Hydrogen transport in superionic system Rb₃H(SeO₄)₂: a revised cooperative migration mechanism

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We performed density functional studies of electronic properties and mechanisms of hydrogen transport in Rb₃H(SeO₄)₂ crystal which represents technologically promising class M₃H(XO₄)₂ of proton conductors (M=Rb,Cs, NH₄; X=S,Se). The electronic structure calculations show a decisive role of lattice dynamics in the process of proton migration. In the obtained revised mechanism of proton transport, the strong displacements of the vertex oxygens play a key role in the establishing the continuous hydrogen transport and in the achieving low activation energies of proton conduction which is in contrast to the standard two-stage Grotthuss mechanism of proton transport. Consequently, any realistic model description of proton transport should inevitably involve the interactions with the sublattice of the XO₄ groups.

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I. INTRODUCTION

Last years demonstrate a continuous increase of research activity in the field of hydrogen conductors. This can be explained by great technological perspectives of hydrogen conducting materials for applications in solid-state hydrogen fuel cells, hydrogen storage and electrochemical devices. A central problem in fuel-cell hydrogen batteries technology is the development of cheap and efficient materials for electrochemical elements which can be used for the chemical storage and transformation of chemical to electrical energy. In the functional properties of hydrogen devices, the transport of hydrogen through the conducting part to cathode plays a key role which makes the proton transport mechanisms one of the central problems of current experimental and theoretical studies.

In the wide range of proton conducting materials, the crystals with superionic phases M₃H(XO₄)₂ (M=Rb,Cs, NH₄; X=S,Se) are of especial interest due to their high proton conductivity coefficients which in the high temperature disordered state can reach values of the order 10⁻² − 10⁻¹ Ω⁻¹ cm⁻¹. In these phases, the quasi-two-dimensional proton transport is characterized by a dynamically disordered network of virtual hydrogen bonds dynamically establishing between the oxygens O(2) of nearest groups XO₄. Although on the first sight the transport of protons in hexagonal (001) planes seems to be quite a strainforward process explained in terms of the two-stage Grotthuss mechanism, the real mechanism of proton migration is still not sufficiently well examined and understood. The reason for this difficulty is a complex cooperative character of proton migration which should strongly interact with the dynamics of the ionic environment, the fact supported by numerous experimental Raman, Infrared, x-ray and NMR spectroscopy studies.

In the theoretical works, the two-stage Grotthuss mechanism is frequently considered within phenomenological free-particle approaches which typically contain two stages: (1) translation of proton within a hydrogen bond between the nearest ionic groups XO₄; (2) inter-bond proton transfer related to reorientations of the ionic groups XO₄. However, the experimental studies demonstrate that the transport of protons is a highly complex process which can be characterized as a transfer of hydrogen ion in the course of the reactions of creation and breaking of HXO₄ bonds. As a consequence of such reacting environment with dynamically redistributing electronic density, the protons in conducting materials cannot be described as almost free particles.

Despite the existing theoretical studies of the low-temperature proton ordered phases and proton conduction in M₃H(XO₄)₂ by phenomenological models, up to date there is no first-principle-investigations of these systems. The recent first-principle molecular dynamics studies of superprotonic phase transition in a related superionic system CsHSO₄ were focused on the structural transformations and reorientational motion of HSO₄⁻ groups, without the studies of the proton migration mechanism. Another ab-initio study of the proton conduction in CsHSO₄ has been devoted to the estimation of diffusion barriers, without a detailed consideration of the role of oxygen network in the proton transport mechanism. The lack of the first-principle investigations of the transport mechanism in M₃H(XO₄)₂ can be explained by highly complicated crystal structure of these systems involving several structural transformations which makes ab-initio calculations extremely time-consuming and challenging. Our present studies of the hydrogen transport are based on the density functional theory (DFT) with the use of the linearized augmented plane wave method (LAPW) implemented in the WIEN2k package. The LDA (Local Density with non-linear core corrections) and GGA (Generalized Gradient) approximations of the DFT developed by Perdew, Burke and Ernzerhof, and Perdew and Zunger have been
employed in our calculations. In the GGA, the additional gradient terms of the electron density are added to the exchange-correlation energy and its corresponding potential, which is beyond the local density approximation (LDA) of the DFT. In our studies of the proton migration paths, we also employ a nudged-elastic-band method within the pseudopotential approach implemented in the Quantum Espresso package, which allows to perform the dynamical relaxation of the atomic surrounding along the steps of the proton conduction processes.

