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X-ray-absorption fine-structure studies of $Hg_{1-x}Cd_xTe$ and $Hg_{1-x}Mn_xTe$ bond lengths: Bond relaxation and structural stability of ternary alloys

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Bond lengths in the narrow-band-gap semiconductor alloys $Hg_{1-x}Cd_xTe$ and $Hg_{1-x}Mn_xTe$ have been deduced using x-ray-absorption fine-structure techniques. The nearest-neighbor bond lengths, for both alloy systems, are found to be constant as a function of alloy composition within the experimental uncertainties of 0.01 Å. These results contradict the predictions of some recent theories for $Hg_{1-x}Cd_xTe$ alloys, finding the Hg—Te and Cd—Te bond lengths to be decreasing in spite of the lattice constant increasing with x. The bond relaxation in several III-V, II-VI, and II-VI-based diluted magnetic semiconductor (DMS) ternary alloys is found to be quantitatively proportional to the ratio of bond bending to bond-stretching force constants. $Hg_{1-x}Cd_xTe$ and DMS alloys, including $Hg_{1-x}Mn_xTe$, are found to have the largest amount of bond relaxation. For DMS, this is attributed to tetrahedral bond weakening resulting from hybridization of anion p and Mn $3d$ orbitals thereby decreasing the amount of charge available for the making of sp^3 bonds.

I. INTRODUCTION

The semiconducting alloys $Hg_{1-x}Cd_xTe$ and $Hg_{1-x}Mn_xTe$ are interesting because their tunable, narrow energy gap make them ideal materials for infrared-detector applications.[1] Aside from having similar physical and optical properties, $Hg_{1-x}Mn_xTe$ is different from the nonmagnetic $Hg_{1-x}Cd_xTe$ because of its magnetic properties, such as the large negative magnetoresistance attributed to the exchange interaction between Mn^{2+} ions and valence-band electrons.[2] The electronic and optical properties of $Hg_{1-x}Cd_xTe$ (Refs. 3–5) and $Hg_{1-x}Mn_xTe$ (Refs. 4 and 6) have been studied extensively in the last decade. However, local-structure studies on these alloys have begun only recently.[7,8] Local-structure studies of $Hg_{1-x}Cd_xTe$ and $Hg_{1-x}Mn_xTe$ are important for the proper determination of the alloys' physical and chemical properties.

This work was undertaken in part due to some interesting predictions, regarding nearest-neighbor (NN) bond-length shift (or simply bond relaxation) in $Hg_{1-x}Cd_xTe$ alloys: using an extension of Harrison's[9] bond-energy formalism, Sher *et al.*[10] found the Hg—Te and Cd—Te bond lengths to be *decreasing* in spite of the lattice constant *increasing* with x.[11] Subsequently, Hass and Vanderbilt[12] found results similar to those of Sher *et al.*, using a self-consistent pseudopotential approach. Both groups attributed the anomalous relaxation to chemical forces arising from a difference in cation electronegativities resulting in charge-transfer effects between the Cd^{2+} and Hg^{2+} ions. According to Hass and Vanderbilt, the anomalous relaxation should be most evident in a system having close lattice matching of end-member compounds, such as $Hg_{1-x}Cd_xTe$. We decided to study $Hg_{1-x}Mn_xTe$ alloys, in conjunction with $Hg_{1-x}Cd_xTe$ ones, because the difference in electronegativities for Hg^{2+} and Mn^{2+} ions is larger than for Hg^{2+} and Cd^{2+} ions, and while the lattice matching for the former system is slightly worse than for the latter, there existed the possibility that $Hg_{1-x}Mn_xTe$ alloys might also show anomalous bond-length relaxation.

In this paper, we first present our x-ray-absorption fine-structure (XAFS) results for the NN bond lengths in $Hg_{1-x}Cd_xTe$ and $Hg_{1-x}Mn_xTe$ alloys. Second, we show our attempts at quantifying the relationship between the amount of bond relaxation and the average ratio of bond-bending to bond-stretching force constants for several III-V, II-VI, and II-VI-based diluted magnetic semiconductor (DMS) ternary alloys.

II. MEASUREMENTS AND ANALYSIS

We have measured the Hg L_{III}-edge and Cd K-edge XAFS spectra of zinc-blende-structured $Hg_{1-x}Cd_xTe$, the samples having $x=0.15$ and 0.19, and the HgTe and CdTe standards, at Stanford Synchrotron Radiation Laboratory (SSRL), Palo Alto, CA using the VII-3 beam line with an electron-beam energy of 3.0 GeV and a maximum stored current of 95 mA. The measurements were made in fluorescence mode using an Ar_2-gas-filled ion chamber. Data were collected using a variable-exit monochromator having two flat Si(220) crystals. Hg L_{III}-edge and Mn K-edge XAFS spectra were also obtained for five zinc-blende-structured $Hg_{1-x}Mn_xTe$ samples, having $x=0.05$, 0.19, 0.30, 0.40, and 0.50, and the HgTe and $MnTe_2$ standards. These measurements were performed in transmission mode, using ion chambers filled with a mixture of N_2 and Ar_2 gas, at both SSRL beam line VII-3 and National Synchrotron Light Source (NSLS) Upton, NY, using the X-11A beam line with an electron beam energy of 2.5 GeV and a maximum stored current of 110 mA. Data were collected using a Si(111) double-crystal monochromator. Energy resolution was estimated to be approximately 2 eV at SSRL and 3 eV at NSLS by the Cu $3d$ near-edge feature. Harmonics were rejected by detuning the monochromator on its rocking curve from 30% to 50% of its maximum transmitted x-ray intensity. The reduction of harmonics was verified using a third ion chamber with 32–64 layers of household aluminum foil (about 64 μm per layer) in front of the incoming beam. All measurements were taken at room temperature.

