Computer Simulation of Superionic Conductors: II. Cationic Conductors. Review

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Abstract—The state of the art of the molecular-dynamics simulation of superionic conductors is reviewed. The main studies devoted to the structural, dynamic, and transport properties of the basic classes of solid electrolytes with conductivity via silver, copper, lithium, sodium, and hydrogen cations are considered. The premelting effect in ionic crystals is discussed.
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1. Ag⁺ IONIC CONDUCTORS: SILVER IODIDE AND SUPERIONIC CONDUCTORS ON ITS BASIS

1.1. Silver Iodide

Among cationic superionic conductors, the model object is silver iodide, in which the high-conductivity state is obtained as a result of the phase transition. Recall that the crystal structure of the high-temperature (T > 420 K) disordered α phase (sp. gr. Im3m) has a bcc anion sublattice, and two silver cations in a unit cell can occupy positions of three types: 12d-tetrahedral, 24h-trigonal, and 6b-octahedral positions. Upon cooling, the α phase of AgI is transformed into the hexagonal β phase with a zinc blende structure (sp. gr. P6/3mc) at a temperature of 420 K.

In molecular dynamic calculations, different types of ion–ion potential were used. Their choice was performed mainly at the phenomenological level and was not based on quantum-chemical calculations [1–6].

The large part of molecular-dynamics calculations was performed for systems composed of 256 or 512 ions (however, systems containing more than 1000 atoms have been considered as well). The effect of the computational box size (the number of particles) and the procedure of calculation of the Coulomb energy on the characteristics of the mobile α-AgI subsystem was analyzed in [7].

1.1.1. Dynamic behavior

Analysis of mean-square displacements shows that silver cations are involved in translational motion, whereas iodine anions vibrate near their equilibrium positions. The calculated values of diffusion coefficient at different temperatures are shown in Fig. 1. An analysis of atomic-density distributions [1, 9] allowed to
draw a conclusion that there is a saddle point $s$ between two tetrahedral crystallographic positions (Fig. 2).

The static structure factor $S(k)$, calculated in [12, 13], indicates that the density distribution of mobile silver cations is mainly determined by the properties of the bcc-anion lattice: $S_A(k)$ peaks are observed at the same distances as the $S_S(k)$ peaks. This conclusion is confirmed by the fact that first peak in the radial pair correlation function for Ag–Ag pairs is located almost at the same distance (~4.3 Å) as the peak for I–I pairs [1, 5]. The dynamic structure factor was calculated in [14].

The microscopic diffusion mechanism was analyzed in [3]. It turned out that jumps occur mainly in the [110] direction, i.e., an ion moves to the nearest tetrahedral position. Note also that in 40% of cases an ion makes a reverse jump to its initial site.

The silver diffusion coefficients were found from the analysis of the velocity autocorrelation function [3, 9]. Such calculations give the values $D_{Ag} = 1.68 \times 10^{-5} \text{ cm}^2/\text{s}$ (at 450 K [3]) and $3.56 \times 10^{-5} \text{ cm}^2/\text{s}$ at 560 K [12].

The Haven ratio is $D/D_{Ag}(\omega = 0) = 1.68/3.4 = 0.5$ (at 450 K) [3] and 0.46 (at 560 K) [12]. The values obtained correspond to the experimental value of 0.6 and are in good agreement with the theoretical estimates [15].

The specific features of the behavior of silver cations in the time ranges 0.1–1 and 10–30 ps in the disordered $\alpha$ phase of AgI were discussed in [16, 17].

Using the molecular-dynamics method, one can describe the specific features of diffuse X-ray and Raman scattering [18]. We should note also the attempts to analyze the trajectories of silver cations within the fractal approach [19].

### 1.1.2. Phase transitions in AgI

To investigate the phase transitions by the molecular-dynamics method, it is necessary to use computer programs that make it possible to take into account the change in the symmetry of a system under consideration (i.e., the shape and size of the unit cell) in calculations, vary the density of the system with time, and maintain a constant pressure in the system. Within the $NPT$ (constant number of particles $N$, constant pressure $P$, and constant temperature $T$) approach, investigation of the $\alpha \rightarrow \beta$ phase transition at zero pressure was performed in [3]. The analysis of the radial pair correlation functions indicates a transition from the bcc lattice to fcc lattice upon cooling. Repeated heating of the system up to 495 K transforms AgI into the $\alpha$ phase. The transition occurs in the temperature range from 472 to 495 K. These temperatures are in good agreement with the experimental value of 420 K.

