Off-centering of Pb and Sn impurities in GeTe

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X-ray-absorption fine-structure studies of the local structure of large Pb and Sn substitutional impurities in GeTe were carried out. The local environment of these atoms in $Ge_{0.9}Pb_{0.1}Te$ and $Ge_{0.85}Sn_{0.15}Te$ solid solutions was shown to be strongly distorted in comparison with that in binary PbTe and SnTe compounds. The neighboring Te atoms were found at two distances, 3.06 and 3.27 Å (for Pb), and 2.97 and 3.18 Å (for Sn atoms). For both impurities the shortest distance appeared to be substantially shorter than that in corresponding binary compounds with the same overall coordination. The off-centering of Pb and Sn impurities is explained by participation of their deeply lying $6s^2$ and $5s^2$ lone electron pairs in chemical bonding in the condition of strong local stress created by these impurities in the lattice. [S0163-1829(97)04814-5]

I. INTRODUCTION

Off-center ions represent an interesting class of substitutional impurities which were discovered in 1965 (Ref. 1) and have been studied since then using various techniques. The displacement of an off-center ion from a regular lattice site in a crystal creates a dipole moment which can change its orientation. The interaction between such dipoles generates many interesting cooperative phenomena that are closely related to phase transitions. The appearance of a disordered (dipolar glass) state exhibiting nonergodic properties at low temperatures[2,3] is such an example. Vugmeister and Glinchuk[4] have recently proposed a mechanism for indirect dipole-dipole interaction in highly polarizable media (usually known as incipient ferroelectrics), which results in the appearance of "impurity ferroelectricity": that is, a polar state induced by off-center ions.[5,6]

X-ray-absorption fine-structure (XAFS) spectroscopy is a powerful direct method for the investigation of local structure and has made a valuable contribution to studies of off-center ions. It has established the off-centering of Ge and S atoms in PbTe,[7,8] which was anticipated from indirect experiments; revealed the off-centering of Ge atoms in SnTe;[9] showed the off-center behavior of Nb atoms in $KTaO_3$.[10] Moreover, XAFS spectroscopy has given important information on the nature of the phase transitions in some crystals. For instance, XAFS studies have revealed that the phase transitions in $Pb_{1-x}Ge_xTe$ (Ref. 7) and $Na_{0.82}K_{0.18}TaO_3$ (Ref. 11) are of the order-disorder type in spite of the fact that the macroscopic properties of these crystals indicate displacive type phase transitions.

It should be noted that all experimental data for off-center ions are restricted to small atoms substituting for larger atoms in crystals.[12] The main reason for the off-center instability of small atoms in ionic crystals is the inability of the decreased repulsive forces to oppose the action of the polarization forces that tend to displace the ion from its centrosymmetric position.[1,13] In covalent crystals the off-centering of small atoms was explained by the chemical rebonding.[14]

In this work we report direct experimental observation of the off-centering of *large* (Pb and Sn) substitutional impurities in GeTe using the XAFS technique and discuss a possible explanation for this phenomenon.

II. EXPERIMENT

Samples of $Ge_{0.9}Pb_{0.1}Te$ and $Ge_{0.85}Sn_{0.15}Te$ were prepared for XAFS investigations by alloying germanium telluride ($GeTe_{1.016}$) with PbTe and $SnTe_{1.016}$ in evacuated quartz ampoules. Before the measurements the alloys were annealed at 545–590 °C for 50 h and quenched in cold water to prevent the possible decomposition of the solid solution. X-ray studies confirmed the homogeneity of the samples and showed that at 300 K they had the rhombohedral structure of α-GeTe. The alloys were then powdered and sieved and the powder was rubbed into the surface of adhesive tape. From 8 to 24 layers of tape were used for the recording of XAFS spectra.

The XAFS experiments were carried out at Daresbury Laboratory on stations 7.1 and 9.3 with an electron beam energy of 2 GeV. The maximum storage ring current was 250 mA (in multibunch mode) in the experiment on station 7.1 and 25 mA (in single-bunch mode) in the experiment on the 5 T wiggler station 9.3. The monochromators used were two flat Si(111) crystals (station 7.1) and two flat Si(220) crystals (station 9.3). Measurements were made at 80 K, at the K edges of Ge (11.103 keV), Sn (29.200 keV), and at the L_{III} edge of Pb (13.055 keV). The XAFS data were collected in transmission mode using ion chambers filled with He+Ar or He+Xe gas mixtures that gave 20 and 80% absorption of incident radiation at the edge under investigation.