The $Hg_{1-x}Cd_xTe$ samples were grown at the Honeywell Corporation and the $Hg_{1-x}Mn_xTe$ samples at the Institute of Physics, Polish Academy of Sciences, all using Bridgman's method.[13] X-ray diffraction measurements showed the $Hg_{1-x}Mn_xTe$ samples to be cubic single-phase crystals. Samples were powdered using ceramic grinding tools, then sieved to 400 mesh (<38 μm) and brushed on tape. Each sample was fabricated using four layers of tape giving a total μx between 1.5 and 2.0 at all edges studied. Thickness effects were checked for by repeating measurements of selective spectra with samples having eight layers of tape. Having checked our sample quality in this way, we estimate the particle size to be predominantly $< 10\ \mu$m. Data analysis was done using variants of the "*UW*" analysis package; these standard procedures have been described elsewhere.[14]

The normalized extended x-ray-absorption fine-structure (EXAFS) oscillations for Hg L_{III} edge and Cd K edge of $Hg_{1-x}Cd_xTe$ and the Hg L_{III} edge and Mn K

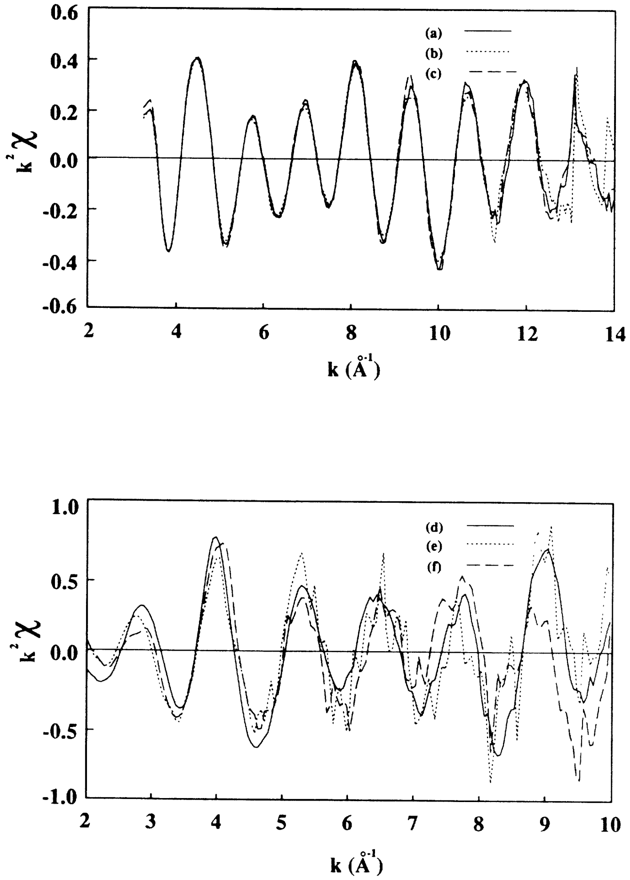

FIG. 1. Normalized EXAFS oscillations for the Hg L_{III} edge of (a) HgTe, (b) $Hg_{0.85}Cd_{0.15}Te$, (c) $Hg_{0.81}Cd_{0.19}Te$, and the Cd K edge of (d) CdTe, (e) $Hg_{0.85}Cd_{0.15}Te$, and (f) $Hg_{0.81}Cd_{0.19}Te$. All data were obtained at room temperature.

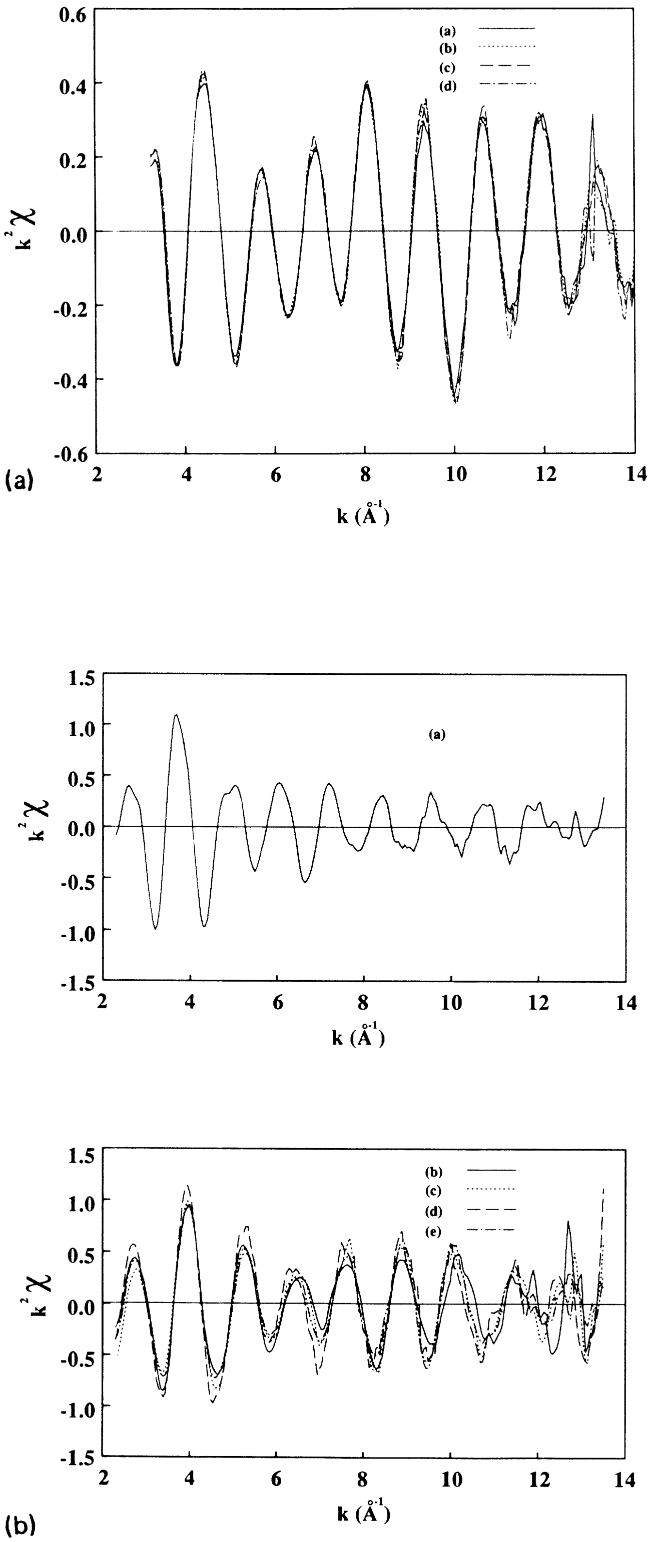

FIG. 2. (a) Normalized EXAFS oscillations for the Hg L_{III} edge of (a) HgTe, (b) $Hg_{0.95}Mn_{0.05}Te$, (c) $Hg_{0.70}Mn_{0.30}Te$, and (d) $Hg_{0.50}Mn_{0.50}Te$. All data were obtained at room temperature. (b) Normalized EXAFS oscillations for the Mn K edge of (a) $MnTe_2$, (b) $Hg_{0.81}Mn_{0.19}Te$, (c) $Hg_{0.70}Mn_{0.30}Te$, (d) $Hg_{0.60}Mn_{0.40}Te$, and (e) $Hg_{0.50}Mn_{0.50}Te$. All data were obtained at room temperature.

