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ENERGY PARAMETERS OF INTRACELLULAR MOVEMENT OF FLUORIDE IONS IN A SUPERIONIC LaF₃ NANOCRYSTAL

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ABSTRACT

The paper presents the results of quantum chemical calculations of the change in the lattice energy and the energy parameters of internal motion in a LaF_3 nanocrystal during a phase transition from a dielectric state to a highly conducting phase. Quantum-chemical calculations were done for three nanogrids with linear dimensions of $2.1 \times 2.0 \times 2.2$ nm, $2.9 \times 2.0 \times 2.2$ nm and $3.5 \times 2.0 \times 2.2$ nm. It has been established that the increment in the magnitude of the lattice energy in all nanolattices decreases with an increase in the number of disordered fluorine ions in them. It was also established that the increment of the lattice energy (with an equal number of disordered fluorine ions) is more significant for nanogrids with a larger number of ions. It is shown that, for all nanogratings, the energy E_a of a single act of disordering of the anion sublattice with an increasing number of disordered ions decreases from 0.16–0.17 eV in the dielectric phase to 0.02–0.04 eV in the superionic state.

KEYWORDS: *Quantum Chemical Calculation, LaF_3 Nanocrystal, Internal Motion*

INTRODUCTION

Superionic (SI) materials form a special class of substances, attracting the attention of a wide range of researchers for their unusual properties, which are extremely interesting both from the standpoint of the fundamental problems of solid state physics and physical chemistry and in connection with purely applied aspects [1–3]. In most cases, the conductivity of typical SI conductors is close to the values characteristic of melts and concentrated solutions of strong electrolytes. So, if the conductivity of ordinary ionic crystals at temperatures sufficiently far from the melting point, as a rule, does not exceed $\sigma_i \approx 10^{-9}$ S / cm, then the ionic conductivity of good SI conductors is $\sigma_i \approx 10^{-1}$ - 100 S / cm. Thus, SI materials have mixed properties: the conductivity of a melt or electrolyte solution on the one hand, and the mechanical strength and elasticity of a solid body on the other. For this reason, SI materials are often called solid electrolytes. In some respects, these are materials that fill the gap between liquids and crystals, and the measure of the disorder of the SI lattice of materials can be controlled with the help of temperature.

In addition to the practical significance of the SI materials, their comprehensive study is a logical continuation of a number of objects that are becoming increasingly complex to study. From the point of view of physical chemistry, SI conductors represent an important link in a vast array of electrically conductive materials. Moreover, for a large class of SI conductors, the transition from the dielectric (DE) state to the highly conducting state often has the character of a phase transition (PT), which is diffuse in a certain temperature range. The interest of specialists in the study of transport processes in solids to fluoride-conducting ionic conductors, in particular, to LnF₃ (Ln-La, Ce, Pr) crystals, is primarily

determined by the wide possibilities of their application in various technical fields. In particular, the SI LnF_3 crystals are extremely perspective as a material for working modules in high-capacity solid-state batteries, electrochromic displays, gas-analytical sensors, and various micro-ion devices.

The use of modern film technologies allows changing and improving the physicochemical properties of ion-conducting materials, as well as significantly expanding the field of application of such materials. In this case, an important factor in various technical applications is the fact that LnF_3 crystals possess a sufficiently high specific conductivity in the region of room temperature. The anion sublattice of LnF_3 crystals consists of three types of structurally nonequivalent fluorine ions, called F_1, F_2, and F_3. The process of active disordering of the anion sublattice, for example, in a LaF_3 crystal, is observed in the range of 240–540 K and continues until the melting point of the material. Moreover, in the range of 240–320 K, the lattice disordering is determined by active motion in the F_1 sublattice. The remaining fluorine ions F_2 and F_3 together with metal cations form anion – cation (base) planes in the lattice structure. The sublattices of these ions are more conservative and disordered at temperatures in excess of 360–420 K.