As an attempt to account for the coupling of mobile protons with the dynamical distortions of the groups XO₄, the existing microscopic description of the proton transport considers the interaction of protons with the displacements of the vertex oxygens O(2) of XO₄ involved in the hydrogen bonding. Such a coupling is presented in terms of the interaction of proton charge with the optical phonon modes corresponding to the anti-phase stretching vibrations of the O(2)-ions and is classified in terms of “protonic polaron” concept. The calculated in this approach coefficients of the proton conductivity are consistent with the experimental measurements performed in the superionic phases. However, the polaronic concept introduced in Ref. 21 involves a number of phenomenological parameters like polaron binding energy which have been estimated by the fitting of the calculated conductivity to the experimentally measured values. To verify the role of the dynamical distortions in the proton migration mechanism, in this work we present a detailed DFT study of the mechanism of hydrogen migration in the system Rb₃H(SeO₄)₂, which belongs to the M₃H(XO₄)₂-class.

To investigate the role of the proton environment, two aspects of the hydrogen transport have been analyzed. The first aspect is related to the structure and positioning of hydrogen-bonded oxygen ions O(2) in the dynamical network. The present DFT calculations demonstrate the strong displacements of O(2) from the high-symmetry positions on the three-fold axis in the equilibrium state, which allows to verify the concepts of the O(2)-structural positioning discussed in the previous x-ray and NMR studies. As the second aspect, we have analyzed the migration paths of protons in the configuration of instantaneously relaxed atoms. The performed DFT calculations allow to derive the energy profiles along the proton migration paths and to investigate the displacements of each atom involved in the proton surrounding. As a result, the present studies give a possibility to obtain the first-principle estimates of the hydrogen-bond lengths and energetic parameters involved in the phenomenological modeling and to verify the concept of protionic polaron introduced in the previous phenomenological description of proton transport. Our findings also allow to improve several experimental conclusions obtained in the previous x-ray and NMR experiments with Rb₃H(SeO₄)₂, in particular to clarify the positioning of the vertex oxygens O(2) during the proton migration and to examine the proton positions on the hydrogen bond at the intrabond proton transfer. As a result, the present DFT results demonstrate a central role of oxygen displacements for the migration of hydrogen and emphasize in this way a key role of the proton environment for the establishing the proton transport.

The rest of the paper is organized in three sections. In Section II the theoretical methods employed in our studies are discussed. Section III presents the results of the electronic structure calculations and of the calculations of the proton migration paths and oxygen positioning. In Section IV we summarize the main results and conclusions of our work.

II. THEORETICAL MODELS AND METHODS

A. Structural concepts of hydrogen-bonded network

In the high-temperature disordered phase of Rb₃H(SeO₄)₂ schematically shown in Fig. I(a), hydrogen transport occurs in a network of “virtual” (equally probable) hydrogen bonds which are occupied by a proton with equal probability 1/3. This network (see Fig. I(b) for details) is established between the vertex oxygens O(2) of the tetrahedra SeO₄ which can be chemically bonded to the three nearest tetrahedra by hydrogen bonds.

The experimentally deduced structure of the network of hydrogen-bonded tetrahedra at T = 456 K projected on (001) plane is represented by the electronic difference density map in Fig. 2. This map has been calculated from the x-ray diffraction data using SHELXL-93 programs. The central feature detected in Fig. 2 is a disorder of the hydrogen-bonded vertex oxygens O(2) (shown by red dots) between three structurally equivalent positions. The hydrogen bonds are schematically presented by the solid lines where the double black dots denote the positions for proton in a double-well potential.

In the earlier work by Baranov et al., a different concept of the structure of hydrogen-bonded network is proposed for the analysis of the x-ray diffraction data. In this concept, the oxygens O(2) are statically located in high-symmetry positions on three-fold axis, which also implies a static character of the of SeO₄ tetrahedra and leads to a possibility of the movement of free protons in the disordered superionic phase. Therefore, the arrangement of the vertex oxygens O(2) is still an open question which has a prime importance for the understanding the nature of proton transfer mechanism in these systems.

In the first concept of the structural arrangement of O(2) in the superionic phase of Rb₃H(SeO₄)₂ signified in Ref. 15, the oxygens O(2) are located in the high-symmetry positions on the three-fold axis and form weak hydrogen bonds with the length of the covalent bond O(2)-H approaching 1.76 Å. In distinction from the high-symmetry case, the second type of oxygen arrangement discussed in Ref. 15,17 assumes the distortions of O(2)
from the three-fold axis towards the hydrogen at the formation of the O(2)-H-O(2)' bond. To prevent a break of high symmetry in the disordered superionic phase caused by such distortions, a dynamical disorder of each O(2) between three equally probable positions is assumed. These positions are related to each other by a rotation by 120 deg around the three-fold axis (see Fig. 2 where the three equivalent positions of distorted O(2) are marked by red dots)). To analyze the equilibrium positions of the oxygens O(2), we performed the GGA calculations of the total energy of the system for the different values of the displacements $\Delta$ of the oxygen O(2) from the positions of the three-fold axis towards a migrating proton, a process which is schematically shown in Fig. 1(b). In the calculations of the electronic structure of Rb$_3$H(SeO$_4$)$_2$, the lattice constants of the unit cell of the trigonal R$\bar{3}$m symmetry in hexagonal coordinates were fixed to the values obtained from the structural analysis: $a = 6.118 \, \text{Å}$ and $c = 22.629 \, \text{Å}$. Technical details include a GGA method developed by Perdew, Burke and Ernzerhof on a $4 \times 2 \times 3$ $k$-point grid representing a mesh of 40 $k$-points in the first Brillouin zone. The comparison of the total energy calculated for the mesh of 80 $k$-points gives the difference between the total energies $E_{\text{tot}}(80) - E_{\text{tot}}(40) = 0.00136 \, \text{eV}$ which allows us to use the 40 $k$-point mesh for the GGA-calculations.

