

NEW METHOD FOR DETERMINING PARAMETERS OF POTENTIAL WELL OF NONCENTRAL ATOMS USING EXAFS SPECTROSCOPY

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A new method to determine parameters of a three-dimensional multiwell potential of noncentral atoms from EXAFS data has been proposed. The main features of this approach are the series expansion of a three-dimensional potential in a cluster in displacement degrees with allowance for constraints imposed by lattice-node symmetry and the exact three-dimensional integration of the distribution function in calculation of EXAFS spectra. Within the framework of this approach, parameters of a multiwell potential were estimated for the first time in classical approximation for a Ge atom in solid solution $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ ($77 \text{ K} \leq T \leq 300 \text{ K}$, $x \geq 0.4$). It is shown that the anharmonic part of the potential is strongly anisotropic and that by its type a ferroelectric phase transition in $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ is intermediate between the displacement and order–disorder transitions.

INTRODUCTION

Noncentral impurities have long attracted investigators' attention due to their unusual properties [1]. In particular, they can give rise to ferroelectric phase transitions in crystals, as, for instance, in the case of a Ge impurity in SnTe, PbTe and PbSe, S impurity in PbTe or Li impurity in KTaO_3 . However, quite often even data on the phase transition type in such crystals are contradictory. For example, in the GeTe–SnTe solid solution the behavior of heat capacity [2] and elasticity moduli [3] in the Curie point vicinity indicate that this phase transition is similar to displacement transitions (in addition, a soft mode is observed in GeTe [4]), whereas studies of an extended fine structure in X-ray absorption spectra (EXAFS) make it obvious that Ge atoms are noncentral both below and above T_c . The latter testifies to 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 noncentral impurity potential $V(\mathbf{r})$.

EXAFS spectroscopy is a powerful tool for studying the interatomic interaction potential in crystals. At present parameters of the anharmonic interatomic potential are determined from EXAFS data by the cumulant expansion method [6, 7]. However, this method has the following limitations: (1) anharmonicity must not be strong so that only the first few terms of expansion in k would be sufficient, and (2) this method is inapplicable to crystals where the potential has several minima. Besides, the cumulant expansion method fails to provide information about atomic motion anisotropy. As the noncentral impurity potential has several equivalent-energy minima corresponding to different directions of atom displacement from a lattice node, another approach is needed to solve the problem.

This paper suggests a new method for determining parameters of a multiwell potential of noncentral impurities which is free of the limitations of the cumulant expansion method. This approach will be used to study the configuration of the potential well of Ge atoms in the $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ solid solution and its behavior with the Ge temperature and concentration variation.

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DESCRIPTION OF METHOD

In the EXAFS theory, in a single scattering approximation the oscillating portion in a spectrum at the K absorption edge (EXAFS function) connected with atoms of the first coordination sphere has the form [8]

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

where summation involves all the nearest neighbors; S_0^2 is the factor taking into account multi-electron effects and inelastic scattering; f is the complex backscattering function; δ_1 is the phase of the escape of a photoelectron with an orbital moment $l = 1$ from an absorbing atom; λ is the mean free path of a photoelectron; k is the photoelectron wave vector related to energy E of an absorbed X-ray quantum and photoionization energy of the level E_0 by the formula $k = \sqrt{2m(E - E_0)}/\hbar$; $\rho(\mathbf{r})$ is the probability of scattering atom location at a point \mathbf{r} (the origin is associated with an absorbing atom), 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 information about the local structure and motion of atoms is contained in the distribution function $\rho(\mathbf{r})$.

The possibility of finding potential well parameters from EXAFS spectra is based on the fact that the function $\rho(\mathbf{r})$ is determined by $V(\mathbf{r})$. The proposed approach to processing EXAFS spectra is as follows. First, we parameterize the three-dimensional potential $V(\mathbf{r})$ with allowance for crystal symmetry, then calculate the normalized distribution function $\rho(\mathbf{r})$ and substitute it into equation (1) in order to calculate the theoretical EXAFS spectrum and compare it with the experimental one. After that, by varying the parameters of the potential and repeating the procedure for calculating the theoretical spectrum, we minimize the root-mean-square deviation of the experimental EXAFS spectrum from the theoretical spectrum and thus determine the potential well shape.

