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Modeling of the properties of the semiconductor solid solution $Lu_{1-x}V_xNiSb$ in the presence of magnetic ordering

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Modeling of the thermodynamic, structural, energetic and magnetic properties of the semiconductor solid solution $Lu_{1-x}V_xNiSb$ was carried out under the condition of the presence of a magnetic moment on the V atoms and the occurrence of spontaneous magnetization. It is shown that the change in the unit cell parameter $a(x)$ and the mixing enthalpy $\Delta H_{mix}(x)$ depends little on the presence or absence of spontaneous magnetization. Modeling of the distribution of the density of electronic states DOS in the presence of a magnetic moment on V atoms revealed the splitting of energy states with spins up and down while preserving the band gap ε_g of $Lu_{1-x}V_xNiSb$. The relationship between the concentration of magnetic V atoms in $Lu_{1-x}V_xNiSb$ and the Curie temperature T_C, when spontaneous magnetization is destroyed and the substance becomes paramagnetic, is established. The solid solution semiconductor $Lu_{1-x}V_xNiSb$, provided spontaneous magnetization is present, can be considered as a promising magnetocaloric.

Key words: magnetic ordering, Fermi level, Curie temperature.

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Introduction

Semiconductor solid solutions based on half-Heusler phases (space group $F\bar{4}3m$ [1]) are one of the most studied thermoelectric materials because they have a high efficiency of converting thermal energy into electrical energy [2]. One of these materials is the semiconductor solid solution $Lu_{1-x}V_xNiSb$, $x = 0 – 0.10$, obtained by doping the *p*-LuNiSb semiconductor with V atoms by substituting atoms of the rare earth metal Lu in the crystallographic position 4*a* [3]. *A priori*, one of the features of such doping was that V atoms have the ability to be in different valence states (from +1 to +5), and this can lead, under certain conditions, to a change in the magnetic state of the material.

A comprehensive study of the structural, electrokinetic, energy, and magnetic properties of $Lu_{1-x}V_xNiSb$ allowed the authors [3] to reveal the complex nature of structural changes, in which V atoms simultaneously occupy different crystallographic positions, generating structural defects of acceptor and donor nature, and in the band gap ε_g appear corresponding acceptor and donor states that determine the conduction mechanisms. Studies have also shown that $Lu_{1-x}V_xNiSb$ solid solution samples are Pauli paramagnets in which the magnetic susceptibility is determined solely by the electron gas.

During the experimental study of the existence of the $Lu_{1-x}V_xNiSb$ solid solution, the authors [3] confirmed the results of the work [4] about the absence of the VNiSb compound (complete replacement of Lu atoms by V) with the MgAgAs structure [1]. It is important that the samples in [3] and [4] were prepared by fusing a charge of components in an electric arc furnace with a tungsten electrode in purified argon atmosphere on a copper water-cooled hearth. On the other hand, while studying the crystal structure of ternary compounds in the Ti(V)-Fe(Co, Ni)-Sn(Sb) systems, P. Krypyakevich and

his colleagues [5] discovered the VNiSb compound with the MgAgAs structure [1]. Note that the technology of obtaining samples in works [3, 4] and [5] was fundamentally different. In work [5], the samples were prepared by fusing a charge of components using the induction method in the presence of a strong electromagnetic field.

It is this circumstance, as well as taking into account the authority of the authors [5] and the ability of V atoms to be in different valence states, that gives reason to assume that the presence of a magnetic field during the preparation of the samples could cause the VNiSb compound with the MgAgAs structure to be obtained. At the same time, in the synthesized samples, V atoms will have a local magnetic moment, and the exchange interaction between electrons will cause parallel orientation of spins, which will lead to spontaneous magnetization in VNiSb samples. We can also assume that in the semiconductor solid solution $Lu_{1-x}V_xNiSb$ V atoms will have a local magnetic moment, and the obtained samples will be magnetically ordered.

