

EXAFS Analysis of the Local Structure of $\text{Cd}_{(1-x)}\text{M}_x\text{Te}$ ($\text{M}=\text{Cr, Fe, Ni}$)

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Abstract. CdTe, doped with transition metals, has received much attention for decades as promising II-VI dilute magnetic semiconductor materials. High purity $\text{Cd}_{(1-x)}\text{M}_x\text{Te}$ ($\text{M}=\text{Cr, Fe, Ni}$) monocrystals have been prepared by the Bridgman method. Because the solubility of transition metals in CdTe is rather small, the zinc-blende phases were prepared in the limit of $x \leq 0.1$. The local structural relaxation and effects of metal ion substitution on CdTe have been studied by measuring the fluorescence detected X-ray absorption fine structure (XAFS) spectra of the M K-edges and Te L_1 -edges. While II-VI compounds show significant variations of band structures, carrier densities and mobilities depending on the amount of donor or acceptor, XANES and EXAFS analysis of the M K-edge spectra reveal that only slight variations of oxidation states and bond lengths appear in no connection with atomic number of substituting metals. On the other hand, Te L_1 -edge spectra, for example of $\text{Cd}_{(1-x)}\text{Fe}_x\text{Te}$, exhibit rather a strong distortion around the central atom as a function of x . This distortion is attributed to the redistribution of Cd atoms from their original locations as the Fe concentration increases.

Keywords: CdTe, II-VI semiconductor, XAFS, XANES

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INTRODUCTION

Cadmium telluride (CdTe), one of the II-VI compounds, has been studied for a long time since it is a dilute magnetic semiconductor (DMS) when doped with transition metal [1,2]. Applications range from X-ray, gamma-ray and IR detectors to substrates for HgCdTe epitaxial layers [3]. Since CdTe exhibits outstanding properties as a substrate for CdS/CdTe solar cells, it is a prospective candidate for replacing more expensive commercial solarvoltaic materials. When the Cd is replaced by Mn, Fe, Co or Ni within certain limits, CdTe shows giant magnetic resistance (GMR) and maintains a zinc blende structure (T_d symmetry) in which the cation is coordinated with four Te atoms. In addition to metal-nonmetallic transition, it shows variations in the binding energy of acceptors as a function of temperature [4]. This is the result of the presence of the bound magnetic polaron (BMP) [5,6]. Because these properties have been attributed to the readjusted electronic configurations as well as structural distortions and disorders, studies of structural properties are necessary as a function of dopant concentration.

In this work, metal doped CdTe single crystals were prepared at concentrations of less than 10 at. % because the solubility of metal is rather small [7]. X-ray absorption fine structure (XAFS) spectroscopy has been applied to characterize the local structural relaxations and variations of electronic structures of $\text{Cd}_{1-x}\text{M}_x\text{Te}$ as a function of x , where $\text{M} = \text{Cr, Fe and Ni}$.

EXPERIMENTAL

CdTe single crystals, doped with transition metal (TM), were grown using the vertical Bridgman method in a vertical electronic furnace. Because the quality and purity of single crystals depend on the speed of crystal growth and the temperature gradient in the furnace, CdTe powder was pulled down at a rate of 1~10 mm/h by using a step motor, and the temperature was maintained by a microcomputer at 1150°C at the furnace center. The measured temperature gradient was 26°C/cm.

The XAFS measurements were carried out at BL3C1 of the Pohang Light Source (PLS) on the K-edges of TM as well as L_1 -edge of Te. A Si(111) double crystal monochromator was used with detuning to 70 % in intensity to eliminate higher-order

harmonics. The XAFS samples were finely powdered and deposited on polyimide tape. To reduce the X-ray absorption of air, a specially designed extensible He chamber was inserted between the Io chamber and sample. Data were taken in transmission and fluorescence, using a 13-element Ge detector for the fluorescence spectra. For the Te L-edges, somewhat large peaking time and long integration time per data point were applied to enhance the data quality and energy resolution and to reduce the effects of overlapping neighboring edges at the expense of count rate and experiment time. In that case, energy resolution was estimated at ~ 150 eV, and more than 3 hours were needed to take a spectrum. The XAFS data were analyzed by conventional procedures published elsewhere [8,9].

RESULTS AND DISCUSSION

The oxidation state of the absorbing atom, correlated with chemical shift, was obtained by comparing X-ray absorption near edge structure (XANES) spectrum with those of references.