At temperatures above the phase transition temperature our crystals have the NaCl structure. In this structure each noncentral Ge atom moves in an octahedron formed by six Te atoms. Since in ferroelectrics the displacement of ferroactive atoms from lattice nodes caused by heat motion is always greater than that of surrounding atoms, in a first approximation the heat motion of Te atoms can be ignored so that only the motion of a Ge atom in a rigid octahedron would be considered. In our experiments Ge atoms are absorbing and Te atoms are scattering. As we are interested in the motion of Ge atoms, it will be more convenient to separate a cluster of seven atoms (Ge + 6Te) and change over to a new frame of reference whose origin is at the center of symmetry of the octahedron. Since $\rho(\mathbf{r})$ is a pair distribution function, equation (1) can be rewritten in the new frame of reference, and it can be shown that the expression for $\chi(k)$ remains the same, except that now the vector \mathbf{r} becomes the coordinate of the Ge atom and $\rho(\mathbf{r})$, the probability of the Ge atom located at the point \mathbf{r} . In the new frame of reference, Te atoms are spaced at a distance $a_0/2$ from the origin along the axes $\langle 100 \rangle$ (a_0 is the lattice parameter). This means that for a Ge atom located at a point $\mathbf{r} = (x, y, z)$, the contribution from the six Te atoms to EXAFS function (1) will be determined by six three-dimensional integrals in which distances r are calculated by the formulas $r^2 = (a_0/2 \pm x)^2 + y^2 + z^2$, $r^2 = x^2 + (a_0/2 \pm y)^2 + z^2$, $r^2 = x^2 + y^2 + (a_0/2 \pm z)^2$.

In the microscopic model of ferroelectricity [9] the effective potential $V(\mathbf{r})$ at which an atom moves consists of two components: a local anharmonic potential $V_{\text{loc}}(\mathbf{r})$ and a term $V_{\text{mf}} = (\mathbf{d} \cdot \mathbf{E}_{\text{mf}})$ that describes interaction between the atom under consideration and other atoms of the same kind and an external field. Let us expand the potential $V_{\text{loc}}(\mathbf{r})$ in the vicinity of the origin of coordinates in powers of atomic displacement components. For a node characterized by the point symmetry group O_h , expansion in powers up to the fourth order has the form

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

where α , β , γ , and δ are the coefficients. As the distribution function does not depend on the selection of the energy origin, we put $\alpha = 0$. 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; $R_{\min}^2 = -\beta/(2\gamma + 2\delta/3)$ is the squared distance 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 in $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$, the Ge atoms are displaced to one of the eight equivalent $\langle 111 \rangle$ directions, therefore, the sign of the parameter d in (3) must be negative.

The experimental data considered in this paper were obtained for samples in a ferroelectric phase; therefore, when processing these data one must take into account the existence of a preferential direction (V_{mf} term) and rhombohedral distortion of the lattice. Let us assess the degree of the influence of these factors and the higher-order invariants on the results obtained. Processing of data with allowance for rhombohedral lattice distortion known from the experiment produces virtually no effect on the agreement between experimental and theoretical spectra and the values of local potential parameters. Consideration of the sixth-order invariants in expansion (2) showed that their effect on the data obtained at least at low temperature is also insignificant. As to the molecular field \mathbf{E}_{mf} , an attempt made at using it as another adjustable parameter in data processing was unsuccessful, even though it can markedly affect the potential's parameters (agreement between experimental and theoretical spectra depended weakly on \mathbf{E}_{mf}). For this reason, in a first approximation we decided to ignore the effects of a molecular field and rhombohedral distortion.

If the temperature exceeds the Debye temperature, the classical approximation is applicable and the probability that an atom is located at an arbitrary point of a crystal depends on potential energy at this point: $\rho(\mathbf{r}) \sim \exp(-V(\mathbf{r})/kT)^*$. Performing exact three-dimensional integration in this approach to calculate EXAFS function (1), permits us to use potentials with an arbitrary degree of anharmonicity, including multiwell potentials. Isolation of a cluster which sets mutual arrangement of Te atoms, makes it also possible to determine parameters of anisotropy of atomic motion.

