Lattice dynamics of cadmium telluride*

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The phonon dispersion relation of CdTe at 300 °K has been measured for the [100], [111], and [110] directions of propagation using neutron inelastic scattering. The CdTe single crystal was grown from the melt with Cd present as ¹¹⁴Cd to reduce the neutron absorption of the specimen. The results have been fitted to a 14-parameter shell model that represents both the neutron data and other measured properties well when the non-neutron data are included in the fit. The present results, along with earlier measurements on α -Sn and InSb, complete the isoelectronic sequence α -Sn · InSb CdTe. The systematic trends in the lattice dynamics of this series of semiconductors (which is characterized by increasing band gap and ionicity) are brought out by comparison of frequency distributions calculated from the shell-model fits.

INTRODUCTION

We present here measurements of the phonon dispersion relation of CdTe. Together with measurements on α -Sn and InSb reported in an earlier paper¹ (hereafter called I), these complete the study of the lattice dynamics of the isoelectronic semiconductor sequence α -Sn - InSb - CdTe. The sequence is characterized by increasing band gap and ionicity, while the structure remains the same (zinc blende) and the lattice spacing and atomic masses change very little; hence it offers an ideal testing ground for theories of the lattice dynamics of semiconductors. A similar sequence exists in the next-higher row of the Periodic Table as $Ge \rightarrow GaAs \rightarrow ZnSe$, but available results² on ZnSe are at present incomplete. In principle, both sequences could be extended to the I-VII members, which exist in the zinc-blende phase as γ -AgI and γ -CuBr, respectively. However, the former is a metastable phase³ that occurs only in very small crystallites, while the latter shows anomalous behavior in the lattice dynamics that has been explained by a mechanism in which the Cu atoms occupy metastable positions.⁴

Owing to the very high thermal-neutron-absorption cross section of ¹¹³Cd found in natural Cd, the experimental measurements were made with a crystal composed predominantly of the isotope ¹¹⁴Cd. The difference between the mass of this isotope (113.9) and the average atomic mass of natural Cd (112.4) is expected to have a negligible

effect on the phonon frequencies. The sample preparation is described in Sec. II.

The neutron-scattering experiments and results for the phonon-dispersion curves are discussed in Sec. III. Section IV contains the results of a shellmodel fit to the data. In principle, one would like to analyze the data in terms of a more fundamental microscopic model.⁵ Unfortunately, at present the information required to apply such models to III-V and II-VI compounds is unavailable.

II. CRYSTAL PREPARATION

Approximately 20 g of the isotope ^{114}Cd (98.8% 114 Cd, 0.47% 113 Cd, 0.32% 112 Cd, 0.40% other isotopes) was obtained from The Oak Ridge National Laboratory Isotope Sales Department. This material was purified by Eagle-Picher Industries, Inc., Miami, Oklahoma, with a vacuum distillation process yielding Cd metal with a purity of approximately 99.99%. $^{114}\mathrm{Cd\,Te}$ crystals were then grown at Hughes Research Laboratories, Malibu, California, using techniques previously developed there.⁶ The Cd was mixed with pure Te in proportions that gave a slight Te excess and sealed under vacuum in a 17-mm diameter quartz ampoule. The crystal was grown by the Bridgman method. The temperature profile of the furnace was adjusted by means of Variac transformers controlling the power input to the seven heating elements. The profile used had a temperature of 1125°C at the hottest point; the freezing point of the material $(1041 \degree C)$ was reached at a point about 145 mm