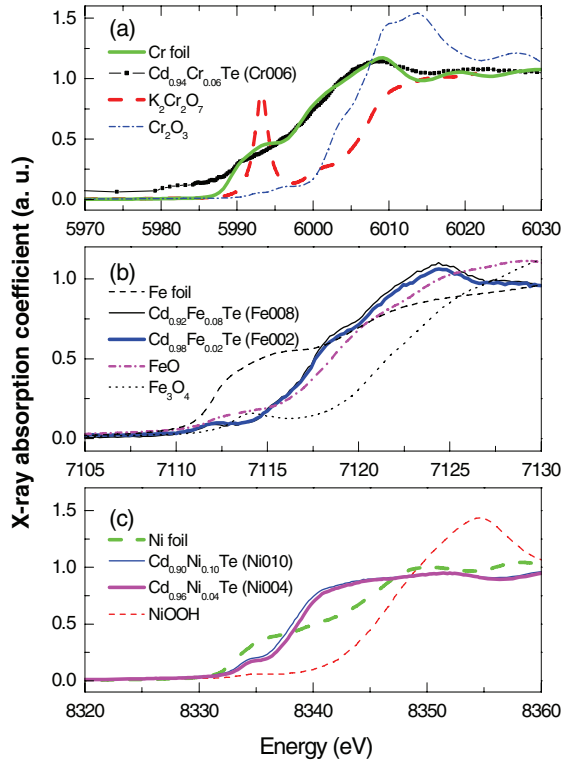


FIGURE 1. XANES spectra of CdTe doped with TM (=Cr, Fe, Ni) at TM K-edges. The oxidation state of Cr-doped CdTe is nearly same with that of Cr metal (a). Fe-doped (b) and Ni-doped (c) XANES spectra show that Fe and Ni cations are at around divalent state and these spectra move to high energy side slightly in line with the TM concentration.

Normalized TM K-edge XANES spectra are presented in Fig. 1. Compared with references, the oxidation states of Fe (Fig. 1b) and Ni (Fig. 1c) appear to be divalent. The XANES spectra of these cations shift to high energy as the dopant concentration increases. Since the oxidation states of Fe and Ni are similar to that of Cd, it can be deduced that these cations are located in the Cd sites. On the other hand, the oxidation state of Cr (Fig. 1a) is nearly the same as Cr foil, which indicates that Cr was not incorporated in CdTe and remained as localized clusters in the compounds. These clusters may form because of limited solubility of Cr; the system of Cr-doped CdTe will not be discussed further in this work.

Fourier transform (FT) magnitudes of the $k\chi(k)$ oscillations of the Ni-doped and Fe-doped samples, taken at the Ni and Fe K-edges, are given in Figs. 2a and b, respectively, as a function of concentrations. The two distinctive peaks in these figures correspond to the TM-Te interaction in the first coordination sphere. In the case of the Ni-doped CdTe (Fig. 2a), the FT shape and the inter-atomic distance change slightly as the dopant concentration increases, indicating that the structure of the nearest shell around the absorbing atom is changed in line with the Ni concentration. However, these small variations could be within the experimental error. As shown in Fig. 2, there are no notable contributions from the farther shells to the FT magnitudes. This could originate from a lack of long-range ordering beyond the first shell.

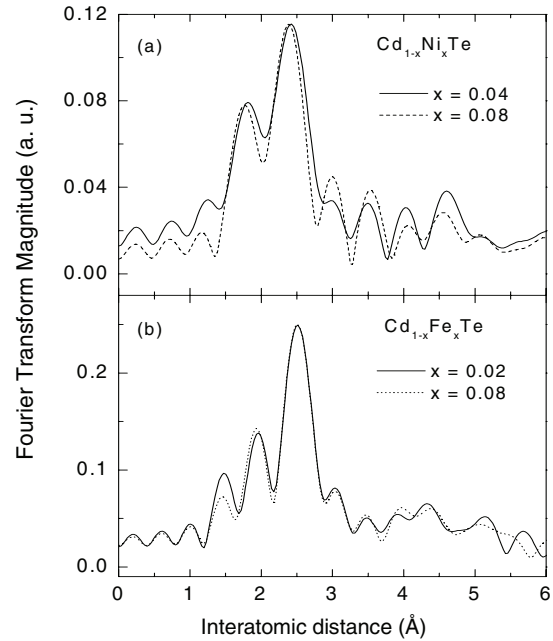


FIGURE 2. Fourier transforms of k -weighted Ni and Fe K-edge EXAFS oscillation for (a) $\text{Cd}_{1-x}\text{Ni}_x\text{Te}$ and (b) $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ as a function of x .

