Abnormal Vibrations of Cd Atoms in $Zn_xCd_{1-x}Te$

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Combined proton-induced x-ray-emission and Rutherford-backscattering channeling measurements on ⟨111⟩ CdTe and $Zn_xCd_{1-x}Te$ ($x=0.04$, 0.1, 0.3) crystals reveal a narrowing of the Cd-sublattice channeling pattern relative to that of Te for $x=0.1$ which does not exist for the other x materials. This observation is attributed to enhanced vibrations of Cd atoms caused by the bonding changes induced by the Zn.

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An important question regarding ternary zinc-blende compound semiconductors is concerned with the structural and dynamic changes that can occur upon replacement of either cations or anions in the binary base material. Both local structural distortions of the lattice or variations in bond strengths in the vicinity of the minority atom may result from such a replacement. Of particular interest in this context are the II-VI compounds based on CdTe of which zinc cadmium telluride is an important member. This material is a mixture of ZnTe and CdTe in which x atoms of Cd have been substituted by Zn. We have found that such substitution ($x=0.1$) dramatically reduces the vibrations of the crystal as a whole, yet strangely, the Cd sublattice vibrates with an amplitude substantially higher than the rest of the atoms.

X-ray diffraction experiments on $Zn_xCd_{1-x}Te$ of various compositions have shown[1] that the average lattice parameter changes almost linearly with x. Extended x-ray-absorption fine-structure studies[2] indicate that the first-nearest-neighbor distances exhibit a bimodal distribution nearly independent of x, with the Cd-Te and Zn-Te distances differing by about 0.12 Å; the cation sublattice has an almost undistorted fcc structure, while the anions exhibit a strongly distorted sublattice. Little is known about the dynamics of atoms in ternary compounds. Resonant Raman measurements on $Ga_{0.85}In_{0.15}P$ revealed[3] peculiar behavior of some modes, attributed to local changes in crystal symmetry caused by the difference between the GaP and InP bond lengths. While Raman measurements yield information on the collective motion of a cluster of atoms in the crystal, knowledge about the motion of individual atoms in a ternary crystal is unavailable from such measurements.

In the present work we deduce information on the dynamics of both cation and anion sublattices in $Zn_xCd_{1-x}Te$ ($x=0$, 0.04, 0.1, and 0.3) from channeling measurements. By performing simultaneous Rutherford-backscattering (RBS) and proton-induced x-ray-emission (PIXE) channeling experiments, we were able to detect relative displacements from the atomic strings of the different constituent atoms of the crystal. Measurements carried out at 298 K and at ≈100 K enabled us to discriminate between dynamic (vibrational) and static effects. Our results not only show that the additional small amounts of Zn atoms to CdTe reduce the vibrational amplitudes of the crystal as a whole, but also give the first evidence for the existence of enhanced thermal amplitudes of Cd atoms.

In typical "angular scan" channeling experiments, the crystal under study is bombarded by energetic light charged particles and the yields of close-encounter atomic processes (such as RBS and PIXE) are measured as functions of tilt angle of a major crystallographic axis with respect to the beam.[4] Under optimal channeling conditions, the projectiles are gently steered along the open channels of the crystal never getting closer to the atomic strings than a certain minimum distance, which is of the order of 10^{-1} Å. Atomic processes which require impact parameters substantially smaller than this value (such as L-shell ionization or direct backscattering, having impact parameters of $\approx 10^{-2}$ and $\approx 10^{-4}$ Å, respectively) are therefore greatly reduced. Backscattered protons or characteristic x rays if detected are thus mainly due to close collisions with atoms of the first surface layer (surface peak) or to collisions with atoms displaced, thermally or statically, from their normal lattice sites into the channels.

The important features of angular-scan curves are their half-width ($\psi_{1/2}$) and depth ($\chi_{\min}$). For near-surface channeling in a monoatomic crystal having cubic symmetry, these quantities were found, by fitting the results of the continuum model to extensive computer simulations,[5] to be given by

$$\psi_{1/2}=0.8\left[\frac{Z_1Z_2e^2}{Ed}\ln\left(\frac{3a^2}{1.44u_1^2}+1\right)\right]^{1/2}, \tag{1}$$