On the other hand, if the magnetic state of matter and its internal energy change under the influence of a magnetic field, heat is released or absorbed. Under adiabatic conditions, for example, when a magnetic field is quickly turned on or off, the temperature of a substance changes due to the magnetocaloric effect. This opens up prospects for the use of solid solutions based on half-Heusler phases as magnetocalorics – one of the most important areas of modern scientific research.

The following results of modeling the thermodynamic, structural, energy and magnetic properties of the semiconductor solid solution $Lu_{1-x}V_xNiSb$ as a possible magnetocaloric in the presence of a magnetic moment on V atoms are the first step in the study of magnetocalorics with a high efficiency of thermal energy conversion in the presence of a magnetic field.

I. Research methods

Thermodynamic, structural, and energetic properties of the semiconductor solid solution $Lu_{1-x}V_xNiSb$ were modeled in the presence of a magnetic moment on V atoms. Calculations of the distribution of the density of electronic states (DOS), electron localization function (ELF), mixing enthalpy (ΔH_{mix}), as well as optimization of crystal structure parameters was carried out using the Koringa-Kohn-Rostocker (KKR) method in Coherent Potential Approximation (CPA) and Local Density Approximation (LDA). Modeling by the KKR method was carried out using the AkaiKKR program package [6] in the local density approximation for the exchange-correlation potential with the Moruzzi, Janak, Williams [7] parameterization in the semi-relativistic account of the core level and spin-orbit interaction. Calculations were performed for a 10×10×10 *k*-grid, and the Brillouin zone was divided into 1000 *k*-points, which were used to calculate the Bloch spectral function (band spectrum) and the density of electronic states. The width of the energy window was chosen to capture the semi-core states of *p*-elements. The accuracy of calculations of the position of the Fermi level ε_F is ±6 meV.

II. Modeling of thermodynamic and structural properties of $Lu_{1-x}V_xNiSb$ in the presence of magnetic ordering

To determine the area of solubility of V atoms in the structure of the LuNiSb compound (the area of existence of the substitution solid solution $Lu_{1-x}V_xNiSb$), modeling of thermodynamic characteristics, in particular, the enthalpy of mixing ΔH_{mix} in the concentration range x = 0–1.0 was carried out for two cases: in the presence of a magnetic moment on V atoms and its absence (Fig. 1).

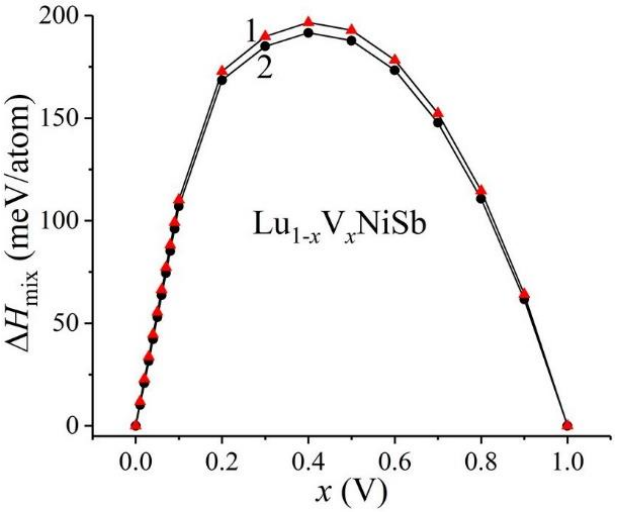

Fig. 1. Modeling of changes in the values of the mixing enthalpy ΔH_{mix} of $Lu_{1-x}V_xNiSb$ in the presence of (1) and the absence (2) of a magnetic moment on V atoms.

As can be seen from the simulation results, the presence or absence of a magnetic moment on V atoms has little effect on the behavior of the mixing enthalpy ΔH_{mix}. High positive values of the mixing enthalpy ΔH_{mix} indicate the absence of solubility of V atoms in the structure of the LuNiSb compound. However, at concentrations of V atoms x=0–0.10 and x=0.9–1.0 (in the vicinity of low values of ΔH_{mix}), there is an energetic feasibility of the existence of a substitution solid solution $Lu_{1-x}V_xNiSb$, as well as the existence of a compound VNiSb (complete replacement of Lu atoms by V atoms) with the MgAgAs structure.

