

LATTICE DYNAMICS AND PHASE TRANSITIONS

A New Method for Determining Parameters of the Potential Well of Off-Center Atoms from EXAFS Data

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Abstract—A new method is proposed that makes it possible to determine the parameters of the three-dimensional (3D) multiwell potential of off-center atoms from extended X-ray absorption fine-structure (EXAFS) data. The main features of this approach are the expansion of the 3D potential of a cluster in a power series of an atomic displacement taking into account the restrictions imposed by the lattice-site symmetry and exact 3D integration of the distribution function in calculations of EXAFS spectra. The parameters of the multiwell potential for Ge atoms in the $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ solid solution as functions of temperature and composition ($77 \leq T \leq 300$ K, $x \geq 0.4$) were obtained in the classical approximation. It is shown that the anharmonic part of the potential is highly anisotropic, and the type of ferroelectric phase transition in $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ is intermediate between the displacive and order–disorder transitions. © 2004 MAIK “Nauka/Interperiodica”.

INTRODUCTION

Off-center impurities have long attracted the attention of researchers due to their unusual properties [1]. In particular, they may give rise to ferroelectric phase transitions in crystals (for example, impurities of Ge in SnTe, PbTe, and PbSe; S in PbTe; and Li in KTaO_3). However, even data on the type of phase transitions in such crystals often turn out to be contradictory. For example, in GeTe–SnTe solid solutions, the behavior of the specific heat [2] and the moduli of elasticity [3] in the vicinity of the Curie point T_c indicate that the phase transitions in these compounds are similar to displacive (in addition, a soft phonon mode is observed in GeTe [4]), whereas the extended X-ray absorption fine-structure (EXAFS) studies indicate clearly that Ge atoms are off-center at temperatures both below and above T_c [5]. The latter circumstance indicates the existence of a multiwell potential and an order–disorder phase transition. These contradictions cannot be explained without direct determination of the parameters of the multiwell potential of an off-center impurity.

EXAFS spectroscopy is a powerful tool for studying the potential of interatomic interaction in crystals. Presently, to determine the parameters of anharmonic interatomic potential from EXAFS data, the cumulant expansion method is used [6, 7]. However, the practical implementation of this approach encounters the following problems. First, the anharmonicity should not be very strong to make it possible to restrict the expansion in terms of the modulus of the wave vector k to a few first terms. Second, the method cannot be applied in practice to crystals in which the potential has several minima. In addition, the cumulant expansion method does not provide information on the anisotropy of

atomic motion. At the same time, the potential of off-center impurities has several energetically equivalent minima corresponding to the displacement of an atom from a lattice site to a particular off-center position; therefore, another approach should be developed to solve the problem stated.

In this study, we propose a new method to solve the problem of determining the parameters of the multiwell potential of off-center impurities, which has no drawbacks inherent in the cumulant expansion method. This approach is used to study the shape of the potential well of Ge atoms in the $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ solid solution under conditions of varying temperature and Ge concentration.

DESCRIPTION OF THE APPROACH

In the EXAFS theory, the oscillating part of the spectrum at the absorption K edge (the EXAFS function) has the following form in the single-scattering approximation [8]:

$$\chi(k) = \sum_i \frac{S_0^2}{k} \text{Im} \left\{ f(k, \pi) \exp(2i\delta_1) \right. \\ \left. \times \int \frac{\rho(\mathbf{r}) \exp(-2r/\lambda)}{r^2} \exp(2ikr) d\mathbf{r} \right\}. \quad (1)$$

Here, the summation is over all the nearest neighbors, S_0^2 is the factor taking into account many-electron effects and inelastic scattering, f is the backscattering function (including the amplitude and phase of scattering), δ_1 is the phase of a photoelectron escaping from an

absorbing atom, λ is the mean free path of a photoelectron, k is the modulus of the wave vector of a photoelectron, $\rho(\mathbf{r})$ is the probability of finding the scattering atom at the point \mathbf{r} , and $r = |\mathbf{r}|$ is the distance between the absorbing and scattering atoms. The functions S_0^2 , f , δ_1 , and λ characterize the absorbing and scattering atoms, and the distribution function $\rho(\mathbf{r})$ contains information on the local structure and motion of atoms.