EXPERIMENTAL

The measurements were made on polycrystalline samples of $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ solid solution with $x = 0.4$, 0.7, and 1.0 which were produced by alloying binary compounds and then were subjected to homogenizing annealing at 620 °C for 48 h. Immediately before measurements the alloys were powdered, the powder was sieved and then deposited on the surface of an adhesive tape.

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

Processing of the EXAFS spectra was conventional [8, 10]. The energy corresponding to an inflection point at the absorption edge was taken to be the photoionization energy of the level E_0 . The jump at the absorption edge varied from 0.19 to 0.5. Information about the first ionization sphere we are interested in was obtained from the experimental spectra $\chi(k)$ by means of direct and inverse Fourier transform using a modified Hanning window [8]. A typical extraction range was $\Delta R = 1.65\text{--}3.55 \text{ \AA}$ in R space, and $\Delta k = 2.8\text{--}12.7 \text{ \AA}^{-1}$ in k space. Further data processing consisted in varying the potential's parameters and finding their magnitudes at which the root-mean-square deviation of a theoretical spectrum $k\chi(k)$ from the spectrum extracted out of the experimental spectrum was minimal. The functions $f(k, \pi)$, $\delta_1(k)$, and $\lambda(k)$ required to calculate the theoretical spectra were computed using the FEFF program [11].

It is known [8] that the number of adjustable parameters used to analyze EXAFS data must not exceed the so-called number of independent parameters in the data $N_{\text{ind}} = (2/\pi)\Delta R\Delta k$. In our case there were six variable parameters (parameters a , d , R_{\min}^2 , S_0^2 , a_0 , and also correction of zero energy dE_0 [8]) at $N_{\text{ind}} = 9\text{--}12$. It is interesting, that the number of variable parameters in our case was the same as that in traditional analysis of the data using two coordination spheres.

* At lower temperatures it is necessary to take into account quantum nature of atomic motion which makes the $\rho(\mathbf{r})$ -vs.- $V(\mathbf{r})$ relationship more complicated. In this work we restrict ourselves to the classical motion case; the case of quantum motion will be considered in another paper.

RESULTS AND DISCUSSION

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

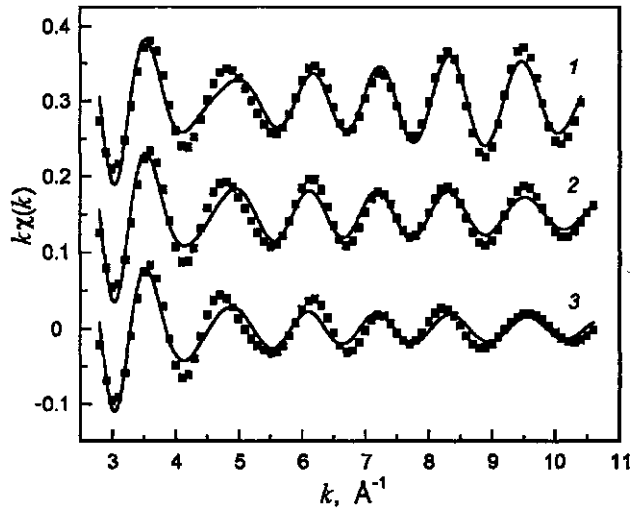


Fig. 1

Comparison of EXAFS experimental (dots) and theoretical (solid lines) spectra for a $\text{Sn}_{0.3}\text{Ge}_{0.7}\text{Te}$ sample at $T = 80$ K (1), 180 K (2) and 275 K (3).

Figure 2 presents a cross section of constant-energy surfaces calculated from the potential's parameters found for a sample with $x = 0.7$ at 80 K. It can be seen that the equal-potential curves are greatly extended in the direction of $\langle 111 \rangle$ and that the fastest growth of potential energy occurs for displacement toward $\langle 100 \rangle$.