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(0,0,ξ)									
ζ	$\Delta_3(A)$	4)	$\Delta_1(A)$	$\Delta_1(O)$	$\Delta_3(O)$				
0.0	0.0		0.0	5.08(10)	4.20(10)				
0.2	0.54	(2)	0.96(3)	5.10(8)	4.25(10)				
0.4	0.91	(2)	1.85(3)	4.90(8)	4,38(10)				
0.6	1.07	(3)	2.62(4)	4.47(8)	4.35(10)				
0.8	1.06	(3)	3.25(4)	4.20(8)	4.46(10)				
1.0	1.05	(3)	•••	• • •	4.44(6)				
(ξ,ξ,ξ)									
ζ	Λ ₃ (Α	A)	$\Lambda_1(A)$	$\Lambda_1(O)$	$\Lambda_3(O)$				
0.0	0.0		0.0	5.08(10)	4.20(10)				
0.1	0.42	(2)	0.91(3)	•••	4.19(5)				
0.2	0.68	(2)	1.82(3)	4.99(8)	4,27(8)				
0.3	0.81	(3)	2,55(5)	4.81(8)	4.20(6)				
0.4	0.88	(3)	3.00(8)	4.55(7)	4.33(6)				
0.5	0.88	(3)	3.25(8)	4.33(7)	4.33(6)				
(と と 0)									
ζ	$\Sigma_2(A)$	$\Sigma_1(1)$	$\Sigma_1(2)$	$\Sigma_1(3)$	$\Sigma_1(4)$				
0.0	0.0	0.0	0.0	5.08(10)	4.20(10)				
0.2	0.56(2)	0.74(2)	1.37(2)	5.00(20)	4.30(10)				
0.4	0.93(3)	1.30(2)	2.41(5)	• • •	4.30(10)				
0.6	1.10(3)	1.58(3)	3.16(8)	4.60(20)ª	4.30(20)ª				
0.8	1.10(3)	1.40(3)	3.74(10)	4.55(10)	•••				
1.0	1.05(3)	1.05(3)	•••	4.44(6)	•••				

TABLE I. Phonon frequencies in CdTe at 300 °K. Frequency (THz) vs. reduced wave vector $\xi = aq/2\pi$.

^aThese values represent the results from a single broad peak fitted to the sum of two peaks of the appropriate resolution width.

lower down, the gradient there being about $0.8 \degree C/mm$. The ampoule was inserted in the inner ceramic tube of the furnace at the hottest point, and then lowered at a rate of 6 mm/h until it reached the bottom of the tube—at a temperature of approximately $800 \degree C$ —at which time it was removed and cooled in air. The inside of the ampoule was initially coated with graphite so that the ingot could be removed easily, when the ampoule was broken. In the first run, with the elemental

material, the ampoule was inserted very slowly into the furnace so that combination took place without large vapor pressures developing. Stoichiometry was obtained in the first run, so that this precaution was unnecessary in subsequent runs. The ampoules were blown with a pointed tip at the bottom on the inside surface; otherwise no special measures were taken to seed the growth.

Grain boundaries and twin planes can easily be identified in CdTe boules by visual examination after light sandblasting of curved surfaces or light lapping of flat ones. The first boule produced had relatively few grain boundaries, but the large number of twin planes made it impossible to obtain a good crystal for the purposes of neutron-scattering experiments.⁷ This boule was then used as the starting material for a second run. The second boule was also polycrystalline, but had a large monocrystalline region in the middle section, from which it was possible to cut out a single crystal weighing 10.58 g, almost entirely free of twin planes. By means of visual examination, x-ray Laue photographs, and neutron-diffraction measurements, it was confirmed that no other crystals of significant size were present. The mosaic spread was less than the angular resolution of the neutron diffractometer $(0, 2^{\circ})$.

III. EXPERIMENTS AND RESULTS

The experiments were carried out using the HB-3 triple-axis spectrometer at the High Flux Isotopes Reactor, Oak Ridge National Laboratory. All measurements were obtained using the constant- \vec{Q} technique with fixed analyzer energies of 7.0 THz and, to a lesser extent, 9.0 THz. The latter analyzer energy was used to allow measurements of some optic modes at more favorable reciprocallattice points. The crystal was mounted with a [110] axis vertical for most of the measurements, but the Σ_2 TA mode ([110] direction) was measured with the crystal oriented to have an [001] axis ver-



FIG. 1. Dispersion relation for CdTe at 300 °K. Symbols represent neutron measurements; solid lines represent shell-model calculation described in text (either I or II, as they give indistinguishable results).