The potential-well parameters can be determined from the EXAFS spectra because the function $\rho(\mathbf{r})$ is determined by the three-dimensional (3D) potential $V(\mathbf{r})$. The approach to processing the EXAFS spectra proposed by us consists of the following stages. First, we parametrize the 3D potential $V(\mathbf{r})$ taking into account the crystal symmetry. Then, we calculate the normalized distribution function $\rho(\mathbf{r})$ and substitute it into Eq. (1) to calculate the theoretical EXAFS spectrum and compare it with the experimental spectrum. Furthermore, varying the parameters of the potential and repeating the procedure of calculation of the theoretical spectrum, we minimize the mean-square deviation of the calculated EXAFS spectrum from the experimental one and thus determine the shape of the potential well.

The crystals under study have a NaCl structure above the phase-transition temperature. In this structure, each off-center Ge atom moves in an octahedron formed by six Te atoms. Since, due to the presence of a soft optical mode, the amplitude of optical vibrations of ferroelectrically active atoms in ferroelectrics is always much larger than the amplitude of relative vibrations of atoms in the same sublattice (it is determined by the energy of phonons at the edge of the Brillouin zone), we can neglect the thermal motion of Te atoms in the first-order approximation and consider only the motion of a Ge atom in a rigid octahedron. In our experiments, Ge and Te atoms are absorbing and scattering atoms, respectively. Since we are interested in the motion of Ge atoms, it will be more convenient to select a cluster consisting of seven atoms (one Ge and six Te atoms) and pass to a new system of reference with the origin at the center of symmetry of the octahedron. Taking into account that $\rho(\mathbf{r})$ is a pair distribution function, we can rewrite Eq. (1) in the new system of reference and show that the expression for $\chi(k)$ remains the same with the only exception: the vector \mathbf{r} is now the coordinate of the Ge atom and $\rho(\mathbf{r})$ is the probability of finding the Ge atom at the point \mathbf{r} . In the new system of reference, Te atoms are located at the distance $a_0/2$ from the origin of coordinates along the $\langle 100 \rangle$ axes (a_0 is the lattice parameter). This means that, for a Ge atom located at the point $\mathbf{r} = (x, y, z)$, the contribution of the six Te atoms to the EXAFS function (1) will be determined by six 3D integrals, in which distances r are calculated by the formula $r^2 = (a_0/2 - x)^2 + y^2 + z^2$.

In the microscopic model of ferroelectricity, the effective potential $V(\mathbf{r})$ (in which an atom moves) consists of two terms: the local anharmonic potential

$V_{\text{loc}}(\mathbf{r})$ and the quantity $V_{mf} = (\mathbf{dE}_{mf})$, which describes the interaction of the atom under consideration with all the other atoms and the external field [9]. Let us expand the potential $V_{\text{loc}}(\mathbf{r})$ in the vicinity of the origin of coordinates in terms of the powers of the atomic-displacement components. For a site characterized by the point symmetry group O_h , the expansion in powers up to the fourth order has the form

$$V_{\text{loc}}(\mathbf{r}) = \alpha + \beta r^2 + \gamma r^4 + \delta(x^2 y^2 + x^2 z^2 + y^2 z^2), \quad (2)$$

$$r^2 = x^2 + y^2 + z^2,$$

where α , β , γ , and δ are some coefficients. Since the distribution function does not depend on the choice of the reference point on the energy scale, we assume that $\alpha = 0$. Then, expression (2) can be rewritten as follows:

$$V_{\text{loc}}(\mathbf{r}) = a(-2R_{\text{min}}^2 r^2 + r^4) + d(x^2 y^2 + x^2 z^2 + y^2 z^2 - r^4/3), \quad (3)$$

where $a = \gamma + \delta/3 > 0$ is the parameter characterizing the isotropic part of the fourth-order anharmonicity, $R_{\text{min}}^2 = -\beta/2(\gamma + \delta/3)$ is the square of the distance corresponding to the potential minimum, and $d = \delta$ is the parameter describing the anisotropic part of the fourth-order anharmonicity. It was shown in [5] that Ge atoms in $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ are displaced to one of the eight equivalent minima in the $\langle 111 \rangle$ directions; therefore, the sign of the parameter d in formula (3) must be negative.

The experimental data considered here were obtained for samples in the ferroelectric phase. Therefore, when processing these data, it is necessary to take into account the existence of a preferential direction (the term V_{mf}) and the rhombohedral lattice distortion. Let us estimate the effect of these factors and higher order invariants on the results obtained. When the data were processed using reasonable values of the molecular field \mathbf{E}_{mf} , agreement between the experimental and theoretical spectra was retained and the values of the local-potential parameters changed only insignificantly. This is no surprise since the contributions of the terms linear with respect to \mathbf{E}_{mf} to the EXAFS function for the first coordination sphere compensate each other. The data processing taking into account the known experimental value of the rhombohedral lattice distortion hardly affects the agreement between the experimental and theoretical spectra and the values of the local-potential parameters. Thus, in the first-order approximation, we may neglect the molecular-field effect and the rhombohedral lattice distortion in the data analysis. Taking into account the sixth-order invariants in expansion (2) showed that their effect (at least, on the data obtained at low temperatures) is also insignificant.