edge of $Hg_{1-x}Mn_xTe$ are shown in Figs. 1, 2(a) , and 2(b), respectively; the corresponding Fourier transforms are shown in Figs. 3(a), 3(b), 4(a), and 4(b), respectively. Further analysis involved use of the "ratio method,"[14] where the alloy data were compared with spectra from standard binary compounds for determining the NN bond lengths in alloys. For the Mn K-edge data of $Hg_{1-x}Mn_xTe$ we used as our standard the NaCl-like structured $MnTe_2$ having a lattice constant $a=6.943$ Å and displacement parameter $u=0.386$, determined using Mössbauer and x-ray diffraction measurements[15] taken at room temperature. From this we obtained a NN Mn—Te bond length of 2.904 Å in $MnTe_2$.

III. EXPERIMENTAL RESULTS

The results for the NN bond lengths in our $Hg_{1-x}Cd_xTe$ samples are shown in Fig. 5. We find that the Hg—Te and Cd—Te bond lengths in $Hg_{1-x}Cd_xTe$ remain constant within 0.01 Å, when compared to the HgTe and the CdTe samples used as standards, although x-ray diffraction measurements[11] show the lattice constant to increase linearly with x. The error bars were calculated from standard formulas for determining uncertainties in linear coefficients in doing a least-squares fit to a straight line. These results are in disagreement with predictions made by Sher *et al.*[10] and Hass and Vanderbilt[12] that the NN bond lengths in $Hg_{1-x}Cd_xTe$ *decrease* while the lattice constant is found to *increase* with x: Hass and Vanderbilt predicted a decrease of ~2% (~0.05 Å) over the full concentration range. Using strain energy calculations, Tsai *et al.*[16] have obtained Hg—Te and Cd—Te bond lengths which are in good agreement with our results (see Fig. 5). Similar results have been obtained by Wei and Zunger[17] using a local-density functional formalism.

As shown in Fig. 6, our results indicate that the Hg—Te and Mn—Te bond lengths in $Hg_{1-x}Mn_xTe$ remain essentially constant with x, within experimental uncertainties, when compared to HgTe and $MnTe_2$ standards. This is in contrast to the mean cation-cation distance (d_c), as determined from x-ray diffraction measurements,[18] decreasing linearly as a function of Mn concentration. The strain energy formalism has been applied by Newman *et al.*[19] to calculate the NN bond lengths for $Hg_{1-x}Mn_xTe$, showing reasonably good agreement with our data (see Fig. 6). Furthermore, $Hg_{1-x}Mn_xTe$ alloys remain in a single zinc-blende-structural phase up to $x \sim 0.75$, not showing significantly increased $\Delta\sigma^2$ (Debye-Waller factor relative to the standards) for the first shell data. This is in contrast to $Zn_{1-x}Mn_xSe$ alloys, which show larger $\Delta\sigma^2$ when x is close to the phase transition range.[20]

It is well established that ionic charge transfer in solids leads to edge energy shifts, for the edges of the ions involved in the charge transfer, and changes in the x-ray-absorption near-edge structure (XANES) depending upon the system studied. Our results show essentially no evidence of edge energy shift or change in the XANES of the Hg L_{III} edge for $Hg_{1-x}Cd_xTe$ alloys when compared to the Hg L_{III}-edge XANES of HgTe. From this we infer

