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Infrared analysis of clustering in the II-VI-VI compound $CdSe_xTe_{1-x}$

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Infrared reflectivity spectra at 82 K for Bridgman-grown $CdSe_xTe_{1-x}$ crystals ($x = 0.05-0.35$) show the two expected transverse-optical phonon modes and an unexpected third mode. Analysis of the data, using the cluster model of Verleur and Barker, shows that these spectra represent substantial nonrandom clustering of the anions around the cations. The magnitude and x dependence of the clustering is similar to that seen in the related compound $CdSe_xS_{1-x}$ grown at the same temperature, although by a different growth method.

INTRODUCTION

The phonon modes of ternary compounds made from group-II and group-VI elements in the form II-II-VI, such as $Hg_{1-x}Cd_xTe$ and $Cd_{1-x}Zn_xTe$, have been extensively studied. The alternate form, II-VI-VI, is far less understood. For $CdSe_xTe_{1-x}$, a II-VI-VI ternary compound with zinc-blende structure for $x < 0.35$ and wurtzite structure for $x > 0.5$, the only complete infrared phonon data of which we know come from Vinogradov, Vodop'yanov, and Oleinik,[1] and Gorska and Nazarewicz.[2,3] However, Verleur and Barker[4] carried out earlier infrared work on the related compound $CdSe_xS_{1-x}$ and also analyzed the data to see whether the anions were randomly distributed around the cations.

The question of nonrandom or clustered atomic distribution in II-VI ternary compounds is important. It affects the fundamental analysis and behavior of these materials.[5,6] Detailed experimental evidence of such clustering has been obtained, for instance, for $Cd_{1-x}Zn_xTe$ and $Hg_{1-x}Cd_xTe$ by nuclear magnetic resonance,[7] and for $Hg_{1-x}Cd_xTe$ by infrared spectroscopy.[8] Infrared spectra for $Cd_{1-x}Zn_xTe$ and $Cd_{1-x}Mn_xTe$ also show features which may be related to clustering, although detailed analyses have not yet been made.[9,10]

A detailed infrared model for clustering comes from Verleur and Barker (hereafter called VB), who applied it to $GaAs_xP_{1-x}$ (Ref. 11) and then to $CdSe_xS_{1-x}$.[4] They considered all possible nearest-neighbor arrangements of anions around the cations. Each such configuration supports a characteristic set of infrared phonon modes. A careful analysis of the measured infrared spectrum then establishes the distribution of configurations, which can be analyzed to determine whether the distribution is random or nonrandom. VB expressed the degree of nonrandomness by a parameter β ($0 \leq \beta \leq 1$), defined for $CdSe_xS_{1-x}$ by

$$P_{SeSe} = x + \beta(1-x) ,$$
$$P_{SS} = (1-x) + \beta x , \tag{1}$$

where P_{SeSe} is the probability of finding a Se ion next to a Se ion, and P_{SS} has the same meaning for a S ion next to a S ion. In a completely random distribution, $P_{SeSe} = x$ and $P_{SS} = (1-x)$. Thus the larger the value of β, the larger the chance of finding a Se ion next to a Se ion, and a S ion next to a S ion, indicating a nonrandom distribution.

VB's reflectivity spectra for $CdSe_xS_{1-x}$ showed three or four clear phonon peaks for all x values, not just the two transverse optical (TO) peaks expected from a conventional two-mode ternary alloy. The additional structure, which appeared even at 300 K but sharpened at the lowest measurement temperature of 15 K, was associated with clustering. The early $CdSe_xTe_{1-x}$ data,[1-3] taken at 300 K only, showed two main phonon peaks for almost all samples, with only the slightest hints of unresolved shoulders, which were probably too indefinite to analyze. In any case they were not included in the analyses, and the spectra were interpreted in terms of typical two-mode behavior.

Our infrared data come from $CdSe_xTe_{1-x}$ samples with $x = 0.05$, 0.15, 0.25, and 0.35. At 300 K, as in the earlier data,[1-3] we see two main peaks and hints of a third unresolved one for $x = 0.25$ and 0.35. But our sharper spectra at 82 K clearly show three shoulders or peaks for $x = 0.15$, 0.25, and 0.35. Given this evidence of clustering behavior like that in $CdSe_xS_{1-x}$, we analyze our data with the VB model and obtain values for β.