It should be noted that, according to [3], molecular-dynamics simulation does not make it possible to reproduce the experimentally observed increase in the sample density at the $\beta \rightarrow \alpha$ transition. However, this statement was disproved in [9, 10].

In the cycle of studies [10, 20, 21], Tallon investigated the phase diagram of iodide silver using the molecular-dynamics calculations under constant pressure conditions. A system composed of 216 or 512 ions was spontaneously transformed from one phase into another upon cooling or heating. The phase diagram shown in Fig. 3, on the whole, is in qualitative agreement with the true phase diagram.
1.2. Solid Electrolytes Based on AgI: Ag₃SI, and Ag₄RbI₅

The molecular-dynamics calculations of the Ag₃SI solid electrolyte were performed in [22] for a system of 1080 particles. For the α phase, the radial pair correlation functions indicate the formation of an anion sublattice having an fcc structure. Silver cations are distributed over interstitial positions, and the coordination number 4 for the first peak in g_{Ag(IS)} indicates the preferential tetrahedral coordination (12d) of silver. The temperature dependences of the Debye–Waller factors and diffusion coefficients indicate good agreement with the experimental results. At 600 K, the Haven ratio is 0.47–0.49 a value that is comparable to the experimental value $H = 0.47$ [23].

To reveal the microscopic mechanism of conductivity in Ag₃SI, van Hove functions were analyzed. Figure 4 shows the second moment $P(t)$. It can be seen that, although the motion of anions in both phases has an oscillatory character, the transport of cations in the β phase is strongly anharmonic, whereas, in the α phase, it has a jump character.

An attempt to calculate the population of positions in the solid electrolyte Ag₄RbI₅ within the simplest model [24] showed reasonable agreement with the experimental results.

1.3. Solid Solutions of Electrolytes Based on α-AgI

It is known that, in a number of quasi-binary systems AgI–AgX ($X = Br, Cl$) [25–28] and AgI–MI ($M = Cu, Cs$) [29–32], solid solutions based on α-AgI exist in a fairly wide range of concentrations and temperatures. The concentration dependences of the ionic conductivity of the solid solutions $\alpha$-AgI$_{1-x}$Cl$_x$ ($0 < x < 0.1$) [28] and $\alpha$-Ag$_{1-y}$Cu$_y$I ($0 < y < 0.1$) [29–34] indicate the decrease in the conductivity of the material with an increase in the dopant content in the sample.

The structural and transport properties of solid solutions based on α-AgI, formed by substitutions in the

![Fig. 3. Calculated phase diagram for AgI [10].](image)

![Fig. 4. The value of $P$ for ions in Ag₃SI at (a) 600 and (b) 450 K [22].](image)

![Fig. 5. Concentration dependences of the diffusion coefficient of Ag⁺ cations in the α-Ag$_{1-x}$Cu$_x$I system [35].](image)
anion ($\alpha$-AgI$_{1-x}$Cl$_x$, $0 < x < 0.25$) and cation ($\text{Ag}_1^{-y}\text{Cu}_y$I, $0 < y < 0.25$) sublattices were studied by the molecular-dynamics method [35–37].

The analysis of mean-square displacements for all solid solutions shows that, in the high-temperature $\alpha$ phase, only cations are involved in the translational motion, whereas anions only oscillate near their equilibrium positions. Figures 5 and 6 show the composition dependences of the diffusion coefficient of silver cations. It can be seen that a decrease in $D_{\text{Ag}}$ with an increase in the copper and chlorine concentrations in the solid solutions is observed at all temperatures.

The concentration dependence of the activation energy of diffusion for the solid solutions $\alpha$-Ag$_{1-x}$Cu$_x$I has a maximum at $x \approx 0.15$ (Fig. 7). The curve $E_{\text{act}}(x)$ [32] has a similar form; however, the maximum is observed at $x \approx 0.25$. The results of molecular-dynamics calculations made it possible to calculate the transport numbers and compare them with the measured values. As can be seen in Fig. 8, good agreement between the data of computational and physical experiment is observed.