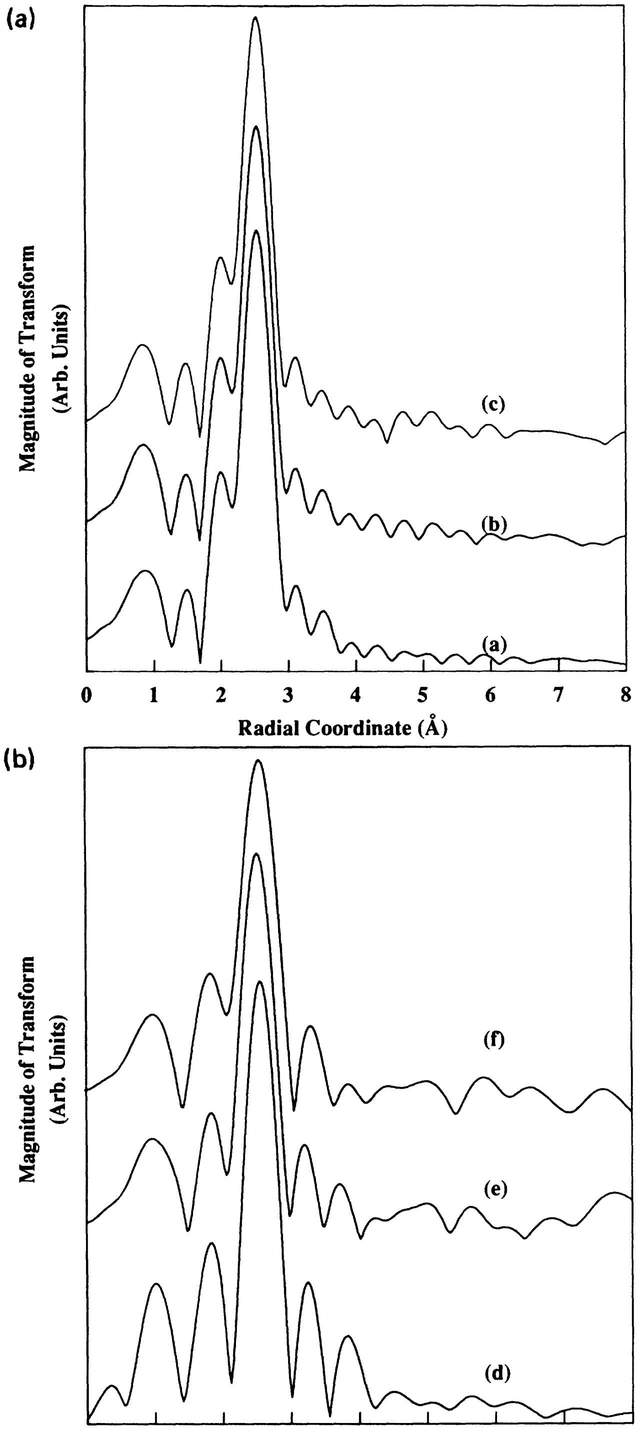

FIG. 3. (a) Magnitude of the Fourier transform of the Hg L_{III}-edge EXAFS $k^3\chi$ data from $k=3.5$ to 12 Å^{-1}; (a) HgTe, (b) $Hg_{0.85}Cd_{0.15}Te$, (c) $Hg_{0.81}Cd_{0.19}Te$. The first shell EXAFS were isolated by inverse-Fourier transforming with a typical r-space window of $|\Delta r|=1.4$ Å. All data were obtained at room temperature. (b) Magnitude of the Fourier transform of the Cd K edge EXAFS $k^3\chi$ data from $k=2.5$ to 9.5 Å^{-1}; (d) CdTe, (b) $Hg_{0.85}Cd_{0.15}Te$, (f) $Hg_{0.81}Cd_{0.19}Te$. The first shell EXAFS were isolated by inverse-Fourier transforming with a typical r-space window of $|\Delta r|=1.5$ Å. All data were obtained at room temperature.

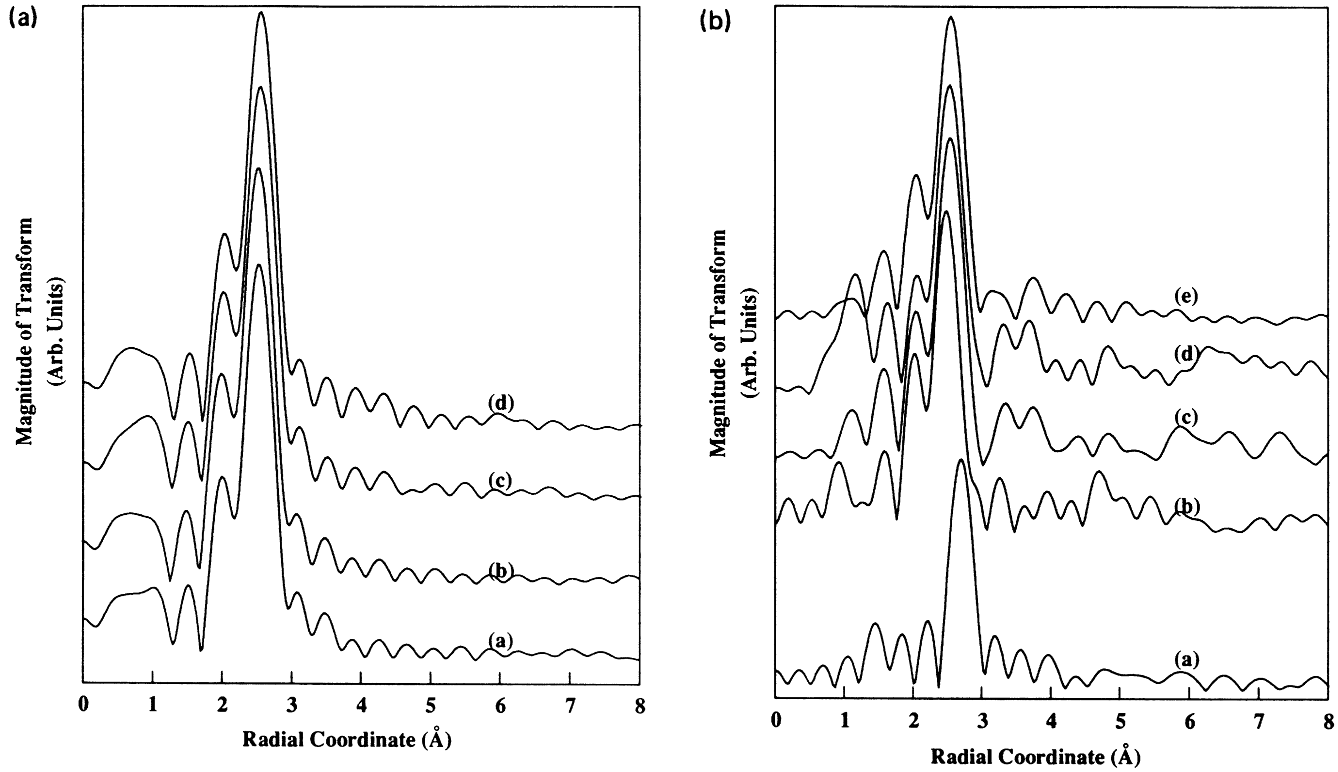

FIG. 4. (a) Magnitude of the Fourier transform of the Hg L_{III}-edge EXAFS $k^3\chi$ data from $k = 3.5$ to 11.5 Å^{-1}; (a) HgTe, (b) $\mathrm{Hg}_{0.95}\mathrm{Cd}_{0.05}\mathrm{Te}$, (c) $\mathrm{Hg}_{0.70}\mathrm{Cd}_{0.30}\mathrm{Te}$, (d) $\mathrm{Hg}_{0.50}\mathrm{Mn}_{0.50}\mathrm{Te}$. The first shell EXAFS were isolated by inverse-Fourier transforming with a typical r-space window of $|\Delta r| = 1.3$ Å. All data were obtained at room temperature. (b) Magnitude of the Fourier transform of the Mn K-edge EXAFS $k^3\chi$ data from $k = 3.5$ to 12.5 Å^{-1}; (a) MnTe_2, (b) $\mathrm{Hg}_{0.81}\mathrm{Mn}_{0.19}\mathrm{Te}$, (c) $\mathrm{Hg}_{0.70}\mathrm{Mn}_{0.30}\mathrm{Te}$, (d) $\mathrm{Hg}_{0.60}\mathrm{Mn}_{0.40}\mathrm{Te}$, (e) $\mathrm{Hg}_{0.50}\mathrm{Mn}_{0.50}\mathrm{Te}$. The first shell EXAFS were isolated by inverse-Fourier transforming with a typical r-space window of $|\Delta r| = 1.3$ Å. All data were obtained at room temperature.

