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Off-Centering of Pb and Sn Impurities in GeTe Induced by Strong Local Stress

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Abstract. The local environment of large Pb and Sn substitutional impurities in GeTe was found to be strongly distorted compared to that in binary PbTe and SnTe compounds. For both impurities the neighboring Te atoms were found at two different distances, the shortest of them being by 0.16–0.17 Å less than that in corresponding binary compound. The off-centering of Pb and Sn impurities is explained by participation of their $6s^2$ and $5s^2$ unshared electron pairs in chemical bonding in the condition of strong local stress created by these impurities in the lattice.

1. INTRODUCTION

XAFS spectroscopy, which is a powerful method for investigation of the local structure, has made a valuable contribution to studies of off-center ions [1,2]. So far all known experimental data for off-center ions were restricted to small atoms substituting for larger atoms in crystals [3]. In this work we report the first experimental observation of the off-centering of large (Pb and Sn) substitutional impurities in GeTe and discuss a possible explanation for this phenomenon.

2. EXPERIMENT

Samples of $\text{Ge}_{0.9}\text{Pb}_{0.1}\text{Te}$ and $\text{Ge}_{0.85}\text{Sn}_{0.15}\text{Te}$ were prepared by alloying germanium telluride ($\text{GeTe}_{1.016}$) with PbTe and SnTe_{1.016} in evacuated quartz ampoules. Before the measurements alloys were annealed at 545–590°C for 50 h. The homogeneity of the samples was confirmed by X-ray studies.

The XAFS experiments were carried out at Daresbury Laboratory on the stations 7.1 and 9.3 with an electron beam energy of 2 GeV and a maximum storage current of 250 mA on the station 7.1 (multi-bunch mode) and 25 mA on the wiggler station 9.3 (single-bunch mode). Measurements were made at 80 K, at the *K*-edges of Ge and Sn, and at the *L*_{III}-edge of Pb in transmission mode. For each sample several measurements were repeated.

The oscillatory EXAFS function $\chi(k)$ was extracted from the absorption curve $\mu x(E) = \ln(I_0/I)$ in a conventional way [4]. The edge steps ranged from 0.08 to 1.4. The information about the two closest shells was extracted from $k\chi(k)$ curve using direct and inverse Fourier transforms. The nonlinear fitting was used to obtain distances, coordination numbers and Debye-Waller factors for each shell. The number of fitting parameters (6–10) was usually about half of the number of independent data points (15–20). The accuracy of the fitting parameters was estimated from the correlation matrix.

The backscattering amplitude and effective phase of a photoelectron were calculated using FEFF software [5] or extracted from standard PbTe and SnTe samples.

3. RESULTS AND DISCUSSION

Figure 1 compares EXAFS functions $k\chi(k)$ obtained at the Pb *L*_{III}-edge for $\text{Ge}_{0.9}\text{Pb}_{0.1}\text{Te}$ and PbTe samples. Different shapes and periods of oscillation for these spectra mean that the local environment of Pb atoms in these crystals is different. Analysis showed that the experimental data can be described well only in the case of a model in which the nearest Te atoms are at two different distances, 3.05 ± 0.015 and 3.27 ± 0.025 Å, with the corresponding coordination numbers of 3.5 ± 0.9 and 2.8 ± 1.2 . The metal atoms in the second shell were revealed at an average distance of 4.30 ± 0.02 Å. The species of the surrounding atoms and interatomic distances revealed by the analysis show that Pb atoms substitute for Ge atoms in GeTe, but due to large difference in sizes of Pb and Ge atoms, impurities create strong local stress in the GeTe lattice.

Two surprising facts in the data for $\text{Ge}_{0.9}\text{Pb}_{0.1}\text{Te}$ have attracted our attention. They are (i) the appearance of two different Pb–Te distances in the first shell instead of a single one and (ii) the fact that the length of the shortest Pb–Te bond is 0.16 Å less than the length of the same bond in PbTe. The latter is surprising because the bond lengths in isovalent solid solutions do not usually differ by more than 0.03–0.04 Å from those in the basic binary compounds.

In our opinion, these facts can be explained by the off-centering of Pb atoms.

The shortest interatomic distance in all earlier studied crystals with off-center ions of small radius is nearly the same as in corresponding binary compound. However the length of the shortest Pb–Te bond in $\text{Ge}_{0.9}\text{Pb}_{0.1}\text{Te}$ is shown to be substantially less than in PbTe. This can indicate the qualitative change in the character of the Pb–Te chemical bond in the solid solution. In our opinion, this change is made possible because the Pb atom has unshared $6s^2$ electron pair that does not participate in chemical bonding in PbTe but can play more active role in $\text{Ge}_{0.9}\text{Pb}_{0.1}\text{Te}$.

Figure 1: $k\chi(k)$ curves obtained at the Pb L_{III} -edge for $\text{Ge}_{0.9}\text{Pb}_{0.1}\text{Te}$ and PbTe samples at 80 K. Points — filtered data ($R = 1.4 - 4.3$ Å), solid line — the best theoretical approximation. Dotted line shows $k\chi(k)$ curve for PbTe.

Figure 2: $k\chi(k)$ curves obtained at the Sn K -edge for $\text{Ge}_{0.85}\text{Sn}_{0.15}\text{Te}$ and SnTe samples at 80 K. Points — filtered data ($R = 1.85 - 4.2$ Å), solid line — the best theoretical approximation. Dotted line shows $k\chi(k)$ curve for SnTe.

The existence of the pressure-induced phase transition in PbTe, which occurs from NaCl to GeS structure at 50 kbar [6] and is accompanied by the distortion of the local environment of the Pb atom, confirms the possibility of participation of the unshared pair in chemical bonding. Moreover, it was shown that this phase transition is accompanied by an appreciable 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.

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 $\text{Ge}_{0.85}\text{Sn}_{0.15}\text{Te}$ and SnTe samples are also qualitatively different. The analysis revealed that the lengths of Sn–Te bonds in $\text{Ge}_{0.85}\text{Sn}_{0.15}\text{Te}$ were 2.97 ± 0.02 and 3.18 ± 0.03 Å (in contrast to a single distance of 3.14 ± 0.01 Å for SnTe). The coordination number corresponding to the distance 2.97 Å was close to 3. The metal atoms in the second shell were located at an average distance 4.20 ± 0.04 Å.

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.

In summary, direct measurements of the local environment of the large substitutional atoms of Pb and Sn in GeTe crystals have discovered a new, previously unknown type of off-centering of impurities of large size. The off-centering of these atoms is attributed to the existence of the unshared s^2 electron pair that becomes stereochemically active under high local stress. Thus, we conclude that the chemical rebonding is probably the main cause for the off-centering of both small and large impurity atoms in crystals.

Acknowledgments

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