On the other hand, *X*-ray phase and *X*-ray structural analyzes showed that the substitution solid solution $Lu_{1-x}V_xNiSb$ exists at concentrations x = 0–0.10 [3]. In particular, on the powder patterns of the $Lu_{1-x}V_xNiSb$ samples, x=0–0.10, there are no traces of impurity phases, except for the main phase, which is indexed in the MgAgAs structure type [1], and microprobe analysis of the concentration of atoms on the surface of the samples showed their correspondence to the original composition of the charge. At higher concentrations of V, $x > 0.10$, delamination (spinoidal phase decomposition) occurs, and the VNiSb compound with the MgAgAs structure was not detected.

Therefore, comparing the obtained results of simulation of the enthalpy of mixing ΔH_{mix} of $Lu_{1-x}V_xNiSb$ in the presence and absence of a magnetic moment on V atoms with the data of structural studies [3]

we find a certain contradiction. Thus, if in the case of insignificant concentrations of V atoms (x = 0–0.10) the results of simulation and experiment agree, then at high concentrations (x = 0.9–1.0) there is a discrepancy. After all, the results of modeling the enthalpy of mixing ΔH_{mix} in the presence and absence of a magnetic moment on V atoms show the energetic feasibility of the existence of the VNiSb compound with the MgAgAs structure, but it was not detected in experimental works [3, 4].

Perhaps the inconsistency will be removed with a method of synthesis of $Lu_{1-x}V_xNiSb$ samples different from that in [3], in particular, in the presence of an external magnetic field, as in [5].

Modeling of changes in the values of the unit cell parameter $a(x)$ of $Lu_{1-x}V_xNiSb$ was carried out for an ordered variant of the crystal structure and 100% solubility of V atoms in the structure of the LuNiSb compound in the presence and absence of a magnetic moment on V atoms (Fig. 2). Under such conditions, all crystallographic positions of $Lu_{1-x}V_xNiSb$ are occupied by atoms corresponding to the MgAgAs structure type [1], and impurity V atoms replace Lu atoms in position 4*a*. From Fig. 2, we can see that the presence or absence of a magnetic moment on V atoms has little effect on the behavior of $a(x)$ dependences of $Lu_{1-x}V_xNiSb$ for both simulation cases, and the dependences themselves show a monotonous decrease in values. This behavior of the dependences $a(x)$ of $Lu_{1-x}V_xNiSb$, x = 0–1.0, for the ordered version of the structure is predicted, since the replacement of large Lu atoms (r_{Lu}=0.173 nm) by smaller V atoms (r_V=0.134 nm) in position 4*a* will inevitably lead to a decrease in the unit cell parameter values. Considering that V atoms ($3d^34s^2$) have more *d*-electrons than Lu atoms ($5d^16s^2$), the substitution of Lu atoms for V atoms in the 4*a* position will lead to the appearance of defects of donor nature in the $Lu_{1-x}V_xNiSb$ structure, and in the band gap ε_g will be generated impurity donor states, which will determine the conductivity of the semiconductor [8].