that, for the range studied, no substantial charge transfer from Cd to Hg takes place in these alloys. This result is in agreement with the predictions made both by Tsai and collaborators and by Wei and Zunger. Nearly identical results were found from the Hg L_{III}-edge XANES for $\mathrm{Hg}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ alloys when compared to the Hg L_{III}-edge XANES of HgTe.

IV. INTERPRETATION

Our results for the NN bond lengths in $\mathrm{Hg}_{1-x}\mathrm{Cd}_x\mathrm{Te}$, showing them to be essentially constant with x, indicate that there is no anomalous relaxation for this system as predicted by Sher *et al.* and Hass and Vanderbilt. Furthermore, we infer from our XANES results that there is no substantial net charge transfer from Cd to Hg in $\mathrm{Hg}_{1-x}\mathrm{Cd}_x\mathrm{Te}$ alloys as predicted by Sher *et al.* and Hass and Vanderbilt. Similar results for the $\mathrm{Hg}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ alloys lead us to generalize that there is no appreciable Mn to Hg charge transfer, as a result of chemical forces between the cations owing to a difference in their electronegativities, causing anomalous bond relaxation. In this context, we are in agreement with the interpretation of Wall *et al.*[21] of their photoemission studies of the electronic structure of $\mathrm{Hg}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ alloys, but not of their conclusions concerning $\mathrm{Hg}_{1-x}\mathrm{Cd}_x\mathrm{Te}$ alloys; they suggest that the dissimilarity in $\mathrm{Hg}_{1-x}\mathrm{Cd}_x\mathrm{Te}$ photoemission spectra to that of the binary narrow-gap parent compound HgTe is due to appreciable change with x of Hg—Te bond lengths associated with substantial charge-transfer effects.

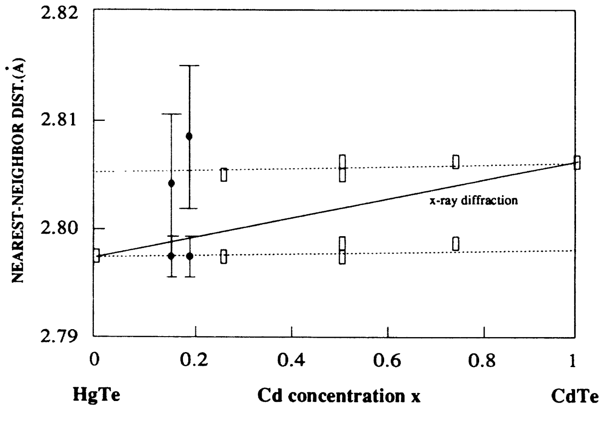

FIG. 5. EXAFS results for Hg—Te (lower solid circles) and Cd—Te (upper solid circles) bond lengths in $\mathrm{Hg}_{1-x}\mathrm{Cd}_x\mathrm{Te}$; the solid line represents the x-ray diffraction determined lattice constant results, multiplied by a $\sqrt{3}/4$ factor, taken from Ref. 11; the dashed lines represent the best fit to theoretical calculations (open squares) of the bond lengths (from Ref. 16).

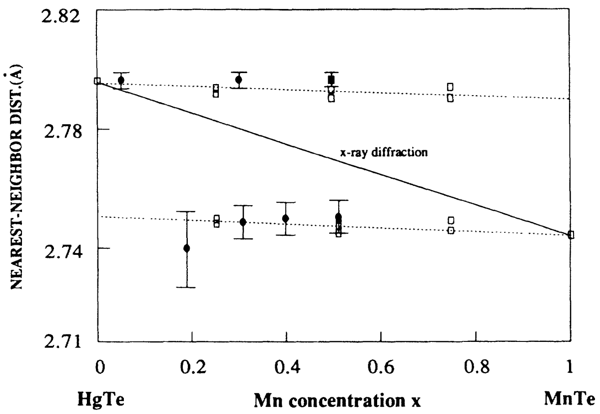

FIG. 6. EXAFS results for Hg—Te (upper solid circles) and Mn—Te (lower solid circles) bond lengths in $Hg_{1-x}Mn_xTe$; the solid line represents the x-ray diffraction determined mean cation-cation distances, multiplied by a $\sqrt{3/8}$ factor, taken from Ref. 18; the dashed lines represent the best fit to theoretical calculations (open squares) of the bond lengths (from Ref. 19).

Although the theoretical calculations of several groups[16,17,19] agree well with our findings for the NN bond lengths of both systems, they have all been made for ordered alloys[22] and evidence for a broad group of II-VI and III-V-based ternary alloys (including DMS) indicates that such bulk samples prepared from the melt are disordered.[20,23] As described by Balzarotti *et al.*,[24] the inconsistency between theory and EXAFS experiment may arise from the differing statistics involved in the accounting for the different tetrahedral configurations of ions in the alloys. For example, all of the tetrahedra containing cations surrounding an anion for the ordered chalcopyrite $A_{0.5}B_{0.5}C$ alloy have the $2A$-$2B$ cation configuration while a randomly populated disordered alloy, having the same concentration, may have a larger combined total of A-$3B$ and $3A$-B cation configurations than the $2A$-$2B$ type. This inconsistency should be greatest for alloys whose end-member binary compounds have the largest lattice mismatch (more accurately, the largest absolute bond relaxation), and therefore, may cause the poorer agreement between theory and EXAFS results for NN bond lengths in $Hg_{1-x}Mn_xTe$ as opposed to in $Hg_{1-x}Cd_xTe$ alloys.

