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Analysis of Chemical Disorder in $Pb_{1-x}Ge_xTe$

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The PbGeTe crystal lattice is locally deformed due to different ionic radii of cations and their random placement in the lattice. It is important to quantitatively characterize such microscopic disorder because local deformations have significant influence on the properties of magnetic ions introduced to such crystal. The simples method to study microscopic disorder is to consider purely classical model of the lattice in which neighboring atoms are connected by springs with properly chosen spring constant and equilibrium lengths. In the present work, using *ab initio* methods we discuss applicability of the springs-atoms model to the real crystal. We also explain results of extended X-ray absorption fine structure experiments performed on PbGeTe mixed crystals.

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1. Introduction

The microscopic local disorder, known also as the chemical disorder is an unavoidable feature of mixed crystals. In such crystals we have two different anions or two different cations, thus in general two different nearest neighbor cation–anion distances. The existence of these two distances, together with lack of perfect long range order leads to microscopic distortions. It means that practically every ion in the crystal lattice has different nearest neighborhood and the symmetries of the neighborhoods are in general lower than the symmetry of the crystal considered as the macroscopic body. From our previous studies it is known that the microscopic disorder strongly influences the properties of magnetic ions introduced to locally deformed lattices. Number of experimentally observed phenomena may be explained taking microscopic disorder into account, for example magnetic specific heat in $Pb_{1-x}Eu_xTe$ crystals [1] or the broadening of EPR lines for Eu^{2+} ions in $Pb_{1-x}Ge_xTe$ with increasing germanium content [2].

In the present work we investigate microscopic disorder in $Pb_{1-x}Ge_xTe$ mixed crystals. These materials are very interesting concerning possible applications in spintronics. It is known that these crystals reveal ferroelectric properties

and after introducing magnetic ions also ferromagnetic properties. The possibility of simultaneous control of ferroelectricity and magnetism may lead to very interesting applications, for example to four state memories. However, in order to fully understand magnetic properties of magnetic ions in such mixed crystal one should characterize the local microscopic disorder in a crystal. The present work is the first step to achieve this goal.

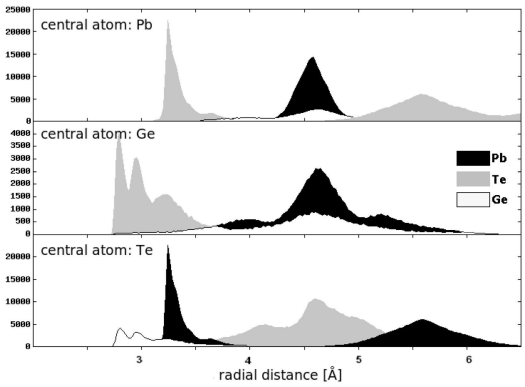

Fig. 1. Radial distribution functions — results of simulations for PbGeTe lattice [2]. Let us notice three tellurium maxima in the second part for germanium as the central atom.

In our previous work [2] we investigated microscopic disorder in $Pb_{1-x}Ge_xTe$ in the framework of purely classical model. The starting point of the model was a perfect PbTe lattice with some Pb atoms randomly replaced by Ge atoms. The nearest neighbors ions were connected by springs with properly chosen spring constants and the equilibrium spring lengths. It is known that in GeTe the germanium atoms are not in the centers of the unit cells but displaced along [111] direction [3]. In order to simulate this effect we introduced two kinds of springs connecting germanium atom and neighboring tellurium atoms, namely three of them had shorter equilibrium length than the other three. After zero temperature Monte Carlo procedure we obtained equilibrium configuration of the lattice. Having equilibrium configuration it was possible to predict theoretically different ion–ion radial distribution functions (see Fig. 1) and compare them to those measured in extended X-ray absorption fine structure (EXAFS) experiments [3]. However, applying the model described above only part of experimental results could be explained, for example for germanium as the central atom (see the second part of Fig. 1) we obtained two tellurium maxima (the left one and the right one). In order to obtain the third maximum, that placed approximately at 3 Å we had to assume that part of the germanium atoms are connected with neighboring tellurium atoms by six identical springs. One of the conclusions of Ref. [2] was that in $Pb_{1-x}Ge_xTe$ mixed crystal only part of germanium atoms were displaced in the unit cells along

[111] direction like in pure GeTe compound. There was also significant part of Ge atoms for which the equilibrium positions were at the centers of the unit cells.

