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# Optical phonons in $Cd_{1-x}Zn_xTe$

S. Perkowitz, L. S. Kim, and Z. C. Feng
*Department of Physics, Emory University, Atlanta, Georgia 30322*

P. Becla
*Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

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We have combined infrared and Raman methods to study the transverse- and longitudinal-optical (TO and LO) phonons in bulk $Cd_{1-x}Zn_xTe$ ($x=0.005-1$), for the first time at temperatures as low as 20 K. The samples were grown by the two-zone Bridgman method. We confirm that, within a two-mode model, both the CdTe- and ZnTe-like TO-mode frequencies increase with $x$, unlike any other II-VI ternary compound with known phonon modes, and unlike a recent report for $Cd_{1-x}Zn_xTe$ films grown on GaAs by molecular-beam epitaxy. The ZnTe-like TO frequency at very low $x$ is near the prediction from impurity-mode theory. The infrared spectra show signs of clustering behavior like that seen in $Hg_{1-x}Cd_xTe$.

## INTRODUCTION

The tunable lattice and band properties of $Cd_{1-x}Zn_xTe$ make it a useful substrate material with potential for devices, and it is an interesting II-VI compound in its own right; yet there has not been much recent optical examination of its unusual phonon modes. In the 1970s, three groups[1-3] used infrared or Raman spectroscopy to study the transverse-optical (TO-) and longitudinal-optical- (LO-) phonon modes in bulk $Cd_{1-x}Zn_xTe$ at 300 and 80 K. All three papers report two-mode behavior, with similar plots of the CdTe- and ZnTe-like TO and LO frequencies versus $x$. All show the remarkable result stated by Vodop'yanov *et al.*[2]; unlike every other two-mode system studied at the time, where one mode's TO frequency increases with $x$ and the other decreases, in $Cd_{1-x}Zn_xTe$ both frequencies grow with $x$.

The latest available compendium of II-VI ternary compounds[4] still shows no other compound with this behavior. In more recent work, Olego *et al.*[5] obtain different results for $Cd_{1-x}Zn_xTe$ films grown on GaAs substrates by molecular-beam epitaxy. Although their Raman data show a ZnTe-like TO-mode frequency increasing with $x$, they report a CdTe-like TO frequency independent of $x$. One motivation for our study of $Cd_{1-x}Zn_xTe$, therefore, is to reexamine the unique mode behavior. Unlike any of the earlier work, we combine infrared data, which emphasize the TO modes, with Raman data, which are superior for the LO modes.

A second motivation is to examine the phonons at very small values of $x$. It is at the low value $x=0.04$ that $Cd_{1-x}Zn_xTe$ is lattice matched to $Hg_{0.78}Cd_{0.22}Te$ for infrared detectors. A deeper reason, given by Wei *et al.*,[6] is that the study of $Cd_{1-x}Zn_xTe$ at low concentrations of ZnTe should help connect impurity theory with the theory of mixed crystals.

A third motivation is not limited to $Cd_{1-x}Zn_xTe$. It is that infrared phonon data can reflect details of clustering behavior in ternary compounds, as Verleur and Barker[7] showed in exhaustive infrared analysis of $GaAs_xP_{1-x}$ and other III-V compounds. The same observation has been made in a II-VI system by Kozyrev *et al.*,[8] who interpreted fine structure in infrared phonon spectra of $Hg_{1-x}Cd_xTe$ as arising from nonrandom clustering. We examine $Cd_{1-x}Zn_xTe$ as part of our continuing infrared and Raman study of such clustering in a variety of II-VI ternary compounds.

## SAMPLES AND EXPERIMENTAL METHODS

The $Cd_{1-x}Zn_xTe$ alloys were made at the Massachusetts Institute of Technology, by reacting the 99.9999%-pure elemental constituents in evacuated and sealed quartz tubes. The sample $x$ values of 0.005, 0.01, 0.03, 0.1, 0.2, 0.3, 0.4, and 0.5 were calculated from the mass densities. These precast alloys were regrown by directional solidification in a Bridgman-Stockbarger-type crystal-growth furnace. Regrowth occurred at the rate of 1.2 mm/h in the furnace adiabatic zone with a temperature gradient of about 15 °C/cm. The resulting boules were sliced perpendicular to the growth direction. The slices used for the infrared and Raman measurements were annealed at 600 °C in a Cd-saturated atmosphere for about 5 d. Their surfaces were prepared by lapping, mechanical polishing, and etching in bromine-methanol solution.