The full-potential method employs an expansion of the electronic potential inside the atomic spheres via a full number of the electronically occupied local orbitals (Rb, Se, O and H atoms in our case), whereas the potential outside the spheres is constructed as a plane-wave expansion with a plane-wave cutoff given by 667 eV. Such a method allows to achieve high accuracy in the description of the electronic structure, total energy and electronic density of states. The dynamical disorder in the superionic state cannot be directly described in the static density functional calculations. As a consequence, in a generated model unit cell, only a single hydrogen bond is selected from the three virtual hydrogen bonds near each SeO$_4$ group which leads to a lowering of the symmetry of the system from the rhombohedral to monoclinic. In this
case, the generated structure can be considered as a static snapshot of the dynamically disordered superionic state. In the studies of the hydrogen transport mechanism we also considered a doubled unit cell, where the initial orientations of the two hydrogen bonds in the cell are chosen randomly, each bond can be dynamically broked and created in a chain of intermediate configurations generated by the nudged elastic band (NEB) method.\textsuperscript{28,31}

In the studies of the transport mechanism, each atomic configuration has been structurally relaxed. The relaxation involves the optimization of the atomic positions by the minimization of the total energy and forces acting on the atoms in the generated unit cell. For the structural optimization, we use a Newton scheme described in Ref.\textsuperscript{31}. A comparison of different relaxed static configurations allows to calculate the energy barriers for the proton migration. With the obtained zero-temperature results, we also analyze the influence of temperature on the activation energies of the proton transport.

B. Modeling the hydrogen migration paths

To analyse in details the paths for the hydrogen migration in the relaxed surrounding, we employed the nudged-elastic-band (NEB) method implemented in the Quantum-Espresso (QE) Package of the DFT calculations with the use of plane-wave basis sets and pseudopotentials.\textsuperscript{28,31} In these calculations, for the atomic cores of Rb, H, Se and O we employ the Perdew-Zunger (PZ) norm-conserving pseudopotentials with nonlinear core corrections.\textsuperscript{27} Our choice of pseudopotentials is justified by the facts that all characteristic features of the electronic structure calculated with the use of the full potential Wien2k GGA code (Fig. 3(a)) and obtained with the PZ-pseudopotentials (Fig. 3(b)) are consistent in the energy window \((E_F - 7.0\,\text{eV}; E_F + 1\,\text{eV})\), where \(E_F\) is the Fermi energy. Specifically, both approaches allow to describe the characteristic DOS-peaks related to the O(2)-2p orbitals (the energy range between \(E_F\) and \(E_F - 5\) eV in Fig. 3) and the DOS-peak related to the 1s-orbital of H at the energy value about \(-6.1\) eV (Fig. 3(a)) which corresponds to the peak at about \(-6.2\) eV in Fig. 3(b). In the GGA-approach, the energy gap between the highest filled and lowest empty electronic states is about 3.5 eV (Fig. 3(a)) which is close to experimentally discussed gap about 4 eV in related compounds. The GGA gap is larger then the gap between \(-1.3\) eV obtained by the LDA-method (Fig. 3(b)) due to the usual underestimation of the gap in the LDA calculations, which does not influence the results of the NEB studies based on the calculations of the total energy. Also, we would like to note that a detailed comparison of the electronic and optical properties of several compounds like Rb\(_2\)O and Li\(_2\)O related to the constituents of Rb\(_3\)H(SeO\(_4\))\(_2\) calculated in the LDA and GGA approaches shows a good consistency with the available experimental results.\textsuperscript{28} As the low-temperature electronic properties calculated by these two approaches are consistent, we conclude that the PZ-pseudopotential approach implemented in the QE-code is sufficient to capture the physical features of the hydrogen migration in our system.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Total density of states calculated (a) in the GGA (Perdew, Burke, Ernzerhof, Ref. 26) using the full potential approach of Ref. 25 and (b) in the LDA using norm-conserving pseudopotential approach with nonlinear core corrections implemented by Perdew, Zunger, see Ref. 27. The zero energies correspond to the Fermi levels.}
\end{figure}