$$\chi_{\min}=6Nd\pi u_1^2[1+(\psi_{1/2}d/2.2u_1)^2]^{1/2}. \tag{2}$$

Here $a=0.4685(Z_1^{2/3}+Z_2^{2/3})^{-1/2}$ Å and N is the atomic crystal density. The important parameters that appear in these equations are the properties of the probing projectile (charge Z_1e and energy E) and the properties of the crystal under study, i.e., its atomic charge (Z_2e), the atomic spacing along the string (d), and its one-dimensional thermal root mean square amplitude of vibration $[u_1(T)]$. For channeling in a mixed crystal along a direction in which the different atoms alternate along the strings, as is the case for the ⟨111⟩ channel in the zinc-blende structure, the equations must be slightly modified; Z_2 and d are replaced by the average atomic charge of the string and the average atomic spacing, respectively. As for the atomic amplitude u_1, which may differ for the different constituent atoms, calculations based on the binary collision model[6] have shown that $\psi_{1/2}$ is mainly determined by the vibrations of those atoms with which close collision have occurred. Thus, if different types of atoms have different vibrational amplitudes, different half-widths should be observed in a channeling experiment which is sensitive to the kind of atom with which the collision has occurred (i.e., PIXE in our case).

The measurements were performed on ⟨111⟩-oriented CdTe and $Zn_xCd_{1-x}Te$ ($x = 0.04$, 0.1, and 0.3) crystals grown by the modified Bridgman method. Protons of 200 keV were used and the beam current was kept low (≤ 1 nA/mm^2) to avoid sample heating. After a preset charge density had been accumulated the beam was moved to a fresh spot in order to minimize surface degradation due to prolonged exposure to the probing beam. Backscattered protons were detected with a surface-barrier detector set at 170°, while characteristic x rays were detected in a Si(Li) detector at an angle of 135° with respect to the beam. Both RBS and PIXE spectra were recorded simultaneously for each crystal tilt angle, scanning through the ⟨111⟩ axis, at 0.1° increments. The angular-scan curves for each element in the crystal were extracted from the PIXE spectra by integrating over the L lines of Zn, Cd, and Te. Raw data of such PIXE angular scans for Cd and Te in CdTe, $Zn_{0.1}Cd_{0.9}Te$, and $Zn_{0.3}Cd_{0.7}Te$ are shown in Fig. 1.

The $\psi_{1/2}$ and $\chi_{\min}$ values were extracted from the measured PIXE angular scans. The $\psi_{1/2}$ results for Cd and Te measured at room and at low (≈ 100 K) temperatures are shown in Fig. 2 for all samples studied. It should be noted that while no significant differences between these parameters exist for CdTe and $Zn_xCd_{1-x}Te$ with $x = 0.04$ and 0.3, the data for the $x = 0.1$ material shows a marked narrowing of the Cd curve with respect to that of Te (see also Fig. 1). Furthermore, for both elements, $\psi_{1/2}$ exhibits a maximum at $x = 0.1$. This is in contrast with the theoretical expected behavior as calculated from Eq. (1), assuming a constant u_1 and using average Z_2 and d values (the dashed-dotted line in Fig. 2).

The results of PIXE angular scans for different elements should usually not be compared directly because of the different effective depths from which the corresponding x rays originate. The greater this depth the more severe is the dechanneling, which is reflected in a shallower and narrower angular dip. However, for the

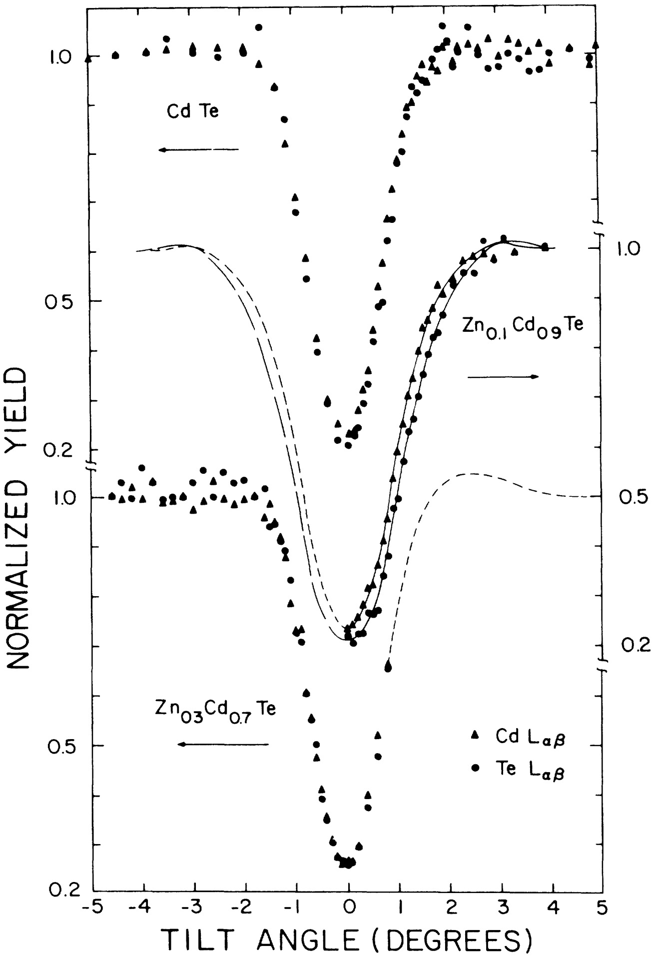

FIG. 1. Results of Cd $L_{\alpha\beta}$ and Te $L_{\alpha\beta}$ angular scans through the ⟨111⟩ axis for CdTe, $Zn_{0.1}Cd_{0.9}Te$, and $Zn_{0.3}Cd_{0.7}Te$.

