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Elastic constants and their pressure dependences in $Cd_{1-x}Mn_xTe$ with $0 \leq x \leq 0.52$ and in $Cd_{0.52}Zn_{0.48}Te$

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We have measured ultrasonic transit times to determine the elastic constants of $Cd_{1-x}Mn_xTe$ crystals with $0 \leq x \leq 0.52$ and of $Cd_{0.52}Zn_{0.48}Te$ at 296 K using hydrostatic pressures up to 4 kbar. It is found that Mn, but not Zn, weakens the zinc-blende crystal structure and makes it less stable under pressure. Applying a modified Born criterion to our data, we deduce the pressure expected to cause the transition to the rocksalt structure in each compound. The influence of Mn we attribute to Mn 3*d* orbitals hybridizing into the tetrahedral bonds.

I. INTRODUCTION

$Cd_{1-x}Mn_xTe$ is one of the semimagnetic semiconductors which have been the subject of extensive studies recently because of their important semiconducting, optical, and magneto-optic properties and the occurrence of a magnetic phase transition at low temperatures.[1–4] For $x \leq 0.7$, $Cd_{1-x}Mn_xTe$ has the cubic, zinc-blende (sphalerite) structure,[5] with a smaller lattice parameter[6] the larger the Mn content, whereas MnTe has the hexagonal NiAs structure[7] at ambient conditions. A desire to determine the influence of Mn on the structural stability prompted us to make ultrasonic transit-time measurements to determine how the elastic constants of $Cd_{1-x}Mn_xTe$, CdTe, and $Cd_{0.52}Zn_{0.48}Te$ crystals depend on hydrostatic pressure.

For $Cd_{1-x}Mn_xTe$ with $x = 0$, 0.06, 0.45, and 0.52, and $Cd_{0.52}Zn_{0.48}Te$ we obtained complete elastic constant versus pressure data at 296 K. In addition we measured the transit time of the piezoelectrically active shear mode in $Cd_{0.55}Mn_{0.45}Te$ as a function of pressure at 196 K for the reasons mentioned later.

As will be seen, our results indicate that substitution of Mn, but not Zn, for Cd makes the zinc-blende lattice less stable and permits us to determine from a modified Born stability criterion[8] what pressure is expected to cause a transition to the rocksalt structure.

Interpretation of our $Cd_{1-x}Mn_xTe$ results will invoke the effect of Mn 3*d* orbitals on the tetrahedral bonding. Justification for this invocation will be discussed in terms of experimental evidence[9,10] for the hybridization of Mn 3*d* states with Te 5*p* states and for the *d* levels of Mn, but not those of Cd and Zn, having energies[11,12] favorable for hybridization with sp^3 bonding orbitals.

II. EXPERIMENTAL DETAILS AND DATA ANALYSIS

Our samples were cut from single crystals grown by one of us (U.D.) using the Bridgman technique in the Central Sample Preparation Facility of the Purdue Materials Research Laboratory. The chemical compositions were determined by electron microprobe analysis using equipment in the Department of Geosciences. After x-ray orientation, the samples were cut with a diamond wire saw and then polished with successively finer SiC and alumina grits down to 0.05 μm to obtain two flat and parallel (to within 2×10^{-4} rad) faces perpendicular to the [110] direction. In addition, a $Cd_{0.55}Mn_{0.45}Te$ sample was prepared with [100] flat faces. The density of each sample was determined by a loss of weight in water method and is listed in Table I along with sample length in the direction of wave propagation. Sample length was measured with a Brown and Sharpe Differential Electronic Gauge using standard gauge blocks as references.

TABLE I. Sample density and length in the direction of wave propagation.

Sample	Density (g/cm^3)	Length (cm)	Propagation direction
CdTe	5.854±0.005	0.5029±0.0001	[110]
$Cd_{0.94}Mn_{0.06}Te$	5.817	0.6360	[110]
$Cd_{0.55}Mn_{0.45}Te$	5.366	0.3089	[110]
$Cd_{0.55}Mn_{0.45}Te$	5.366	0.5603	[100]
$Cd_{0.48}Mn_{0.52}Te$	5.316	0.5207	[110]
$Cd_{0.52}Zn_{0.48}Te$	5.811	0.4745	[110]

TABLE II. Elastic constants of $Cd_{1-x}Mn_xTe$ and $Cd_{0.52}Zn_{0.48}Te$ at 296 K at atmospheric pressure in units of 10^{11} dyn/cm^2.