To obtain quantitative information of the local structure around the X-ray absorbing atoms, the inverse FTs were performed on the first peak at around 2.2 ~ 3.0 Å in the FTs of Te L_1 -edge spectra of the Ni-doped and Fe-doped samples. Curve fitting was carried out for the obtained $k\chi(q)$ functions using the iterative nonlinear least-square curve fitting technique and the parameters given by FEFF8.2 [10]. The fits include two single scattering paths, a Te-Cd and a Te-TM interaction. k -weighted Te L_1 -edge spectra of 4 at. % and 8 at. % Ni concentration and 2 at. % and 8 at. % Fe concentration were fitted in r -space and the results are shown in Figs. 3a. and b, respectively. The resulting fit parameters are given in Table 1. In the curve fits, only the coordination numbers among the fitting parameters were fixed according to crystallographic data. In the case of the Ni-doped samples, the amplitudes of the peaks decrease in line with Ni concentration, but no further significant variations are observed. On the other hand, the peak of the nearest shell for the Fe-doped sample broadens in width and decreases in intensity and shifts to longer bond lengths with the increase in Fe concentration. This result is contrary to for the Ni-doped case. However, when the coordinated atoms are not distributed at a uniform distance, the FT magnitude decreases and the width broadens. Since the interatomic distance of the Fe-Te bond was not changed, as observed in Fig. 2, these variations for the peak could be attributed to the redistribution of Cd atoms from their original location.

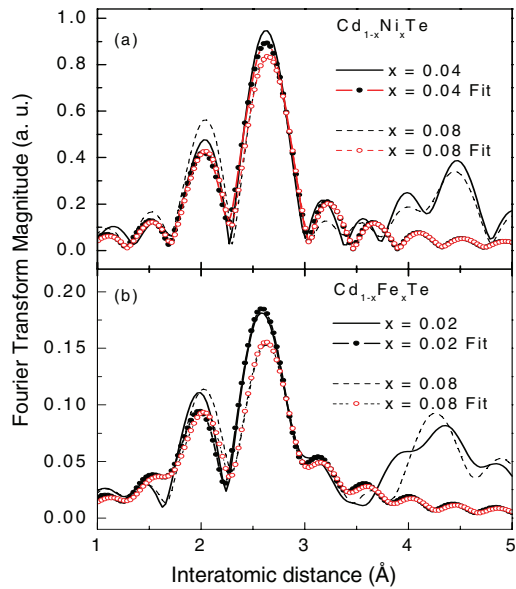


FIGURE 3. Fourier transforms of k -weighted Te L_1 -edge EXAFS oscillation for (a) $\text{Cd}_{1-x}\text{Ni}_x\text{Te}$ and (b) $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ as a function of x . The results of curve fits are shown as same type lines with different symbols.

TABLE 1. The fitted parameters of the Fe and Ni doped samples in different concentration. Two single scattering paths, Te-Cd and Te-M interaction, are used in curve fits, where M = Fe and Ni. One standard deviation errors on the least significant figures are indicated in the brackets.

samples	r (Å)		$\sigma^2 (\times 10^{-3} \text{ Å}^2)$	
	Te-Cd	Te-M	Te-Cd	Te-M
$\text{Cd}_{0.98}\text{Fe}_{0.02}\text{Te}$	2.77(9)	2.77(7)	6.15(9)	4.67(1)
$\text{Cd}_{0.92}\text{Fe}_{0.08}\text{Te}$	2.79(5)	2.78(1)	6.76(7)	0.2(8)
$\text{Cd}_{0.96}\text{Ni}_{0.04}\text{Te}$	2.80(5)	2.84(5)	4.35(4)	0.6(6)
$\text{Cd}_{0.92}\text{Ni}_{0.08}\text{Te}$	2.82(0)	2.84(7)	4.39(4)	1.7(6)

The second peak at around 4~5 Å in Fig. 3 corresponds to the Te-Te interaction of the second nearest shell. In the case of Fe-doped samples, the shapes and magnitudes of the second peak are changed with the increase of Fe concentration. It is attributed to the superposition of double scattering by way of redistributed Cd atoms of the first shell and the Te-Te single scattering.

CONCLUSION

The local and electronic structures of $\text{Cd}_{1-x}\text{TM}_x\text{Te}$ single crystals (where TM is Cr, Fe and Ni) were studied using the XAFS technique. Only the Fe-doped samples show significant local structural variations upon further Fe concentration. It is mainly attributed to the redistribution of Cd atoms from their original locations.

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