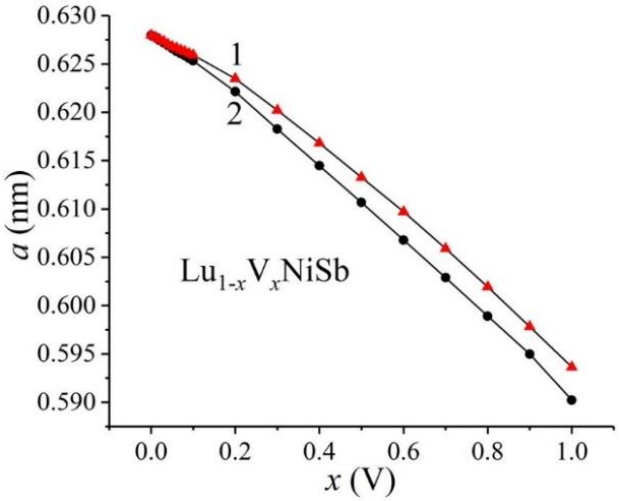

Fig. 2. Modeling of changes in the values of the unit cell parameter $a(x)$ of $Lu_{1-x}V_xNiSb$ in the presence (1) and absence (2) of the magnetic moment on V atoms.

Therefore, the results of modeling the change in the unit cell parameter $a(x)$ of $Lu_{1-x}V_xNiSb$ in the presence and absence of a magnetic moment on V atoms are similar in behavior and the nature of the change in values. In other words, the possible magnetic ordering of $Lu_{1-x}V_xNiSb$ cannot be detected by structural studies.

III. Modeling of energy and magnetic properties of $Lu_{1-x}V_xNiSb$ in the presence of magnetic ordering

The results of modeling the distribution of the density of electronic states (DOS), the behavior of the Fermi level ε_F and the band gap ε_g of $Lu_{1-x}V_xNiSb$ for the ordered variant of the crystal structure in the presence of magnetic ordering are shown in Fig. 3. To understand and compare the influence of the magnetic moment on the V atoms on the electronic structure of $Lu_{1-x}V_xNiSb$ in Fig. 4 shows the calculation of DOS in the absence of magnetic ordering. We can see that the presence of a magnetic moment on V atoms leads to the magnetic ordering of $Lu_{1-x}V_xNiSb$ and the splitting of energy states with opposite spins (Fig. 3). The addition of the lowest concentration of V atoms in the simulation (x=0.01) forms in the band gap ε_g of $Lu_{1-x}V_xNiSb$ near the conduction band ε_C in states with up spin a band of donor states ε^V_D (impurity donor band), on which the Fermi level ε_F is localized. This is characteristic of semiconductors of the electronic conductivity type, in which electrons are the main current carriers [8]. In contrast, spin-down states do not undergo any change. At higher concentrations of V atoms, for example, x = 0.03 and x = 0.05, the concentration of impurity donor states ε^V_D increases significantly, which at $x > 0.05$ intersect with the bottom of the conduction band ε_C: a dielectric-metal electrical conductivity transition occurs, which is an Anderson transition [9].

Crossing the edge of the conduction band ε_C by the Fermi level ε_F will change the type of conductivity of the semiconductor from activation (for $x < 0.05$) to metallic (for $x > 0.05$) [8]: on the temperature dependences of the specific resistance $\ln(\rho(1/T))$ the activation parts will disappear, and resistance values ρ will increase with temperature [10].

The nature of changes in the values of the distribution of the density of electronic states (DOS) of $Lu_{1-x}V_xNiSb$ in the presence (Fig. 3) and absence (Fig. 4) of magnetic ordering are practically the same for states with upward spins. We can predict that the behavior of the kinetic properties of the semiconductor solid solution $Lu_{1-x}V_xNiSb$ in the presence and absence of magnetic ordering will be similar at temperatures higher than the Curie temperature (T_C), when the magnetic ordering disappears. At the temperature of the phase transition of the second kind, which is the Curie temperature T_C, when spontaneous magnetization is destroyed under the action of thermal motion of atoms, there will be a sudden change in the properties of the substance, in particular, magnetic and kinetic.

