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Elastic constants of Zn1-xMnxSe: Tetrahedral bond weakening due to Mn 3d(t2)aaSe 4p hybridization

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Elastic constants of $Zn_{1-x}Mn_xSe$: Tetrahedral bond weakening due to Mn $3d$ (t_2)-Se $4p$ hybridization

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We have made ultrasonic transit time measurements at 296 K on $Zn_{1-x}Mn_xSe$, with $x = 0.20$, 0.37, and 0.53, which reveal that Mn causes elastic constant reductions indicating a decrease in structural stability due to hybridization of Mn $3d$ (t_2) with Se $4p$ orbitals reducing the availability of the latter for tetrahedral bond formation. Comparison with previous results on $Cd_{1-x}Mn_xTe$ reveals that elastic constant reduction is greater the larger the anion-mediated superexchange between Mn ions.

I. INTRODUCTION

The elastic constants of the $A_{1-x}^{II}Mn_xC^{VI}$ compounds measured hitherto [$Hg_{1-x}Mn_xTe$ (Ref. 1) and $Cd_{1-x}Mn_xTe$ (Ref. 2)] *decrease* as Mn content increases. This reduction is in contrast to the *increase* expected from the fact that the lattice parameter a_L decreases as Mn content increases and the rule[3] that in a series of tetrahedrally bonded semiconductors the elastic constants are about proportional to $1/a_L^4$. In both $Hg_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xTe$ the shear elastic constants, C_{44} and $C_s \equiv (C_{11} - C_{12})/2$, exhibit greater percentage reductions than does the longitudinal wave constant C_{11}. In $Cd_{1-x}Mn_xTe$, a semiconductor with a wide gap which increases with x, these effects have been attributed[2] to weakening of tetrahedral bonding since in type IV elemental and III-V and II-VI compound semiconductors resistance to shear distortion (and structural stability) is mainly due to the covalent component of crystal bonding.[4,5] Such bond weakening is probably the main effect of Mn on the elastic constants of the $Hg_{1-x}Mn_xTe$ also, despite the fact that $Hg_{1-x}Mn_xTe$ changes[6] from being a semimetal at low x to being a small gap semiconductor when $x > 0.07$.

Interpretation of bond weakening by Mn in $Cd_{1-x}Mn_xTe$ was initially attributed[2] to Mn $3d$ orbitals hybridizing with the sp^3 tetrahedral bonding orbitals. Later a modified hybridization interpretation[7] was suggested because of photoemission evidence[8] for Mn $3d(t_2)$-Te $5p$ hybridization in $Cd_{1-x}Mn_xTe$ and the realization that stronger, covalent bonds can be formed when d orbitals as well as s and p orbitals are available.[9] The modified interpretation suggested that the effect most important for elastic constant reduction and bond weakening in $Cd_{1-x}Mn_xTe$ was Mn $3d(t_2)$-Te $5p$ hybridization leaving fewer Te $5p$ orbitals available for the tetrahedral bonds.

The magnetic exchange interaction between Mn ions in wide-gap, $A_{1-x}^{II}Mn_xC^{VI}$ diluted magnetic semiconductors (DMS) is thought to be via superexchange through the nearest anion[10,11] with the exchange integral J depending on the fourth power of matrix elements involving anion p orbitals with Mn $3d$ admixture and Mn $3d$ orbitals. Since the size of J depends on the type of anion,[10,12] the elastic constant reduction by Mn ought to also. Thus we have investigated $Zn_{1-x}Mn_xSe$ since it is a wide-gap selenide and has a larger J than does $Cd_{1-x}Mn_xTe$.

