

CHANGE IN THE ELECTRON DENSITY OF Sb_2Te_3 AS A RESULT OF THE FORMATION OF NANOOBJECTS

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Nanoobjects - nanoislands and localized patterns that play a deforming role in the distribution of electron density are revealed. Changes in the van der Waals bond between quintets in the Sb_2Te_3 structure are associated with the formation of impurities and nanoobjects in the interlayer space of the crystal matrix. Van der Waals forces affect the charge density distribution and chemical bonding in these crystals. The parameters of the critical points and the nature of the charge density distribution in their vicinity indicate the coexistence of several types of chemical bonding in Sb_2Te_3 crystals: covalent, semimetallic, and also a bond type characterized by charge density fluctuations.

Keywords: structure, localized patterns, nanoislands, electron density, critical points, percolation.

PACS: 62.20Fe, 61.72.Cc, 61.72.Lk

INTRODUCTION

Antimony telluride Sb_2Te_3 has a high thermoelectric figure of merit and belongs to the class of topological insulators. The hexagonal structure of layered Sb_2Te_3 crystals consists of close-packed quintets that interact with each other using van der Waals forces. Depending on the concentration, impurities embedded in them can be localized both in the interlayer space and defective cavities, and penetrate into the layers of the crystalline matrix.

Of practical interest is the type of defects, in the presence of which a high charge transfer density is achieved with maximum phonon scattering, which makes it possible to increase the thermoelectric figure of merit of the material by reducing the thermal conductivity in Sb_2Te_3 .

Some defects can take part in the transformation of the material structure during thermally activated processes, affecting the nature of the charge distribution and changes in interatomic distances.

For the convenience of considering the processes of formation of nanoobjects leading to a redistribution of charges in layers and between them, it is desirable to analyze the method for finding the electron density $\rho(\mathbf{r})$ of Sb_2Te_3 molecules based on the analysis of the matrix of second derivatives of the electron density with respect to coordinates, called the Hessian matrix to identify the location of critical points $(\partial^2\rho/\partial x_i \partial x_j)$, where $i, j = 1, 2, 3$, $x_1 = x$, $x_2 = y$, $x_3 = z$. In this case, $\rho(\mathbf{r})$ - the electron density is found either from experiments or by calculation. The points \mathbf{r}_c at which the electron density gradient vanishes $\nabla\rho(\mathbf{r}_c) = 0$ are called critical. At these points, the electron density has extreme properties (has a minimum or maximum, and can also be a saddle point). Diagonalizing the symmetric Hessian matrix ρ , one can find its eigenvalues λ_i ($i = 1,$

2, 3) and the coordinate axes, the principal axes of curvature, for which the off-diagonal elements of the matrix are equal to zero. Sum of Diagonal Matrix Elements – Laplacian $\nabla^2\rho = \partial^2\rho/\partial x^2 + \partial^2\rho/\partial y^2 + \partial^2\rho/\partial z^2$ plays an important role in the analysis of features in the electron density distribution[1,2].

Let us note some features of the sign of the Laplacian and its magnitude at the critical point, which determine the signs of a chemical bond, while highlighting the following points [1]:

- In the classification of the types of chemical bonding in crystals, the sign of the Laplacian of the electron density $\nabla^2\rho_b$ at the saddle critical point of the bond type, the signs and ratios of the absolute values of the principal values of the curvature λ_i ($i = 1, 2, 3$) at a given critical point, the magnitude of the charge ρ_b , as well as the nature of the electron density distribution in the interatomic region of the crystal.

- The negative sign of the Laplacian $\nabla^2\rho_b < 0$ indicates that charge flows into the critical point from Sb atoms, between which this critical point is located, the covalent bond is characterized by the negative sign of the Laplacian, negative values $\lambda_{1,2} < 0$, larger in absolute value $\lambda_{1,2} > \lambda_3$, a large value of the electron density at the critical point ρ_b .

- The positive sign $\nabla^2\rho_b > 0$ indicates the expulsion of the charge from the region near the critical point. For ionic bond $\nabla^2\rho_b > 0$, $\lambda_{1,2} \ll \lambda_3$, ρ_b is small, the charge density is concentrated mainly in the regions where atoms are located

- The eigenvalues λ_i of the symmetric Hessian matrix are real, can have any sign, and can also be equal to zero.