For the $\alpha$-AgI$_{1-x}$Cl$_x$ solid solutions, the activation energy of diffusion is $E_0 = 0.14 \pm 0.01$ eV. This value is close to the values $E_0 = 0.15$ eV for nonstoichiometric $\alpha$-Ag$_{1-x}$Cu$_x$I phases with substitutions in the cation sublattice.
1.4. Ag⁺ Ionic Conductors: Silver Chalcogenides

Ag₂X silver chalcogenides are mixed ionic–electronic conductors. They are of great interest for many researchers [39, 40]. Silver sulfide and selenide (Ag₂S and Ag₂Se) have a high-temperature disordered phase of the α-AgI type, in which sulfur (selenium) forms a bcc lattice, whereas silver cations (their concentration is a factor of 2 larger than that in silver iodide) are disordered over interstitial positions.

The results of [39–44] indicate the presence of silver cations not only in tetrahedral but also in octahedral positions. The diffusion coefficients shown in Fig. 9 are in good agreement with the experimental data [39, 40].

The analysis of density maps of silver atoms (Fig. 10) shows that the density distribution of silver ions in the octahedral position, \( \rho_o \), (with respect to the Ag⁺ density distribution in tetrahedra, \( \rho_t \)) at 646 K is \( \rho_o/\rho_t = 0.55 \), and the density distribution of Ag⁺ in the intermediate \( M \) position is \( \rho_M/\rho_t = 0.2 \). The value \( \rho_M/\rho_t \) remains almost invariable at all temperatures, whereas \( \rho_M/\rho_t \) increases with an increase in temperature. In addition, we can conclude that the \( s \) point is not a saddle point (as in \( \alpha \)-AgI). Since the density distribution of silver in the octahedral position is sufficiently high, jumps from octahedral to tetrahedral positions play an important role and we can speak about the existence of conductivity channels in the [100] direction.

Molecular-dynamics calculations make it possible to determine the static structure factors [39, 43] and explain the anomalously high intensity in the spectra of quasi-elastic neutron scattering in the vicinity of the wave vector \( \mathbf{Q} = (1.6, 1, 0) \) [45] and the presence of low-energy excitations (~2 meV) at temperatures below the phase-transition temperature. It was revealed that silver–silver correlations dominate in the system. With an increase in temperature, the width of the quasi-elastic peak increases, whereas its intensity decreases.

In [44], the transition of silver sulfide from the high-temperature disordered phase into the monoclinic phase (sp. gr. \( P2_1/c \)) was modeled.

In investigation of Ag₂Se [46–49], additional information was obtained from the analysis of the angular correlation functions.

The dynamics of silver cations was investigated using the analysis of mean-square displacements and the autocorrelation functions. The values of diffusion coefficient determined by different methods coincided with each other; the temperature dependence \( D(T) \) is shown in Fig. 9. The Haven ratio ranges from 0.41 (595 K) to 0.58 (804 K), i.e., is in good agreement with the experimental values in the range 0.42–0.50 [23, 50].

The phase transition to the low-temperature ordered phase was discussed in [49]. A detailed study of crystallization processes in Ag₂Se was performed in [51]. The calculated value of the melting temperature (~1000 K)
is in agreement with the experimental result: \( T_m = 1170 \text{ K} \).

The third representative of the family of silver chalcogenides \( \text{Ag}_2\text{Te} \) has another disordered structure—the antifluorite structure. For molecular-dynamics calculations [52], a system composed of 324 particles was chosen. The analysis of radial pair correlation functions indicates the formation of an fcc lattice by tellurium anions; in this lattice, silver cations are located in tetrahedral voids. More detailed information was obtained from consideration of the density distribution \( \rho_{\text{Ag}} \) of \( \text{Ag}^+ \) cations. The density distribution of silver in the \((110)\) plane at 650 K is shown in Fig. 11. As can be seen, silver cations spend most time in the vicinity of \( t \) positions and move to a neighboring tetrahedral position through an octahedral one.

The distribution obtained is in good agreement with the suggestion of Okazaki [50], according to which jumps of cations occur along a zigzag curve connecting \( t \) and \( o \) positions in the \((110)\) plane through the common triangular plane.

The dependences of temperature on the diffusion coefficient that were obtained from the analysis of mean-square displacements are shown in Fig. 12. The activation energy is 0.14 eV, a value that is in good agreement with the direct experimental data. Use of autocorrelation functions of the velocity and current makes it possible to find the conductivity of silver telluride (Fig. 12) and calculate the Haven ratio: \( H \sim 0.5 \). This value is somewhat lower than the experimental value \( 0.63 \) [23, 50].