In contrast to the almost free motion of the hydrogen implemented in a wide range of the models of hydrogen transport, in the present work we consider the migration of hydrogen as a cooperative process, the feature which can be described by the NEB-approach.\textsuperscript{28,31} Specifically, for each stage of the hydrogen transport, this process involves a relaxation of the atomic positions and of the distances between the different atoms. In our analysis, to better relax the positions of the atoms neighbouring to H, we perform a doubling of the unit cell which now includes four SeO\(_4\) groups and two protons (see Fig. 3(a) for details). For each position of the hydrogen in the unit cell, the coordinates of all neighbouring atoms were relaxed until the forces acting on the atoms reached their minima. In these calculations, we use the plane-wave cutoff 1020 eV and the energy cutoff for charge and potential given by 2040 eV.

In the NEB-approach, the relaxation of the atomic positions along the hydrogen migration path is performed by the minimization of the total energy of each intermediate configuration (image). These images correspond to different positions of H on the migration path and produced by the optimization of a specially generated object functional (action) with the consequent minimization of the spring forces perpendicular to the path. In our calculations, the convergence criteria for the norm of the force orthogonal to the path is achieved at the values below 0.05eV/Å.
III. RESULTS AND DISCUSSION

A. Vertex oxygens O(2)

The experiments (see Ref. 29) show that in M₃H(XO₄)₃-crystals the temperature of the superionic phase transition Tₛ does not depend on the deuterization. Moreover, the neutron diffraction results do not distinguish two distinct hydrogen positions on the bonds and justify a representation of hydrogen atom in flat single-minimum potentials. Consequently, in the present studies of the positioning of O(2), the initial proton positions are fixed to the centers of hydrogen bonds. In Fig. 1, such a single-well approximation is identified by the centering of proton between the oxygens O(2).

To study the modification of the total energy caused by the relaxation of the vertex oxygens, the positions of O(2) on a selected hydrogen bond were shifted by a distance 5 Å, while the coordinates of other atoms were kept in the undistorted high-symmetry state. Fig. 4 demonstrates the variation of the total energy of the system E(Δ)−E(Δ = 0) with the increase of the O(2) displacement parameter Δ. One can see that the lowest value of E(Δ) corresponds to Δ = 0.5 Å which implies a stabilization of a short hydrogen bond O(2)-H of a length 2.54 Å where the length of the covalent bond O(2)-H equals 1.27 Å. It is remarkable that despite the central-point approximation for the proton within the hydrogen bonds, the obtained length of the H-bond is typical for double-well H-bonds and is consistent with the results of x-ray and neutron scattering studies 15,17,22, which becomes clear from the comparison of different data with the present results presented in Table I Consequently, our findings clearly support the second concept of the oxygen-distorted network structure which is characterized by the two types of dynamical disorder in the superionic phase: (i) the statistical disorder of the hydrogens between the virtual hydrogen bonds in hexagonal planes and (ii) the disorder of the vertex oxygens between three symmetry-related positions around the three-fold axis indicated in Fig. 1(b).

To demonstrate the influence of the displacements of O(2) on the electronic properties, we have analyzed the projected atomic densities of electronic states for Δ = 0 and Δ = 0.5 Å which are presented in Fig. 5. The considered two types of the structural positioning of O(2) can be characterized by a substantial electronic hybridization of H 1s orbitals and 2p orbitals of O(2). In Fig. 5, the s-p hybridization can be identified by the density peaks at the energies about −3.5 eV and in the range (−5.5) − (−6) eV below the Fermi energy (for Δ = 0.5 Å, these peaks are marked by a dashed line). The DOS peaks at about −18 eV imply also a strong hybridization between H 1s and O(2) 2s orbitals. The displacements of O(2) from the high-symmetry positions lead to a shortening of the O(2)-H distances and consequently to a significant increase of the s-p hybridization peaks at −6 eV. Moreover, the O(2)-distortions result in the emergence of new strongly hybridized state at −9.5 eV. In addition, the displacements of O(2) induce the distortions of the SeO₄ tetrahedra which results in the lowering of the local symmetry and in the split of high hybridized peaks around −18 eV (Fig. 5, case Δ = 0.5 Å). In the considered model unit cell, instead of the virtual H-bonds we consider a number of selected configurations with the fixed H-bonds near each SeO₄ group. In a real statistically disordered system one may expect that the obtained split of the hybridization peaks will be smoothed by the dynamical disorder.

FIG. 4: Total system energy as a function of the O(2) distortion parameter Δ. Here Δ is the displacement of O(2) with respect to its high-symmetry position on the three-fold axis.