$Zn_{1-x}Mn_xSe$ crystals suitable for our ultrasonic measurements were available with x up to 0.53. We have used them for investigating the transit time and attenuation of ultrasound down to 1.5 K.[13,14] Reference 14 also includes low-temperature attenuation measurements on $Cd_{1-x}Mn_xTe$. A preliminary report on some of the $Zn_{1-x}Mn_xSe$ results has been published elsewhere.[13] In this paper we shall confine our attention to the room temperature elastic constants of $Zn_{1-x}Mn_xSe$ and compare them to results deduced from previous experiments on ZnSe (Ref. 15) and $Cd_{1-x}Mn_xTe$.[2]

Since our $Zn_{1-x}Mn_xSe$ samples with $x = 0.37$ and 0.53 had the hexagonal, wurtzite structure (as expected), while ZnSe and $Cd_{1-x}Mn_xTe$ have the cubic, zinc-blende (sphalerite) structure, we shall use equations based on Martin's transformations[16] to deduce hexagonal elastic constants for ZnSe and $Cd_{1-x}Mn_xTe$ from their measured cubic elastic constants.[15,2] We shall use average cation-cation spacing, d_c, to help characterize different samples since in a given DMS system d_c is the same linear function of x in both the zinc-blende and wurtzite structures.[17]

II. EXPERIMENTAL DETAILS AND DATA ANALYSIS

Our $Zn_{1-x}Mn_xSe$ samples were obtained from boules grown by one of us (U.D.) using the Bridgman technique in the Central Sample Preparation Facility of the Purdue Materials Research Laboratory. Pairs of flat, parallel faces were cut and lapped perpendicular to simple crystallographic directions located by Laue x-ray back reflection. The Laue photographs indicated that our $x = 0.37$ and 0.53 samples were hexagonal, wurtzite-structured single crystals as was expected and that even our 0.20 sample seemed to show spots indicating hexago-

nal symmetry although it was expected to have the cubic, zinc-blende structure.

Debye Scherrer x-ray diffraction from powdered $x = 0.20$ material revealed rings that could be indexed in both the cubic and the hexagonal systems with the cubic fit being better, but also contained rings forbidden in the cubic structure but allowed in the hexagonal system. Debye Scherrer patterns for $x = 0.53$ indicated that it was hexagonal in agreement with our Laue photographs and expectations. Our x-ray results for $x = 0.20$ probably indicate that polytypism is occurring as has been noticed previously by other people.[18] The polytypism is thought to consist of close-packed planes having alternatively cubic and hexagonal close packing. These planes are perpendicular to the [111] cubic direction or the [0001] hexagonal direction.

The fractional Mn concentration x was determined to within about ± 0.01 by energy-dispersive, x-ray fluorescence analysis using a Kevex XRF-0700 unit and the Kevex Micro-X700 analytical spectrometer. Sample density was measured to within about 0.20% by the liquid immersion method using distilled water.

The distance between each pair of parallel faces on a sample was measured to within one part in 10^4 using a commercial Brown and Sharpe (BS) sensor-differential amplifier system and standard gauge blocks. The BS system was used to determine that face parallelism was within about 5 s of arc. Sample flatness was checked with a helium light source and an optical flat to be within about 1 μm.

To one face of each pair on a sample a commercial (Valpey Corp.) X-cut or AC-cut quartz transducer plated with chrome gold and having a fundamental frequency of 30 MHz was bonded with Dow Corning 200 fluid or Nonaq stopcock grease.

The pulse echo overlap technique[19] was employed to determine the round-trip transit time of 2-μs pulses of longitudinal or transverse ultrasonic waves using commercial electronic instrumentation. Proper matching of cycles within each echo was accomplished following the procedure in Ref. 19. The velocity is given by $2Lf$ where L is the sample length in the direction of propagation and f, the frequency needed to overlap successive echoes, is the reciprocal of the transit time of the ultrasonic pulse. An elastic stiffness modulus, C (which may be a single elastic constant C_{ij} or combination of such constants), is obtained using the relation $C = \rho v^2$ where ρ is the sample density. To relate C to individual C_{ij} elastic constants, we used expressions in the literature.[20]

Sample properties are summarized in Table I that also indicates the propagation and polarization directions of the ultrasonic wave pulses we used. In view of the x-ray results indicating polymorphism in our $x = 0.20$ sample we have included in Table I both cubic and hexagonal designations for each mode.