	CdTe	$Cd_{0.94}Mn_{0.06}Te$	$Cd_{0.55}Mn_{0.45}Te$	$Cd_{0.48}Mn_{0.52}Te$	$Cd_{0.52}Zn_{0.48}Te$
C_L[a]	6.52 ±0.05	6.5 ±0.1	6.1 ±0.1	6.1 ±0.1	7.3 ±0.1
C_S[b]	0.832±0.005	0.83±0.01	0.78±0.01	0.78±0.01	1.07±0.01
C_{44}[c]	1.99 ±0.01	1.98±0.02	1.84±0.02 (1.87±0.02)[d]	1.82±0.02	2.38±0.02
C_{11}	5.36 ±0.05	5.3 ±0.1	5.1 ±0.1	5.1 ±0.1	6.0 ±0.1
C_{12}	3.7 ±0.05	3.7 ±0.1	3.5 ±0.1	3.5 ±0.1	3.8 ±0.1
B[e]	4.25 ±0.05	4.2 ±0.1	4.0 ±0.1	4.0 ±0.1	4.5 ±0.1
C_{44}[f]			1.85±0.02		

[a] $C_L=(C_{11}+C_{12}+2C_{44})/2$ from [110][110] waves.
[b] $C_S=(C_{11}-C_{12})/2$ from [110][$1\bar{1}0$] waves.
[c] From [110][001] waves.
[d] From [100][001] waves at 196 K.
[e] $B=(C_{11}+2C_{12})/3$.
[f] From [100][001] waves.

Commercial X- and ac-cut quartz transducers plated coaxially with chrome-gold and having a fundamental frequency 30 MHz were bonded to each sample.

The pulse-echo-overlap technique[13] was employed to determine the round-trip transit time of both longitudinal and transverse ultrasonic waves. The procedure of McSkimin and Andreatch[14] was used to determine proper echo overlap at 1 bar.

Other experimental details (including pressure generation and measurement) and methods for obtaining the elastic constants and their pressure dependences from our transit-time data were similar to those used previously in this laboratory.[15,16] In determining the pressure dependences of the elastic constants we used the specific heat and thermal expansivities of CdTe (Refs. 17 and 18) and ZnTe (Ref. 19) to make the small adiabatic-isothermal correction.

III. RESULTS AND DISCUSSION

Elastic constant values for our samples at atmospheric pressure are listed in Table II; C_L, C_S, and C_{44} are the stiffness moduli directly determining the velocities of the ultrasonic waves we employed. Figure 1 shows how the shear wave moduli $C_S=(C_{11}-C_{12})/2$ and C_{44}, the bulk modulus B, and the lattice parameter a_L depend on Mn or Zn concentrations. It can be seen that substitution of either Zn or Mn for Cd causes a decrease in a_L. This is to be expected since Zn and Mn are smaller and lighter than Cd. From their smaller a_L's, samples containing Zn or Mn might be expected[20] to have larger elastic constants than CdTe. We find that this expectation is fulfilled in the case of $Cd_{0.52}Zn_{0.48}Te$ but not in the case of $Cd_{1-x}Mn_xTe$. We believe this indicates that Mn $3d$ orbitals exert considerable influence on bonding, whereas the d orbitals of Zn and Cd do not, as will be discussed later.

The pressure dependences of the elastic constants of all our samples except $Cd_{0.94}Mn_{0.06}Te$ are shown in Figs. 2 and 3. Results for $Cd_{0.94}Mn_{0.06}Te$ are not shown since they were within experimental error of those for CdTe. Actual data points have been omitted from Figs. 2 and 3 to avoid clutter. Experimental errors are indicated by the symbol on each line which is the locus of the data points.

