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INFLUENCE OF Se, Pb AND Mn IMPURITIES ON THE FERROELECTRIC PHASE TRANSITION IN GeTe STUDIED BY EXAFS

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EXAFS was used to study the local environment of Se, Pb and Mn impurity atoms in germanium telluride. It is found that the three impurity atoms do not occupy fixed on-center positions in GeTe and that the origin and magnitude of the displacements are different. It is shown that the rate of decrease of T_c when doping GeTe with these impurities is determined primarily by the size of impurity atoms and the type of chemical bond between impurity and main atoms of the crystal.

Keywords: Ferroelectric phase transition; impurities; Curie temperature; off-center ions; EXAFS spectroscopy.

1 INTRODUCTION

It is well known that impurities and defects exert strong influence on the ferroelectric phase transitions in crystals. From the theoretical point of view, the strength of this influence is determined by whether defects are centrosymmetric or have their own dipole moment and whether the dipoles are frozen or can readily change their orientation. The influence of each of these types of defects on the ferroelectric phase transition has been considered in terms of a phenomenological approach (Halperin and Varma, 1976; Levanyuk, Osipov and Sigov, 1978; Thomas, 1981; Levanyuk and Sigov, 1988). Unfortunately, at present, there is no way to predict the type of defect that will be created when doping ferroelectrics with impurities.

The purpose of this work was to study the local environment of impurity atoms and off-center Ge atoms in doped GeTe crystals using EXAFS and to establish a relationship between the structural position of the impurities and the change of Curie temperature in doped crystals. The study of extended X-ray absorption fine structure (EXAFS) seemed to be an ideal method for these investigations.

In the present work, GeTe crystals doped with various impurities were studied. Germanium telluride is a well-known ferroelectric having one of the simplest crystal structures in the paraelectric phase (NaCl cubic structure with two atoms in a primitive cell). GeTe was therefore chosen as a model material for studies of ferroelectric phenomena. Doping impurities Se, Pb and Mn were chosen because of their qualitatively different influence on the phase transition temperature T_c . The effect of isoelectronic impurity Se on T_c is very weak, while that of Pb and Mn is much stronger, although Pb is an isoelectronic impurity, and Mn is a nonisoelectronic one.

2 EXPERIMENTAL

The samples of solid solutions $\text{GeTe}_{1-x}\text{Se}_x$ ($x = 0.1-0.3$), $\text{Ge}_{0.9}\text{Pb}_{0.1}\text{Te}$ and $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$ ($x = 0.1$ and 0.2) were prepared by alloying germanium telluride (composition $\text{Ge}_{0.496}\text{Te}_{0.504}$) with GeSe, PbTe or MnTe in evacuated quartz ampoules. The alloys were annealed for from 50 to 165 hours at temperatures of 545, 640 and 650°C for $\text{GeTe}_{1-x}\text{Se}_x$, $\text{Ge}_{0.9}\text{Pb}_{0.1}\text{Te}$ and $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$, respectively. The homogeneity of the samples was confirmed by X-ray studies. At 300 K all the samples, except for $\text{Ge}_{0.8}\text{Mn}_{0.2}\text{Te}$, had the rhombohedral structure of α -GeTe, while the $\text{Ge}_{0.8}\text{Mn}_{0.2}\text{Te}$ sample had a cubic structure. Before each measurement the alloys were powdered and sieved, and the powder was rubbed into the surface of adhesive tape. The optimal thickness of the absorbing layer necessary to get good EXAFS spectra was achieved using from 8 to 12 layers of the tape.

EXAFS data were collected in transmission mode at 77 K on station 7.1 at the SRS at Daresbury Laboratory with an electron beam energy of 2 GeV and a maximum stored current of 250 mA. The measurements were carried out at the K absorption edges of Mn (6.539 keV), Ge (11.103 keV), Se (12.658 keV) and the L_{III} -edge of Pb (13.055 keV). The intensities of incident (I_0) and transmitted (I) radiation were recorded by ion chambers. Two flat Si(111) crystals were used as a monochromator.