FIG. 5: Projected density of states of the oxygens O(2) and hydrogens calculated by the GGA method. The cases Δ = 0 and Δ = 0.5 Å correspond to the hydrogen bonds between SeO₄ groups (a) with high-symmetry positions of O(2) on the three-fold axis and (b) with the displacements of O(2) from the three-fold positions towards the proton. The zero energy corresponds to the Fermi level.

The redistribution of the electronic charge density due...
to the distortions of O(2) causes the accumulation of the electron charge on the obtained short hydrogen bonds, the effect observed in the contours of the difference charge density in Fig. 6. Consequently, in the superionic phase the formation of the strong virtual hydrogen bonds should be also identified by a remarkable increase of the electron density between the O(2) ions, which is consistent with the experimentally obtained electron density map of Fig. 1.

**FIG. 6**: Electronic difference density contours (crystalline renormalized by the superimposed atomic densities) for the hydrogen bonds O(2)-H-O(2). Here the oxygens O(2) are located on the three-fold axis (left panel), and displaced from this axis towards the hydrogen on the bond (right panel).

**TABLE I**: Hydrogen bond length parameters (in Å) in the superionic phase of Rb₃H(SeO₄)₂ determined from the experiments and calculated by the O(2)-relaxation in the full-potential GGA.

| GGA (O(2)-relaxation) | Ref. 15 | Ref. 30 | Ref. 11 |
|------------------------|---------|---------|---------|
| 2.54                   | 2.51    | 2.594   | 2.58    |

B. Rotational stage in the full potential calculations

Based on the results obtained for the positions of the hydrogen-bonded O(2), it is possible to study the mechanisms and paths of the hydrogen migration. In our analysis, the special focus is put on the rotational stage of the Grotthuss transport mechanism. In its classical description, this stage involves the rotational motion of the HSeO₄ group around the three-fold axis determined by a rotation angle α (see Fig. 7b) where the rotation stage is schematically shown), and the consequent formation of a new hydrogen bond between the rotated group and the nearest SeO₄ tetrahedron approached by this rotation.

First, we analyze a possibility of the rotational step as an independent stage of the proton transport mechanism. In this case, the hydrogen with the covalently bonded oxygen O(2) is allowed to rotate around the nearest SeO₄-group while the positions of all the surrounding atomic groups are fixed. In such a rotational stage, we have calculated the variation of the total energy of the system due to the rotations. Similar to the studies of the O(2) network in the previous section, we consider here two possible structural concepts for the rotational motion. In the first high-symmetry case, the oxygen O(2)¹ of the H(SeO₄)¹ group is fixed on the three-fold axis (Δ = 0), whereas in the second configuration the oxygen O(2)¹ is relaxed (displaced) by a distance Δ = 0.5 Å from the three-fold axis and rotates jointly with the hydrogen by the angle α (the rotation of O(2)¹-H covalent bond). The resulting dependences of the total energy on α are presented in Fig. 7.

It is remarkable that both, high-symmetry and O(2)¹-H-rotated configurations are characterized by high-energy barriers (about 2.6–3 eV) between the initial position of proton and the transition state (TS) (Fig. 7a) which corresponds to the intermediate value of the rotation angle α about π/3. The high energy barriers absolutely exclude any independent motion of proton in the conducting system, a concept which is widely applied for the free electrons in metals. We also note the obtained values for the energy barriers are at the same order as the rotational barrier 1.54 eV calculated in Ref. 24 for the system CsHSeO₄ which prompts on the common physical aspects of the transport mechanisms in these classes of proton conductors.

Despite the high energy of the TS state, the dashed energy profile in Fig. 7 demonstrate a possibility for a partial rotation of the covalent bond O(2)¹-H by α = 20–25 deg which has considerably low barriers of about 0.3–0.7 eV. In the superionic state, such a partial rotation can be also accompanied by the displacements of the oxygen O(2)² of a neighbouring group (SeO₄)² towards the hydrogen which would lower the energy barrier and could result in the formation of the new hydrogen bond O(2)¹-H-O(2)² with the consequent proton transfer to the group (SeO₄)². As a conclusion, the rotational motion of protons should also involve the relaxation of the oxygens O(2) of more distant SeO₄ groups.

C. Hydrogen migration as a cooperative process

In the studies of hydrogen migration in a fully relaxed surrounding, we employ the NEB-method discussed in section IIIB. Fig. 8 shows the snapshots of the migration of the hydrogen H1 between the complexes (SeO₄)¹-(SeO₄)² and (SeO₄)²-(SeO₄)³ calculated by the NEB method. The obtained proton migration path can be
FIG. 7: (a) Energy profiles for the rotation of hydrogen around the group (SeO₄)₁. The case Δ = 0 corresponds to the oxygen O(2)¹ located on the three-fold axis and fixed during the rotation of H. For Δ = 0.5 Å, O(2)¹ is displaced by a distance Δ and rotates jointly with the hydrogen. (b) Schematic view of the rotation stage of the transport mechanism. The short arrows indicate the displacements of the oxygens O(2) from the three-fold positions towards the proton, the large circles denote SeO₃ groups, α is the rotation angle of O(2)-H covalent bond.