III. RESULTS AND DISCUSSION

The elastic constants we determined experimentally for our $Zn_{1-x}Mn_xSe$ samples are listed in Table II. Since $C_{66}^H \equiv (C_{11}^H - C_{12}^H)/2$, four of the five independent hexagonal elastic constants have been obtained for $x = 0.37$ and 0.53. The other elastic constant C_{13}^H could not be determined because of our not having enough material to prepare an appropriate sample (with faces perpendicular to a direction 45° away from the c axis). Only three elastic constants are given for $x = 0.20$ because of the ambiguity in some transit time data caused by the polytypism of this sample. The value of C_{33}^H is firmly established even in the presence of polytypism. However, experimental results yield values for C_{11}^H and C_{44}^H which depend on whether cubic or hexagonal structure is assumed. Therefore we list two alternative values for each of these constants. In Fig. 1 we used the average of the alternatives for each of these constants. Actually the results for

TABLE I. Characteristics of $Zn_{1-x}Mn_xSe$ samples at 296 K and ultrasonic modes used.

x	Length (cm)	Density (g/cm^3)	Mode Propag.	Mode Polariz.
0.20	0.5731	5.111	[0001]^a [111]^b	[0001]^a [111]^b
			[0001]^a [111]^b	$\perp$[0001]^a [1$\bar{1}$0]^b
0.20	0.5434	5.111	[110]	[110]
0.37	0.4100	4.886	[10$\bar{1}$0]	[0001]
			[10$\bar{1}$0]	[0100]
			[10$\bar{1}$0]	[10$\bar{1}$0]
0.37	0.4348	4.886	[0001]	[0001]
			[0001]	$\perp$[0001]
0.53	0.3551	4.758	[0100]	[10$\bar{1}$0]
			[0100]	[0001]
			[0100]	[0100]
0.53	0.5629	4.758	[0001]	$\perp$[0001]
			[0001]	[0001]

^{a}If hexagonal.
^{b}If cubic.

TABLE II. Hexagonal elastic constants C_{ij}^H (in 10^{11} dyn/cm^2) determined experimentally for $Zn_{1-x}Mn_xSe$ with $x = 0.20$, 0.37, and 0.53 in this work and those calculated for ZnSe using experimental cubic constants from Ref. 15 in equations from Ref. 6 given in the Appendix and average cation-cation spacing d_c (in Å) from Ref. 17. Since $x = 0.20$ is polymorphic, we give C_{11}^H and C_{44}^H values deduced assuming both hexagonal and cubic symmetry.

x	0	0.20	0.37	0.53
C_{11}^H	10.42	9.81 hex. 9.58 cub.	8.77	8.25
C_{12}^H	4.76		4.67	4.56
C_{13}^H	3.53			
C_{33}^H	11.65	10.89	10.06	9.34
C_{44}^H	2.40	2.18 hex. 1.92 cub.	1.83	1.68
C_{66}^{Ha}	2.83		2.05	1.84
d_c	4.0090	4.0419	4.0699	4.0962

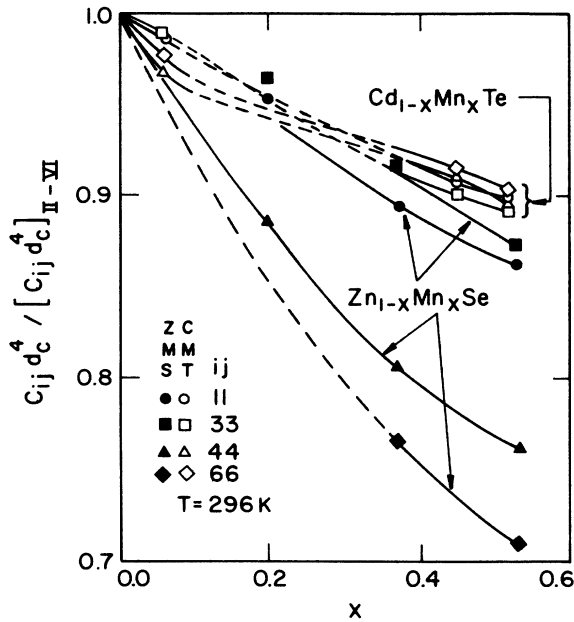$^a C_{66}^H \equiv (C_{11}^H - C_{12}^H)/2$.