A linear pressure dependence was found for the directly determined elastic moduli in all cases. The pressure derivatives of the elastic constants are listed in Table III. The longitudinal mode modulus $C_L=(C_{11}+C_{12}+2C_{44})/2$ increased with pressure in all samples. The largest increase was in $Cd_{0.52}Zn_{0.48}Te$ and the smallest increase in $Cd_{0.48}Mn_{0.52}Te$. The slow shear wave modulus

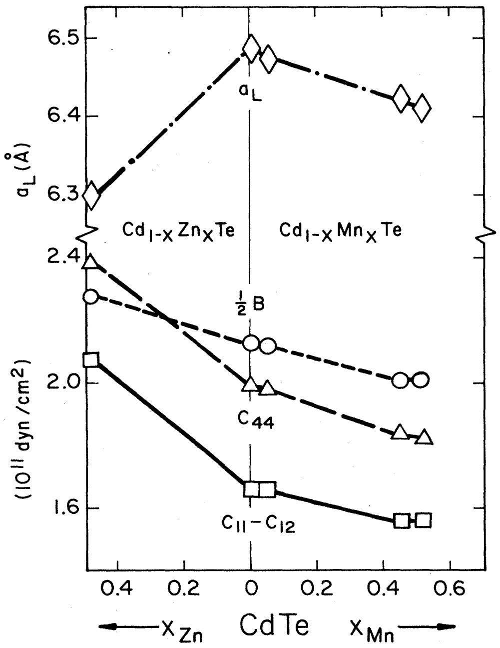

FIG. 1. Lattice parameter a_L, and elastic stiffness moduli at 296 K versus concentration of Zn or Mn substituted for Cd in CdTe. (a_L values are from Ref. 6 for $Cd_{1-x}Mn_xTe$ and from the density of $Cd_{0.52}Zn_{0.48}Te$.)

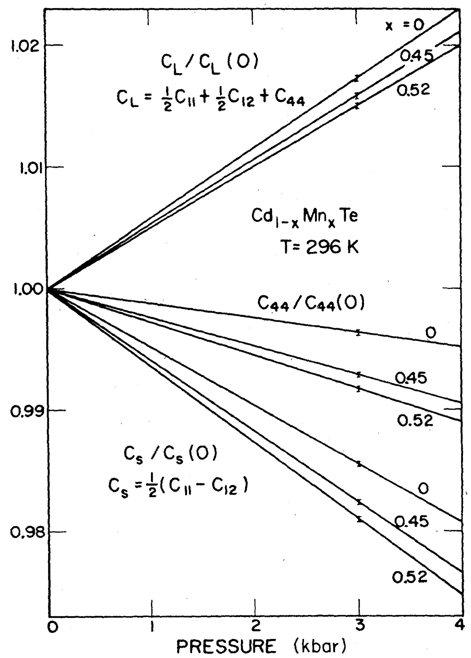

FIG. 2. Relative elastic constants versus hydrostatic pressure for $Cd_{1-x}Mn_xTe$ crystals at 296 K.

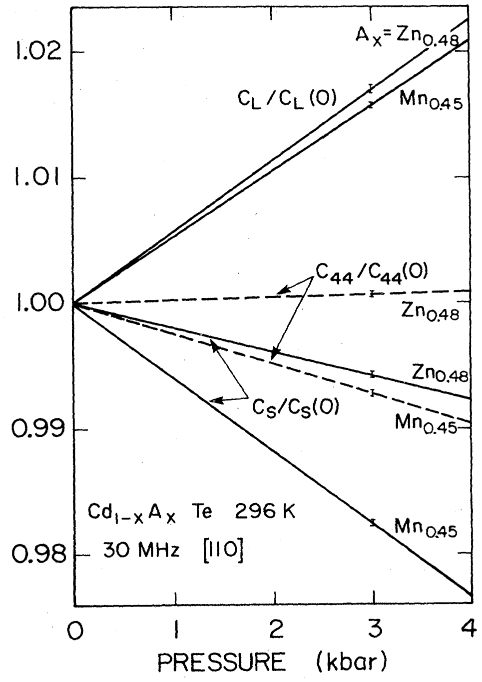

FIG. 3. Relative elastic constants versus hydrostatic pressure for $Cd_{0.55}Mn_{0.45}Te$ and $Cd_{0.55}Zn_{0.48}Te$ crystals at 296 K.