The oscillatory extended XAFS (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 normal way.[15] After removing the pre-edge background, splines were used to extract the smooth atomic part of the absorption, $\mu x_0(E)$, and 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 energy origin, E_0, was taken to be the position of the inflection point on the absorption edge. The edge steps ranged from 0.08 to 1.4. For each sample
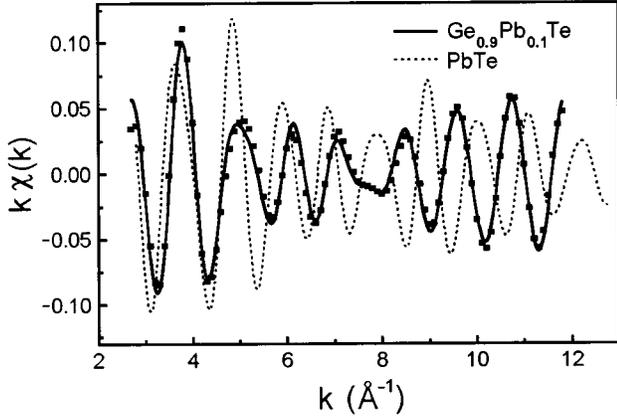
FIG. 1. EXAFS function $k\chi(k)$ obtained at the Pb L_{III} edge for $Ge_{0.9}Pb_{0.1}Te$ and PbTe samples at 80 K. Points indicate filtered data ($R = 1.4 - 4.3$ Å); solid line is the best theoretical approximation within the model with two Pb-Te distances in the first shell and equal Pb-Ge and Pb-Pb distances in the second shell. The dotted curve shows $k\chi(k)$ data for PbTe.

several measurements were repeated. The records were all independently processed and the resulting $\chi(k)$ curves finally averaged.

Direct and inverse Fourier transforms with modified Hanning windows[16] were used to extract the information about the first and second 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 δE_0 were simultaneously varied to obtain the minimum root-mean-square deviation between the experimental and calculated $k\chi(k)$ curves. The number of fitting parameters (from 6 to 10) was usually about half of the number of independent data points [$N_{\mathrm{ind}} = 2\Delta k\Delta R/\pi = 15-20$ (Ref. 15)]. The accuracy of the fitting parameters was estimated from the correlation matrix and the errors presented in this work correspond to 95%-confidence level interval of variation in the parameters. To increase this accuracy additional constraints and relations between the parameters were taken into account (e.g., equal energy corrections δE_0 for all shells and known relation between coordination numbers for known structures).

FEFF software[17] was used to calculate the dependence of the backscattering 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 GeTe, PbTe, and SnTe samples.

III. RESULTS AND DISCUSSION

Figure 1 shows EXAFS function $k\chi(k)$ obtained at the Pb L_{III} edge for $Ge_{0.9}Pb_{0.1}Te$ and PbTe samples. Comparison between these data shows that the shape and the period of oscillation for these spectra are different. It means that the local environment for Pb atoms in $Ge_{0.9}Pb_{0.1}Te$ and PbTe is different. Quantitative analysis shows that the model, in which all Te atoms in the first shell of Pb in $Ge_{0.9}Pb_{0.1}Te$ are located at the same distance, cannot describe the experimental data satisfactorily. We achieved good agreement between experimental and theoretical curves (see Fig. 1) only in the case of a model in which the first shell of the Pb atom consists of two Te subshells at distances $R_1 = 3.06$ Å and $R_2 = 3.27$ Å (see Table I). The coordination numbers corresponding to these distances were 4.2 ± 0.6 and 1.8 ± 0.7.[18] Debye-Waller factors for the Pb-Te bonds in $Ge_{0.9}Pb_{0.1}Te$ ($\sigma_1^2 = 0.002$ Å^2 and $\sigma_2^2 = 0.005$ Å^2) were lower than that for PbTe (0.006 Å^2). The metal atoms in the second shell (Ge and Pb) were at an average distance of $R_3 = 4.30$ Å, which coincides with the distance determined from x-ray data.

The species of the surrounding atoms and interatomic distances in the first and second shells revealed by the analysis show that Pb atoms substitute for Ge atoms in GeTe. However Pb atoms are much larger than Ge ones ($r_{Ge^{2+}} = 0.73$ Å, $r_{Pb^{2+}} = 1.26$ Å) and so they must create strong local stress in the GeTe lattice. This conclusion is confirmed by the fact that both found Pb-Te distances exceed the corresponding Ge-Te interatomic distances in GeTe (see Table I). The strong local stress around the Pb atom is a reason of the decreased Debye-Waller factors for Pb-Te bonds, while the increased Debye-Waller factor for the second shell (compared to the GeTe data, see Table I) is due to the disorder in the solid solution.