FIG. 8: Snapshots demonstrating hydrogen migration between the neighbouring groups (SeO₄)₁ and (SeO₄)³. Here Se, O and H atoms are represented by yellow, red and blue circles. Sections (a) and (b) show configurations with rotated (SeO₄)₁; (c) resulted from the transfer from (1) to (2) and rotation around (SeO₄)², configuration (d) is obtained after the transfer of hydrogen between two tetrahedra (SeO₄)² and (SeO₄)³.

In the further rotation of O(2)¹-H1 the H1 coordinate r changes from r = 0.8 to r = 2 Å which leads to a small increase of the total energy by about 0.2 eV in Fig. 9(a). In Fig. 9(a), the minimum of the total energy at r = 0.8 Å corresponds to the nearly zigzag alignment of the O(2)-H-dimers (configuration presented in part (b) of Fig. 8), similarly to the low-temperature ordered phase III stabilized below the superionic transition temperature, see Refs. 16, 20, 34 for the detailed description of the structure of this phase. The rotation part in the range 0.8 ≤ r ≤ 2 Å corresponds to the rotation stage of the Grotthuss transport mechanism.

described via several steps:

1) the O(2)¹-H1 covalent bond is rotated around SeO₃-group which corresponds to the variation of the rotation angle α from its initial value π/3 to the value α = 0 (part (a) in Fig. 8 is schematically shown in Fig. 9(c)). We note that this rotation fully corresponds to the rotational motion of H studied in the previous section III B within the full potential approach, whereas the rotation in section III B is performed in the opposite direction shown in Fig. 9(b) with the angle α changing from 0 to π/3. The comparison of the corresponding energy profiles calculated by the NEB-method (Fig. 8(a), H1 coordinate r in the range 0 ≤ r ≤ 0.8 Å) and in the full-potential approach (Fig. 5) shows that despite the similar parabolic form, the energy barrier in the QE-case ∆E(QE) = E(0) − E(r = 0.8) is about 1.0 eV which is much lower then the full-potential GGA-value obtained from the difference ∆E(FP) = E(α = π/3) − E(α = 0) = 2.72 eV. This comparison clearly demonstrates the key role of the structural relaxation in the NEB-approach for the lowering the energy barriers for the proton transport.
In Fig. 9(a), the energy barrier for the hydrogen rotation step approaches 0.2 eV. Here the rotation barrier is estimated from the energy dependence between r = 0.8 Å and r = 2Å.

(2) The hydrogen is transferred from the oxygen ion O(2)\(^{1}\) (part (b) in Fig. 6) to the oxygen O(2)\(^{2}\) (part (c) in Fig. 3). Fig. 6 presents the displacements of the oxygen O(2) and the changes of the O(2)-O(2) distances during the migration of the hydrogen derived from the DFT(NEB)-calculations. The proton transfer stage occurs in the range (2 < r < 3) of the proton coordinate. It is remarkable that this range of r is characterized by significant displacements of O(2)\(^{1}\) and O(2)\(^{2}\) by 0.2-0.25 Å towards the hydrogen and by the corresponding strong decrease of the distance between O(2)\(^{1}\) and O(2)\(^{2}\) from its initial value about 3Å to the value 2.51Å, which is very close to the results of the full-potential GGA studies (see Table I). In Fig. 6 the occurrence of the transfer of the hydrogen between O(2)\(^{1}\) and O(2)\(^{2}\) is identified by the minimal O(2)-O(2) distance and maximal displacement of O(2)\(^{1}\) which is indicated by the red arrow in the plots.

Table II presents the maximal (d\(^{\text{max}}\)) and minimal (d\(^{\text{min}}\)) lengths of the hydrogen bond during the transfer step calculated in the NEB approach which are compared to the corresponding experimentally obtained values. Despite the good agreement with the experimental maximal bond length, the calculated value of d\(^{\text{min}}\) = 2.51 Å is in coincidence with the estimates of Ref. 15 for the superionic Rb\(_{3}\)H(SeO\(_{4}\))\(_{2}\). The difference is possibly related to the influence of the dynamics of NH\(_{4}\)\(^{+}\) groups in the superionic state which leads to additional softening of the structure and to the consequent increase of the O(2) displacements.