While our EXAFS results do not show anomalous local-structure relaxation in the two alloy systems, we find that they exhibit the largest bond relaxation when compared to other III-V, II-VI, and DMS ternary alloys, for which such data are available. In order to understand why this is so, we first concentrated upon studying the variation of these compounds' local relaxation with their ionicities. (Simply put, the ionicity f_i is defined as the fractional measure to which a compound is ionic as opposed to covalent.) However, as will be shown later, the treatment of ionicity in DMS is not very straightforward. A better parameter perhaps, is the ratio of the compounds' bond-bending force constant β to bond-stretching force constant α, which were first used by Keating[25] in his application of the valence-force-field model[26] to the calculation of the elastic properties of diamond-structured crystals. It seems reasonable that bond relaxation would depend on the β/α parameter since it is directly related to the microscopic strain in the crystal. In the remainder of this paper, we discuss the variation of bond relaxation with β/α and f_i for zinc-blende- and wurtzite-structured III-V, II-VI, and DMS ternary alloys.

We define the B—C bond relaxation, for $A_{1-x}B_xC$-type alloy systems, in the usual way: $\epsilon_{BC} = \{r_{BC}(x\rightarrow 0)-r_{AC}^0\}/\{r_{BC}^0-r_{AC}^0\}$, where $r_{BC}(x\rightarrow 0)$ is the NN bond length for the B-type impurity atom in the AC compound and r_{BC}^0 and r_{AC}^0 are the end-member compound NN bond lengths. The AC bond relaxation ϵ_{AC} is defined using an exactly analogous equation. The reason for the normalization, by the difference in the end-members' NN bond lengths, is to compensate for the variation in lattice matching among the alloy systems. Our calculated values for ϵ_{AC}, ϵ_{BC}, and $\bar{\epsilon}=(\epsilon_{AC}+\epsilon_{BC})/2$, for all III-V (Ref. 27) and II-VI-based[24] ternary semiconductors and DMS (Refs. 20, 24, and 28) having been studied, are compiled in Table I.

Martin[29] applied Keating's model to the study of zinc-blende-structured compounds and determined the theoretical dependence of the cubic elastic constants C_{ij} on α, β, and point-ion Coulombic forces. The Coulomb terms are directly proportional to the dynamic effective charge, which is related directly to the optic-mode splitting $(\omega_l^2-\omega_t^2)$. This is an approximation because it is assumed that the dynamic effective charge differs little for

TABLE I. Bond force constants and the bond ionicity parameters for III-V semiconductors, II-VI semiconductors, and the hypothetical tetrahedrally coordinated end-member compounds MnSe and MnTe.

Material	$\alpha(N/m)$[a]	$\beta(N/m)$[a]	β/α[a]	f_i[b]
AlSb	35.35	6.77	0.192	0.43
GaP	47.32	10.44	0.221	0.33
GaAs	41.19	8.95	0.217	0.31
GaSb	33.16	7.22	0.218	0.26
InP	43.04	6.24	0.145	0.42
InAs	35.18	5.50	0.156	0.36
InSb	29.61	4.77	0.161	0.32
ZnS	44.92	4.78	0.107	0.62
ZnSe	35.24	4.23	0.120 (0.123)[c]	0.63
ZnTe	31.35	4.45	0.142	0.61
CdTe	29.02	2.43	0.084 (0.089)[d]	0.72
HgTe	28.0	2.57	0.092[d]	0.75
MnSe	28.3	2.0	0.070[c]	
MnTe	25.4	2.2	0.087[d]	0.72[e]

[a] Reference 29.
[b] Reference 48.
[c] Reference 34.
[d] This paper.
[e] Reference 43.

either acoustic or optic modes of a crystal. Using elastic and optical data and his relations, Martin has calculated the β/α values for most of the end-member binary compounds that we are interested in analyzing, except for DMS: hypothetical zinc-blende-structured MnTe for $Hg_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xTe$ alloys, and wurtzite-structured MnSe for $Zn_{1-x}Mn_xSe$ alloys. We have obtained β/α values for the hypothetical tetrahedrally structured compounds MnTe and MnSe by using Martin's relations and resorting to extrapolation methods described below.

In order to calculate the bond-force values for the hypothetical zinc-blende-structured MnTe, we found it necessary to linearly extrapolate the C_{11} and C_{12} elastic constants for $Cd_{1-x}Mn_xTe$ to $x=1$, yielding $C_{11}\approx 4.8\times 10^{11}$ dyn/cm^2 and $C_{12}\approx 3.3\times 10^{11}$ dyn/cm^2, since the reported C_{ij} cover an incomplete concentration range: $0\leq x\leq 0.52$.[30] The dynamic effective charge for the hypothetical compound MnTe can be approximately calculated using extrapolated results for the optic-mode phonon frequencies, having values $\nu_l\approx 210$ cm^{-1} and $\nu_t\approx 180$ cm^{-1}, from a Raman-scattering study made on $Cd_{1-x}Mn_xTe$.[31] We made similar calculations for CdTe, using $\nu_l\approx 166$ cm^{-1} and $\nu_t\approx 142$ cm^{-1}, so as to make a most reliable comparison of β/α for the two end-member compounds of $Cd_{1-x}Mn_xTe$. Our results for β/α are 0.089 and 0.087 for CdTe and MnTe, respectively.

The $Zn_{1-x}Mn_xSe$ alloys system provides a complication for this sort of analysis because it undergoes a phase transition from zinc blende to wurtzite structure occurring near $x=0.35$. In order to make a proper comparison across the phase transition, it becomes necessary to transform between cubic and hexagonal elastic constants of the alloy system. The most straightforward way to estimate the β/α parameter, for the hypothetical MnSe compound, is to transform the hexagonal elastic constants to equivalent cubic elastic constants using Martin's[32] transformations. The $Zn_{1-x}Mn_xSe$ hexagonal elastic constants have been reported and the justification for such transformations in this system has been discussed in a previous paper.[33] The results for β/α, detailed in a fuller account elsewhere,[34] are 0.123 and 0.070 for ZnSe and the MnSe hypothetical compound, respectively. The large difference in β/α values for the end members of $Zn_{1-x}Mn_xSe$ is indicative of a considerable decrease in that alloys' structural stability first mentioned in a previous work on room-temperature elastic constants of the alloys.[33]

We have also calculated $\beta/\alpha=0.091$ for HgTe, based on room-temperature elastic constants $C_{11}=5.36\times 10^{11}$ dyn/cm^2 and $C_{12}=3.66\times 10^{11}$ dyn/cm^2.[35] Because room-temperature optic-mode phonon frequencies for HgTe were unavailable, we used values measured at 77 K instead [$\nu_l=138$ cm^{-1} and $\nu_t=118$ cm^{-1} (Ref. 36)] for our calculations of that compound's dynamic effective charge. Assuming the difference in the two sets of values is small, this approximation is valid since β/α does not change significantly with small variations in the Coulomb terms.