TABLE II. Observed and calculated elastic and dielectric properties for CdTe at 300 °K.

			Calculated	
Property	Units	Observed	I ^{a,b}	IIc,b
C ₁₁	10 ¹²	0.533(2) ^d	0.556	0.554
C_{12}	$dynes/cm^2$	0.365(2)	0.349	0.359
C_{44}		0.204(1)	0.210	0.210
€∞		7.1(1) [•]	6.9	6.8
ϵ_0		10.2(1)•	10.2	10.0
ν_{TO}		4.20(10)	4.20	4.19
	$\mathbf{T}\mathbf{H}\mathbf{z}$	4.22(2)•		
ν_{LO}		5.08(10)	5.10	5.07
		5.03(2) ^e		
e_{14}	10^4 esu/cm^2	$1.0(1)^{f}$	13.4	1.00
a	Å	6.486		
M	amu	113.9,127.6		

^aModel I; e_{14} not included in data to be fitted.

^bIn both model I and model II, all non-neutron data were assigned low weights in the fitting procedure corresponding to standard deviations equal to 10% of the measured values.

^cModel II; e_{14} included in data to be fitted. ^dReference 11.

Reference 8.

^fReference 12.

tical. A limited number of other mode frequencies were checked in both orientations; good agreement was obtained.

The measured frequencies and estimated errors (95% confidence limits) are shown in Table I for the three directions measured. The dispersion relations are shown graphically by the symbols in Fig. 1. Where no error bars are shown, the errors are smaller than the symbols. The continuous lines represent the fitted shell-model results (discussed more fully in Sec. IV). The neutron results for the frequencies of the optic modes at the origin Γ are $\nu_{LO} = 5.08 \pm 0.10$ THz and $\nu_{TO} = 4.20 \pm 0.10$ THz, in good agreement with the infrared results⁸ of 5.03 and 4.22 THz, respectively.

The character of the various branches and symmetry points have been discussed fully in I and will not be repeated here. A more detailed comparison of the present results for CdTe to those for α -Sn and InSb will be given in Sec. IV, in terms of the shell-model fits to the three substances.

IV. SHELL-MODEL FITS

The present results have been fitted to the shell model developed by Cochran⁹ and by Dolling.¹⁰ This model, and our notation for it, have been described fully in I. Therefore, we shall give only a brief description of the model here, and point out that the model can be used to describe all of the available data, including the piezoelectric and dielectric constants. The model used has 14 parameters, and, as such, the parameters are not expected to have much physical significance. The 14 parameters used are $\alpha_R = \alpha_T$, a first-neighbor ion-ion and/or ion-shell short-range force constant; γ_R , γ_T , and γ_S , the ratio of the two independent first-neighbor force constants for ion-ion, ion-shell, and shell-shell forces; Z_1 , the charge on the negative Te ion; $S_R = \alpha_S / \alpha_R$; π_1 , and π_2 , the atomic polarizabilities of Te and Cd, respectively; d_1 , and d_2 , the mechanical polarizabilities; and μ , λ , γ , δ , and general second-neighbor force constants. The expressions for the dynamical matrix and for various physical quantities in terms of these parameters are given in I.

This model was fitted to the measured frequencies and to the elastic constants, ¹¹ dielectric constants, ⁸ and piezoelectric constant. ¹² The latter quantities were assigned a weight corresponding to 10% errors during the fitting procedure, so that the model would be most sensitive to the measured neutron results. The fit converged slowly to a reasonably well-defined but shallow minimum with a final value of $\chi^2 = 1.65$. This represents an extremely good fit, so that one would expect the model to give a good representation of the disper-



FIG. 2. Dispersion relations for α -Sn (solid lines), InSb (dashed lines), and CdTe (chain lines) derived from shell-model calculations using the parameters of Table III.

TABLE III. Shell-model parameters for α -Sn, InSb, and CdTe.