FIG. 1. Hexagonal elastic constant times fourth power of the cation-cation separation for $Cd_{1-x}Mn_xTe$ and $Zn_{1-x}Mn_xSe$ divided by the respective values for CdTe and ZnSe. Hexagonal elastic constants were deduced for ZnSe and $Cd_{1-x}Mn_xTe$ using their experimentally determined cubic elastic constants in equations based on Martin's transformations.

criterion[22] which states that, for stability, a shear-to-bulk modulus ratio must be larger than some small, but nonzero, value since the behavior of the longitudinal moduli is dominated by the volumetric (i.e., bulk modulus) component.

More quantitative estimates also indicate that the shear-to-bulk modulus ratios decrease as Mn content increases in $Zn_{1-x}Mn_xSe$ thus implying that Mn decreases structural stability according to the modified Born criterion. One type of estimate we made by assuming that the bulk modulus is proportional to $1/d_c^4$, where d_c is the average separation between cations.[17] The results are shown in Fig. 1, where we see that the $C_{44}^H d_c^4$ and $C_{66}^H d_c^4$ products for $Zn_{1-x}Mn_xSe$ are considerably and progressively smaller for $x = 0.37$ and 0.53 than for ZnSe. The, $1/d_c^4$ variation for the bulk modulus is consistent with the fact that in zinc-blende-structured semiconductors the bulk modulus is approximately proportional to $1/a_L^4$ where a_L is the lattice parameter.[3] Our other way of estimating shear-to-bulk modulus ratios involved calculation of the bulk modulus by using our experimental C_{ij}^H's and values estimated for C_{13}^H by assuming that the C_{13}^H/C_{33}^H ratio had the same value as in ZnSe. This procedure yielded greater decreases in the bulk modulus than that deduced from $1/d_c^4$ but still gave considerable percentage decreases in shear-to-bulk modulus ratios at $x = 0.37$ and 0.53 since the experimental shear moduli decreased about twice as much as did the bulk modulus obtained from the C_{ij}^H's. We have shown results obtained using d_c^4 since d_c values are well known and facilitate comparison with $Cd_{1-x}Mn_xTe$ data.

To discuss structural stability further we review some specifics about tetrahedrally bonded, compound semiconductors. First of all, their elastic constants[4] depend primarily on the forces needed to stretch and bend the tetrahedral bond between neighbor ions (although there are smaller ionic contributions also). Furthermore, in the cubic zinc blende structure the C_{ij}^c's are related simply to the bond-stretching (α) and bond-bending (β) force constants.

The longitudinal wave elastic constants (e.g., C_{11}^c, etc.) and the C_{44}^c shear constant depend on linear combinations of α and β while the slow shear wave constant $C_s^c \equiv (C_{11}^c - C_{12}^c)/2$ depends on β, but not on α. Stability against shear strain depends on interatomic bond-bending forces describable by β and thus on the C_s^c shear constant.

The β/α ratio is approximately proportional to $1 - f_i$ where f_i is the Phillips ionicity.[23] Dielectric theory has been used to derive a relation between β itself and $1 - f_i$ which seems to be valid for III-V but not for II-VI compound semiconductors.[5]

Unfortunately in the hexagonal, wurtzite structure neither of the shear elastic constants depends simply on a bond-bending force constant.[24] However, since the same basic tetrahedral building blocks are involved in wurtzite as in zinc blende, we infer that the reduction of the shear constants by Mn in $Zn_{1-x}Mn_xSe$ indicates a reduction in bond-bending forces and thus of the tetrahedral bond's ability to resist shear. Furthermore we infer that the

$x = 0.20$ are not crucial for interpreting the effect of Mn on the elastic constants of $Zn_{1-x}Mn_xSe$ since we have more accurate and complete results for $x = 0.37$ and $x = 0.53$ samples.

