

XAFS STUDY OF THE  $\text{Ge}_{1-x}\text{Eu}_x\text{Te}$  and  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  THIN LAYERSA. Wolska<sup>\*</sup>, B.J. Kowalski, M. Pietrzyk, W. Knoff, and T. Story

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Diluted magnetic semiconductors (DMS) have been shown to be the very promising materials for spintronic purposes. Usually, II-VI and III-V materials are considered and very intensively investigated in pursuit of the compound with the Curie temperature ( $T_C$ ) above room temperature. On the other hand, the IV-VI type semiconductors, like the GeTe crystals doped with transition metals and/or rare earth elements also show properties interesting from spintronics point of view. In case of GeTe doped with Mn, Curie temperature ( $T_C$ ) depends on the Mn concentration and can reach 140 K for  $\text{Ge}_{0.5}\text{Mn}_{0.5}\text{Te}$  [1]. Adding another dopant, like Eu, influences magnetic properties even further.  $T_C$  becomes relatively high at markedly lower Mn content and it becomes, in case of  $\text{Ge}_{0.89}\text{Mn}_{0.07}\text{Eu}_{0.04}\text{Te}$ , comparable to that of  $\text{Ge}_{0.6}\text{Mn}_{0.4}\text{Te}$ . Apparently, the interaction between  $d$  and  $f$  states of both dopants changes magnetic order in the system. Therefore, it is important to determine energy distribution and positions of Mn  $3d$  and Eu  $4f$  states. What's more, the knowledge about the position and local structure around magnetic ions is also necessary to broaden the understanding of the origin of ferromagnetism in the investigated system.

The best tool for examining an average local atomic structure around selected element is EXAFS (Extended X-ray Absorption Fine Structure). This technique is sensitive to the specific element and gives the information about the number and type of neighbouring atoms, as well as the structural disorder. However, some limits exist in this method too. The Mn K-edge (6539 eV) and Eu  $L_3$ -edge (6977 eV) are too close to obtain a full-range EXAFS spectrum for Mn and can influence XANES (X-ray Absorption Near Edge Structure) spectrum for Eu. Therefore, it is important to investigate also materials without co-doping and, as a first step, the results of analysis for the samples with one type of dopant are presented here.

The  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  ( $x = 0.08, 0.10$ ) and  $\text{Ge}_{1-x}\text{Eu}_x\text{Te}$  ( $x = 0.005, 0.007$ ) thin layers were grown on  $\text{BaF}_2$  (111) substrates by the MBE method. The substrate temperature was kept at 400–450°C. The obtained layers were of 0.25  $\mu\text{m}$  thick. The XANES and EXAFS spectra were measured at the HASYLAB, A1 station. Measurements were carried out at the Ge K-edge, Mn K-edge and Eu  $L_3$ -edge using a 7-element Ge fluorescence detector. During measurements the samples were cooled to liquid nitrogen temperature in order to minimize thermal disorder. The FEFF8.4 code [2] was used to

calculate theoretical XANES spectra. The Artemis and Athena programs [3], using IFEFFIT data analysis package, were applied to analysis of the EXAFS data.

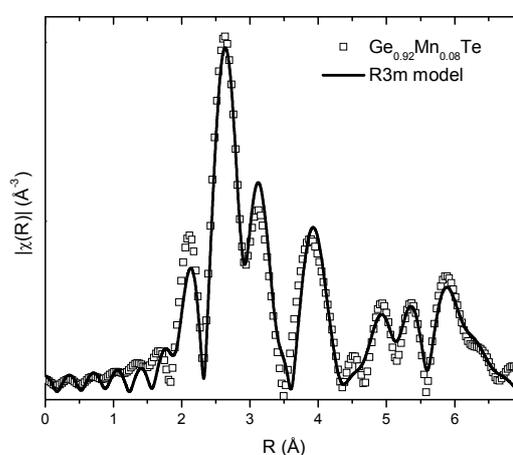


Figure 1. FT experimental EXAFS spectrum (squares) and fit of theoretical model (solid line) of the Ge K-edge in the  $\text{Ge}_{0.92}\text{Mn}_{0.08}\text{Te}$  sample.