We have made a plot of $\bar{\epsilon}$ as a function of $\overline{\beta/\alpha}=(\beta/\alpha_{AC}+\beta/\alpha_{BC})/2$ for all of the alloy systems discussed above (Table II). Physically, the significance of using $\overline{\beta/\alpha}$ as the variable in this plot is due to a mixed environment of bond-force strengths around any one ion in an alloy system. Obviously, the simplest way to handle this problem is by averaging β/α values belonging to the end members. Considerations of this mixed bond-force environment brings up a question of how it might change with concentration. In fact, the bond relaxation, as calculated from EXAFS results, appears to be independent of x (at least for the alloy systems discussed in this paper, for which we generally have $x>0.05$) implying that the use of average $\overline{\beta/\alpha}$'s is appropriate.

As Fig. 7 shows, the bond relaxation is smallest for III-V alloy systems, having the largest $\overline{\beta/\alpha}$ parameters, and largest for II-VI and DMS alloy systems, which have the smallest $\overline{\beta/\alpha}$ parameters. This is reasonable because as $\overline{\beta/\alpha}$ decreases, in tetrahedrally coordinated compounds, it becomes more energetically favorable to have greater bond-angle distortion and less bond-length change while for large $\overline{\beta/\alpha}$ the situation reverses. Furthermore, it can be inferred from Fig. 7 that there exists a direct relationship between bond relaxation and the $\overline{\beta/\alpha}$ parameter. There is generally much less scatter in the plot for III-V compounds than for II-VI and DMS compounds, which may partially be due to greater inaccuracies in Martin's definitions of the bond forces for compounds having small β/α parameters. This point is addressed in more detail below in the discussion of calculating these compounds' ionicities.

The largest bond relaxation occurs in DMS and $Hg_{1-x}Cd_xTe$ when compared to other II-VI and III-V compounds studied in this paper. For DMS alloys, we believe that this is confirmation of a suggestion made previously that the Mn^{2+} ions play a significant role in weakening the tetrahedral bond: this results from the hybridization of Mn $3d$ orbitals, having t_2 symmetry, with

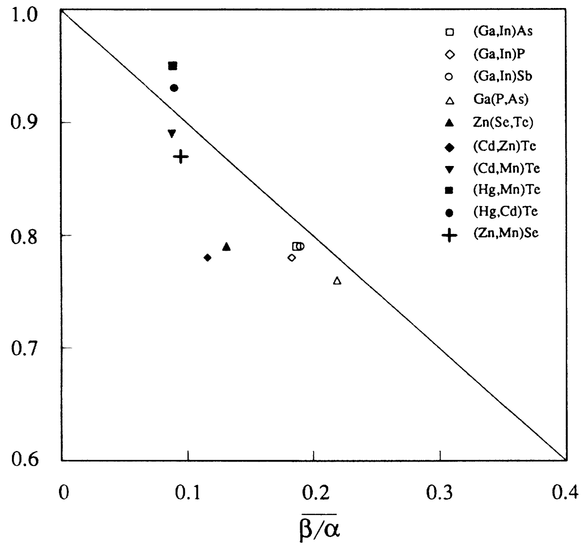

FIG. 7. EXAFS results for III-V-, II-VI-, and II-VI-based DMS ternary semiconductors' nearest-neighbor bond-lengths relaxation [normalized to the total variation predicted by the virtual-crystal approximation (VCA)] $\bar{\epsilon}=(\epsilon_{AC}+\epsilon_{BC})/2$ as a function of a mean A-C and B-C ratio of bond-force constants $\overline{\beta/\alpha}$. The solid line represents the ideal case $\bar{\epsilon}=1-\overline{\beta/\alpha}$.

TABLE II. Nearest-neighbor bond-length difference between the end-member compounds of the alloy system, the difference between the EXAFS determined nearest-neighbor bond length of the impurity atom and the end-member compound measured at the respective end, the nearest-neighbor bond-length relaxation for the two types of bonds in the alloy system, and its average value for III-V, II-VI, and II-VI-based ternary DMS.

Alloy $(A,B)C$ or $A(B,C)$	$\lvert r^0_{AC}-r^0_{BC}\rvert$ (Å)	$\lvert r^{x=1}_{AC}-r^0_{BC}\rvert$ (Å)	$\lvert r^{x=0}_{BC}-r^0_{AC}\rvert$ (Å)	ϵ_{AC}	ϵ_{BC}	$\bar{\epsilon}$
(Ga,In)As[a]	0.174	0.134	0.139	0.77	0.80	0.79
(Ga,In)P[a]	0.181	0.145	0.138	0.80	0.76	0.78
(Ga,In)Sb[a]	0.156	0.125	0.122	0.79	0.78	0.79
Ga(P,As)[a]	0.088	0.067	0.066	0.76	0.75	0.76
Zn(Se,Te)[a]	0.182	0.146	0.142	0.80	0.78	0.79
(Cd,Zn)Te[b]	0.161	0.124	0.127	0.77	0.79	0.78
(Cd,Mn)Te[b]	0.059	0.057	0.048	0.97	0.81	0.89
(Zn,Mn)Se[c]	0.102	0.095	0.082	0.93	0.80	0.87
(Zn,Mn)S[d]	0.087	0.084	0.083	0.97	0.95	0.96
(Hg,Mn)Te[e]	0.051	0.05	0.046	1	0.90	0.95
(Hg,Cd)Te[e]	0.009	0.0086	0.008	0.96	0.89	0.93

[a] Reference 27.