In order to compare the elasticity of our hexagonal $Zn_{1-x}Mn_xSe$ samples with that of cubic ZnSe and $Cd_{1-x}Mn_xTe$ (and also with that of $Zn_{0.80}Mn_{0.20}Se$ when it is assumed to be cubic) we calculated hexagonal elastic constants for the cubic materials using the equations given in the Appendix. These equations are based on the assumptions[16] that elastic behavior depends mainly on atomic interactions within the basic tetrahedral building blocks in both structures, and that the wurtzite structure is obtained by rotating the tetrahedral building blocks of zinc blende into two inequivalent trigonal orientations having different internal strains. The equations have been validated by their successful application to ZnS (Ref. 16) for which experimental elastic constants are available for both the zinc-blende and wurtzite structures.

From Table II we can see that all the elastic constants of $Zn_{1-x}Mn_xSe$ decrease as Mn content increases and that the C_{44}^H and C_{66}^H shear elastic constants show much greater decreases than the C_{11}^H and C_{33}^H longitudinal ones. The shear constant decreases imply a reduction in structural stability since C_{44}^H and C_{66}^H are two of the eigenvalues of the hexagonal elastic constant matrix and, according to the Born criterion,[21] elastic eigenvalues must be nonzero for structural stability. The greater decreases in C_{44}^H and C_{66}^H than in C_{11}^H and C_{33}^H imply reduction of structural stability according to a modified Born

lesser reductions in the longitudinal than in the shear $d_c^4 C_{ij}^H$ products implies that the ratio of bond-bending to bond-stretching forces decreases as x increases in $Zn_{1-x}Mn_xSe$, and that the tetrahedral bond is progressively weakened as Mn content increases. The reason why we have not deduced cubic elastic constants for $Zn_{1-x}Mn_xSe$ from our experimental hexagonal ones and used them to deduce the α and β force constants [as has been done in AgI (Ref. 24)] is that we could not determine C_{13}^H experimentally. The method we used to estimate C_{13}^H provides values which are probably not accurate enough for use in deducing cubic elastic constants but were nevertheless good enough for deducing the bulk modulus since the latter depends on C_{11}^H, C_{12}^H, and C_{33}^H as well as C_{13}^H.

Before suggesting an explanation for bond weakening in $Zn_{1-x}Mn_xSe$ we see from Fig. 1 that Mn causes smaller decreases in the $d_c^4 C_{ij}^H$ products in $Cd_{1-x}Mn_xTe$ than in $Zn_{1-x}Mn_xSe$. Comparison of these products rather than the C_{ij}^H's themselves is more appropriate because Mn causes d_c to decrease in $Cd_{1-x}Mn_xTe$ but to increase in $Zn_{1-x}Mn_xSe$. The similarity between the fractional decreases of the shear $d_c^4 C_{ij}^H$ products and the longitudinal ones in $Cd_{1-x}Mn_xTe$ is not deemed to be significant because all reductions are much smaller, and thus more difficult to interpret, in $Cd_{1-x}Mn_xTe$ than in $Zn_{1-x}Mn_xSe$. Furthermore, although not shown in Fig. 1, we found that the $C_{ij}^H d_c^4$ products, calculated from the experimental cubic elastic constants and d_c values,[7] were smaller for $Hg_{0.8}Mn_{0.2}Te$ (Ref. 1) than for HgTe,[25] and that Mn caused larger percentage reductions in the shear products (8%) than in the longitudinal ones (5%). We have not presented these $Hg_{1-x}Mn_xTe$ results in detail because their interpretation may be clouded by the fact that HgTe is a semimetal and $Hg_{0.8}Mn_{0.2}Te$ is a small gap semiconductor (as mentioned in the Introduction).

Weakening of the tetrahedral bonds by Mn in widegap, dilute magnetic semiconductors is due, we believe, to some hybridization of Mn $3d(t_2)$ orbitals into anion p orbitals causing there to be fewer p orbitals available for forming the sp^3 tetrahedral bonds and thus less charge in these bonds.

