

Orientationally degenerate $(\text{OH})^-$ centers in perovskite-type proton-conducting oxides: Low-temperature thermodynamics and H/D isotope effects

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It is shown that proton-associated dipole centers $(\text{OH})^-$ can provide significant, glass-like, contributions to the low temperature properties of perovskite-type proton conducting oxides, such as ABO_{3-y} doped with cations of lower valence. These contributions result from the splitting of the orientationally degenerated states of dipole centers by random crystal fields and protons tunneling. It is demonstrated that H/D (or H/T) substitution leads to large and abnormal isotope effects for the properties caused by $(\text{OH})^-$ degenerated states.

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Introduction. Much interest has been focused on the defect structure and transport properties of different perovskite oxides such as $\text{A}^{\text{II}}\text{B}_{1-x}^{\text{IV}}\text{R}_x^{\text{III}}\text{O}_{3-y}$ due to their importance as high-temperature proton conductors. Such proton conducting oxides are now considered as candidates for use in high temperature sensors, fuel cells, electrolyzers and other electrochemical devices to be applied in cleaner energy technologies based on natural gas and hydrogen [1, 2]. At elevated temperatures these materials can dissolve a significant amount of protons in atmosphere containing hydrogen and/or water vapor [3]. Protons in oxides are attached to the oxygen ions forming $(\text{OH})^-$ centers, which possess dipole moment themselves and form more complex dipoles $\text{R}^{3+}-\text{(OH)}^-$ with dopant ions R^{3+} . There exist equivalent potential minima for protons at oxygen and for $(\text{OH})^-$ centers near the dopant in the perovskite lattice ([3–5] and refs therein). Both types of multi-well states without regard for the interactions between different “dipoles” and their interactions with other imperfections are orientationally degenerate.

Evidently, such degenerated states can significantly affect different properties under appropriate conditions, and, in principle, the studies of these effects can provide additional information on the state and dynamics of protons in proton-conducting oxides. In particular, information on the local dynamics parameters (e.g., tunneling near the single oxide ion) and on the $(\text{OH})^-$ centers concentration could be expected. Nevertheless, we are unaware of any results in this field. The low-

temperature dielectric relaxation in the proton containing $\text{A}^{\text{II}}\text{B}_{1-x}^{\text{IV}}\text{R}_x^{\text{III}}\text{O}_{3-y}$ oxides was investigated in several works of Novick et al. [6, 7], but possible manifestations of $(\text{OH})^-$ degenerated states were not considered there.

The study of the proton-associated degenerate dipole centers (DDC) manifestations is of interest for various reasons. First of all, the process of protons migration in oxides is complex enough (it is strongly coupled with the oxygen dynamics) [3], and the role of local dynamics of protons is not quite clear. Next, not all the questions concerning the protons dissolution and their state in oxides are clear (the effect of the dopant nature on the solubility, the possibility of various hydrogen charge states in oxide, etc.). Furthermore, the proton-associated DDC represent an additional example of degenerate tunnel centers with several distinctive features, including abnormal isotope dependencies of their contribution to different properties, see below.

This communication reports our theoretical considerations on the manifestations of the proton-associated DDC in the low-temperature properties of proton conducting oxides. The energy spectrum of such tunnel centers has been considered and different mechanisms of the degenerate states splitting have been analyzed. The attention is focused on the systems with moderate content of reoriented centers. A number of low-temperature physical properties of such degenerate systems at arbitrary ratio between the tunnel splitting and the dispersion of random crystal fields have been considered. Isotope effects H/D/T for the properties under study are also discussed. The studies were performed for the com-

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pounds ABO_{3-y} with the acceptor doping in the B or A sublattices: $A^{II}B_{1-x}^{IV}R_x^{III}O_{3-y}$ and $A_{1-x}^{III}C_x^{II}B^{III}O_{3-y}$, respectively.

The model and Hamiltonian. We have focused on the low temperature region where the $(OH)^-$ dipoles reorientation is due to the protons tunneling between the local potential minima near the single oxide ion and for the effects under study one can neglect the protons transfer between oxide ions. We are unaware of the precise data for these potential minima positions and energetics. Nevertheless, the available results demonstrate that the height of potential barriers between these minima is about 0.1 to 0.2 eV, see, e.g. [5]. A set of positions for protons near the single oxide ion, suggested in [4], is shown in Fig.1.