The main aim of the present paper is to investigate disordered $Pb_{1-x}Ge_xTe$ lattice, using *ab initio* methods. In particular we want to study to what extent the simple model based on atoms connected by springs may serve as a proper description of the mixed crystal and to check whether quantum mechanical calculations lead to the presence of more than one equilibrium position for Ge.

2. Calculation details

In calculations we used two packages: OpenMX [4] and Quantum Espresso [5]. The atoms building the investigated system are heavy atoms, in particular lead. Thus it is necessary to use methods in which relativistic effects (the spin–orbit coupling) are taken into account. Starting the density functional theory calculations it is very important to choose properly the exchange-correlation energy functional and the pseudopotentials, i.e. number of valence electrons and cut-off radii. For problems considered in the present paper the basic check of the appropriateness of these choices is comparison of system's equilibrium lattice constant a_0 and the bulk modulus B obtained from calculations with the corresponding experimental values. Both packages provide codes for calculations of pseudopotentials. We spent a lot of time trying to obtain pseudopotentials for Pb, Te and Ge assuming that the valence electrons are only s and p electrons from the most outer shells of the atoms. Unfortunately, for pseudopotentials with such small numbers of valence electrons the calculated values of a_0 and B for PbTe were not in agreement with experiment. Eventually we used pseudopotentials distributed with the packages. In the case of Quantum Espresso calculations we used available pseudopotentials which, unfortunately, did not take into account spin–orbit effects. For OpenMX, it turned out that the best pseudopotentials are those with local density approximation (LDA) for exchange-correlation energy functional. This is interesting, because it is usually accepted that the generalized gradient approximation (GGA) should be better than LDA. Comparison of the energy of the unit cell as a function of lattice constant is presented in Fig. 2. For LDA we obtained for PbTe $a_0 = 6.5$ Å, $B = 46$ GPa which corresponds quite well to the experimental values $a_0^{\text{exp}} = 6.46$ Å and $B^{\text{exp}} = 43$ GPa [6].

Unfortunately, because of the large number of valence electrons:

— 20 for Pb, 16 for Te and 14 for Ge in case of OpenMX (the necessity of taking into account s, p, and d orbitals as the basis orbitals: 24 orbitals for Pb, 18 for Te and Ge),

— 14 for Pb, 6 for Te and 4 for Ge in case of Quantum Espresso, the calculations are time consuming and dimensions of the systems in calculations are limited.

In order to justify the atoms-springs model of the lattice one should know if the force acting on an atom which is moved from its equilibrium position is

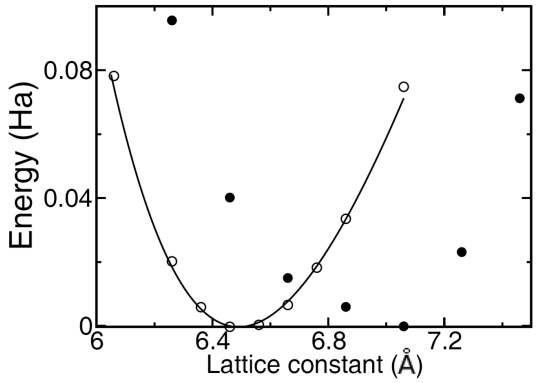

Fig. 2. Comparison of the energy of the unit cell of PbTe as the function of the lattice constant for two exchange-correlation functionals. Open points LDA approximation, closed points GGA approximation, the line is the Birch–Murnaghan [7] energy dependence (OpenMX calculations).

proportional to the displacement Δx or, in other words, if the energy is a quadratic function of Δx. In our studies we considered three types of structures. The first structure was 27-atom cluster which allows us to check the shape of the total energy dependence on displacement of ions in pure PbTe. The second structure considered by us was $2\times2\times2$ supercell (64 atoms, part of the infinite crystal). This structure was to model regions in $Pb_{1-x}Ge_xTe$ mixed crystal where concentration x of Ge is low (of the order of 0.03 or smaller). In order to simulate regions with higher concentration (x of the order of 0.2–0.3) we calculated energy of the third structure: $1 \times 1 \times 1$ supercell for $Pb_{0.75}Ge_{0.25}Te$ crystal, it means the perfect crystal with the unit cell consisting of four Te atoms, three Pb atoms and one Ge atom. In all cases the energy was calculated as a function of the displacement of the central atom.

3. Results

As it is seen from Fig. 3 in the case of lead the energy as a function of displacement is nearly quadratic. This is not the case for tellurium, but the deviations from parabola (thin solid line) are only for small Δx.