The oscillatory EXAFS function $\chi(k)$ was extracted from the absorption curve $\mu x(E) = \ln(I_0/I)$ (where E is the energy of radiation) in the conventional way described by Lee, Citrin, Eisenberger and Kincaid (1981) and Sayers and Bunker (1988). After removing the pre-edge background, splines were used to extract the smooth atomic part of the absorption $\mu x_0(E)$ and then the dependence $\chi = (\mu x - \mu x_0)/\mu x_0$ was calculated as a function of the photoelectron wave vector $k = (2m(E - E_0)/\hbar^2)^{1/2}$. The position of the inflection point on the absorption edge was taken as the energy origin, E_0 . The edge steps ranged from 0.12 to 0.95. For each sample 3 to 4 independent measurements were made. The records were then processed and the resulting $\chi(k)$ curves finally averaged.

Direct and inverse Fourier transforms with modified Hanning windows (Sayers and Bunker, 1988) were used to extract the information about 2 to 4 nearest shells from the experimental curve $\chi(k)$ (the ranges of extraction in R -space are presented in the captions for each figure). The distances R_j , coordination numbers N_j and Debye-Waller factors σ_j^2 for each shell as well as the energy origin correction dE_0 were varied simultaneously to obtain the minimum of the root-mean-square deviation between the experimental and calculated $k \cdot \chi(k)$ curves. The number of fitting parameters (from 6 to 13) was usually about half of the number of independent data points ($N_{\text{ind}} = 2\Delta k \Delta R/\pi = 13 - 21$ (Lee *et al.*, 1981)). The accuracy of determination of the fitting parameters was estimated from the correlation matrix; the errors presented in this work correspond to a 95% confidence level interval for the variation of parameters. To increase the accuracy, additional constraints and relations between the parameters were taken into account (equal energy corrections dE_0 for all shells and known relation between coordination numbers for known structures).

The FEFF software developed by Mustre de Leon, Rehr, Zabinsky and Albers (1991) was used to calculate the dependence of back-scattering amplitude and phase, the central atom phase shift and the mean free path of a photoelectron on its wave vector. The adequacy of the data processing method was checked on the GeTe sample.

3 RESULTS

A typical EXAFS function $k \cdot \chi(k)$ obtained at the Ge K -edge for GeTe_{0.7}Se_{0.3} sample is presented in Figure 1. Analysis of the data reveals that (i) the first

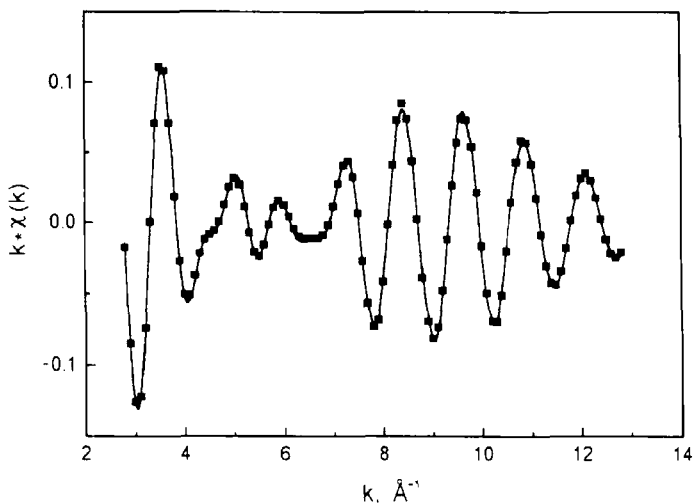


FIGURE 1 EXAFS function $k \cdot \chi(k)$ obtained at the Ge K -edge for $\text{GeTe}_{0.7}\text{Se}_{0.3}$ sample at 77 K. Points are the filtered data ($R = 1.65\text{--}4.35 \text{ \AA}$); the solid line represents the best theoretical approximation within the model with two Ge–Te and one Ge–Se distances in the first shell and one Ge–Ge distance in the second shell.