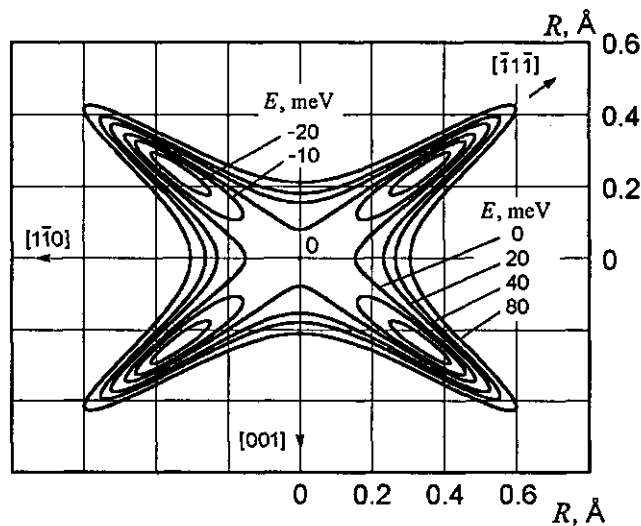


Fig. 2

Constant-energy surfaces obtained for a $\text{Sn}_{0.3}\text{Ge}_{0.7}\text{Te}$ sample at 80 K by sectioning a potential well by a plane perpendicular to axis $\langle 110 \rangle$.

The temperature behavior of the parameters a , R_{\min}^2 and $|d|$ for all the $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ samples studied are illustrated in Figs. 3, 4, and 5. The comparison of Figs. 3 and 5 demonstrates that the anharmonicity parameter d is about two orders of magnitude larger than the parameter a . This means that the sought-for parameter is characterized by strong anisotropy. Indeed, as follows from angular potential dependence (3), the minimal value of the coefficient at r^4 (equal to a) is attained when the Ge atom moves toward $\langle 111 \rangle$, and the maximal value (equal to $a + |d|/3$), when it moves in the direction of $\langle 100 \rangle$. This is not surprising, since adjacent Te atoms are located in the direction $\langle 100 \rangle$ from the Ge node and, therefore, displacement of a Ge atom in this direction is accompanied with strong nonlinear repulsion. At the same time, $\langle 111 \rangle$ is a direction to a lunge at a close-packed atomic plane, and the shift of noncentral Ge atoms in this direction is much easier.

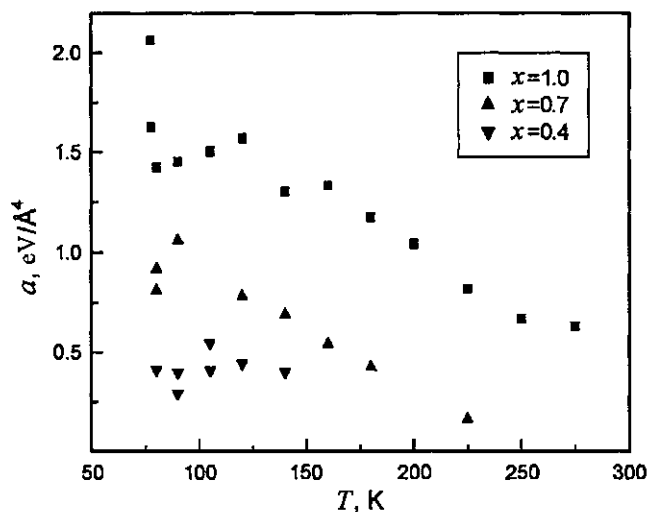


Fig. 3

Temperature dependence of the parameter a for $\text{Sn}_{0.3}\text{Ge}_{0.7}\text{Te}$ samples with different x .