Fig. 5 presents the results of modeling the behavior of the Curie temperature T_C of the semiconductor solid solution $Lu_{1-x}V_xNiSb$ under the condition of the presence of a magnetic moment on V atoms, which is accompanied by magnetic ordering. We can see that there is a close to linear dependence of the Curie temperature T_C of the

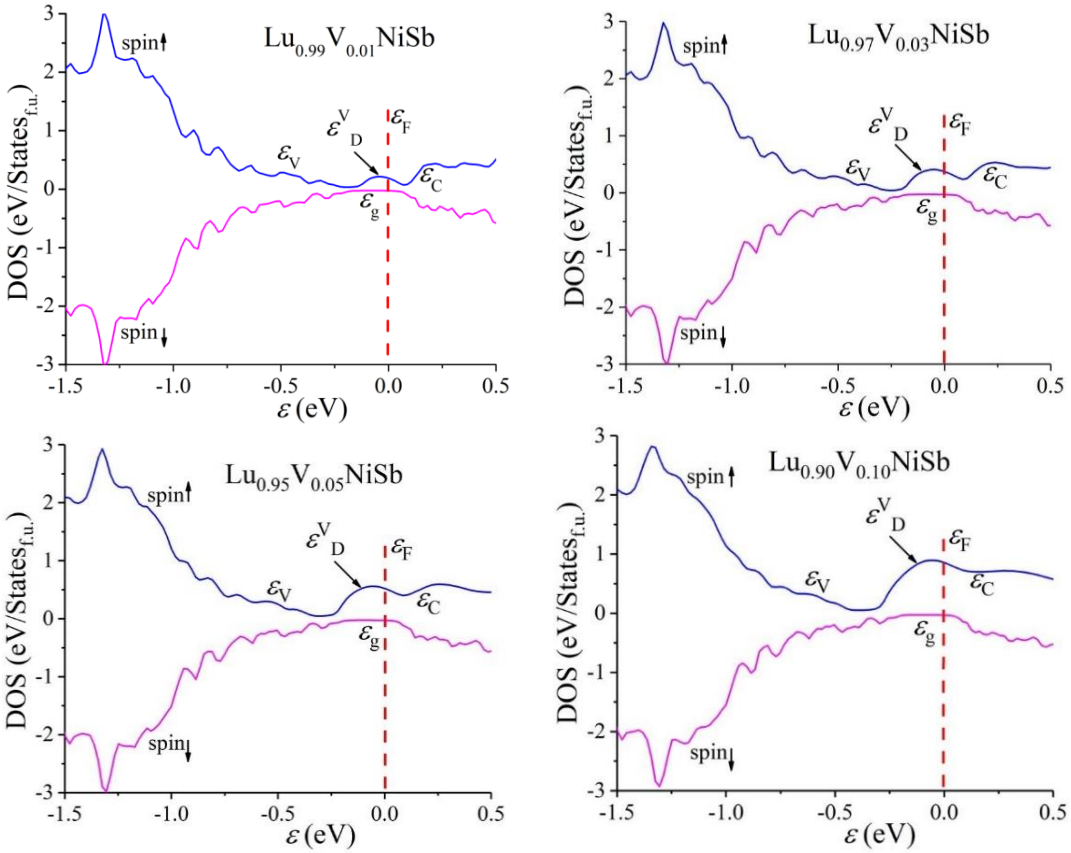

Fig. 3. Modeling of the distribution of the density of electronic states DOS of $Lu_{1-x}V_xNiSb$ when available magnetic ordering.

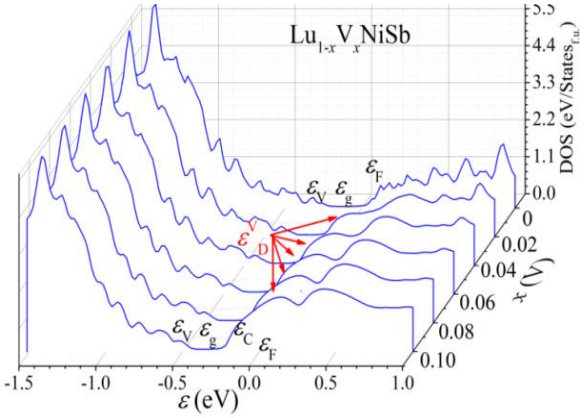

Fig. 4. Modeling the distribution of the density of electronic states of DOS $Lu_{1-x}V_xNiSb$ in the absence of magnetic ordering.