Two surprising facts in the data for $Ge_{0.9}Pb_{0.1}Te$ have attracted our attention. They are (i) the appearance of two different Pb-Te distances in the first shell instead of a single distance and (ii) the fact that the shortest Pb-Te bond is 0.16 Å less than the length of the same bond in PbTe (3.22 Å at 80 K, see Table I). The latter is in contradiction with the results of earlier EXAFS studies, which have shown that bond lengths in isovalent solid solutions usually do not differ by more than 0.03–0.04 Å from those in the basic binary compounds.

TABLE I. Interatomic distances and Debye-Waller factors for the first and second shells for $Ge_{0.9}Pb_{0.1}Te$, $Ge_{0.85}Sn_{0.15}Te$ solid solutions and PbTe, SnTe, and GeTe binary compounds at 80 K.

Sample	The first shell				The second shell	
	R_1, Å	σ_1^2, 10^{-3} Å^2	R_2, Å	σ_2^2, 10^{-3} Å^2	R_3, Å	σ_3^2, 10^{-3} Å^2
$Ge_{0.9}Pb_{0.1}Te$	3.055 ± 0.005[a]	2.30 ± 0.56	3.266 ± 0.009[a]	5.74 ± 0.88	4.302 ± 0.014[a]	21.4 ± 2.2
PbTe	3.222 ± 0.005[a]	5.54 ± 0.63			4.621 ± 0.026[a]	18.2 ± 4.7
$Ge_{0.85}Sn_{0.15}Te$	2.965 ± 0.007	1.26 ± 0.80	3.154 ± 0.025	8.97 ± 2.68	4.236 ± 0.059	31.0 ± 10.3
SnTe	3.135 ± 0.006	4.39 ± 0.86			4.450 ± 0.016	3.71 ± 2.68
GeTe	2.795 ± 0.002	3.69 ± 0.32	3.148 ± 0.004	6.41 ± 0.54	4.199 ± 0.007	16.9 ± 1.1

[a]All the distances found at the Pb edge were increased by 0.03 Å to take into account systematic error probably originating from central atom phase calculation for heavy Pb atom in FEFF.

There are two ways to interpret the appearance of two Pb-Te bond lengths: to state that either all Pb atoms are off-center or that there exist two different sorts of Pb atoms in Ge sites. Despite the unlikely possibility of a displacement of a Pb atom from its lattice site in conditions where strong local stress exists, we think that this interpretation is the only one possible. Indeed, the only reason for the distinction in the Pb-Te bond lengths in the model with two different sorts of Pb atoms may simply be the difference between the charge state of Pb atoms. However the transition of roughly half of the Pb atoms to a state with higher valence (which could explain the reduction in the interatomic distance to 3.06 Å) should inevitably be accompanied by a drastic change in the electrical properties of crystals (in contradiction with known experimental data[19]).

Therefore, in our opinion the interpretation of the data in terms of the off-centering of the Pb atoms is much more reasonable. In contrast to studies of all other crystals with off-center ions of small radius (where the shortest interatomic distance is nearly the same as in corresponding binary compound), the length of the shortest Pb-Te bond in $Ge_{0.9}Pb_{0.1}Te$ is shown to be substantially less than in binary PbTe. This fact enables us to reach some conclusions about the nature of the observed phenomenon. The appreciable reduction of the Pb-Te bond length clearly indicates the qualitative change in the character of the Pb-Te chemical bond in the solid solution. This change is made possible because the Pb atom has a lone (unshared) $6s^2$ electron pair that is stereochemically inactive in PbTe but which can become stereochemically active when promoting one of its s electrons.[20] An obvious consequence of participation of $6s$ states in chemical bonding will be the reorganization of the local environment of the Pb impurity atom and its displacement from the centrosymmetric position.

Results from investigations into the pressure-induced phase transition in PbTe, which occurs from NaCl to GeS structure at 50 kbar,[21] shed additional light on the nature of off-centering of Pb atoms in GeTe. These investigations showed that the change in the local coordination of Pb atoms from 6 to $2+1+2+1$ at the phase transition is accompanied by an appreciable (from 2 to 5 %, according to different data) reduction in the volume of the primitive cell. Thus, the reorganization of the local environment of Pb atoms may be considered to be a way in which the elastic energy of a crystal can be lowered. In this case the off-centering of Pb atoms becomes energetically favorable.