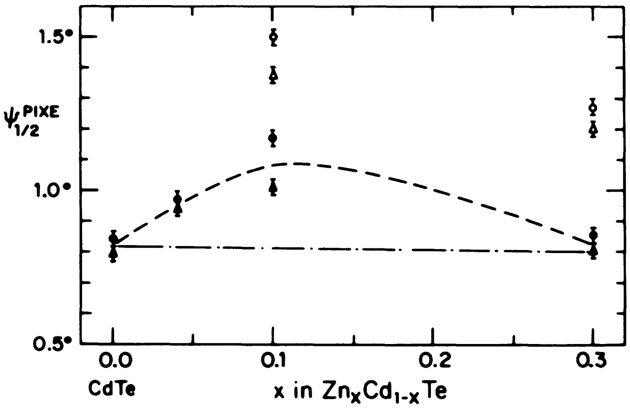

FIG. 2. $\psi_{1/2}$ values extracted from PIXE angular-scan curves of Cd (triangles) and Te (circles), for various compositions. Closed symbols, $T = 300$ K; open symbols, $T = 126$ K and $T = 103$ K for $x = 0.1$ and 0.3, respectively. The dashed line connecting the room temperature values is meant to guide the eye only. The dashed-dotted line (normalized to the $x = 0$ data) represents the expected trend, as explained in the text.

case of Cd ($Z=48$) and Te ($Z=52$), calculations[7] have shown that the expected difference between PIXE angular dips for these two elements is negligible for all $\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{Te}$ compositions studied here. Direct comparison of the raw PIXE angular-scan data can thus be done without the application of any depth correction. Hence the differences between Cd and Te, noticeable in Figs. 1 and 2 for the $x=0.1$ crystal, are significant.

The overall response of the crystal to the addition of Zn has been deduced from the near-surface RBS angular-scan data. The measured $\psi_{1/2}(0)$ and $\chi_{\min}(0)$ values, extrapolated to the crystal surface, were used to calculate the average thermal vibration amplitudes $\langle u_1 \rangle$ according to Eqs. (1) and (2), and are shown in Fig. 3. As can be seen, 4%–10% additions of Zn drastically reduce the vibrations of the crystal as a whole.

The present results clearly indicate that addition of small quantities of Zn ($x \approx 0.1$) to CdTe induces major changes in the crystal properties, which are (a) a marked narrowing of the Cd angular-scan curve as compared to that of Te $[\Delta\psi = \psi_{1/2}(\mathrm{Te}) - \psi_{1/2}(\mathrm{Cd})]$ and to the corresponding expected weighted RBS dip[7] and (b) a drastic decrease in the thermal vibrations of the ZnCdTe crystal as a whole. These effects disappear with further addition of Zn ($x=0.3$).

The observed effects cannot be attributed to instrumental factors since all data for a given x were taken simultaneously. Furthermore, the crystals used were all of high quality as reflected by the extrapolated surface $\chi_{\min}(0)$ which was always close to the expected value (when reasonable thermal vibrational amplitudes were taken[8]) and was internally consistent with the corresponding $\psi_{1/2}$ (note the agreement between full circles and crosses in Fig. 3).