Figures 4 and 5 show that the behaviors of Ge atom in $1\times1\times1$ and $2\times2\times2$ are quite different. For $2\times2\times2$ supercell which is to model $Pb_{1-x}Ge_xTe$ with low Ge concentration the absolute minimum is at the center of the cell. For $1 \times 1 \times 1$ supercell which corresponds to higher Ge concentration the minimum is displaced from the center. The differences between OpenMX and Quantum Espresso results may be due to different pseudopotentials and due to small plane wave or atomic orbital basis taken in the calculations. However, the qualitative behaviors of the presented curves are the same.

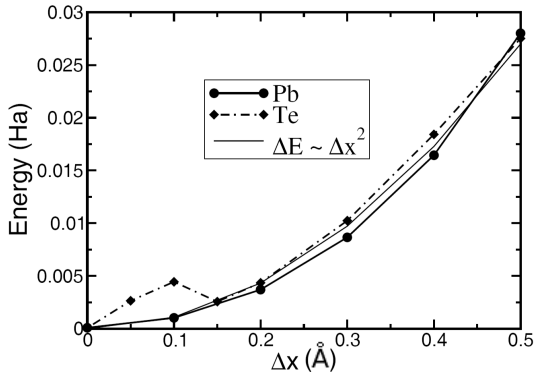

Fig. 3. Dependence of the energy of 27-atom cluster (OpenMX calculations) on the displacement Δx of the central atom from the cluster's center along [100] direction.

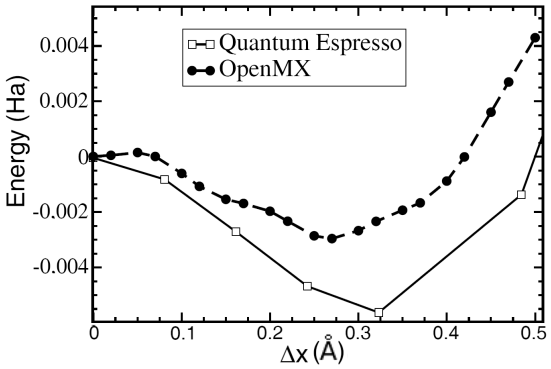

Fig. 4. Comparison of dependences of the total energy on the displacement Δx of the Ge ion from the lattice point along [111] direction for $1 \times 1 \times 1$ supercell. Δx is measured along [100] direction.

We think that these results explain the presence of three peaks observed in EXAFS experiments (see the second part of Fig. 1 and Ref. [3]). In $Pb_{1-x}Ge_xTe$ the distribution of Ge atoms is not homogeneous. Due to fluctuations there are regions in which the local concentration of germanium is smaller and the regions where the concentration is larger. The regions with smaller concentration are responsible for the central peak in the second part of Fig. 1, the regions with larger concentrations produce two other peaks.

In the present paper we studied number of atomic configurations in disordered $Pb_{1-x}Ge_xTe$ mixed crystal using *ab initio* methods. Three main conclusions may be drawn.

1. Concerning elastic properties of PbTe the local density exchange--correlation functional gives better results than generalized gradient approximation.

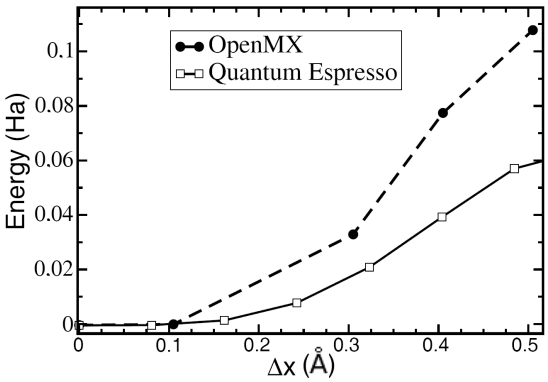

Fig. 5. Comparison of dependences of the total energy on the displacement Δx of the Ge ion from the lattice point along [111] direction for $2\times2\times2$ supercell. Δx is measured along [100] direction.

2. The atom-spring model of the disordered crystal lattice may serve as a crude approximation only. In particular, from Figs. 4 and 5 it is seen that the forces acting on germanium atom depen not only on the nearest neighborhood of an atom but also on an average germanium concentration in the region.

3. Results of quantum mechanical calculations explain presence of three maxima for germanium–tellurium radial correlation function obtained from EXAFS experiments.

Acknowledgments

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