To answer the question about the microscopic nature of the ion transport in \( \text{Ag}_2\text{Te} \), the times of existence of silver cations in different polyhedra, which can be selected in the anion sublattice around the corresponding positions, were analyzed [55, 56]. It was found that the lifetime \( \tau_o \) in the tetrahedral position is larger than in the octahedral one (\( \tau_t \)).

The phase transition in \( \text{Ag}_2\text{Te} \), as a result of which the anion fcc lattice is transformed into a bcc lattice, was modeled in [57]. It was found that the diffusion coefficient in an fcc structure is lower than in a bcc structure and the activation energy in an fcc structure is higher than in a bcc structure. These relations are in qualitative agreement with the experimental results.

2. \( \text{Cu}^+ \) IONIC CONDUCTORS

For CuI, the direct phase transition from the \( \gamma \) phase to the \( \alpha \) phase was studied in [3, 58]. It was stated in these studies that the intermediate \( \beta \) phase does not play a significant role. The molecular-dynamics calculations were performed for a system composed of 216 particles. The change in a number of physical characteristics as a result of the order–disorder transition is shown in Fig. 13. With an increase in temperature to ~680 K, the total energy of the system \( E \), the diffusion coefficient \( D \), and the specific heat \( C_V \) increase. Then, the system exists in the intermediate state. With a further increase in temperature, \( E \) and \( D \) sharply increase (the latter from \( 1 \times 10^{-5} \) to \( 4 \times 10^{-5} \) cm\(^2\)/s), whereas \( C_V \) undergoes discontinuity (the latent heat of transition is 1.33 kcal/mol, a value that is comparable with the experimental value of 2.47 kcal/mol).

The diffusion data are shown in more detail in Fig. 14. These data demonstrate qualitative agreement between the calculated and experimental values of \( D \), although the calculated values depend strongly on the choice of the potential. From the analysis of the density distribution maps of silver cations, it was concluded in [3, 58–60] that, in the \( \alpha \) phase of CuI, copper cations are statistically distributed over all \( t \) positions (with a probability of \( \sim 0.5 \)) and a small fraction of \( \text{Cu}^+ \) ions are in \( o \) posi-
tions. Copper ions spend most time vibrating in tetrahedral positions (with strong anharmonicity), but sometimes move to octahedral sites.

To obtain the best agreement between the calculated and experimental data, the parameters of the potential [61–63] were varied. The best results were obtained with the three-body (Tersoff) potential) [64] (Fig. 14).

The molecular-dynamics calculations revealed the specific features of the cation transport in the γ phase. An example of collective motion of cations is shown in Fig. 15. The first ion (1) moves to the nearest interstitial position at the “step” period. After a short time, at step 108, ion 2 (which is located at a distance of about 10 Å) likewise moves to an interstitial site followed by ion 3 at step 111 and ion 4 at step 115. Then, ions 2, 3, and 4 rapidly move (at steps 116, 117, and 129) to fill vacancies and complete a chain. This phenomenon indicates that the ion motion is strongly correlated and looks like a caterpillar’s motion. In the α phase, the motion can likewise be correlated, but, nevertheless, it is described well within the jump model [67, 68].

The molecular-dynamics calculations of high-pressure phases in CuCl and CuBr showed the presence of cation transport in them [69].

3. Li⁺ IONIC CONDUCTORS

3.1. Li₃N Ionic Conductor

Among Li-conducting superionic materials, one of the most interesting and well-studied is Li₃N. The crystal structure of lithium nitride (hexagonal symmetry, sp. gr. P6₃/mmc) is formed by alternation of layers of Li(1) atoms and Li₂N groups. Since all positions are occupied in an ideal lattice, defects must be formed to provide ion transport.

The molecular-dynamics calculations were performed within the simplest rigid-ion model [70–73]. The radial pair correlation functions obtained at 300 K for N–N and Li(1)–Li(1) pairs have a form that is characteristic of an ordinary strictly ordered crystal. At the same time, the shape of the curves g₃(2)–Li(2) indicates some loss of the long-range order, although it is not so

![Fig. 13. Temperature dependences of (a) the total energy of the system, (b) the diffusion coefficient of copper, and (c) the specific heat [3].](image)

![Fig. 14. Temperature dependences of the copper diffusion coefficient in CuI: the data of (○) [3], (+) [65, 66] (experiment), (○) [59], (Δ) [61], and (▼) [64]; the dashed line shows the temperature dependence of the copper diffusion coefficient in CuCl (P = 128 kbar) [69].](image)

![Fig. 15. Schematic representation of the correlated motion of Cu⁺ cations in γ-CuI at 588 K [63].](image)
significant as that for such superionic conductors as CaF$_2$ or AgI.