SAMPLES AND EXPERIMENT

The single-crystal $CdSe_xTe_{1-x}$ samples were made at the Massachusetts Institute of Technology. Precast alloys were formed by reacting the 99.9999% pure elemental constituents at approximately 1150 °C in evacuated, sealed quartz tubes. The constituents were mixed to give x values of 0.05, 0.15, 0.25, and 0.35. These alloys were regrown by directional solidification in a Bridgman-Stockbarger-type furnace, at rates of 0.8–1 mm/h. Slices from the resulting boules, cut perpendicular to the

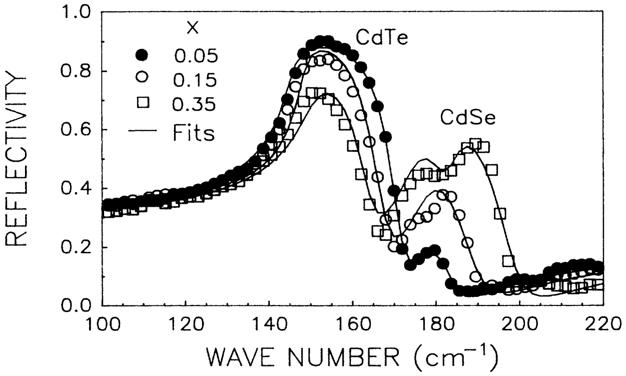

FIG. 1. Infrared reflectivity spectra from CdSe$_x$Te$_{1-x}$ at 82 K. Individual points are measured results. Lines are fits using the VB model with the parameters in Table I. The results for $x=0.25$ are omitted for clarity. The CdTe-like peak at 150 cm^{-1} and the single and split CdSe-like peaks near 180 cm^{-1} are indicated.

growth direction, were annealed at 650 °C in a Se atmosphere. Sample crystallinity and orientation were characterized by x-ray data and metallographic etching. Optical transmission measurements of the band gap, combined with the known linear relation between gap and composition,[12] gave x values within 3% of the calculated values. The samples were lapped, polished, and etched in a bromine-methanol solution prior to infrared measurements.

Infrared data were obtained at sample temperatures of 300 and 82 K, using a Fourier spectrometer operating at a resolution of 2 cm^{-1}. The radiation was not intentionally polarized; since the samples were of cubic structure, polarization should not have been a factor. The spectra are shown in Fig. 1. One noteworthy feature is that down to our lowest wave number of 20 cm^{-1} (not shown) we do not see the rising reflectivity which would indicate free-carrier effects. Hence, assuming that the alloy's electronic effective mass is near the value $0.1m_0$ for CdTe, we estimate that these samples have no more than 10^{16} carriers/cm^3.

DATA ANALYSIS

Before analyzing our more informative low-temperature data, we examined our results at 300 K. We did not carry out a cluster analysis, but simply fitted the spectra with a conventional two-oscillator Lorentzian dielectric function to find the transverse optical-phonon frequencies. The results agreed closely with the earlier data at 300 K.

TABLE I. Parameters for CdSe$_x$Te$_{1-x}$ which yield the fits in Fig. 1, using the Verleur-Barker model (Ref. 11). The fits all use the fixed set shown, except that the total and local ionic charges vary by 10% for different values of x. The values shown are for $x=0.35$. The notation is that of Verleur and Barker. e is the electronic charge, β is the nonrandom clustering parameter defined in Eq. (2).

	CdSe	CdTe
High-frequency dielectric constant	6.0	7.49
Lattice constant (10^{-10} m)	6.052	6.481
(Total ionic charge)/e	2.52	2.37
(Local ionic charge)/e	1.48	2.35
Nearest-neighbor force constants (kg/s^2)		
$k_1(1)$	58.5	
$k_1(2)$	81.4	
$k_1(3)$	110.3	
$k_1(4)$	601.0	
$k_2(2)$		1.3
$k_2(3)$		50.4
$k_2(4)$		66.1
$k_2(5)$		68.6
k_7	41.1	
k_8		43.6
Next-nearest neighbor force constants (kg/s^2)	Between atoms	Force constant
k_3	Se-Se	−25
k_4	Se-Te	0.5
k_5	Te-Te	24.4
k_6	Cd-Cd	48.9
Sample x value	β	
0.05	0.2	
0.15	0.46	
0.25	0.48	
0.35	0.29	

The present sharper spectra at 82 K display (Fig. 1) three clear peaks or shoulders for $x=0.15$, 0.25, and 0.35. The structureless peak centered at 150 cm^{-1} comes from the alloy's CdTe-like mode. The peak near 180 cm^{-1} for the sample with $x=0.05$ lies near the TO frequency for cubic CdSe, and splits at larger values of x.

We analyzed the data with the VB cluster model for the dielectric function. The model requires several parameters, given in Table I. To fit the data, we fixed the dielectric constants and lattice constants of the constituent compounds at their well-established values. The remaining quantities, the total and local ionic charges of CdTe and CdSe, and the force constants among the atoms were allowed to vary simultaneously to give the best fit, starting from VB's results for the force constants in $\text{CdSe}_x\text{S}_{1-x}$.