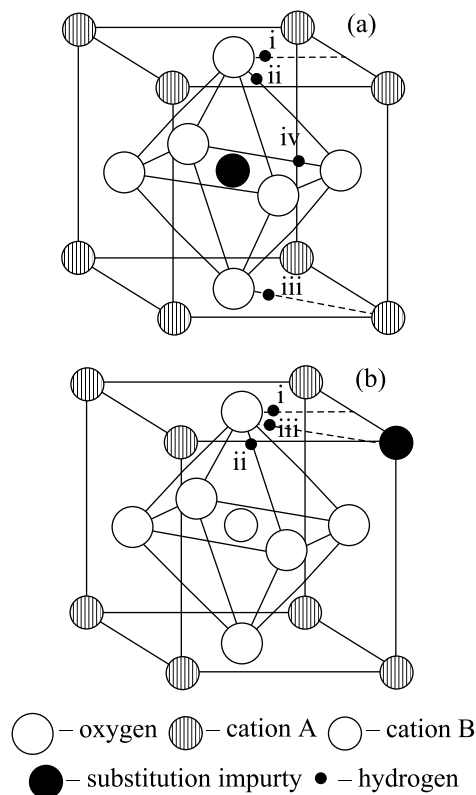


Fig.1. Possible types of proton positions in the cubic perovskites

The authors of [4], on the basis of atomistic computer modeling results for $LaMnO_3$, stated that protons are mainly located in the positions i and ii, see Fig.1. A precise experimental determination of proton positions is difficult. Some experimental results obtained by different experimental techniques, however, have shown some consistencies and confirm a model in which protons lie in the potential minima between the

two neighboring oxygen ions, ii and iv positions, see [5] and refs therein. Nevertheless, several computer modeling techniques give a deviation of the potential minima for protons from the oxygen-oxygen lines, see, e.g. [4, 8].

Let us consider in brief the degeneracy of the energy levels, without regard for tunneling, of the $(OH)^-$ groups located in the nearest neighborhood of dopant, and far from it: “bounded” and “free” states, respectively. For the intermediate cases the splitting of DDC states caused by the interaction of DDC with dopants and (or) with other imperfections will be taken into account via interaction of DDC with random fields of appropriate symmetry.

For the sake of simplicity, we restrict the considerations below to cubic perovskites. It is clear, see Fig.1a, that free DDC states for the i and iii positions are 4-fold degenerated and the other are 8-fold degenerated (4 and 8 equivalent potential minima of each type for protons in the lattice). For the protons located in the neighborhood of the dopant in the B sublattice the “bounded” 8-fold degenerated states, due to the interaction with the dopant, are split into two 4-fold degenerated levels. It is easy to see that the bounded states located in the neighborhood of the dopant in the A sublattice are split as follows. The DDC levels for the i and ii type positions are split into two 2-fold and 4-fold degenerated levels, respectively, and the iii state is split into a ground singlet and an excited doublet and singlet. Thus, the ground state of the proton-associated dipole centers is degenerated (except the case of the bounded DDC of the type iii near the dopant in the A sublattice).

Next we concentrate on the consideration of the bounded states of protons, when $(OH)^-$ groups are located near the dopant R^{3+} in the B sublattice (see Fig.1a). This case is quite general and the results for the other situations could easily be obtained using the ones derived below. In particular, the contribution of the “free” states of OH^- groups would not change qualitatively the results reported.

It should be noted here that a possible deviation of the potential minima for protons from the oxygen-oxygen lines does not change the type of degeneracy considered, and, accordingly, does not change the main results.

