or $1 - x$) of dipoles associated with each band. The rate of change of γ_{TZ} with x is shifted of about 2.2 cm^{-1} above that of γ_{LZ} . The rate of variation of γ_{TC} is about three times higher than that of γ_{LZ} , γ_{LC} being shifted by 7 cm^{-1} above γ_{TC} . At 300 K, the γ_s are more scattered and, on the average, increase with a higher rate with x than at 80 K. Reflectivity measurements near normal incidence are not precise enough to give the detailed variation of ϵ_∞ with composition between the values of the end binaries which are very close to each other ($\epsilon_\infty = 7.4$ for CdTe and 7.3 for ZnTe). Moreover the small $\epsilon_\infty(x)$ variation of defect free materials is hidden by the polarizability contribution of all defects present in tellurides as seen on ZnTe [24].

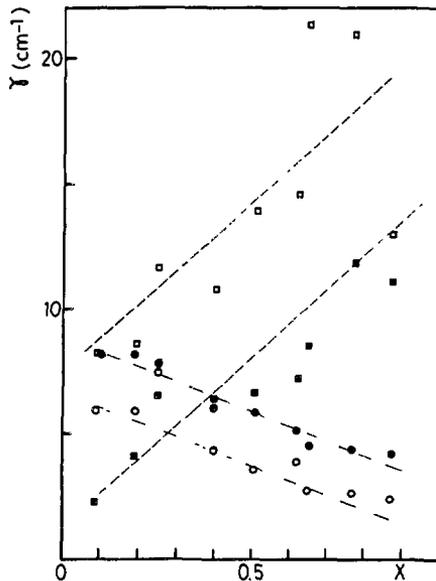


Fig. 4. — Damping parameter at 80 K : (○) γ_{LZ} , (●) γ_{TZ} , (□) γ_{LC} , (■) γ_{TC} .

4. Discussion.

In the range of compositions $x < 0.5$ the values of the transverse and longitudinal frequencies given here are the same within experimental uncertainties, as those given in [15] and near those reported previously [12, 13]. The differences with the results obtained on epitaxial layers [14] remain beyond the experimental errors and should not be assigned to the experimental techniques used. The most realistic assumption rests on the residual strain the lattice undergoes during the epitaxial growth although the layers are considered relaxed as their thickness is very large compared to the critical one on ZnTe [25] or GaAs.

The description of vibrational modes is complicated due to disorder in the cation sublattice [26, 27] and a detailed study needs to be undertaken to understand the difference between both materials to show what parameters are changed on epitaxial layers as compared to bulk crystals. In the contribution of vibration modes to the low frequency polarizability which is given by the Lyddane Sachs Teller relation : $\epsilon_s = \epsilon_\infty (\nu_{LZ}/\nu_{TZ})^2 \cdot (\nu_{LC}/\nu_{TC})^2$ the part of the Cd-Te type mode remains about the same in bulk and epitaxial CZT when the one coming from the Zn-Te type band (ν_{LZ}^2/ν_{TZ}^2) is higher for bulk crystals than for epitaxial layers. This indicates a higher polarizability contribution of the Zn-Te band in bulk CZT as compared to epitaxial ones.

CZT epilayers probed by Raman Scattering have a (001) orientation for $x > 0.1$ and it appears interesting to probe the polarizability contribution of vibration modes on epilayers of (111) orientation for which orientational lattice relaxation can be easier. The (111) direction appears to be the trigonal deformation direction associated with the ferroelectric transition [11].

Summary.

Reflectivity measurement performed for the first time in whole the composition range of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ bulk mixed crystals are reported. The results for $x < 0.5$ agree well with the results of Perkowitz *et al.* [15] which were grown with another method but are different from those obtained on epitaxial layers. The difference is attributed to a non complete relaxation of the epilayers.

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