(3) The O(2)\(^{2}\)-H1 covalent bond rotates and the hydrogen H1 moves towards the group (SeO\(_{4}\))\(^{3}\). The process of the O(2)\(^{2}\)-H1 rotation in the group (SeO\(_{4}\))\(^{2}\) is accompanied by the elongation of the covalent bond between the oxygen O(2)\(^{3}\) and another proton H2 (shown in the left corner of part (c)) and by a strong displacement of O(2)\(^{3}\)

FIG. 10: (a) Displacements of the vertex oxygens O(2) and (b) the change of the distance between the nearest O(2) along the migration path of H1. The red arrows identify the transition state of the proton between the hydrogen atoms O(2)\(^{1}\) and O(2)\(^{2}\).

TABLE II: Hydrogen bond parameters (minimal and maximal (O(2)-O(2) distances d\(^{\text{min}}\) and d\(^{\text{max}}\) in Å), protonic polaron transport parameter ∇V (eV/Å) and the transport activation energy E\(_{a}\) (eV) in the superionic phase of Rb\(_{3}\)H(SeO\(_{4}\))\(_{2}\) calculated by the NEB-method and estimated experimentally.

| method     | d\(^{\text{min}}\) | d\(^{\text{max}}\) | ∇V   | E\(_{a}\) |
|------------|-------------------|------------------|-------|---------|
| NEB (full relaxation) | 2.51  | 2.7   | 2.55  | 0.33    |
| Refs. 17,29 | 2.4   | 2.7   | -     | 0.37    |
| Ref. 15    | 2.51  | 2.67  | -     | 0.49    |
the oxygen O(2)³ towards the hydrogen H1 (part (d) in Fig. 11). The displacement of the oxygen O(2)³ leads to a decrease of the distance between O(2)² and O(2)³ from its initial value 4.2 Å to the value 3.22 Å (Fig. 11(b)) and is essential for the successful hydrogen migration to the group (SeO)³. At the transfer of H1 between O(2)² and O(2)³, the lengths of the bonds Se-O(2)³ (vertex oxygen) and Se-O(1)³ (basis oxygen) in the group (SeO)³ are also changed by about 0.08–0.16 Å. After the proton is transferred from O(2)² to O(2)³, the length of the Se-O(2)² bond is returned to its previous value 1.76 Å.

![Fig. 11: Electronic density contours showing the redistribution of the valence charge density of the hydrogen bond O(2)¹–H-O(2)² during the intrabond proton transfer (a)-(d) and during the rotational motion of H covalently bonded to O(2)² (d)-(f). The valence charge has been obtained by the integration of DOS in the energy window (E_F – 4 eV; E_F) where E_F is the Fermi level.](image)

Fig. 11 demonstrates the redistribution of the valence charge density during the migration of the hydrogen. The intrabond proton transfer step between the vertex oxygen O(2)¹ and O(2)² corresponds to the contours (a)-(d) of the plot. One can see that the hydrogen transfer has a character of a continuous redistribution of the electronic charge density between the two different positions near O(2)² and near O(2)¹ detected in the plots (b) and (c). This finding allows to improve the conclusions of the neutron scattering studies in Ref. 30 about the absence of the two distinct proton positions within a hydrogen bridge in the conducting phase of Rb₃H(SeO)₂ which can be explained by the limited resolution of the experiments. Furthermore, in the rotational step (plots (d)-(f)), the rotational displacements of the oxygen O(2)² follow the proton rotation and lead to significant modifications of the charge density contours near O(2)² which obtain a distinct dumbbell character.

As the consequence of our findings, we propose to consider the obtained in our studies significant displacements of the oxygens O(2) during the migration of the hydrogen as an additional feature of the proton transport mechanism. It is also remarkable that the well established in the literature standard Grotthuss proton transport mechanism contains two main (rotational and translational) stages and does not involve the oxygens displacements as a decisive factor in the proton migration process, which is in contrast to the results of the present work.

To see the role of O(2) displacements in the establishing the hydrogen transport, we examine more closely the change of the total system energy along the proton migration path presented in Fig. 9.

Fig. 9 shows that the energy barrier for the hydrogen rotation step approaches 0.2 eV and is substantially lower than the barrier for the proton transfer between neighbouring groups which is about 0.6 eV in Fig. 9(b). The relation between the obtained rotation and translation barriers is consistent with the conclusion about the decisive role of the intrabond proton transfer in the determining the activation energy for proton conductivity reported in Refs. 9, 17.

In M₃H(XO)₂ systems, the dominant role of the intrabond translational step in the formation of the transport activation energy is in contrast to the quasi-one-dimensional proton conductors MHXO₄, where the proton conduction process is determined by the rotational energy barriers. This fact is also supported by the recent DFT studies of CsHSO₄ where the intrabond proton barrier 0.16 eV was found to be substantially lower than the rotational barrier 0.52 eV, and is also consistent with the ab-initio molecular dynamics calculations of the related systems 35 which show strong fluctuations of the hydrogen bond lengths between 2.4 and 2.8 Å during the proton migration and fast almost barrierless proton transfer on the hydrogen bonds characterized by the extremely short lengths about 2.4 Å. The fast intrabond proton transfer in the quasi-one-dimensional proton conductors is similar to the proton transport properties in water mixtures where the recent ab-initio molecular dynamics simulations demonstrate the existence of two different time scales and identify the faster process with the intrabond proton transfer, while the slower time scale corresponds to local rearrangements of the hydrogen-bond network 36. In this context, the unique two-dimensional character of the transport mechanism in the M₃H(XO)₂ introduces qualitative changes in the translational and rotational energy barriers with a consequent importance of the intrabond transfer in the determination of the transport energy barriers.