In [3], the electronic structures of Bi_2Te_3 and Sb_2Te_3 crystals were calculated using the first principle of the full potential linearized plane wave method. Here, only unrelaxed crystals, which have the

experimental lattice parameters, were studied. However, by varying the structural parameters of Sb_2Te_3 , it is possible to create an electronic topological transition, in which the number of edges of the valence and conducting band changes between 6 and 12. Atoms and clusters formed between $Te^{(1)}-Te^{(1)}$ must have a changed charge at critical points.

The aim of the work was to reveal the process of formation of nano-objects affecting the distribution of electron density in the Sb_2Te_3 crystal.

EXPERIMENT AND DISCUSSION

Based on the results of a number of experimental and theoretical studies [4-7], defects in the crystal structure and their electron microscopic images were found, which were obtained on an atomic force microscope (AFM) of the NC-AFM brand.

Level lines of electron density distribution.

As follows from [1], all three critical points of the bond type in the electron density distribution in the Sb_2Te_3 crystal have a positive Laplacian $\nabla^2\rho_b > 0$ and the ratio between the principal values of the curvature $|\lambda_{1,2}| < \lambda_3$ are similar to those found for Sb and Te. If neglect the slight ellipticity in the electron density distribution near critical points of the bond type in Sb_2Te_3 and approximately assume that $|\lambda_1| \approx |\lambda_2|$ for these substances, then can use the ratio $|\lambda_{1,2}| / \lambda_3$ for critical points of the bond type as some characteristic of the degree of covalence of a chemical bond in a substance. For all critical points of the bond type in the studied substances, it follows that the chemical bond in the Sb_2Te_3 compound has the lowest degree of covalence. These parameters are shown in the table.

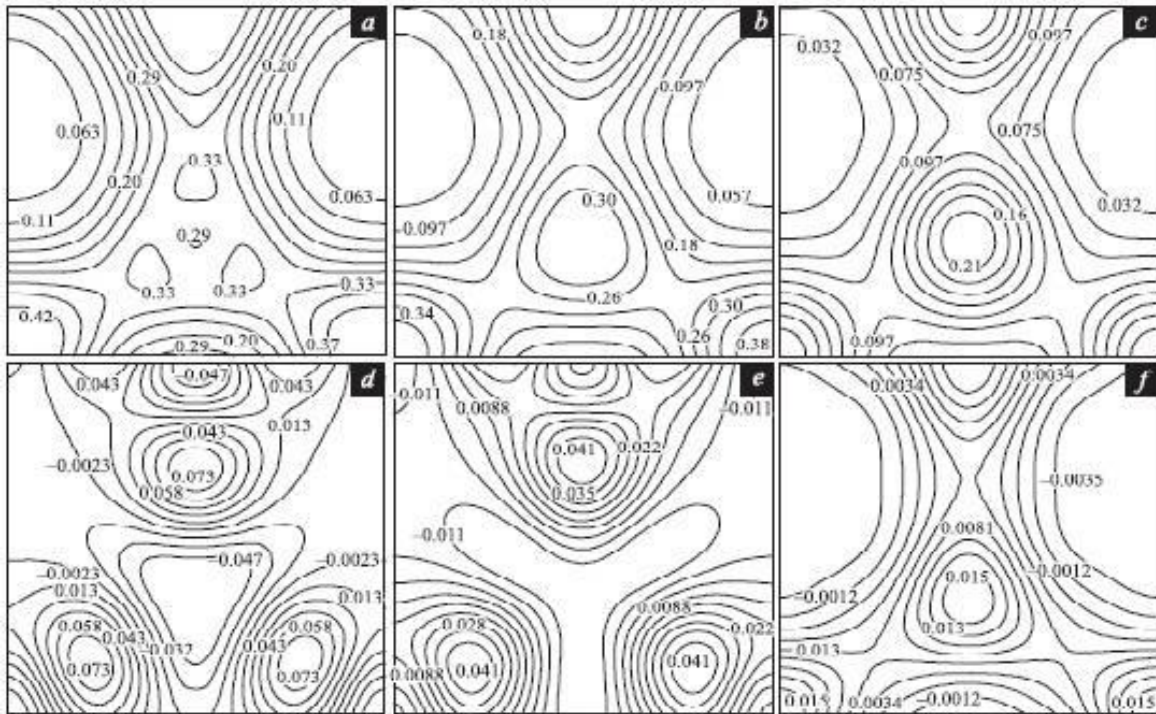


Fig.1. Level lines of the electron density distribution in the planes of the crystal structure of the Sb_2Te_3 compound containing critical points of the bond type. Designation: a, b and c - total electron density, d, e and f - electron density obtained by the CDD method (charge density difference — the difference between the charge density in the substance and in the atoms that make up the substance).