If the crystal temperature exceeds the Debye temperature, the classical approximation is valid and the probability of finding an atom at an arbitrary point of the crystal is determined by the potential energy at this

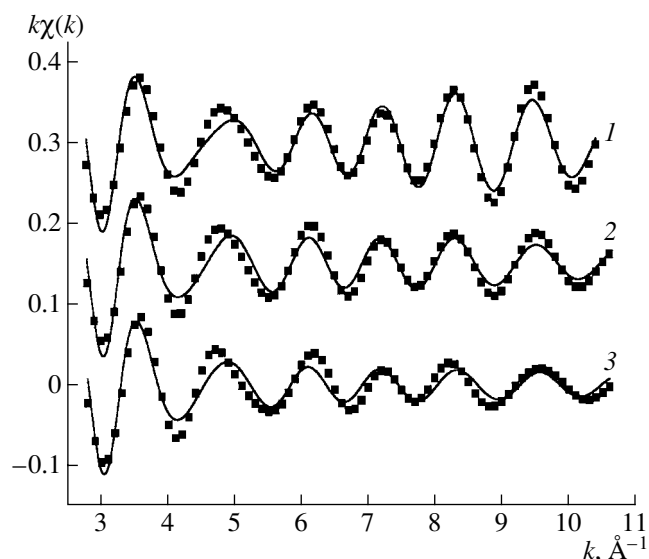


Fig. 1. Experimental (squares) and calculated (solid lines) EXAFS spectra for a $\text{Sn}_{0.3}\text{Ge}_{0.7}\text{Te}$ sample at $T = (1)$ 80, (2) 180, and (3) 275 K.

point: $\rho(\mathbf{r}) \sim \exp(-V(\mathbf{r})/kT)$.¹ Since the EXAFS function (1) is calculated by exact 3D integration in our approach, we can use potentials with an arbitrary degree of anharmonicity, including multiwell potentials. The selection of a cluster, which sets the mutual positions of Te atoms, makes it possible to determine also the anisotropy parameters of the atomic motion.

EXPERIMENTAL

The measurements were performed with polycrystalline samples of the $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ solid solution with $x = 0.4, 0.7$, and 1.0 obtained by alloying binary compounds with subsequent homogenizing annealing at 620°C for 48 h.

Immediately before the measurements, each alloy was grounded into powder, sieved, and deposited onto the surface of a scotch tape.

EXAFS spectra in the vicinity of the Ge-K absorption edge (11.103 keV) were measured at station 7.1 of the Daresbury synchrotron radiation source (energy of electrons 2 GeV, current 240 mA) in the temperature range 77–300 K. The radiation was monochromized by a double-crystal Si(111) monochromator. The spectra were recorded in transmission geometry; the intensities of the incident and transmitted radiation were measured using ionization chambers.

The EXAFS spectra obtained were processed conventionally [8, 10]. The energy corresponding to the

¹ At low temperatures, the quantum character of excitations should be taken into account and the relation between $\rho(\mathbf{r})$ and $V(\mathbf{r})$ becomes more complex. In this study, we restrict ourselves to the classical approximation. The quantum case will be considered in a future publication.

inflection point at the absorption edge was taken as a reference point. The jump at the absorption edge varied from 0.19 to 0.5. The information on the first coordination sphere (the one we are interested in) was derived from the experimental spectra $\chi(k)$ by Fourier transform and reverse Fourier transform using a modified Hanning window [8]. The typical selection ranges in the R - and k spaces were $\Delta R = 1.65\text{--}3.55 \text{ \AA}$ and $\Delta k = 2.8\text{--}12.7 \text{ \AA}^{-1}$, respectively. The further data processing consisted in varying the potential parameters and determining the values at which the mean-square deviation of the calculated spectrum $k\chi(k)$ from the corresponding part of the experimental spectrum is minimum. The functions $f(k, \pi)$, $\delta_1(k)$, and $\lambda(k)$, which are necessary to calculate theoretical spectra, were found using the FEFF software [11].

As is well known, the number of fitting parameters in analysis of EXAFS data should not exceed the number of independent parameters in the data analyzed ($N_{\text{ind}} = (2/\pi)\Delta R\Delta k$) [8]. In our case, the number of variable parameters is equal to six (the parameters a , d , R_{min}^2 , S_0^2 , a_0 , and the correction dE_0 to the zero energy in the spectra [8]) at $N_{\text{ind}} = 9\text{--}12$. Interestingly, the number of variable parameters in our case is the same as in conventional analysis taking into account two coordination spheres.