A stoichiometric crystal was modeled in [70–72]; therefore, as the calculations showed, the Li(2) sublattice became slightly disordered with an increase in temperature. The most interesting results were obtained from the analysis of the trajectories of lithium cations directed perpendicularly to the c axis at 400 K (in the Li$_2$N plane). Since the number of vacancies is small in the lithium sublattice (a stoichiometric composition), a lithium ion reaches a vacancy not by a direct jump but via successive jumps of several ions, as schematically shown in Fig. 16.

Detailed investigations showed that all six ionic transitions occur simultaneously in this case, and we can speak about realization of the soliton-wave mechanism of conductivity [72]. Along with the situation considered, other types of collective motion of lithium ions were observed. This fact indicates strongly correlated motion resembling the motion of a caterpillar [15].

The diffusion coefficients measured for the cases of motion of Li$^+$ ions in Li$_2$N planes and perpendicularly to them differ insignificantly [74] ($D_{\parallel}/D_{\perp} \approx 2/3$). The molecular dynamic calculations from the first principles [75] were performed for a system composed of 32 atoms and containing one lithium vacancy. The lithium trajectories (Fig. 17) are an example of typical diffusion. At the beginning of the calculation, the vacancy was in position 7. Lithium ions moved simultaneously from position 3 to 8 and from 8 to 7. Then, the ion from position 2 tried to move to position 3 but failed. Then, the ion from position 4 reached position 8 but returned back at once. The lithium ions in positions 5, 6, and 1 were not involved in diffusion and vibrated near their equilibrium positions. This scheme demonstrates an important role of vacancies in lithium migration.

### 3.2. Li$_2$SO$_4$ Ionic Conductor

Lithium sulfate in the high-temperature (848–1133 K) fcc $\alpha$ phase has a high ionic conductivity. The nature and mechanism of the ionic conductivity in the $\alpha$ phase of Li$_2$SO$_4$ have not been completely established until now. Direct structural investigations of Li$_2$SO$_4$ indicate orientational disordering of SO$_4^{2-}$ tetrahedra. The molecular-dynamics calculations of a Li$_2$SO$_4$ crystal were performed for systems composed of 96 and 324 atoms [76–79] in which S$^{6+}$ and O$^{2-}$ ions formed SO$_4^{2-}$ groups. In the high-temperature (cubic) phase, motion of lithium ions can be clearly seen, whereas sulfur atoms vibrate near their equilibrium positions.

The temperature dependences of the diffusion coefficient of lithium ions show that the calculated values of $D_{\parallel}$ are somewhat lower than the experimental values. In addition, there is no sharp difference in the cation diffusion both at the transition from the low-temperature phase to the $\alpha$ phase and upon melting of the crystal.

The mechanism of diffusion of Li$^+$ ions was discussed in [79]. It turned out that octahedral positions play a key role in the diffusion mechanism.

For mixed lithium potassium sulfate LiKSO$_4$, similar results were obtained in [80].

### 3.3. Li$_2$MgCl$_4$ Ionic Conductor

The solid electrolyte Li$_2$MgCl$_4$ has an inverse spinel structure. Its formula can be written in the form [Li]$_{76}$[Li,Mg]$_{108}$Cl$_4$. This notation indicates the existence of two lithium sublattices: “tetrahedral” and “octahedral.” The calculations by the molecular-dynamics method were performed for a box consisting of 112 atoms in the temperature range from 500 to 720 K [81]. It was found that, at low temperatures (<600 K), diffusion ($D_{\parallel} = 5.5 \times 10^{-6}$ cm$^2$/s at 500 K) is mainly related to jumps of lithium ions in the octahedral sublattice via tetrahedral positions. At higher temperatures...
(\(D_{Li} = 2.4 \times 10^{-5}\) cm\(^2\)/s at 720 K), lithium ions from the tetrahedral sublattice take part in the diffusion.

3.4. Ionic Glasses

The molecular-dynamics method has been actively used in structural and transport investigations of silicate [82–87] and phosphate [88–90] glasses.