The table lists the parameters of the critical points of the electron density distribution in the Sb_2Te_3 crystal

| position type, N_c | x | y | z | $\lambda_1, e/A^5$ | $\lambda_2, e/A^5$ | $\lambda_3, e/A^5$ | $\nabla^2\rho_c, e/A^5$ | $\rho_c, e/A^5$ |
|----------------------|-------|-------|-------|--------------------|--------------------|--------------------|-------------------------|-----------------|
| 6h | 0,416 | 0,890 | 0,416 | -0,882 | -0,878 | 1,788 | 0,029 | 0,342 |
| 6h | 0,208 | 0,208 | 0,687 | -0,564 | -0,553 | 1,580 | 0,463 | 0,234 |
| 3d | 0,500 | 0,000 | 0,000 | -0,206 | -0,202 | 0,990 | 0,582 | 0,103 |

Weakening of the bond between quintets of the crystal structure of Sb_2Te_3

The structure of Sb_2Te_3 is also often represented in hexagonal axes with 15 layers of the structure

depicted in fig.2 and consisting of three sets of five layers of atoms each, the so-called “quintuple layers of atoms”. The quintet form layers four through eight and nine through thirteen. On Fig.2 3 sets of closest

distances between atoms in the Sb_2Te_3 structure are shown, represented as lines connecting the atoms.

The bond-type critical points in the electron density distribution are located between the atoms: $Sb-Te^{(2)}$ (the first set of bond-type critical points), $Sb-Te^{(1)}$ (the second set), and $Te^{(2)} - Te^{(2)}$ (the third set). They are located in planes parallel to the plane of the hexagonal axes (a, b) and perpendicular to the c axis. Each of the atoms has 3 nearest neighboring atoms and, accordingly, 3 critical points of the bond type. The first two sets of bond-type critical points in the Sb_2Te_3 structure characterize the bond between atoms within a quintet of atomic layers, while the third set of bond-type critical points determines the parameters of a much weaker bond between quintets. The electron density distribution in three Sb_2Te_3 planes, each of which contains three critical points of the bond type, is shown in Fig. 1. In Fig. 1, a-c shows the distribution of the total electron density and in Fig. 1, d-f - distribution of electron density from s- and p-electrons of Sb and Te atoms, obtained by the CDD (charge density difference) method. Fig. 1, a and d represent the electron density distribution for the first set of critical points of the bond type, Fig. 1, b and e - for the second set and Fig. 1, c and f - for the third set. The planes containing critical points of the bond type are drawn parallel to the plane (a, b) of the coordinate system in the hexagonal axes of Sb_2Te_3 . On fig. 1d and e obtained by the CDD method, three critical points are clearly visible in the form of maxima in the electron density distribution. The location of the electron density level lines in Fig. 1, f noticeably differs from that in Fig. 1, d and e. In this plane, there are no clearly pronounced maxima of the electron density, which provides the connection between the quintets in the Sb_2Te_3 structure. This plane is the cleavage plane for the crystal. The parameters of the critical points and the nature of the charge density distribution in their vicinity indicate the coexistence of several types of chemical bonding in Sb_2Te_3 crystals: covalent, semimetallic, and also a bond type characterized by charge density fluctuations. Van der Waals forces, essential for finding the equilibrium parameters of crystal lattices, affect the charge density distribution and chemical bonding in these crystals. The temperature dependences of the elastic constants in layered crystals revealed a tendency for a more rapid change in the interlayer elastic constants in comparison with the intralayer ones [8]. It is noted that the change in the values of the elastic constants with temperature is an anharmonic phenomenon and occurs due to two processes: phonon-phonon interaction and lattice deformation due to thermal expansion. The anharmonicity of the bond forces between the layers is substantially greater than the anharmonicity of the intralayer forces. In this case, the fraction of the contribution of thermal expansion to this change is much higher for the "interlayer" elastic constant than for the "intralayer" one [8]. Interlayer (inside a five-layer quintet package) bonds in antimony chalcogenides are sensitive to changes in the value of interlayer interaction. The enhancement of the polarity of the bond and the redistribution of the electron density, depending on the broadening of the interlayer