[b] Reference 24.

[c] Reference 20.

[d] Reference 28.

[e] This paper.

anion $4p$ or $5p$ orbitals leaving fewer anion p orbitals available for tetrahedral bonding.[30,33] Anion p–Mn $3d$ hybridization effects in wide gap DMS have been studied theoretically, in their connection with the superexchange mechanism which mediates the magnetic interaction between the Mn ions,[37–39] and experimentally with angle-resolved ultraviolet photoelectron spectroscopy,[36] ellipsometry,[40] and photoemission spectroscopy.[41,42] Our conclusions are in agreement with those made by Qadri *et al.*,[43] who base theirs on energy-dispersive x-ray diffraction and electrical resistivity measurements made under pressure on $Cd_{1-x}Mn_xTe$ samples. $Zn_{1-x}Mn_xS$ has the largest average bond-relaxation value ($\bar{\epsilon}=0.96$) of all alloy systems considered in this paper. This may in part be due to p-d hybridization becoming stronger as the anion is changed from Te→Se→S in $Zn_{1-x}Mn_xC^{VI}$ alloy systems: this is supported by photoemission measurements on $Cd_{1-x}Mn_xC^{VI}$ (C^{VI}=S,Se,Te) alloy systems[41] and electronic band-structure calculations.[44]

The reason why there is such large bond relaxation for both $Hg_{1-x}Cd_xTe$ and $Hg_{1-x}Mn_xTe$ may in part be due to HgTe being a semimetal with relatively low covalent bonding character (which may explain its very low $\beta/\alpha=0.092$ value). $Hg_{1-x}Mn_xTe$, like other DMS, exhibits tetrahedral bond weakening due to p-d hybridization effects described above while $Hg_{1-x}Cd_xTe$ alloys may have similar Cd $4d$–Te $5p$ hybridization effects.[44]

Ideally, it would be very useful to correlate the bond relaxation, as deduced from EXAFS measurements, with the ionicity f_i for the materials of concern in this paper for two reasons: (i) Martin's[29] empirical discovery that, for the restricted set of diamond and zinc-blende-structured materials he considered, the decrease in shear elastic constants with ionicity can be expressed by the relation $\beta/\alpha \propto (1-f_i)$, and (ii) because p-d hybridization in DMS lessens the availability of p orbitals for sp^3 tetrahedral bonds, it therefore also decreases the amount of charge in these bonds, which should in turn have ramifications for the ionicity of these alloys in the context of their structural stability. Unfortunately, the restricted set of materials Martin considered does not include DMS and although some attempts have been made, a proper treatment of their ionicity and its relationship with their structural stability is still lacking.

The calculation of the ionicity for DMS is complicated

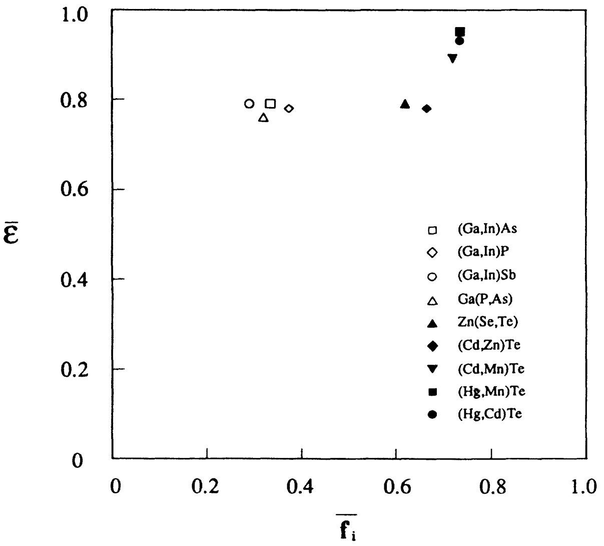

FIG. 8. EXAFS results for III-V-, II-VI-, and II-VI-based DMS ternary semiconductors' nearest-neighbor bond-lengths relaxation (normalized to the total variation predicted by the VCA) $\bar{\epsilon}=(\epsilon_{AC}+\epsilon_{BC})/2$ as a function of the mean A-C and B-C ionicity $\bar{f}_i$.

by the hopping mechanism of electrons occupying p-d hybridized orbitals, thereby participating in the superexchange process and our lack of understanding in the proper accounting of the charge on these electrons as covalent or ionic. Perkowitz *et al.*[45] found from infrared reflectivity measurements that f_i *decreases* in $Cd_{1-x}Mn_xTe$, from 0.72 for CdTe to 0.54 for the hypothetical MnTe compound, in contradiction with tetrahedrally coordinated structure of $Cd_{1-x}Mn_xTe$ becoming unstable at $x \approx 0.7$. This appears contradictory because studies by Phillips[46] and Van Vechten[47] indicate that in general f_i increases with NN coordination number; Phillips found that $f_i = 0.785$ is a critical value separating fourfold covalently bonded and sixfold ionically bonded compounds. Furthermore, Perkowitz *et al.* calculated f_i using the local effective-charge method,[48] which becomes more unreliable with increasing compounds' ionicity and questionable when applied to materials such as DMS, which have highly delocalized majority d bands. Perhaps a more reliable measure of f_i for $Cd_{1-x}Mn_xTe$ alloys is provided by Qadri *et al.*,[43] from fractional volume change experiments, who find the ionicity of the system alloys to be basically constant ($f_i = 0.72$) throughout the $x = 0$–0.70 region. As pointed out by the authors, their calculation also suffers to some extent from the same problems as mentioned above, but probably to a lesser degree.

Nevertheless, we have also plotted, as shown in Fig. 8, the bond relaxation as a function of the mean end-member compounds' ionicity $\bar{f}_i$. While the general trend is somewhat in agreement with the results shown in Fig. 7 [(i.e., $\beta/\alpha \propto (1-f_i)$], there is more scatter in the plot and a much weaker dependence of the bond relaxation on the ionicity $\bar{f}_i$. In view of this and the problems associated with its calculation covering a wide range of compounds, we conclude that, for the alloy systems considered in this paper, the ionicity (as calculated by Martin[29]) is an inappropriate parameter for the bond relaxation.[49]

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