4. Na\(^{+}\) IONIC CONDUCTORS

4.1. Na-\(\beta\)-Alumina Crystals

The materials from the \(\beta\)-aluminas family are 2D conductors in which charge transport occurs in 2D conductivity gaps separating spinel blocks [38, 91].

The conductivity of Na-\(\beta\)-alumina is mainly determined by the deviation of the sample composition from stoichiometry. For a purely stoichiometric sample, the conductivity is minimum since sodium ions are ordered (all \(BR\) positions are occupied, and \(aBR\) positions are vacant). Introduction of additional sodium cations leads to disordering in the sodium sublattice and, as a result, to an increase in \(\sigma\).

To reveal the specific features of ion transport at the microscopic level, molecular-dynamics calculations of the Na-\(\beta\)-alumina were performed. In the first studies [92–94], a simple two-particle potential was used. Later, a combined two- and three-body ion-interaction potential was applied [95].

Analysis of sodium ion trajectories shows that all \(BR\) positions are occupied at low temperatures and excess Na ions are localized in (or near) \(aBR\) positions. A particular role of additional oxygen atoms in the \(mO\) states should be noted: The interstitial oxygen decreases the mobility of sodium ions. Indeed, the \(BR\) and \(aBR\) positions that are nearest to \(mO\) are almost always vacant, whereas the next positions (\(nnn\)) are almost always occupied by Na\(^{+}\) ions, whose migration activity is low.

Superstoichiometric sodium cations induce an additional transition of Na ions from \(BR\) to \(aBR\) positions. The number of sodium ions in the state of transition (flight) from one position to another is very small (a few percent). Therefore, we can speak about the jump mechanism of migration. At the same time, jumps are strongly correlated (especially at low temperatures); thus, it is necessary to consider the motion of an ensemble of sodium ions.

Analysis of the time and number of jumps of sodium cations from \(BR\) to \(aBR\) positions [93] showed that the average time of flight \((\tau_f)\) is much shorter than the time of residence \((\tau_r)\) in a crystallographic position. This fact also confirms the jump mechanism of conductivity.

The temperature dependences of diffusion shown in Fig. 18 indicate a small gradual change in the activation energy. Such behavior of \(E_a\) can indicate a change in the mechanism of ion transport (it was also noted in [94]). In the low-temperature range (below 900 K), the activation energy is 0.2 eV for doped samples and 0.6 eV for stoichiometric ones. These values are in good agreement with the experimental results. The high activation energy for a stoichiometric sample is related to the large energy expenditures on the generation of defects in the ordered Na sublattice.

4.2. Na-\(\beta\)\(^{II}\)-Alumina Crystals

Na-\(\beta\)\(^{II}\)-alumina crystals have a layered structure and their conductivity has a 2D character. The stoichiometric compound has the \(Na_3MgAl_9O_{17}\) composition; however, the nonstoichiometric modifications \((Na_{1+x}Mg_{Al_{11-x}}O_{17}\ (x < 1))\) are more widespread. The conductivity gap contains the bridge oxygen atoms and sodium atoms.

The results of the molecular-dynamics calculations [96–99] show that the distribution of Mg\(^{2+}\) ions significantly affects the mobile Na\(^{+}\) sublattice. As follows from the analysis of the motion paths of sodium and oxygen in the conductivity gap, oxygen atoms vibrate near their equilibrium crystallographic positions, whereas Na\(^{+}\) cations diffuse in the conductivity plane. The analysis of the radial pair correlation functions [99] gave grounds to suggest that ordering of sodium ions around vacancies occurs at low temperatures. At high temperatures, the lifetimes of vacancies are very low and do not affect additional ordering of Na cations. The main peak is related to unrelaxed Na ions (which have no vacancies in the neighborhood) as well as to the same undisplaced ions and relaxed ions.
In [97], from the analysis of Na\(^+\) cation trajectories in the conductivity plane, it was concluded that 18\(h\) positions around an empty BR position are populated.

Figure 19 shows the temperature dependences of the diffusion coefficient for the calculated systems with different concentrations and initial positions of Mg cations. From this figure, we can draw two main conclusions: (i) non-Arrhenius behavior of \(D(1/T)\) is observed and (ii) the distribution of magnesium in spinel blocks affects the diffusion of sodium cations significantly.