The Ge K-edge EXAFS was measured for the doped samples and for the reference GeTe layer. Since, the amount of Ge atoms was relatively high, the existence of self-absorption effect was checked using the Booth and Bridges algorithm for thin samples. The calculations excluded the need of correction. EXAFS analysis was carried out using the same model and the same set of parameters in each case. In this way the comparison between the samples was possible. For the GeTe sample, in addition to the regular Ge-Te bonds, around 12% of Ge-Ge bonds were found. This behaviour was also observed by Kolobov *et al.* in the thin GeTe layers. [4] However, in case of doped samples, adding additional Ge atoms in the first shell led to the unphysical parameters. It appears that presence of dopants eliminates the additional Ge-Ge bonds.

The EXAFS analysis of Ge K-edge shows that all samples possess the GeTe structure with  $R3m$  space group. Figure 1 presents the fitting results for  $R3m$  model in a range up to 7 Å for one of the samples doped with Mn. The analysis of Mn K-edge for the same sample,

$\text{Ge}_{0.92}\text{Mn}_{0.08}\text{Te}$ , is shown in Figure 2. In this case, a model with  $R\text{-}3m$  structure fits the spectrum better. There is no contradiction between both results. EXAFS gives average information about structure around investigated element in a short radial distance. It means that the dopants can modify their neighbourhood but this does not affect the whole structure (unless when their amount stays at the low level). Table 1 presents the bond lengths found from EXAFS analysis. For the central Ge atom the first shell consists of two subshells where 3 Te and 3 Ge atoms are located at slightly different distances (2.83 Å and 3.14 Å). The Mn atoms are located in the substitutional Ge positions but they modify the nearest neighbourhood in such a way that the Te atoms form one shell only. The distances to the second shell consisting of two Ge subshells are very close in both cases.

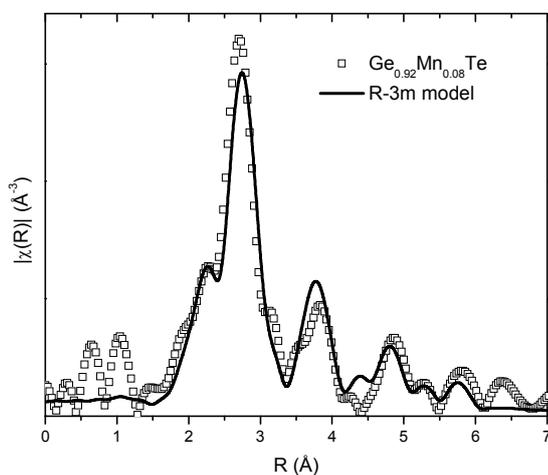


Figure 2. FT experimental EXAFS spectrum (squares) and fit of theoretical model (solid line) of the Mn K-edge in the  $\text{Ge}_{0.92}\text{Mn}_{0.08}\text{Te}$  sample.

In case of the  $\text{Ge}_{1-x}\text{Eu}_x\text{Te}$  samples, the amount of Eu dopant was too low to give good quality EXAFS data. Therefore, only the XANES spectra were recorded. In order to check the possible Eu surrounding, the calculations of XANES spectra were performed. There

were four models considered: Eu in the Ge substitutional position ( $\text{GeEu}_{\text{Ge}}\text{Te}$ ),  $\text{EuTe}$ ,  $\text{EuO}$  and  $\text{Eu}$ . The comparison with the experimental data enabled to exclude the presence of Eu and  $\text{EuO}$  inclusions in the investigated samples.

Table 1. The distances found between the absorbing Ge or Mn atoms and the two neighbouring shells (each consisting of two subshells).

	$R_{\text{Te1}}$ [Å]	$R_{\text{Te2}}$ [Å]	$R_{\text{Ge1}}$ [Å]	$R_{\text{Ge2}}$ [Å]
Ge	$2.83 \pm 0.01$	$3.14 \pm 0.01$	$4.15 \pm 0.01$	$4.29 \pm 0.01$
Mn	$2.93 \pm 0.01$	$2.93 \pm 0.01$	$4.10 \pm 0.01$	$4.23 \pm 0.01$

We conclude that Mn dopants substitute the Ge atoms in the  $\text{GeTe}$  layers and slightly modify the first shell consisting of Te atoms. In case of Eu dopants, it seems that Te atoms are also preferred as the first neighbours in the  $\text{GeEu}_{\text{Ge}}\text{Te}$  compound and/or the  $\text{EuTe}$  inclusions.

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