Unfortunately, we did not perform XAFS studies on our samples above the temperature of the ferroelectric phase transition (which is well above the room temperature) to finally confirm the off-centering of the Pb atom. However it is extremely unlikely that such an essential reduction in the Pb-Te bond length could be associated with the polarizing effect of the ferroelectric state on the position of the Pb atom.

Similar results were obtained for the Sn impurity in GeTe. As follows from Fig. 2, the functions $k\chi(k)$ obtained at the Sn K edge for $Ge_{0.85}Sn_{0.15}Te$ and SnTe samples are also qualitatively different. The data at the Sn edge had lower signal-to-noise ratio (compared to $Ge_{0.9}Pb_{0.1}Te$ data) and the spectra were contaminated by glitches. Nevertheless the analysis revealed that the lengths of Sn-Te bonds in $Ge_{0.85}Sn_{0.15}Te$ were 2.97 and 3.18 Å (in contrast to a single
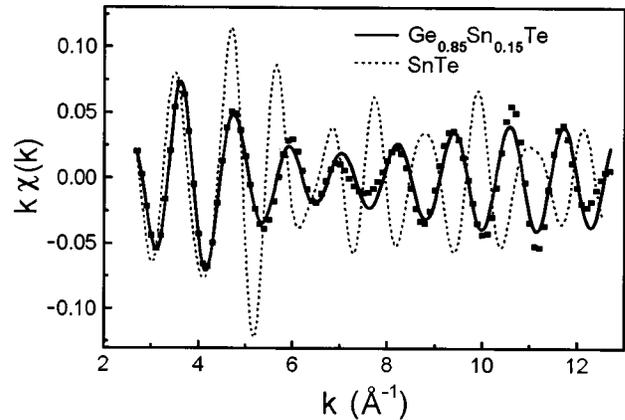
FIG. 2. EXAFS function $k\chi(k)$ obtained at the Sn K edge for $Ge_{0.85}Sn_{0.15}Te$ and SnTe samples at 80 K. Points indicate filtered data ($R = 1.85 - 4.2$ Å); solid line is the best theoretical approximation within the model with two Sn-Te distances in the first shell and equal Sn-Ge and Sn-Sn distances in the second shell. The dotted curve shows $k\chi(k)$ data for SnTe.

distance of 3.14 Å for SnTe, see Table I). The coordination number corresponding to the distance 2.97 Å was close to 3. The Ge and Sn atoms in the second shell were located at an average distance 4.20 Å.

These results clearly demonstrate the essential change in the character of the Sn-Te chemical bond in $Ge_{0.85}Sn_{0.15}Te$ in comparison with SnTe. Therefore we can assume that Sn atoms are also off-center in GeTe crystals, and that the reason for the off-centering is identical to that for Pb atoms. Qualitatively similar results obtained for Pb and Sn impurities in GeTe enable us to conclude that the proposed mechanism for lowering the elastic energy is probably quite general.

We note that $Pb_{1-x}Ge_xTe$ and $Sn_{1-x}Ge_xTe$ samples with low Ge concentration ($x \leq 0.2$) already have been investigated using the XAFS technique.[7,9] The off-centering of Ge atoms was established in these cases. However no anomalies have been found in Pb-Te and Sn-Te bond lengths except that of the increase of the Debye-Waller factor for the Pb-Te bond in $Pb_{1-x}Ge_xTe$ indicating the relative shift of sublattices in the polar phase.

IV. CONCLUSIONS

We have made direct structural measurements of the local environment of the large substitutional atoms of Pb and Sn in GeTe crystals using the XAFS technique and have discovered a new type of off-centering of impurities of *large* size. In our opinion, the off-centering of these atoms is closely related to the existence of the lone s^2 electron pair that becomes stereochemically active under high local stress thus providing a gain in elastic energy of the crystal. Thus, we conclude that chemical rebonding is probably the main cause for the off-centering of both small and large impurity atoms in crystals.

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[18] Using another method, in which the backscattering amplitude and phase functions for Pb-Te pair were extracted from the PbTe standard sample, the following distances and coordination numbers were obtained: $R_1 = 3.05 \pm 0.015$ Å, $R_2 = 3.27 \pm 0.025$ Å, $N_1 = 3.5 \pm 0.9$, $N_2 = 2.8 \pm 1.2$. They are in good agreement with the data calculated using FEFF amplitudes and phases.

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