The attempts to consider the mechanism of cation transport in terms of the formalism of the van Hove autocorrelation function [97] indicate a change in this mechanism (Fig. 20) from a simple jump mechanism at room temperature to the liquid-like mechanism at high temperatures.

Furthermore, we note another interesting study [100] where Na-β\(^+\)-alumina was analyzed as a matrix for design of laser media through Na → Er\(^3+\) substitution.

5. PROTONIC CONDUCTORS

It is known that the high-temperature (at \(T > 415\) K) phase of CsHSO\(_4\) is characterized by a disordered network of hydrogen bonds, which is responsible for the high ionic conductivity of this compound. To reveal the specific features of the dynamic behavior of both the rigid sublattice (especially sulfate tetrahedra SO\(_4^{2-}\)) and protons, molecular-dynamics calculations were performed in [101] within the classical approach using pair potentials. In this case, a SO\(_4^{2-}\)-tetrahedron was considered as a whole (to avoid problems related to covalent S–O bonds), and a proton was considered to be a cation with a charge +1e.

The results obtained in [101] indicate that the microscopic mechanism of proton transport includes two stages:

(i) transition of a proton from one oxygen atom to another, a process that is related to a neighboring tetrahedron;

(ii) structural reorganization of a crystal, a process that is mainly related to the reorientation of tetrahedra.

Both these processes occur with different rates; i.e., develop on different time scales. The first stage cannot be correctly described with neglect for quantum chemical effects. At the same time, to describe the second stage, it is sufficient to take into account the hydrostatic interaction. The diffusion coefficient was determined from the slope of the time dependences of the mean-square displacement of protons: at a temperature of 510 K, \(D_H = 8 \times 10^{-7} \text{ cm}^2/\text{s}\). The value obtained is in good agreement with the experimental value of \(10^{-7} \text{ cm}^2/\text{s}\).

To reveal the specific features of the microscopic mechanism of proton transport in the high-temperature protonic conductor SrTi\(_{1-x}\)Sc\(_x\)O\(_3\) (\(x = 1/8\)), the molecular-dynamics calculations were performed within the quantum-mechanical approach [102–105]. Figure 21 shows the 3D proton trajectories in the time-averaged rigid lattice composed of oxygen, titanium, and strontium. The proton begins its motion from vibrations between O(1) and O(2) oxygen ions, then migrates to the O(3) ion, and, finally, starts vibrating between the O(2) and O(3) ions.

The crystal structure of SrCeO\(_3\) is orthorhombic, i.e., differs from the cubic structure of SrTiO\(_3\). This difference may lead to a change in the mechanism of pro-
proton diffusion. Indeed, as was shown on the basis of ab initio molecular-dynamics calculations [105], migration of H\(^+\) occurs through three different diffusion paths. First, as in the case of strontium titanate, the proton moves around an oxygen ion with conservation of the hydrogen bond. Then, proton diffuses between two oxygen ions belonging to the same octahedron formed by six O\(^2\) ions. Finally, the proton moves to an oxygen ion belonging to a neighboring octahedron.

6. COMPUTER SIMULATION OF THE PREMELTING EFFECT

6.1. Premelting Effect in AgBr

It is known that the so-called premelting effect is observed in silver bromide and chloride crystals. At high temperatures (but lower than the melting temperature by 150–200 K), the conductivity significantly increases, and a deviation from the Arrhenius behavior of conductivity (that is typical of ionic crystals) is observed [106–108]. Note that AgBr does not undergo any structural phase transitions up to the melting temperature (\(T_m = 701\) K). However, just before melting of a crystal, its conductivity reaches \(~1.3\ \Omega^{-1}\ \text{cm}^{-1}\), a value that is comparable with the conductivity of typical superionic conductors [109].

Investigation of the thermodynamic, transport, and structural characteristics of silver bromide in the temperature range from 300 to 1500 K (i.e., in a wide range before and after the melting temperature) was performed in [110, 111] by the molecular-dynamics method. At low temperatures, well-resolved and fairly narrow peaks were observed in all radial pair correlation functions \(g_{ij}(r)\). The distances between the centers of peaks are consistent with the corresponding distances between the positions of ions in the crystal lattice. With an increase in temperature, the cation–cation correlation function \(g_{\text{Ag–Ag}}\) undergoes the largest changes. Even at \(T > 1000\) K, only the first (characterizing the position of the nearest neighbors) peak is pronounced, whereas all other peaks are strongly smoothed. This shape of pair correlation functions is characteristic of the superionic state of \(\alpha\)-AgI.