An analysis of recent work has shown that directly describing the dependence of the energy parameters of internal motion on the degree of disordering of the SI lattice of materials in the framework of classical thermodynamics is rather difficult [4]. As a rule, the physical approaches and mathematical methods used in this case lead, on the one hand, too complex mathematical calculations related to the thermally activated nature of the lattice disordering process, and, on the other hand, to a significant increase in computer simulation time.

At the same time, the problem of describing the magnitude of the energy parameters of intracellular motion depending on the degree of disordering of one of the sublattices can be largely successfully solved nowadays on the basis of modern software. We note in particular the fact that modern computer simulation makes it possible at the microscopic (atomic) level to investigate and describe in detail the features of the motion of individual ions in a wide temperature range (both in the DE phase and in the SI state). Moreover, quantum – chemical modeling of the process of moving ions in a disordered sublattice in some cases can provide new, more detailed information about the intracellular movement of ions, which is very difficult or impossible in laboratory experiments. For this reason, the data obtained by means of the quantum chemical simulation are, as a rule, original, describing in detail the atomic picture of internal motion in the lattice of the conductor under investigation.

For quantum – chemical calculations of the energy parameters of intracellular motion of fluoride ions for nanoscale LaF_3 lattices, we used the package of quantum – chemical programs MOPAC 2016 [5]. For calculating the lattice energy of bonds and the energy parameters of the internal motion we used the semi-empirical method PM7 with an extended set of elements, including the elements lanthanum and fluorine. In the process of calculations using quantum – chemical programs, the bond energy of a system of particles (ions) was determined by a large number of "energy" members, which are determined by interactions of various types (core – core, electron shell – core, etc.) taking into account both long-range and short-range potentials . Thus, the energy of interparticle bonds in LaF_3 nano-lattices, in solid-state physics called the lattice energy of cohesion, was calculated in a physically sufficiently adequate approximation. The methodology for such model calculations is described in detail, for example, in [6].

As already noted, the unusual physicochemical properties of SI materials make them attractive objects for widespread use in a wide variety of applied fields of physics, chemistry, and technology. For example, instrument electronics is characterized by the complexity and miniaturization of working modules using modern film technologies.

Therefore, electronic instrument-making is actively expanding its functionality with new technical devices based on unconventional physical approaches and principles. However, it is obvious that the problem of a significant reduction in the size and mass of such devices can be solved through the use of both new technological methods and new materials, in particular, solid electrolytes as a functional material with a wide range of unusual properties [7, 8]. It is also obvious that further expansion of the applied use of SI materials is possible only on the basis of a deep and successful study of physical phenomena that determine the patterns of high internal mobility and the atomic picture of internal motion in the lattice of a solid body. In terms of the practical use of SI conductors, it should also be noted that the processes occurring in nanoscale systems form the basis of modern and promising solid-state nanotechnologies. In the context of the above, it is interesting to study and predict the properties of nanostructured materials based on the study of some characteristic parameters in nanoscale SI conductors with the number of particles from several tens to 1100-1200.

In the present work, based on the data of computer simulation of structural disorder in a nanosized LaF₃ crystal in a wide temperature range, including a phase transformation region, the change in some energy parameters determining the efficiency of intracellular movement of fluorine ions is investigated. In particular, the dependence of the magnitude of these parameters on the degree of disordering of the anion sublattice during the transition from the DE to superion state is described and analyzed.

RESULTS AND DISCUSSIONS

For model calculations and a detailed description of the physical picture of changes in the lattice binding energy and the specific energy E_a of the disordering of the anion sublattice, three SI nanogrids of LaF₃ crystals with linear dimensions of $2.1 \times 2.0 \times 2.2$ nm (720 ions), $2.9 \times 2.0 \times 2.2$ nm (960 ions) and $3.5 \times 2.0 \times 2.2$ nm (1200 ions). Quantum-chemical calculations of the features of the disordering process of the LaF₃ anion sublattice were carried out for the case of gradual (step-by-step) disordering of the F_1 sublattice in the studied nanolattices. The process of thermal disordering of the anion sublattice was simulated on the F_1 sublattice, whose ions make up $\sim 70\%$ of the total number of fluoride ions.