RESULTS AND DISCUSSION

Typical EXAFS spectra obtained by the procedure described above and their best theoretical approximations for a $\text{Sn}_{0.3}\text{Ge}_{0.7}\text{Te}$ sample at three different temperatures are shown in Fig. 1. The small discrepancy between the spectra is due to the fact that the procedure of selecting a signal from the first coordination sphere does not completely suppress the contribution from the second coordination sphere.

Figure 2 shows the constant-energy map calculated on the basis of the derived parameters of the potential for a sample with $x = 0.7$ at $T = 80 \text{ K}$. It can be seen that the equipotential lines are highly extended in $\langle 111 \rangle$ directions and the potential energy increases most rapidly at displacement in $\langle 100 \rangle$ directions.

The temperature dependences of the parameters a , R_{min}^2 , and $|d|$ for all the $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ samples investigated are shown in Figs. 3–5. Comparison of Figs. 3 and 5 shows that the anharmonicity parameter d exceeds a by about two orders of magnitude. As follows from the angular dependence of the potential (3), the minimum value (equal to a) of the factor at r^4 is obtained for the motion of a Ge atom in one of the $\langle 111 \rangle$ directions. This factor is maximum (equal to $a + |d|/3$) for motion in one of the $\langle 100 \rangle$ directions. This is no surprise since the neighboring Te atoms are located in $\langle 100 \rangle$ directions (with respect to the average position of the Ge atom); therefore, displacements of the latter in these directions are accompanied by strong nonlinear

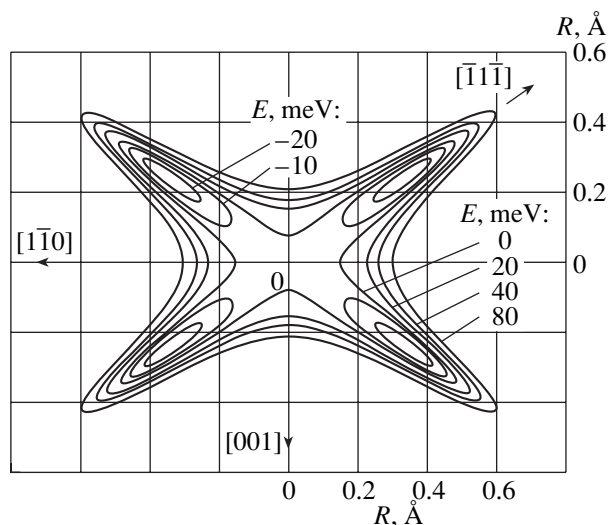


Fig. 2. Constant-energy map for a $\text{Sn}_{0.3}\text{Ge}_{0.7}\text{Te}$ sample at 80 K obtained by crossing the potential well with a (110) plane.

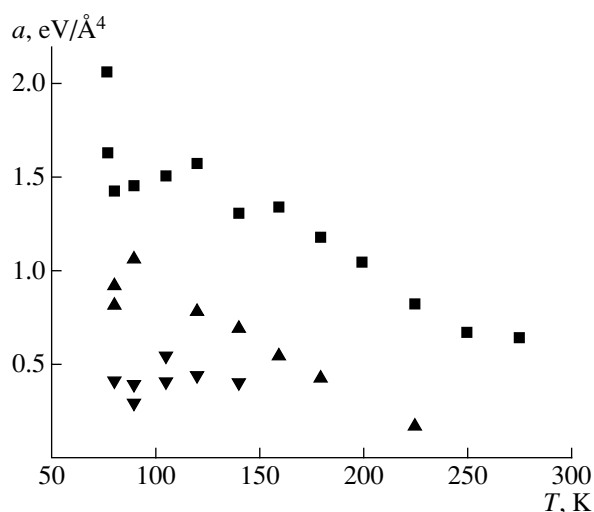


Fig. 3. Temperature dependence of the parameter a for $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ samples with $x = 1.0$ (■), 0.7 (▲), and 0.4 (▼).