The results of the molecular-dynamics calculations of mean-square displacements of silver cations and bromine anions indicate that, at \(T \geq 1000\) K, only Ag\(^+\) cations are involved in translational motion, whereas Br\(^-\) anions vibrate near their equilibrium positions. The temperature dependences of the diffusion coefficient \(D_{\text{Ag}}\) of silver cations are shown in Fig. 22. Here, for comparison, the experimental values of the cation diffusion coefficient are shown, which were obtained by the radioactive-tracer technique [112–115].

Taking into account the above specific features of the behavior of pair correlation functions in the vicinity of the melting point of a crystal and the high values of diffusion coefficient \((D_{\text{Ag}} = 3.34 \times 10^{-6}\ \text{cm}^2/\text{s} \text{ at } 1095\) K), we can draw a conclusion about the matched character of

![Fig. 21. Proton trajectories in SrTi\(_{1-x}\)Sc\(_x\)O\(_3\) (\(x = 1/8\)). Small gray spheres indicate the positions of the proton. Connecting lines are shown for clarity [103].](image1)

![Fig. 22. Temperature dependences of the diffusion coefficient of silver cations in AgBr crystals: (1) experiment [112–115] and (2) molecular-dynamics calculation.](image2)
the motion of silver cations. The observed dynamics of disordering of Ag⁺ ions suggests melting of the cation subsystem, similar to the diffuse phase transition in MF₃ fluorites (M = Ca, Ba, Sr, or Pb) [109], as a result of which a high-conductivity state arises. However, it is known that the superionic state is characterized by low activation energies (about 0.1 eV); therefore, the high activation energy of diffusion (1.05 eV) indicates that the premelting effect in AgBr may be related only to the initial stage of the transition to the superionic state.

6.2. Premelting Effect in MgSiO₃

The premelting effect in MgSiO₃—a material the deep Earth’s mantle is formed of—was studied in [116]. The molecular-dynamics calculations were performed for a cell composed of 540 atoms (108 Mg, 108 Si, and 324 O atoms). At a transition from the orthorhombic to cubic (or pseudocubic) phase at T > 4200 K, the perovskite MgSiO₃ becomes a solid electrolyte containing a disordered oxygen sublattice. The diffusion coefficient of oxygen anions is $1 \times 10^{-5}$ cm$^2$/s at 500 K. Similar data were obtained in [117].

6.3. Premelting Effect in Cr₂O₃

The effect of surface melting in a Cr₂O₃ crystal was studied in [118]. The direct analysis of the patterns of atomic arrangement on the (0001) surface indicates structural disordering at temperatures of about 2500 K, a value that is 900 K lower than the melting temperature of crystal.

For detailed investigation of the specific features of atomic motion, the diffusion coefficients of ions were calculated for the first four surface layers. In the first two layers, diffusion of oxygen atoms begins approximately at 2100 K, whereas in the third and fourth layers, it begins at 2500 and 2660 K, respectively. The cause of this effect is that chromium atoms undergo “melting” at higher temperatures and hinder oxygen diffusion in the lower layers.

CONCLUSIONS

Application of methods of computational experiment to study phenomena at the microscopic level is an actively developing line of research in modern physics and chemistry of the condensed matter. The capacity of modern computers makes it possible to simulate such calculation problems that seemed to be unsolvable a short time ago. Currently, we can consider systems composed of several thousand interacting particles and systems with phase boundaries, model topochemical reactions, and construct new states of matter (for example, form water in the superionic state). The results of computer simulation of a large number of anionic (the first part of this review, [119]) and cationic solid electrolytes convincingly indicate good prospects of molecular-dynamics investigations of the processes of ion transport in such complex materials as superionic conductors. In addition, we should indicate the actual possibilities of predicting properties of new functional materials and constructing new solid electrolytes. Currently, increasing attention is being paid to the quantum-chemical simulation of systems since in many cases it is necessary to take into account the electric charge transport. The equations of classical physics are insufficient to describe this process correctly. For example, the method of quantum molecular-dynamics makes it possible to investigate processes of ions’ intercalation into layered structures and propose models of ions’ intercalation into cathodes of current sources. In addition, this method is a correct approach to simulation of nanomaterials.

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COMPUTER SIMULATION OF SUPERIONIC CONDUCTORS

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