Quantum-chemical calculations were carried out for all nanolattices with a consistent increase in the number of F_1 ions transferred to the nearest interstices. When modeling the process of thermal disordering of the anion sublattice, the number of ions transferred to the internode increased with each successive step for all nanogrids in the same way - by ten disordered F_1 ions. At the same time, all ten fluorine ions moved in the interstices shifting in the XY plane. An increase in the "quasi-liquid" array of ions in the F_1 sublattice was carried out by attaching to it (at the next quantum chemical calculation) ten more disordered ions. In Figure Figure 1 shows the dependences of the change (increments along the ordinate axis) of the ΔE value of the lattice binding energy for three LaF₃ nanolattices, due to the sequential increase in the number of disordered F_1. The abscissa axis shows the numbers of such disordered ions. The zero value of the lattice energy on the ordinate axis corresponds to a fully ordered lattice when all the ions are located in their site positions. The increments ΔE of the bond energy in such a nanolattice are absent. The first step corresponds to the formation of arrays of ten disordered F_1 ions in all nano-lattices. In this case, the bonding energy in nanolattices increases by ~ 1.7–1.8 eV (Figure 1). The second step is associated with the formation of ten more disordered F_1 ions in each nanolattice, which doubles the already existing arrays of point defects. In this case, the total increment of the lattice energies in the three nanolattices lies in the interval ~ 3.1–3.3 eV. The numbers 1, 2, and 3 with the curves of variation of the lattice energies correspond to those containing 720, 960, and 1200 ions.
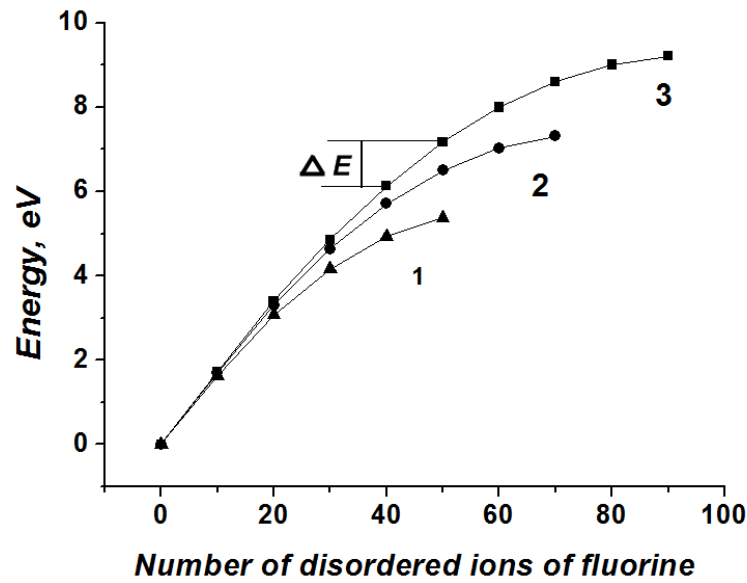
Figure 1: Changes in the Lattice Energy in the SI Nano-Lattices of the LaF$_3$ Conductor Depending on the Number of Disordered Ions F$_1$

It can be clearly seen that each next step inside any of the three curves increases the energy of the nanogrids by an ever smaller value. Moreover, the increment of the lattice energy ΔE is most significant for nano-grids with a larger number of ions. So, for a nanolattice with the number of ions 1200 (curve 3), the increments of its energy ΔE_3 from pitch to pitch significantly exceed the corresponding increments of energy ΔE_1 and ΔE_2 for nano-grids containing 720 and 960 ions. Thus, the lattice binding energy (as expected) is the largest for a nano-lattice with the largest number of ions. From which it follows that in the studied nano-lattices with the corresponding changes in the number of disordered ions, the $\Delta E_3 > \Delta E_2 > \Delta E_1$ ratios are fulfilled.