shell of Ge atoms in $\text{GeTe}_{1-x}\text{Se}_x$ is distorted, as in GeTe; (ii) there are two sorts of Te atoms at $2.80 \pm 0.01 \text{ \AA}$ and $3.12 - 3.14 \text{ \AA}$; (iii) the impurity Se atoms are located at a distance of $2.63 \pm 0.02 \text{ \AA}$. Germanium atoms in the second shell are at an average distance of about 4.2 \AA . On decreasing x from 0.3 to 0.1 the length of the shorter Ge–Te bond does not change, but the length of the longer Ge–Te bond increases systematically from 3.12 ± 0.01 to $3.14 \pm 0.01 \text{ \AA}$ and, in the limit $x \rightarrow 0$, tends to the corresponding value for undoped GeTe ($3.15 \pm 0.01 \text{ \AA}$).

Figure 2 shows the EXAFS function $k \cdot \chi(k)$ for the same sample as in Figure 1 ($\text{GeTe}_{0.7}\text{Se}_{0.3}$), but derived from data at the Se K -edge. These data enable us to establish the local environment of the Se impurity in the crystal. It turns out that experimental data are not in good agreement with the model, where the impurity atom is assumed to enter the Te site and has the same local environment (3 short and 3 long bonds). Analysis shows that the number of neighboring Ge atoms that are at $2.61 \pm 0.01 \text{ \AA}$ from Se atoms is equal to 2.3 ± 0.2 , and reveals other Ge atoms at an average

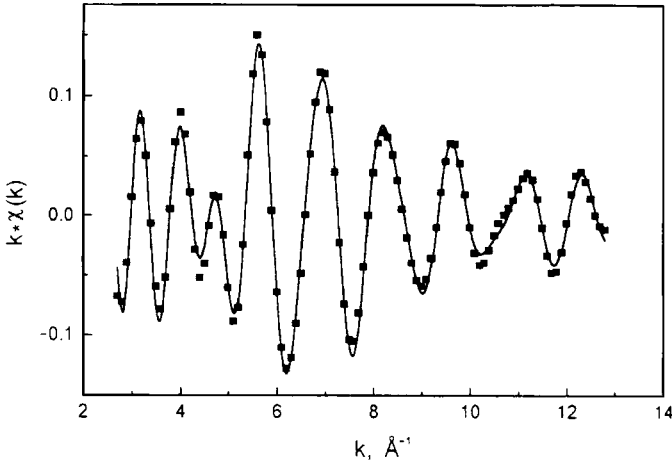


FIGURE 2 EXAFS function $k \cdot \chi(k)$ obtained at the Se K -edge for $\text{GeTe}_{0.7}\text{Se}_{0.3}$ sample at 77 K. Points are the filtered data ($R = 1.40\text{--}4.55 \text{ \AA}$); the solid line represents the best theoretical approximation within the model with two different Se–Ge distances in the first shell and one Se–Te distance in the second shell.

distance $3.08 \pm 0.01 \text{ \AA}$. The structure corresponding to the second shell is complex and the only reliable result of the analysis is that roughly four Te atoms surround selenium at a distance of $4.07 \pm 0.02 \text{ \AA}$. This value is significantly less than 4.17 \AA , the average distance between second neighbors calculated from X-ray data. These results show that on entering the Te sites, Se atoms experience additional local distortion and are displaced from the centrosymmetric position towards one of the edges of slightly deformed Ge octahedra.

The dependence $k \cdot \chi(k)$ obtained at the Pb L_{III} -edge for $\text{Ge}_{0.9}\text{Pb}_{0.1}\text{Te}$ sample is presented in Figure 3. The analysis shows that the model, in which all the neighboring Te atoms in the first shell are at the same distance, gives poor agreement between the experimental and calculated data. However if one assumes that the Te atoms are located at two distances, 3.03 ± 0.01 and $3.24 \pm 0.02 \text{ \AA}$,^a the agreement improves (see Figure 3). The coordination

^a All the distances found at the Pb edge should be increased by 0.03 \AA to take into account systematic error probably originating from central atom phase calculation for heavy Pb atom in FEFF.