The change of the total energy profile along the transfer path in Fig. 9(b) can be directly compared with the corresponding displacements of hydrogen bonded O(2) in Fig. 11(a). From this comparison, we obtain that the increase of the total energy up to ΔE = 0.55 eV is accompanied by the O(2)-displacements ΔO = 0.25 Å. In the phenomenological description of the proton transport 36, the anti-phase displacements of O(2) induced by the
hydrogen-bonded proton have been classified in terms of the "proton-polaronic" effect where the protonic polaron is formed due to the interactions of proton with the anti-phase stretching displacements of the nearest O(2)-oxygens and the energy for the formation of the protonic polaron $E_a = (8\pi V^3)^2/2M(\omega_0)^2$ depends on the energetic parameter $\nabla V = \partial E/\partial V_0$ (here $M$ is the oxygen mass) and on the characteristic frequency $\omega_0$ of of the O(2)-stretching vibration mode. From the ab-initio-profiles shown in Fig. 5(b) and Fig. 10(a), one can derive the value of $\nabla V = 2.55$ eVÅ$^{-1}$ which appears to be very close to the value 2.4 eVÅ$^{-1}$ used in the phenomenological calculations in Ref. 21. Using the value $\omega_0 \approx 850$ cm$^{-1}$ which is in the range of the characteristic frequencies of the HSeO4 stretching vibrations of Rb3H(SeO4)2 reported in Ref. 37, we obtain the estimate for the protonic polaron binding energy: $E_a = 0.2$ eV. With this value, using a high-temperature estimate $E_a \approx 5E_0/3$ obtained in the weak proton interaction limit from Ref. 21, we find the activation energy for the proton transport $E_a = 0.33$ eV. Table II compares the activation energies for the proton conductivity derived on the basis of the present DFT-calculations and reported in different experimental measurements. The obtained here value 0.33 eV is very close to the experiment which confirms a central role of the O(2)-distortions for the proton migration mechanism.

It is also worth noting that the snapshot in Fig. 5(d) corresponds in fact to the two protons located near the same ionic group (SeO4)3, a configuration similar to the high-energy Bjerrum (rotational) defect 35. The energy barrier for the creation of such type of defects is calculated from the obtained energy profile and is about 1.5eV which is twice as high as the estimated translation barrier and which supports negligibly small probability for the creation of the Bjerrum defects in this family of proton conductors.

IV. CONCLUSIONS

We have performed the density functional studies of the electronic properties and the mechanisms of hydrogen migrations in the system Rb3H(SeO4)2 which belongs to the technologically promising class of proton conductors of M3H(XO4)2 crystal family (M=Rb,Cs, NH3; X=S,Se). The results of the electronic structure calculations show a central role of the lattice dynamics in the process of the proton migration. Our findings verify several experimen-

tal conclusions obtained in the previous x-ray and NMR experiments with Rb3H(SeO4)2, which allow to clarify the positioning of the vertex oxygens O(2) during the proton migration and to examine the proton positions on the hydrogen bond at the intrabond proton transfer. The principal conclusion obtained in this work is that the free rotational motion of protons without the corresponding complex distortions of SeO4 groups cannot be considered as an independent part of the Grotthuss transport mechanism. In contrast to the almost free proton motion implemented in a wide range of the models of proton transport, in our work we have considered the migration of hydrogen as a cooperative process which involves a relaxation of the atomic positions and of the distances between the different ionic groups X(SeO4). We have shown that the migration of the hydrogens is connected with the significant displacement of the vertex oxygens O(2). These displacements play a decisive role in the formation of the protonic polaron and in the consequent decrease of the activation energy for the proton conductivity, a concept introduced in the previous phenomenological description of the proton transport. The present DFT results allow to obtain the first-principle estimates of the hydrogen-bond lengths and energetic parameters involved in the existing phenomenological modeling of the proton transport and to prove the validity of the protonic polaron model. Due to their key role in the formation of new hydrogen bonds and in the establishing the successful intrabond proton transfer, the oxygen displacements should be considered as essential feature of the obtained revised mechanism of the hydrogen transport. The developed approach can be also implemented for the modelling of a wide range of the proton conductors which in our view substantially increases the degree of scientific and possible technological applications of the obtained results.

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