It is equally interesting to consider the change in the specific energy E_a of the disordering of the F$_1$ sublattice as a function of the number of disordered fluorine ions and the number of ions in the nano-lattice. Figure 2 shows such changes in the energy E_a for the three LaF$_3$ nano-grids. Analysis of curves 1, 2, and 3, which (as before) correspond to nano-lattices with the number of ions 720, 960 and 1200, allows us to draw the following conclusion. The specific energy E_a of disordering of one F$_1$ ion with an increasing number of disordered F$_1$ ions gradually decreases in all nanolattices from ~ 0.16–0.17 eV in the DE phase (when the fraction of disordered F$_1$ is minimal and not more than ten) to 0.02–0.04 eV in the SI state, when the number of disordered fluorine ions is tens. Moreover, the smallest energy value of $E_a = 0.02$ eV was obtained for a lattice of 1200 ions, containing the largest number of disordered F$_1$ ions (90 ions of this type). Accordingly, the "highest" energy value $E_a = 0.04$ eV was obtained in the SI phase for curve 1, corresponding to the lattice with the total number of ions 720, in which 50 F$_1$ ions are disordered (Figure 2).
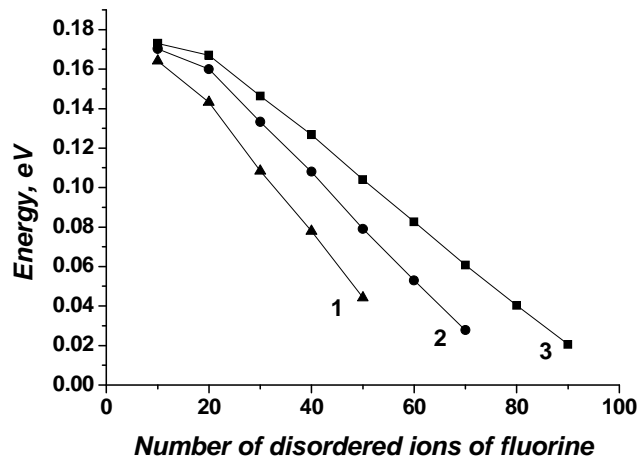
Figure 2: Change in the Specific Energy E_a of Disordering of the F_1 Sublattice as a Function of the Number of Disordered Fluoride Ions in the LaF₃ Nano-Lattices

Such a decrease in the specific energy E_a is determined by the fact that when a disordered ion is formed in an array of already existing interstitial anion – anion vacancy defects, the effect on the energy parameters of the so-called collective interactions in the quasi-liquid sublattice should be taken into account [4]. Such collective interactions determine the characteristics of the process of disordering of one of the SI sublattices of the conductor; in particular, they significantly reduce the value of energy parameters in certain crystallographic directions. Thus, an analysis of the results of quantum chemical calculations for MOPAC 2016 shows that when there is a relatively large number of disordered fluorine ions in the F_1 sublattice (SI phase), the energy parameters in some crystallographic directions decrease by 4–8 times compared to their values in DE phase.

From Figure 2 it also follows that with an increase in the fraction of disordered fluorine ions and a decrease, in this connection, of the energy parameters, in particular, the activation parameter E_a, these parameters take a number of intermediate values: 0.16, 0.14, 0.12, 0.10, 0.08 and 0.06 eV. This series of E_a values, converging in the SI phase to the minimum values of three grades of 0.04 eV (curve 1), 0.03 eV (curve 2) and 0.02 eV (curve 3), were obtained for the first time for the SI crystal of LaF₃.

Moreover, the parameter E_a varies from ~ 0.14 eV (curve 1), ~ 0.16 eV (curve 2) and ~ 0.17 eV (curve 3) in the DE phase to values ~ 0.02 - 0.04 eV in the SI state is almost linear. From this circumstance, it can be concluded that if the increase in the number of disordered ions in the crystal lattice of the crystal occurs in a linear fashion, then the change in the activation energy E_a will correspond to a certain linear function. It can also be expected that if the change in the number of disordered ions with increasing temperature is described by another more complex function (for example, as in Figure 3 taken from [9]), then the change in the energy E_a in the FP region will follow a more complex law.