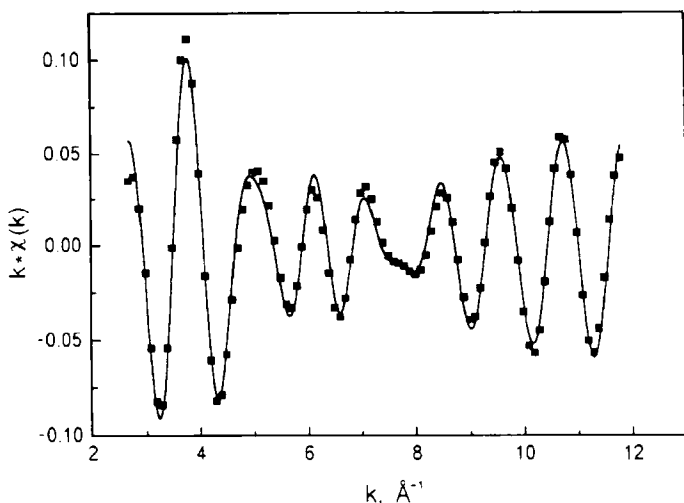


FIGURE 3 EXAFS function $k \cdot \chi(k)$ obtained at the Pb L_{III} -edge for $\text{Ge}_{0.9}\text{Pb}_{0.1}\text{Te}$ sample at 77 K. Points are the filtered data ($R = 1.40\text{--}4.30 \text{ \AA}$); the solid line represents the best theoretical approximation within the model with two Pb–Te distances in the first shell and equal Pb–Ge and Pb–Pb distances in the second shell.

numbers corresponding to these distances are 4.2 ± 0.6 and 1.8 ± 0.7 . The atoms (Ge, Pb) in the second shell are located at an average distance $4.27 \pm 0.02 \text{ \AA}$, which coincides with the corresponding distance calculated from the X-ray data.

Lower values of the Debye-Waller factor for both Pb–Te bonds in $\text{Ge}_{0.9}\text{Pb}_{0.1}\text{Te}$ ($\sigma_1^2 = 0.002$ and 0.005 \AA^2) compared with that for PbTe ($\sigma_1^2 = 0.006 \text{ \AA}^2$) indicate strain around Pb atoms in the structure, in accordance with the fact that both bond lengths exceed the average interatomic distance in GeTe (2.99 \AA).

A typical dependence of $k \cdot \chi(k)$ obtained at the Mn K -edge for $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$ sample is presented in Figure 4. The analysis shows that Mn atoms substitute for metal sites and are surrounded by Te atoms at $2.91 \pm 0.01 \text{ \AA}$ (the first shell) and by (Ge, Mn) atoms at an average distance of $4.18 \pm 0.01 \text{ \AA}$ (the second shell). Attention should be paid to the high value of the Debye-Waller factor for the first shell ($\sigma_1^2 = 0.010 \pm 0.001 \text{ \AA}^2$ for $x = 0.1$ and $0.008 \pm 0.001 \text{ \AA}^2$ for $x = 0.2$ at 77 K), which is probably