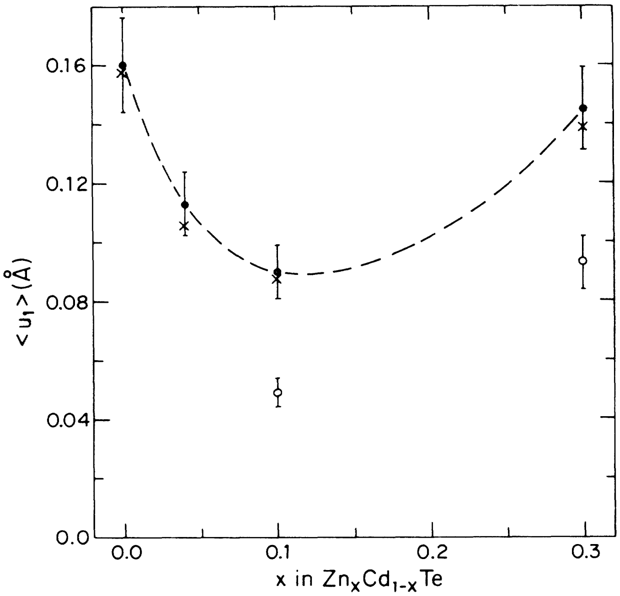

FIG. 3. Average thermal amplitudes at room temperature as deduced from the near-surface RBS data, by the use of Eqs. (1) (full circles) and (2) (crosses). The open circles correspond to the low-temperature measurements, as indicated in the caption of Fig. 2. The dashed line is meant to guide the eye only.

In order to determine whether the above observations are caused by static displacements, or are the result of increased thermal vibrations, we have repeated some of the measurements at lower temperatures (≈ 100 K). If the observed narrowing of the Cd angular-scan curve is due to static displacements of these atoms, then by cooling the sample, the Cd dip should broaden very little, being mainly determined by the equilibrium position of the Cd atoms. If, on the other hand, the Cd dip is determined by thermal vibrations, then cooling the sample should strongly reduce u_1, which in turn would lead to a considerable broadening of the dip [according to Eq. (1)]. The latter is indeed the case, as can be seen in Fig. 2. We therefore conclude that the observed $\Delta\psi$ phenomenon is due to enhanced vibrations of Cd atoms.

The vibrational amplitude determined in the present experiment for pure CdTe is in good agreement with that inferred from x-ray diffraction data[8] [$u_1(\mathrm{Cd})=0.15$ Å and $u_1(\mathrm{Te})=0.13$ Å] but disagrees with theory[9] [$u_1(\mathrm{Cd})=u_1(\mathrm{Te})=0.125$ Å]. By the addition of small amounts (4%–10%) of Zn, the average vibrations observed here are strongly reduced. Indeed, it is known that $\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{Te}$ with $x=0.04$ is a substantially stronger crystal than CdTe; the compressibility decreasing from[10] 0.0322 to 0.0193 GPa^{-1}. However, rough estimates, which convert the compressibility to elastic constants and these to vibrational amplitudes show that the reduction of the average amplitude observed here (Fig. 3) is larger by about a factor of 4 than can be accounted for by the measured changes in compressibility. It should be noted that while compressibility results depend on the macrostructure of the crystal (defects, etc.), vibrational amplitudes are governed by bonding properties only. The observed reduction of $\langle u_1 \rangle$ at the lower temperature is in general agreement with the accepted temperature dependence of thermal amplitudes.

The effects observed in the present work are peculiar; the replacement of some Cd atoms in CdTe by Zn to form $\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{Te}$ ($x<0.1$) strongly reduces the vibrations of both Cd and Te atoms, with the Cd atoms substantially less influenced than Te. Even though we have no explanation for these phenomena, we suggest that they may be associated with the fact that the ZnTe bond is stronger, less ionic, and shorter (by 6%) than the CdTe bond. Hence the electron density around a Te atom, which has both a Cd and Zn neighbor, will tend to be concentrated between the Te and Zn, so as to satisfy the more covalent nature of this bond. The electron density on the CdTe bond will therefore be reduced, causing a relative weakening of this bond which results in the observed enhanced vibrations of the Cd. In the higher-concentration sample ($x=0.3$) the observed average amplitude returns to a value close to that found in pure CdTe, and the $\Delta\psi$ effect almost disappears. This behavior may probably be understood in terms of the linear-chain model of vibrations with two alternating coupling constants between atoms. In the limit of this model in which one of the coupling constants is much larger than the other, the acoustic modes are mostly determined by the smaller of the two force constants. The acoustic modes have been shown[11] to be predominantly responsible for the thermal amplitudes of atoms in many binary crystals, including CdTe and ZnTe. At 30% Zn concentration, the strong ZnTe bonds nearly alternate with the weaker CdTe bonds. Hence the thermal amplitudes in $Zn_{0.3}Cd_{0.7}Te$ will be determined by the CdTe bonds and will thus resemble those of pure CdTe, just as observed in the present experiments.

An alternative explanation for the observations presented here is related to the clustering effect recently proposed by Srivastava, Martins, and Zunger.[12] It has been predicted by these authors that particular configurations of isovalent foreign atoms will be energetically favored in mixed zinc-blende structures. As quoted in Ref. 12, such configurations will locally release the strain normally present in diluted ZnCdTe. This, in turn, can lead to a local lowering of the force constant and hence to the enhanced vibrations of Cd atoms in the vicinity of the Zn cluster.

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