$C_S = (C_{11} - C_{12})/2$ decreased linearly with increasing pressure in all samples. The smallest decrease was in $Cd_{0.52}Zn_{0.48}Te$ and the largest decrease was in $Cd_{0.48}Mn_{0.52}Te$. The fast shear mode modulus C_{44} increased with pressure in $Cd_{0.52}Zn_{0.48}Te$ but decreased with increasing pressure in our other samples.

Since we have observed[21] much more piezoelectric stiffening of the fast shear mode propagating along [110] and polarized along [001] in $Cd_{0.55}Mn_{0.45}Te$ and $Cd_{0.48}Mn_{0.52}Te$ than in CdTe, we decided to determine if the elastic behavior being studied in this work would exhibit any observable effects of electromechanical coupling such as those found in CuCl.[22] Actually there was only a small chance that such effects would be observable in our $Cd_{1-x}Mn_xTe$ samples with $x = 0.45$ and 0.52 since the [110] [001] shear mode in them is stiffened by only about 1%. In any event, for $Cd_{0.55}Mn_{0.45}Te$ we measured the transit time as a function of pressure for the nonpiezoelectrically active shear mode propagating along [100] and polarized along [001] as a function of pressure at 296 K and for the [110] [001] fast shear mode at 196 K, where this mode is piezoelectrically stiffened (as well as having measured the pressure dependence of this mode at 296 K).

At 296 K our results for the [100] [001] mode yielded values for C_{44} and $\partial C_{44}/\partial P$ which were within experimental error of those obtained for the [110] [001] mode (see Tables II and III). The fact that both the [110] [001] and [100] [001] modes yield the same value for C_{44} is understandable since at 296 K mobile charge carriers screen out the piezoelectric field associated with the [110] [001] mode. In addition, the equal pressure depen-

TABLE III. Isothermal pressure derivatives of elastic stiffness moduli $C' \equiv (dC/dP)_T$ at 296 K except as indicated. Waves used to determine moduli and the relationship of the later to the C_{ij}'s are given under Table II.

	CdTe	$Cd_{0.94}Mn_{0.06}Te$	$Cd_{0.55}Mn_{0.45}Te$	$Cd_{0.48}Mn_{0.52}Te$	$Cd_{0.52}Zn_{0.48}Te$
C'_L	3.8 ± 0.1	3.8 ± 0.1	3.3 ± 0.1	3.1 ± 0.1	4.2 ± 0.1
C'_S	-0.40 ± 0.02	-0.40 ± 0.02	-0.44 ± 0.02	-0.49 ± 0.02	-0.21 ± 0.02
C'^{a}_{44}	-0.24 ± 0.01	-0.24 ± 0.01	-0.43 ± 0.02 $(-0.44 \pm 0.02)^b$	-0.50 ± 0.02	0.07 ± 0.02
C'_{11}	3.6 ± 0.1	3.6 ± 0.1	3.3 ± 0.1	3.1 ± 0.1	4.0 ± 0.1
C'_{12}	4.4 ± 0.1	4.4 ± 0.1	4.1 ± 0.1	4.1 ± 0.1	4.4 ± 0.1
B'	4.2 ± 0.1	4.2 ± 0.1	3.9 ± 0.1	3.7 ± 0.1	4.3 ± 0.1
C'^{c}_{44}			-0.42 ± 0.02		

[a] From [110] [001] waves.
[b] At 196 K.
[c] From [100] [001] waves.

dences of these modes at 296 K indicate that pressure does not cause the combination of enhanced electromechanical coupling and reduction of screening which would be necessary to produce a clearly measurable difference between the moduli of the [110] [001] and [100] [001] modes.

The nearly identical pressure dependences of the [110] [001] mode at 196 and 296 K indicate that pressure does not cause a significant enhancement of electromechanical coupling since the piezoelectric field is not screened out at 196 K whereas it is at 296 K.