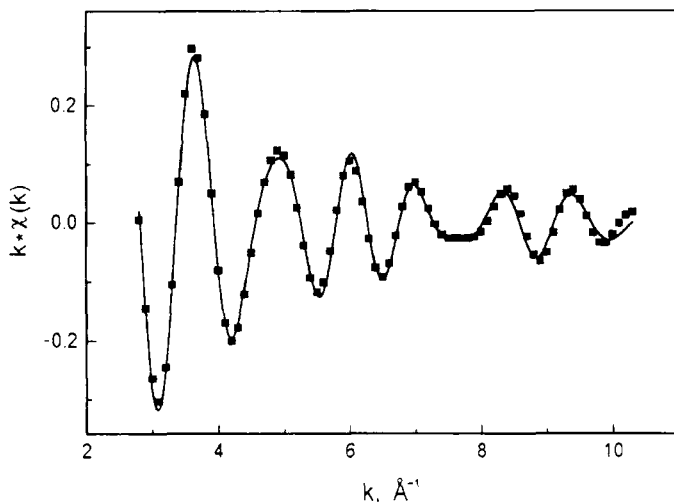


FIGURE 4 EXAFS function $k \cdot \chi(k)$ obtained at the Mn K -edge for $\text{Ge}_{0.9}\text{Mn}_{0.1}\text{Te}$ sample at 77 K. Points are the filtered data ($R = 1.60\text{--}4.10 \text{ \AA}$); the solid line represents the best theoretical approximation within the model with one Mn–Te distance in the first shell and equal Mn–Ge and Mn–Mn distances in the second shell.

due to a small static displacement of the Mn atom from the centrosymmetric position in the Te environment; the value of the shift however does not exceed 0.1 to 0.15 \AA .

4 DISCUSSION

The results obtained in this work enable us to understand more of the mechanisms by which various impurities influence the phase transition temperature in GeTe. The dependence of T_c on the impurity concentration in GeTe doped with Se, Pb and Mn is shown in Figure 5.

We start our discussion with the Se impurity, the influence of which on T_c in GeTe is very weak. Our data allow us to suggest that on entering the Te sites, Se atoms (which are smaller than Te) become “off-center” and acquire an additional degree of freedom for movement. The Se atoms are displaced towards the edge of octahedra, i.e., they move along the polar axis

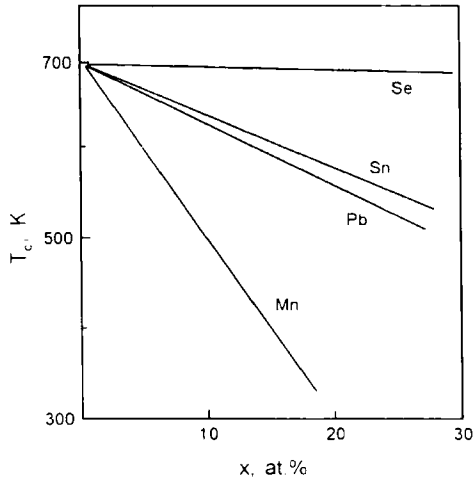


FIGURE 5 Dependence of Curie temperature on the impurity concentration in solid solutions of GeTe with GeSe (Abrikosov *et al.*, 1984), SnTe (Bierly *et al.*, 1963), PbTe (Hohnke *et al.*, 1972) and MnTe (Abrikosov *et al.*, 1980).

and perpendicular to it simultaneously. If we assume that these displacements are independent, the Se atoms and the Te sublattice will move in the polar direction as a whole, and the perpendicular displacements of Se atoms will not affect their movement along the polar axis. The weak dependence of Curie temperature on the Se content in the solid solution may serve as evidence of this supposition. The existence of an additional degree of freedom for Se atoms allows us to predict a possible ordering of perpendicular displacements of impurity atoms at low temperatures. Our results show that according to the classification, Se atoms in GeTe should be considered as noncentrosymmetric defects, the dipole moments of which can easily change their orientation.

As follows from Figure 5, Pb atoms exert a qualitatively different influence on T_c . Two unusual facts found in this work attracted our attention: (i) two different Pb-Te bond lengths appear in the first shell; (ii) the length of shorter Pb-Te bond length is 0.16 Å shorter than that in PbTe (according to our EXAFS data, the Pb-Te distance in PbTe is 3.19 ± 0.01 Å at 77 K).

Two different interpretations of the appearance of two Pb-Te bond lengths in $\text{Ge}_{0.9}\text{Pb}_{0.1}\text{Te}$ are possible. Either (i) all Pb atoms are identical and off-center or (ii) there are two sorts of on-center Pb atoms located in different

cells. Despite the difference in sizes of Pb and Ge atoms (leading to the appearance of strong local strain in the crystal structure around the Pb atom) we find the first interpretation more reasonable.