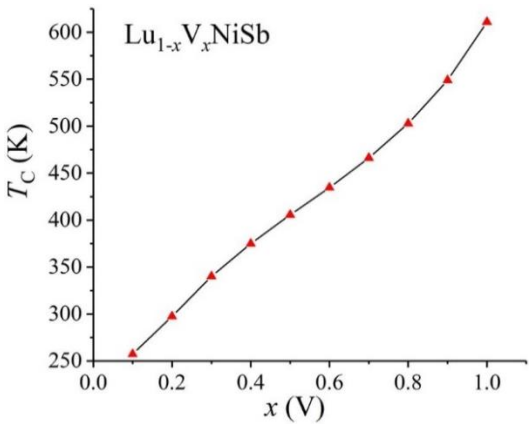

Fig. 5. Modeling of changes in the Curie temperature T_C values of the $Lu_{1-x}V_xNiSb$ in the presence of magnetic ordering.

$Lu_{1-x}V_xNiSb$ on the concentration of V impurity atoms.

The obtained result is understandable, because the greater the concentration of V atoms, the stronger the exchange interaction between electrons will be, and the more difficult it is for the thermal motion of atoms to destroy (disorient) the spontaneous magnetization.

Conclusions

Modeling of the thermodynamic, structural, energetic and magnetic properties of the semiconductor solid solution $Lu_{1-x}V_xNiSb$ was carried out under the condition of the presence of a magnetic moment on the V atoms and the occurrence of spontaneous magnetization. It is shown that the change in the unit cell parameter $a(x)$ and the mixing enthalpy $\Delta H_{mix}(x)$ depends little on the presence or absence of spontaneous magnetization. Modeling of the distribution of the density of electronic states DOS in the presence of a magnetic moment on V atoms revealed the splitting of energy states with spins up and down while preserving the band gap ε_g of $Lu_{1-x}V_xNiSb$. The relationship between the concentration of magnetic V atoms in $Lu_{1-x}V_xNiSb$ and the Curie temperature T_C, when spontaneous magnetization is destroyed and the substance becomes paramagnetic, is established. The solid solution

semiconductor $Lu_{1-x}V_xNiSb$, provided spontaneous magnetization is present, can be considered as a promising magnetocaloric.

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Моделювання властивостей напівпровідникового твердого розчину $Lu_{1-x}V_xNiSb$ за наявності магнітного упорядкування

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Проведено моделювання термодинамічних, структурних, енергетичних та магнітних властивостей напівпровідникового твердого розчину $Lu_{1-x}V_xNiSb$ за умови наявності магнітного моменту на атомах V та виникнення спонтанної намагніченості. Показано, що зміна періоду елементарної комірки $a(x)$ та ентальпії змішування $\Delta H_{mix}(x)$ мало залежить від наявності або відсутності спонтанного намагнічення. Виконані розрахунки ентальпії змішування $\Delta H_{mix}(x)$ за наявності та відсутності магнітного моменту на атомах V показують енергетичну доцільність існування сполуки VNiSb зі структурою MgAgAs. Моделювання розподілу густини електронних станів DOS за наявності магнітного моменту на атомах V виявило розщеплення енергетичних станів зі спінами вгору та вниз при збереженні забороненої зони ε_g $Lu_{1-x}V_xNiSb$. Встановлено залежність між концентрацією магнітних атомів V у $Lu_{1-x}V_xNiSb$ та температурою Кюрі T_C, коли спостерігається перехід від спонтанної намагніченості до парамагнітного стану. Напівпровідниковий твердий розчин $Lu_{1-x}V_xNiSb$ за умови наявності спонтанного намагнічення можна розглядати як перспективний магнетокалорик.

Ключові слова: магнітне упорядкування, рівень Фермі, температура Кюрі T_C.