Elastic constant reduction is due then to more anions having neighbor Mn ions and thus there being more bonds weakened as Mn content increases even though the *length* of each type of cation-anion bond remains almost the same in a given DMS system regardless of the amount of Mn present.[25,26] The plausibility of elastic constant reduction by Mn in DMS being due to reduction in tetrahedral bond charge is supported by the fact that in cubic III-V and II-VI compound semiconductors the amount of bond charge decreases as ionicity increases[27] in almost the same way as the β/α force constant ratio does.[4]

There is photoemission evidence for hybridization of Mn $3d(t_2)$ orbitals with Te $5p$ orbitals in $Cd_{1-x}Mn_xTe$ (Ref. 8) but not for p-d hybridization in $Zn_{1-x}Mn_xSe$.[28]

However, the latter investigation was less extensive than the former using only $x = 0$ and $x = 0.20$ samples whereas the $Cd_{1-x}Mn_xTe$ work involved a number of Mn concentrations up to $x = 0.65$. Photoemission measurements should be done on $Zn_{1-x}Mn_xSe$ with larger Mn concentrations.

Comparison of our $Zn_{1-x}Mn_xSe$ elastic constant results with those for $Cd_{1-x}Mn_xTe$ imply that there is a greater amount of Mn $3d$-Se $4p$ hybridization than of Mn $3d$-Te $5p$ hybridization resulting in fewer Se $4p$ orbitals than Te $5p$ orbitals available for sp^3 bond formation. This inference is in accord with $Zn_{1-x}Mn_xSe$ having a larger exchange integral than $Cd_{1-x}Mn_xTe$ (Ref. 10) since the exchange integral depends on superexchange through the anion and the fourth power of matrix elements between p-d hybridized anion orbitals and Mn $3d$ orbitals.[11]

Before concluding it is appropriate to point out that although magnetic ions can cause a direct reduction in certain elastic constants of nonmetallic solids, we estimate that in our samples the amount of such reduction is much smaller than that which we have observed. Our estimate was made using theoretical expressions in the literature[29] and the experimental susceptibility.[10]

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APPENDIX

The equations[4,24] we used to deduce hexagonal elastic constants, C_{ij}^H, for ZnSe and $Cd_{1-x}Mn_xTe$ which actually have in the cubic, zinc-blende structure the elastic constants C_{ij}^{ZB} are

$$C_{11}^H = \overline{C}_{11} - \Delta^2/\overline{C}_{44}, \quad \overline{C}_{11} = \tfrac{1}{2}(C_{11}^{ZB} + C_{12}^{ZB} + 2C_{44}^{ZB}),$$

$$C_{12}^H = \overline{C}_{12} + \Delta^2/\overline{C}_{44}, \quad \overline{C}_{12} = \tfrac{1}{6}(C_{11}^{ZB} + 5C_{12}^{ZB} - 2C_{44}^{ZB}),$$

$$C_{13}^H = \overline{C}_{13} = \tfrac{1}{3}(C_{11}^{ZB} + 2C_{12}^{ZB} - 2C_{44}^{ZB}),$$

$$C_{33}^H = \overline{C}_{33} = \tfrac{1}{3}(C_{11}^{ZB} + 2C_{12}^{ZB} + 4C_{44}^{ZB}),$$

$$C_{44}^H = \overline{C}_{44} - \Delta^2 \overline{S}_{11}^H, \quad \overline{C}_{44} = \tfrac{1}{3}(C_{11}^{ZB} - C_{12}^{ZB} + C_{44}^{ZB}),$$

$$C_{66}^H = \tfrac{1}{2}(C_{11}^H - C_{12}^H),$$

$$\Delta = \frac{\sqrt{2}}{6}(C_{11}^{ZB} - C_{12}^{ZB} - 2C_{44}^{ZB}),$$

$$\overline{S}_{11}^H = \frac{\overline{C}_{33}}{2\overline{C}_{33}(\overline{C}_{11} + \overline{C}_{12}) - 2\overline{C}_{13}^2} + \frac{1}{2(\overline{C}_{11} - \overline{C}_{12})}.$$

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