We now consider criteria for elastic stability because we shall use one of them to deduce the pressure expected to cause the zinc-blende structure to transform to the rocksalt structure in our crystals containing Mn or Zn. The Born criterion[23] for a lattice to be mechanically stable states that the elastic energy density must be a positive definite quadratic function of strain. This requires that the principal minors (alternatively the eigenvalues) of the elastic constant matrix should all be positive. For cubic crystals these eigenvalues are $C_{11}+2C_{12}=3B$, $C_{11}-C_{12}=2C_S$, and C_{44}. Demarest *et al.*[8] developed a modified criterion which states that in all phase transitions involving a finite shift of the atoms, the transition will take place before any of the shear elastic constants reach zero. The ratio $\alpha=C_t/B$, where C_t is the smallest shear constant, will reach a critical low value at the transition. We deduced a critical value for C_S/B to be used for our ternary compound crystals by making a linear extrapolation of C_S and B for CdTe up to a pressure of 32 kbar where the structural (zinc blende to rocksalt) transition is known to occur in this binary compound.[24] It is pertinent to note that the critical values of the C_S/B ratio deduced from linear extrapolation of low-pressure elastic data on HgSe (Ref. 25) and HgTe (Ref. 26) agree very well with those deduced from experimental values of C_S and B obtained at a pressure just below that where the transition from the zinc blende to the cinnabar structure occurs in these Hg compounds.

Using the 0.126 critical value of C_S/B obtained for CdTe and our elastic data on $Cd_{0.55}Mn_{0.45}Te$, $Cd_{0.48}Mn_{0.52}Te$, and $Cd_{0.52}Zn_{0.48}Te$, we deduce for these three compounds structural transition pressures of 29, 27.5, and 67 kbar, respectively.

These results indicate that the substitution of Zn for Cd in the zinc-blende lattice makes the lattice more stable, whereas substitution of Mn makes the lattice less stable. The difference is due to, we believe, Mn but not Zn $3d$ orbitals hybridizing into the tetrahedral bonds because the $3d$ electrons are less tightly bound[11] in Mn than in Zn.

The occurrence of p-d hybridization in $Cd_{1-x}Mn_xTe$ has been inferred from the pressure[10] and temperature[9] dependences of the optical-absorption edge since these dependences are similar to those occurring in compounds which have a spin-orbit-splitting energy attributable to the combined effect of p and d contributions.[27,28] The likelihood of Mn $3d$ orbitals hybridizing with sp^3 Mn—Te bonding orbitals we infer from photoemission data[11] which indicate that Mn $3d$ levels lie within the valence band mainly in an energy range slightly higher than that of the sp^3 bonding orbitals. These energetics suggest that the Mn $3d$—containing hybrids have somewhat higher energy and less bond strength than the sp^3 orbitals. The Mn $3d$-sp^3 hybridization does not result in an excessive amount of charge in the bond since photoemission data[11] indicate that a large fraction of the Te $5p$ electrons are in energy states lying higher in the valence band than where most of the Mn $3d$ electrons are.

On the other hand, photoemission studies[12] reveal that Cd and Zn d states have much lower energies than the sp^3 states in CdTe, $Cd_{1-x}Mn_xTe$, and ZnTe. Thus the Cd and Zn d levels do not hybridize with the sp^3 bonding orbitals.

The importance of the above consideration for elastic behavior we have observed resides in the fact that the stability of the tetrahedrally coordinated structure against shear is due mainly to the charge in the tetrahedral bonds.[29] Thus factors which affect those bonds may alter the amount, location, or resistance to stress of the bonding charge. Reduction in bond charge has been associated with loss in bond strength and stability.[30] Finally we note that CuCl, which has much smaller elastic constants[22] than do II-IV compounds, is characterized[31] by a very large amount of p-d hybridization, and presumably sp-sd hybridization also, and is more ionic (i.e., has less bond charge) than II-VI compounds.

IV. CONCLUSION

Investigation of the ultrasonic transit times in CdTe, $Cd_{1-x}Mn_xTe$ ($x \leq 0.52$), and $Cd_{0.52}Zn_{0.48}Te$ as a function of pressure reveals weakening of the zinc-blende lattice when Mn but not when Zn is substituted for Cd in CdTe. The hybridization of the Mn $3d$ orbitals into the tetrahedral bonds is thought to be responsible.

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