			CdTe	
Parameter	α –Sn ^a	InSb ^a	Ip	IIc
α _R	12.81	12.08	9.63	9.10
\boldsymbol{Z}_1	0.0	-0.061	-0.440	- 0.270
π_1	0.0841	0.0852	0.0659	0.0529
π_2	0.0841	0.0685	0.0195	0.0397
d_1	0.695	0.677	0.466	0.322
d_2	0.695	0.823	0.447	0.581
S_R	0.953	1.491	3.246	3.677
γ_R	0.352	0.577	0.763	0.745
γ_T	-0.880	0.226	0.488	0.392
γ_s	-7.001	-1.163	0.404	0.269
μ_R	0.048	0.055	0.122	0.188
λ_R	0.115	-0.470	-0.015	-0.175
ν_R	1.256	0.499	0.321	0.332
δ _R	1.048	0.534	0.323	0.186
A	-	0		

^aReference 1. ^cSee Table II, footnote c. ^bSee Table II, footnote a.

sion relations in unmeasured directions. The fitted model results are shown in Fig. 1, from which it can be seen that, with the exceptions of the $\Sigma_2 TA$ and $\Lambda_3 TA$ modes, the agreement is excellent. The failure of the shell model to predict these two branches has been noted previously for the zinc-blende semiconductors. The fit of the model to the non-neutron data is shown in Table II; once again the agreement is fairly good.

It should be noted, however, that some of the model parameters are quite sensitive to the input data. For example, a fit to all of the data except the piezoelectric constant e_{14} converged to an excellent fit ($\chi^2 = 1.60$), but predicted $e_{14} = 13.0 \times 10^4$ esu/cm^2 , as opposed to the value of $1.0 \times 10^4 esu/cm^2$ cm² found when this constant was included in the fitting data. The parameters that changed most dramatically with the inclusion of e_{14} were Z_1 and λ , although other parameters also shifted by lesser amounts to accomodate the different data sets. The two sets of parameters found are shown in Table III. No other quantities calculated differed significantly for the two models. Hence, as stated earlier, the exact values found for the shell-model fits cannot be assigned much physical significance, in spite of the fact that the final model (Model II in Table III) represents all of the available data well. The parameters found for α -Sn and InSb in I are also shown in Table III for completeness.

The shell-model parameters listed in Table III for α -Sn and InSb and CdTe were used to compare the three substances in two ways. First, the calculated dispersion relations are shown in Fig. 2. The splitting of the LO and TO modes at Γ is larger for CdTe than for InSb, as expected from the larger band gap. A general "softening" of the optic and LA modes in the sequence α -Sn-InSb-CdTe is also evident from the figure, while the tranverse acoustic modes are much less affected. It should be noted that the average mass and the lattice constants for the three materials are almost identical. These results are summarized in Fig. 3, which shows the frequency distributions $[g(\nu)]$ obtained for the three materials using the method of Gilat and Raubenheimer¹³ and the shell-model parameters. The effects discussed above are clearly evident in this figure.

V. CONCLUSIONS

The phonon-dispersion relation of CdTe at 300° K has been measured for the three major symmetry directions. This completes the sequence α -Sn-InSb-CdTe (IV-IV, III-V, and II-VI), which cannot be extended to AgI because the zinc-blende structure is only metastable for this compound. It is hoped that the trends observed in this sequence will help to stimulate further theoretical work on the lattice dynamics of semiconductors and lead to models with more physical content than is apparent in the shell model. The shell model is, as expected, more successful for CdTe than for InSb or α -Sn, but the parameters found still seem to have little significance, so that the model serves only as an interpolation scheme. The same defects have been noted for the other II-VI semiconductors¹⁴ for which measurements of the dispersion relations are available.

The present results are in good agreement with infrared results at Γ and in moderate agreement with macroscopic measurements of the elastic constants.

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FIG. 3. Frequency distributions $g(\nu)$ for α -Sn (solid line), InSb (dashed line) and CdTe (chain line) derived from shell-model calculations.

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produce two essentially distinct crystals.

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