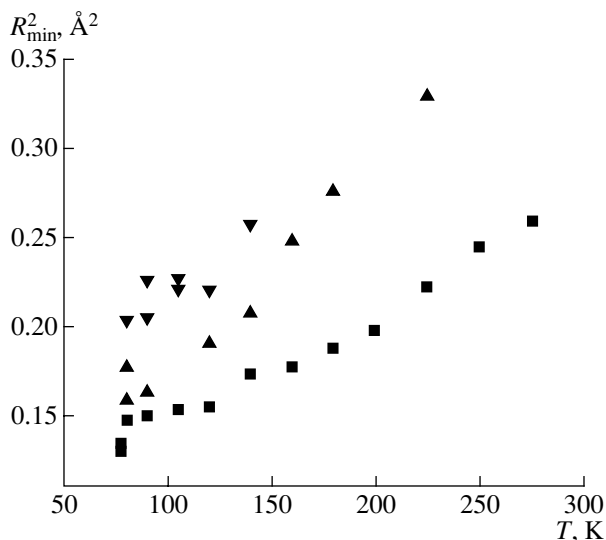


Fig. 4. Temperature dependence of the parameter R_{\min}^2 for $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ samples with $x = 1.0$ (■), 0.7 (▲), and 0.4 (▼).

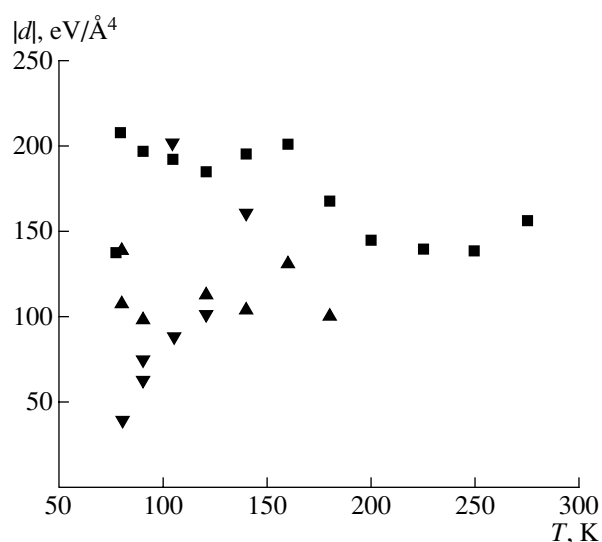


Fig. 5. Temperature dependence of the parameter d for $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ samples with $x = 1.0$ (■), 0.7 (▲), and 0.4 (▼).

repulsion. At the same time, pits of the close-packed atomic plane are located in $\langle 111 \rangle$ directions; hence, off-center Ge atoms can easily displace in these directions. Thus, the condition $|d| \gg a$ and formula (3) suggest that the sought potential is characterized by a strong anisotropy.

An unexpected result obtained in this study is the strong temperature dependences of the parameters a and R_{\min} . It follows from Figs. 3 and 4 that, in the samples with $x \geq 0.7$, a decreases and R_{\min} increases with increasing temperature; at the same time, the depth of the potential well $U_w = aR_{\min}^4$ remains almost invari-

able. Presently, we cannot explain this behavior of the potential parameters, although it is clear that one of the reasons for the change in R_{\min} is the thermal expansion of the crystal. Note that the significant temperature changes in the parameters of the distribution function established here do not suggest a significant change in the average displacement of an atom from the lattice site, which was determined by the formula $\langle r \rangle = \int_0^\infty \rho(\mathbf{r})|\mathbf{r}|d\mathbf{r}$. The dependence $\langle r(T) \rangle$ obtained corresponded to the change expected for the thermal expansion of the lattice.

As follows from Eq. (3), the depth of the potential wells is $U_w = aR_{\min}^4$. Estimation of U_w yields approximately 40, 30, and 20 meV for the samples with $x = 1$, 0.7, and 0.4, respectively. It is known from the microscopic model of ferroelectric phase transitions that the type of phase transition is determined by the dimensionless parameter $s = U_w/kT_c$ [9]. In our case, s is approximately equal to 0.65 for all the samples studied. This means that the type of phase transition in $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ is intermediate between the displacive and order–disorder phase transitions.

CONCLUSIONS

A new method is proposed, which makes it possible to determine the parameters of the 3D multiwell potential of off-center atoms from EXAFS data. The main features of this approach are the expansion of the 3D potential in a cluster in a series, taking into account the restrictions imposed by the lattice-site symmetry and exact 3D integration of the distribution function in calculations of EXAFS spectra. Within this approach, the temperature and composition dependences of the parameters of the multiwell potential of the Ge atom are found in the classical approximation for a series of samples of the $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ solid solution ($77 \leq T \leq 300$ K, $x \geq 0.4$)

It is shown that the anharmonic part of the potential is highly anisotropic and that the type of ferroelectric phase transition in $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ crystals is intermediate between the displacive and order–disorder phase transitions.

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