We also varied the $\text{CdSe}_x\text{Te}_{1-x}$ randomness parameter β, defined by

$$\begin{aligned} P_{\text{SeSe}} &= x+\beta(1-x)\ , \\ P_{\text{TeTe}} &= (1-x)+\beta x\ , \end{aligned} \qquad (2)$$

where P_{SeSe} is the probability of finding a Se ion next to a Se ion, and P_{TeTe} has the same meaning for a Te ion next to a Te ion. When we assumed a completely random distribution, that is, set $\beta=0$, we were never able to make a good fit. Like VB, we included damping terms (not shown in Table I) in the dielectric function and obtained values of magnitude similar to theirs.

Our best-fit parameter set, including the values of β, is given in Table I. One test of the model's validity is whether all four sample spectra can be fitted with the same parameters. We found that the set in Table I served for all the samples, except that the total and local ionic charges varied some 10% from sample to sample. VB had also found that the total effective ionic charge had to be varied for different x values to fit their data for $\text{CdSe}_x\text{S}_{1-x}$.

Figure 1 shows our best fits. Despite extensive efforts, the model yielded only two, not three, separate features for $x=0.15$ and 0.25. However, as the figure shows for $x=0.15$, the fitted peak at 180 cm^{-1} clearly encompasses both Se-like peaks, with similar behavior (not shown) at $x=0.25$. The fit is good at $x=0.05$ and 0.35, with all three peaks reproduced at $x=0.35$.

DISCUSSION AND CONCLUSIONS

To gain insight into nonrandom clustering, we compare our values for β to VB's results for $\text{CdSe}_x\text{S}_{1-x}$ and $\text{GaAs}_x\text{P}_{1-x}$.[11,4] Figure 2 shows that β for both $\text{CdSe}_x\text{Te}_{1-x}$ and $\text{CdSe}_x\text{S}_{1-x}$ lies between 0.3 and 0.5 in the midrange $x=0.2-0.8$, and drops off at high and low values of x. If nonrandom clustering is indeed similar for these two different compounds, what is the reason? Our $\text{CdSe}_x\text{Te}_{1-x}$ samples and VB's $\text{CdSe}_x\text{S}_{1-x}$ samples were made by different methods, so similarity of growth techniques is not the answer. However, both alloys were grown at about the same temperature, approximately 1200 °C for $\text{CdSe}_x\text{S}_{1-x}$ and approximately 1150 °C for $\text{CdSe}_x\text{Te}_{1-x}$, which hints at fundamental thermodynamic considerations.

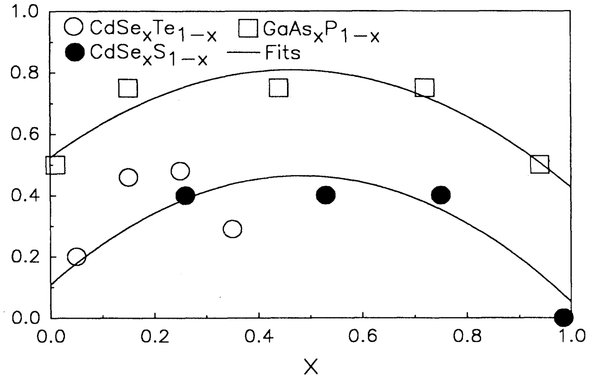

FIG. 2. Dimensionless clustering parameter β [defined in Eq. (2)] vs x for $\text{CdSe}_x\text{Te}_{1-x}$ (present results), $\text{CdSe}_x\text{S}_{1-x}$ (Ref. 4), and $\text{GaAs}_x\text{P}_{1-x}$ (Ref. 11). The lines are quadratic least-squares fits to the combined $\text{CdSe}_x\text{Te}_{1-x}$ and $\text{CdSe}_x\text{S}_{1-x}$ data, and to the $\text{GaAs}_x\text{P}_{1-x}$ data. Both fits are approximately of the form $\beta \propto x(1-x)$.

Figure 2 shows that β for $\text{GaAs}_x\text{P}_{1-x}$ is larger than for either II-VI alloy, but also falls off at high and low values of x. The least-squares fits to the data shown in the figure cannot be considered definitive because the data are limited and their scatter is large. Nevertheless, the fits to the combined II-VI data and to the data for $\text{GaAs}_x\text{P}_{1-x}$ have similar and suggestive shapes. Both fits are nearly of the form $\beta \propto x(1-x)$, that is, the incidence of nonrandom clustering is proportional to the product of the concentrations of the anions. This may be further evidence for universal behavior.

Our low-temperature infrared spectra from $\text{CdSe}_x\text{Te}_{1-x}$ cannot be fitted within the VB model without including nonrandom clustering. We obtain a short-range clustering parameter $\beta=0.2-0.5$, comparable in size and x dependence to VB's results for $\text{CdSe}_x\text{S}_{1-x}$. This similarity occurs in spite of different growth methods; hence it may reflect a basic factor, the thermodynamics of anion mixing during growth. Further infrared analysis of other II-VI-VI and II-II-VI compounds, now under way, should help convert these quasispeculations to definitive understanding.

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