The infrared measurements at Emory University used a Fourier spectrometer and a Golay detector, for good signal-to-noise ratios between 40 and 240 $cm^{-1}$. Data were taken at near-normal incidence and at sample temperatures of 300, 80, and 20–30 K. The main features of the infrared spectra did not change significantly between 80 and 20–30 K, but small features sharpened noticeably at the lowest temperatures. The incident angle was about 9°, a negligible deviation from normal incidence. The reflection coefficient was measured by ratioing the intensity of the light reflected from the sample against that reflected from a reference mirror made of coin silver with about 98% reflectance.

Raman measurements, also performed at Emory University, were made in the near-backscattering geometry on the same samples held at 80 K. The exciting light came from an $Ar^+$ laser with a focused beam of diameter $<0.3$ mm. The scattered light was dispersed by a triple spectrometer and accumulated by an optical multichannel analyzer (OMA), which gave high sensitivity with resolutions of $\sim 2$ $cm^{-1}$.

## RESULTS AND ANALYSIS

Figures 1 and 2 show our main infrared and Raman data, respectively, at low temperatures. In the infrared data, the CdTe-like peak is prominent at all values of $x$. The ZnTe-like structure is not visible for $x=0.005$, but appears as a shoulder near 175 $cm^{-1}$ for $x=0.01$ and is clear for all larger values of $x$. Both primary modes show additional small structure on or near the peaks, as indicated in Fig. 1. The figure also shows theoretical fits to the data, which come from a two-Lorentzian model for the dielectric function $\epsilon(\omega)$,

$$\epsilon=\epsilon_\infty+\sum_{j=1}^{2}\frac{S_j\omega_{Tj}^2}{\omega_{Tj}^2-\omega^2-i\omega\Gamma_j}\ , \tag{1}$$

where $\epsilon_\infty$ is the high-frequency dielectric constant and $S_j$, $\omega_{Tj}$, and $\Gamma_j$ are the strength, TO frequency, and damping constant, respectively, for the $j$th mode. We assigned one Lorentzian oscillator to each main peak, ignoring subsidiary structure on top of the CdTe-like or near the ZnTe-like peak.

A computer program used $\epsilon(\omega)$ in standard expressions to calculate the theoretical reflectivity, varying the parameters in Eq. (1) to give the best least-squares fit. The results are shown in Fig. 1. The fits follow each main peak sufficiently well to give the CdTe- and ZnTe-like TO frequencies, but with some discrepancies in shape.

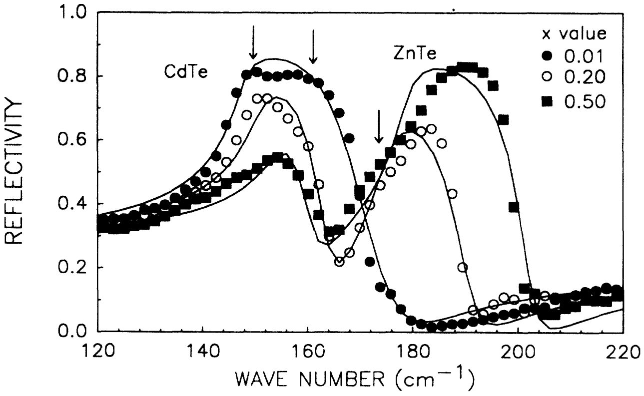

FIG. 1. Representative infrared-reflectivity data (symbols) and Lorentzian fits (solid lines) for bulk $Cd_{1-x}Zn_xTe$ at temperatures of 20–80 K. The primary CdTe- and ZnTe-like peaks are indicated. The primary ZnTe-like peak starts as a shoulder near 175 $cm^{-1}$ for $x=0.01$ and grows to prominence as $x$ increases. Arrows mark some of the additional small peaks or shoulders that may be related to clustering (see text).