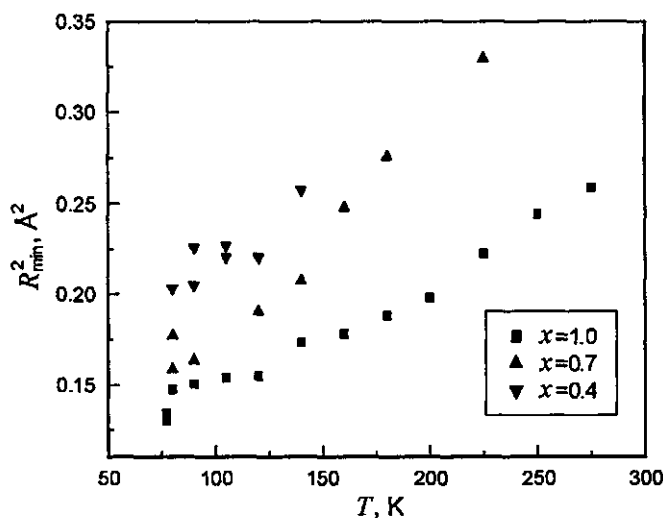


Fig. 4

Temperature dependence of the parameter R_{\min}^2 for $\text{Sn}_{0.3}\text{Ge}_{0.7}\text{Te}$ samples with different x .

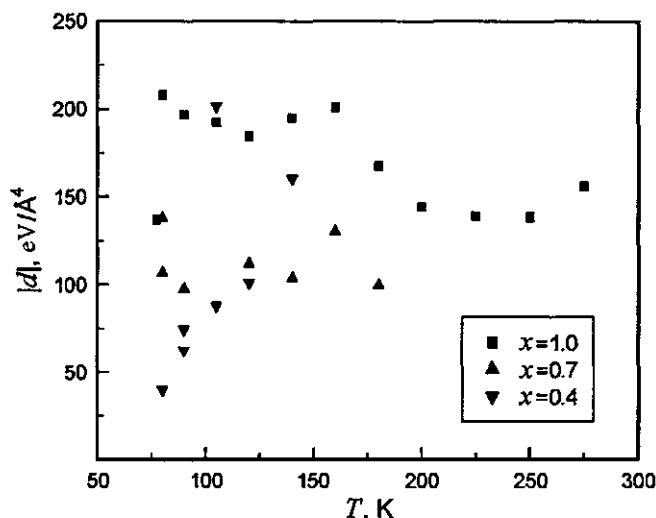


Fig. 5

Temperature dependence of the parameter d for $\text{Sn}_{0.3}\text{Ge}_{0.7}\text{Te}$ samples with different x .

As follows from equation (3), the depth of potential wells $U_w = aR_{\min}^4$, it is estimated at about 40 meV for a sample with $x = 1$, about 30 meV for a sample with $x = 0.7$, and about 20 meV for a sample with $x = 0.4$. It is known from the microscopic model of ferroelectric phase transitions [9] that the phase transition type is determined by the dimensionless parameter $s = U_w/kT_c$. In all the $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ test samples, the parameter s is found to be about 0.65, i. e., the phase transition here is intermediate between the displacement and order-disorder transitions.

An unexpected result obtained in this study was a strong temperature dependence of the parameters a and R_{\min} . It follows from Figs. 3 and 4 that in samples with $x \geq 0.7$, a decreases and R_{\min} increases with the rise of temperature, the potential well depth $U_w = aR_{\min}^4$ remaining virtually unchanged. It should be noted that these rather strong changes of the potential parameters do not lead to a noticeable change in the root-mean-square shift of a particle from a lattice node. Calculation of the temperature dependence of

$$\langle r^2 \rangle = \int \rho(\mathbf{r}) r^2 d\mathbf{r} \quad (4)$$

showed that the shift of the “center-of-gravity” of the distribution function caused by a rise in the temperature from 80 to 300 K did not exceed 0.04 Å (12%). One of the factors responsible for such a change is thermal expansion of a crystal, although other factors may also be involved.

CONCLUSION

A new method has been proposed for determining the parameters of a three-dimensional multiwell potential of noncentral atoms from EXAFS data. The main features of this approach are series expansion of a three-dimensional potential in a cluster with allowance for constraints imposed by lattice-node symmetry, and exact three-dimensional integration of the distribution function for calculating EXAFS spectra. Within the framework of this approach the parameters of a multiwell potential were estimated for the first time in a classical approximation for a Ge atom in $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ solid solution ($77 \leq T \leq 300$ K, $x \geq 0.4$). It is shown that the anharmonic part of the potential is strongly anisotropic. The estimated potential well depth (20–40 meV) indicates that by its type the ferroelectric phase transition in these crystals is intermediate between the displacement and order-disorder transitions.

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