distance, can be traced by the shift up the energy scale of the negative CLTE (coefficient of linear thermal expansion) [9-11] values of the doped crystals. The negative CLTE, accompanied by the overlap of the electronic wave functions of neighboring layers within the quintet, is a consequence of the redistribution of the electron density when the parameters of bonds between the metal and the central chalcogen layer are affected. The ...- $Sb-Te^{(2)}$ - Sb ... connection diagram can explain the mechanism of changes in interatomic distances depending on temperature, as well as the applied uniaxial pressure [12]. At temperatures comparable to the energy of interlayer interaction, this interaction is weakened and the electron density is redistributed into the quintets. The structure of the ion pair can change depending on the temperature, which leads to changes in the perturbing effect of the cation on the electronic system. The shift of the charge to the center of the quintet can lead to an increase in the degree of orbital overlap and an increase in the ionic component of the - $Sb-Te^{(2)}$ bond, since this is energetically favorable, the spin-orbit interaction

can also be enhanced: in an ionic pair, an unpaired electron is partially delocalized on the cation and this leads to an increase spin-orbit interaction. As a result, the elastic properties change due to a decrease in the interatomic distances in the $Te^{(1)}$ - $Sb-Te^{(2)}$ - $Sb-Te^{(1)}$ quintet. A change bonds in the between several different positions can explain the anomaly in thermal expansion of crystals of the Sb_2Te_3 type and a reduction in interatomic distances. The transformation of the structure during thermally activated processes can lead to the destruction of some bonds and the formation of other bonds, and the presence of metastable and defective centers can enhance this effect. For example, studies of the switching effect in chalcogenide glasses have revealed the competition between the resonance bonds of the crystalline phase and the disorder of the amorphous one [13-15]. A decrease in the interatomic distances in bismuth and antimony chalcogenides [9-11] at negative CLTE values can be associated with fluctuations in the magnitude of the interlayer interaction, which affects the parameters of atomic bonds within the quintet. When activated, defect centers create perturbations and an additional potential that distorts bonds; an increase in disorder leads to disorderly forming of bonds and displacement of atomic positions, thereby affecting the magnitude of the spin-orbit interaction. These centers affect the parameters of the hybrid bond, where the chalcogen ions of the inner layer and bismuth play a decisive role; accordingly, the interaction can be accompanied by the formation or strengthening of chemical bonds. The main elements of the defect centers in Sb_2Te_3 are intralayer defects and interlayer islands: intralayer defects are sources of disorder, interlayer defects are covalent bridges [16].

The phenomena described by the percolation theory refer to the so-called critical phenomena, which are due to the properties of the entire set of particles, and not the individual properties of each particle, and are characterized by the presence of a critical point at which the properties of the system change dramatically.

In percolation theory, this critical point is called the percolation threshold. However, there is a direct analogy between the theory of percolation and the fluctuation theory of phase transitions of the second kind, which are also accompanied by critical phenomena. In both cases, they proceed from the empirical fact of the increase in the inhomogeneity of the substance, which, as it were, breaks up into blocks, the size of which grows indefinitely when approaching the critical point. The percolation threshold in this case is determined by the number and size of interlayer nanoobjects, as well as the density of their distribution, at which they radically affect the interlayer interaction. This ultimately leads to a redistribution of the electron density in the quintet and changes in the interatomic distances.

The broadening of the van der Waals space in these crystals is mainly of two types:

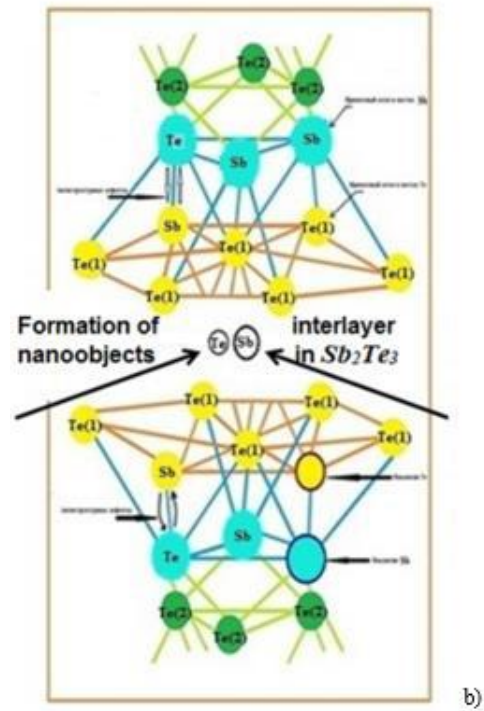
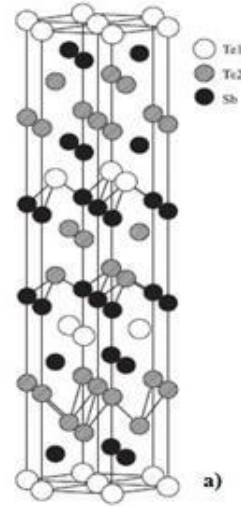
- an increase in the interlayer distance by fractions of an angstrom due to the penetration of a stoichiometric excess or impurities into the interlayer space;
- an increase in the interlayer distance by several nanometers and the formation of defective cavities due to the formation of nanoislands.

A shift of the charge density into the depth of the layer upon broadening of the Van der Waals gap [17], as well as an increase in the number of electrons from donor impurities, can lead to mutual repulsion of lone electron pairs at the Sb-Te⁽²⁾ bond and a change in the bond angle. As a result of such a charge shift [18], a greater splitting of molecular orbitals of various types occurs, in this case, non-bonding orbitals are involved in the formation of covalent orbitals. The Sb orbitals combine with the Te orbitals, with the formation of new bonding orbitals instead of the original nonbonding orbitals, i.e. the bond takes on a metastable ionic-covalent form. When the bonds between the Te⁽²⁾ and stibium atoms are hybridized, the initial system overlaps with the Te⁽²⁾ p-orbital and the lone electron pair of stibium is transformed into a conjugated system, accompanied by a redistribution of the electron density.

The AFM images studied on an atomic force microscope are given in Fig.3. Nanoislands formed between quintets in Sb₂Te₃ defective cavities, their formation does not appear in all interquintet layers, which should affect the uniformity of the distribution of electron density level lines containing critical points.

In the process of coalescence and the formation of localized structures, deformations arise that lead to the

disruption of van der Waals bonds between quintets. The size distributions of nanoislands, coalescence, and island orientations are analyzed.



Crystal structure of the Sb₂Te₃ compound in hexagonal coordinate axes. – a. The model of the crystal structure of Sb₂Te₃ with nanodefects, which are shown by fragments of AFM images in Fig.3. – b.

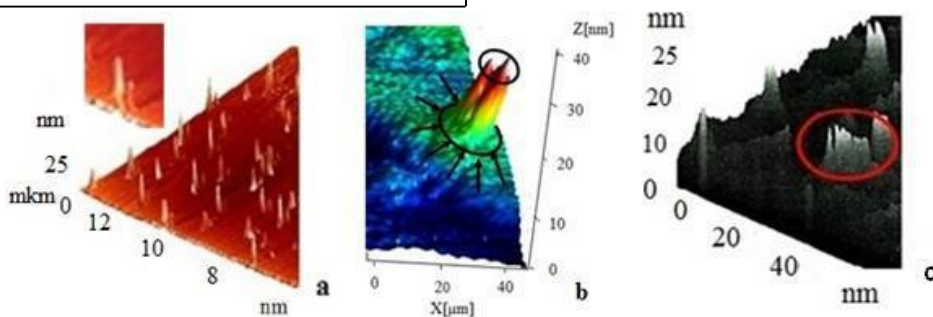


Fig.3. Localized Sb₂Te₃-Se patterns. Nanoislands that are not completely coalesced – a); localized nanoislands (patterns) – b); full localization – c).

We note the following conclusions:

- Critical points in Sb_2Te_3 atoms appear in planes perpendicular to the “C” axis, in which deformed nanoformations are also formed.
- Apparently, during the formation of nanoislands, deformation occurs, mainly between quintets,

which affects the redistribution of the electron density in Sb_2Te_3 .

This work was supported by the Foundation for Science Development at the President of the Azerbaijan Republic- grant № EİF/MQM/ Elm-Tehsil-1-2016-1(26)-71/16/1-M-01.

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