Indeed, the only cause for the difference in bond lengths within the second interpretation may be the difference in charge states of the Pb atoms. This supposes that charge redistribution between Pb atoms takes place. Charge redistribution evidently should result in substantial changes in the electrical properties of crystals. However the experiment does not show any noticeable change in their electrical properties, and so we conclude that the second interpretation is less probable.

The conclusion about off-centering of large Pb atoms in GeTe is quite unexpected. Indeed, earlier EXAFS studies of isovalent solid solutions have established that the difference between the local bond lengths in binary compounds and solid solutions usually does not exceed 0.03 \AA . In our case we obtained two different Pb-Te bond lengths, one of them being essentially shorter (0.16 \AA) than in PbTe. We suppose that the off-centering of the Pb atom is associated with transformation of the stereochemically inactive electron pair on the $6s$ -shell of the Pb atom into a stereochemically active one. This transformation should obviously be accompanied by the reorganisation of the local environment. X-ray studies performed by Kabalkina, Serebryanaya and Vereshchagin (1968) of the pressure-induced phase transition in PbTe, which occurs from NaCl to GeS structure above 50 kbar, support this interpretation. These studies showed that the change of local coordination of Pb atoms from 6 to $(2+1+2+1)$ at the phase transition was accompanied by an appreciable (about 5%) reduction of the primitive cell volume. Thus, the reorganisation of the local environment of Pb impurity atoms under high stress in the GeTe structure may be considered to be a way in which the elastic energy in the crystal can be reduced.

The appearance of two bond lengths in the first shell and the reduction of the shorter bond were found recently when studying EXAFS of the Sn impurity in GeTe (Lebedev, Sluchinskaya, Demin and Munro, 1996). Similar results obtained for Pb and Sn impurities show that the proposed mechanism for lowering the elastic energy may be quite general. The strong local distortion around Sn and especially Pb atoms in the crystal structure and the reduction of the local polarisability of the structure induced by the distortion are the main causes of the strong decrease of T_c when doping GeTe with these impurities.

The large Debye-Waller factor found for Mn atoms in $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$ enables us to conclude that these atoms are slightly displaced from centrosym-

metric positions. However it is hard to believe that they move in multiwell potential because, as follows from Figure 5, Mn atoms exert the strongest influence on T_c . The physical picture occurring in $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$ can be presented as follows. It is known that MnTe crystallizes in the NiAs structure, typical almost exclusively of chalcogenides of $3d$ transition elements. This is explained by the active participation of $3d$ states in the formation of hybrid sp^3d^2 orbitals. The saturated Mn–Te chemical bond constructed on sp^3d^2 orbitals is much more rigid than the unsaturated Ge–Te bond on the p^3 orbitals. This character of the chemical bond in MnTe forces Mn atoms to occupy on-center positions in the crystal structure, thus strongly decreasing T_c . The experimental finding of a small displacement of Mn atoms from the crystal sites can be explained by their polarisation by the structure (which is in the ferroelectric state). Therefore, when speaking about the Mn impurity in GeTe, we can consider it as an on-center defect polarised by polar media.

5 CONCLUSION

The results of this work show that atomic sizes and the type of chemical bond are the main factors that determine the effect of impurities on the Curie temperature in IV–VI semiconductors-ferroelectrics. The importance of these factors was identified earlier by Lebedev and Sluchinskaya (1993). Direct EXAFS studies on the local environment of impurities, performed in this work, has confirmed completely this supposition and has yielded detailed information about the local structure of impurities that could not be obtained from the earlier indirect experiments. The most interesting among the new results is the displacement of the Pb atom from an on-center site position and the formation of a multiwell potential under high local stress. In short, EXAFS data enabled us to explain the specific effects of different atoms on the ferroelectric phase transition based on the structural information obtained at a microscopic level, thus overcoming the limitations of a phenomenological approach.

Acknowledgements

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