It should be noted that the obtained values of the activation parameter E_a are well correlated with the values of the energy E_a of the single act of disordering of the F_1 sublattice obtained in a completely different way - for example, from experimental data on Raman scattering [10] or direct quantum chemical calculations of the parameter E_a - single act disordering of the F_1 sublattice in the DE and SI phases (the results of such calculations are shown in Figure 4 of [11]). Figure 4 shows that the parameter Ea, which determines the change in the energy of the lattice when the F_1 ion moves to

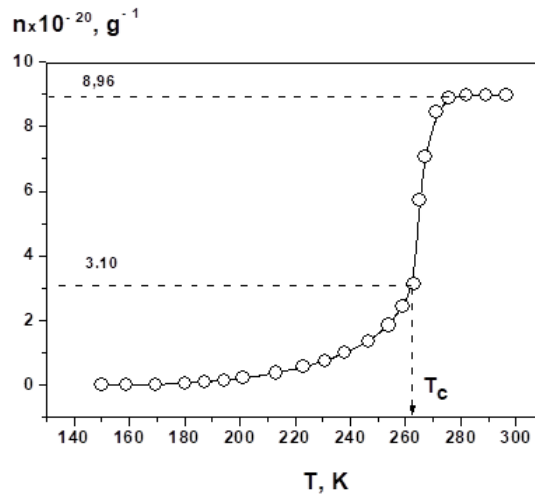the nearest interstitial site, is 0.16 eV (curve 1 for the DE phase)

Figure 3: Temperature Dependence of the Concentration of Disordered F$_1$ Ions in the Region of Phase Transformations in LaF$_3$
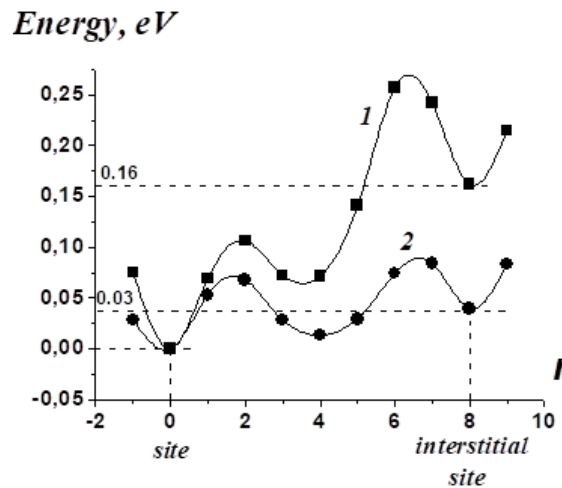

Figure 4: Profiles of Potential Reliefs in the LaF$_3$ Nano-Lattice of 1200 Ions with a Thermally Activated

Displacement of the F$_1$ Ion From the Node To the Nearest Interstitial Site: Curve 1 - Dielectric Phase (T <Tc), Curve 2 - Superionic Phase (T ≥Tc).and 0.03 eV (curve 2 for the SI phase). It is clearly seen that these values almost coincide with the values of E_a for the nano-grids in the DE and SI phases, shown above in Figure 2

CONCLUSIONS

In the work, quantum chemical calculations based on the MOPAC 2016 software package show a consistent change in the energy parameters that determine the efficiency of fluoride ion transfer in the SI nano-lattice of the LaF$_3$ crystal, depending on the degree of disordering of the anion sublattice. It should be particularly noted that the new data obtained through quantum – chemical calculations, as a rule, reveal and describe the microscopic picture of the features of thermally activated processes, in particular, the processes of mass transfer of fluoride ions in the SI lattice of the LaF$_3$ conductor.

It is also obvious that the conclusions obtained in the work can be attributed to the entire SI series of LnF$_3$ crystals with a slight change in the numerical values of the corresponding energy parameters due to the so-called lanthanoid compression of the lattice parameters.

The model schemes developed by the authors for obtaining microscopically small values (on the order of hundredths of eV) of energy parameters are based on positions widely known in crystal physics. Therefore, the model approaches used in the work are applicable to the description of the energy characteristics of internal motion in an extensive SI class of conductors with diffuse phase transitions.

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