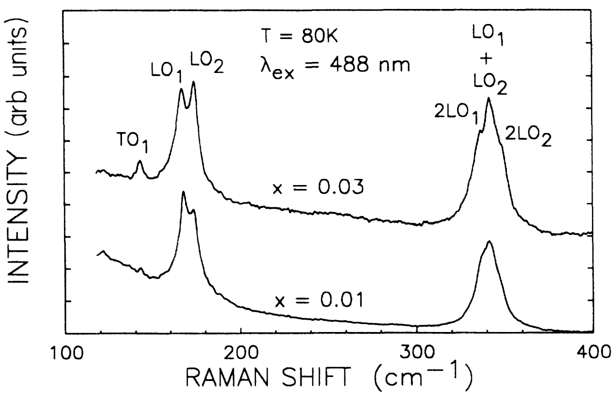

FIG. 2. Representative Raman-scattering data for bulk $Cd_{1-x}Zn_xTe$ at 80 K. CdTe-like (subscript 1) and ZnTe-like (subscript 2) TO and LO modes are marked. Higher-order overtones of the LO modes also appear strongly.

The LO frequencies came from Raman data like those in Fig. 2, which show clear CdTe- and ZnTe-like LO modes, denoted $LO_1$ and $LO_2$, respectively. We also show the higher-order overtones—$2LO_1$, $LO_1+LO_2$, and $2LO_2$—that we observed, to illustrate the excellent sample quality. As a check, we generated a set of LO frequencies from the fits to the reflectivity data. These were identified as the frequencies where $\mathrm{Re}[\epsilon(\omega)]=0$. The infrared values agreed with the Raman values to within a few $cm^{-1}$, but the direct Raman measurements are more accurate. We also note that the forbidden CdTe-like $TO_1$ mode, which appears weakly for the sample with $x=0.01$, strengthens for $x=0.03$. This suggests increased disorder.

Figure 3 displays the infrared TO frequencies and the Raman LO frequencies versus $x$. The ZnTe-like TO frequency at very low $x$ starts near the local-mode value predicted by Wei *et al.*, 171 $cm^{-1}$, and then increases with $x$ as previously observed.[1–3] The CdTe-like TO frequency also increases significantly with $x$. Both behaviors reconfirm the early observations.[1–3] This leaves unexplained why Olego *et al.* observed a constant CdTe-like TO frequency versus $x$ for their $Cd_{1-x}Zn_xTe$ films on GaAs. Possibly the stress from the lattice mismatch between film and substrate (10–14 %, depending on the $x$ value) influences the TO frequencies. Another possibility is that the TO modes are not sufficiently sharp in Raman data to give reliable frequencies.

The secondary structure in Fig. 1 has suggestive implications. The small peaks atop the main CdTe-like peak are very similar to those seen by Kozyrev *et al.*[8] in $Hg_{1-x}Cd_xTe$ and ascribed by them to nonrandom clustering. We speculate that the secondary peaks or shoul-

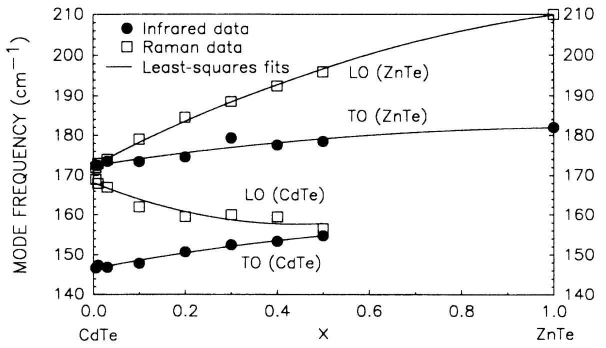

FIG. 3. TO- and LO-mode frequencies in $Cd_{1-x}Zn_xTe$ at 20–80 K vs $x$, from infrared and Raman data like those in Figs. 1 and 2. The data are fitted with quadratic curves as guides to the eye.

ders seen near and below the ZnTe peak also represent clustering behavior. Zamir *et al.*[9] have already used nuclear magnetic resonance to demonstrate the existence of clustering in bulk $Cd_{1-x}Zn_xTe$.

## CONCLUSIONS

Our results again show the anomalous character of the phonon modes in $Cd_{1-x}Zn_xTe$. As in earlier work, our analysis, based on simple two-mode behavior, gives a TO frequency for each mode which increases with $x$. This is a unique property, as far as is known. However, our preliminary observation of what may be cluster modes suggest that this model is too simple. A full-scale clustering fit is now under way, using the detailed model developed by Verleur and Barker.[7] If our surmises are correct, this may clarify the observed TO-mode behavior, provide fits to the additional small structure, and account for the deviations in shape between our two-Lorentzian fit and the main peaks.

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