Let us consider the potential minima located between the two neighboring oxygen ions, ii and iv positions. Then the Hamiltonian H of $(OH)^-$ centers (for the 4-fold symmetry axis Z) in the space of wave functions respondent to the irreducible representations $(A_1 + B_1 + E)$ of the group C_{4v} can be written as follows:

$$\begin{array}{cccccc}
 H = & & A_1 & & E_x & & E_y & & B_1 \\
 A_1 & & \Delta_t & & h_3 + V_3 e_{xz} - pE_x & & h_4 + V_4 e_{yz} - pE_y & & h_1 + V_1(e_{xx} - e_{yy}) \\
 E_x & & h_3 + V_3 e_{xz} - pE_x & & h_1 + V_1(e_{xx} - e_{yy}) & & h_2 + V_2 e_{xy} & & h_3 + V_3 e_{xz} - pE_x \\
 E_y & & h_4 + V_4 e_{yz} - pE_y & & h_2 + V_2 e_{xy} & & -h_1 - V_1(e_{xx} - e_{yy}) & & -h_4 - V_4 e_{yz} + pE_y \\
 B_1 & & h_1 + V_1(e_{xx} - e_{yy}) & & h_3 + V_3 e_{xz} - pE_x & & -h_4 - V_4 e_{yz} + pE_y & & -\Delta_t
 \end{array} \quad (1)$$

Here Δ_t is the splitting parameter for the (OH)⁻ center due to the proton tunneling between adiabatic potential minima near the single oxygen ion; V_i are the interaction constants of the (OH)⁻ center with strains $e_{\alpha\beta}$; p is the dipole moment of the (OH)⁻ when proton is localized in one of the potential minima; E_x and E_y are x and y components of the electric field intensity, and h_i are the components of many-dimensional crystal fields which transform under symmetry transformations as proper components of the strain tensor.

Note that the Hamiltonian (1) is quite general, and also allows considering the properties of DDC for the A-substituted perovskites (Fig.1b) if the appropriate low symmetry field caused by a substitution in the cation sublattice A is specified.

DDC contribution to the low-temperature properties in the absence of random crystal fields. One can consider possible orientations of R³⁺-OH⁻ groups in the crystal as equiprobable. Then, the energy spectrum of DDC in the absence of random crystal fields can be written as follows²⁾:

$$E(A_1) = \Delta_t; \quad E(B_1) = -\Delta_t; \quad E(E_x) = E(E_y) = 0. \quad (2)$$

It is seen that due to the tunneling effect the 4-fold orientational degeneration is removed and several low lying excited states appear in the energy spectrum of DDC. As a result, the contribution of the DDC to the heat capacity ΔC , elastic moduli ΔC_{11} , ΔC_{66} and the dielectric susceptibility $\Delta \epsilon_{\alpha\alpha}$ is as follows:

$$\begin{aligned}
 \Delta C &= \frac{1}{2} N_0 k_B \left(\frac{\Delta_t}{k_B T} \right)^2 \cosh^{-2} \left(\frac{\Delta_t}{2k_B T} \right), \\
 \Delta C_{11} &= -\frac{1}{3} N_0 \left(\frac{V_1^2}{k_B T} \right) \left[\cosh^{-2} \left(\frac{\Delta_t}{2k_B T} \right) + \left(\frac{2k_B T}{\Delta_t} \right) \tanh \left(\frac{\Delta_t}{2k_B T} \right) \right], \quad (3)
 \end{aligned}$$

²⁾The structure of the lowest energy states of such R³⁺-(OH)⁻ center is analogous to that observed for Jahn-Teller ions Tb³⁺ in crystals with zircon structure (TbVO₄, TbAsO₄) [9].

$$\begin{aligned}
 \Delta C_{66} &= -\frac{1}{24} N_0 \left\{ \left(\frac{V_2^2}{k_B T} \right) \cosh^{-2} \left(\frac{\Delta_t}{2k_B T} \right) + \right. \\
 &\quad \left. + 4 \left(\frac{V_{3,4}^2}{\Delta_t} \right) \tanh \left(\frac{\Delta_t}{2k_B T} \right) \right\}, \\
 \Delta \epsilon_{xx} = \Delta \epsilon_{yy} = \Delta \epsilon_{zz} &= \frac{2}{3} N_0 \frac{p^2}{\Delta_t} \tanh \left(\frac{\Delta_t}{2k_B T} \right).
 \end{aligned}$$

where k_B is the Boltzmann constant and N_0 is the number of DDC (N_0 in our case is about the hydrogen content). The typical temperature dependence of ΔC (3) is shown in the Fig.2 (curve 1). It is clear that the DDC

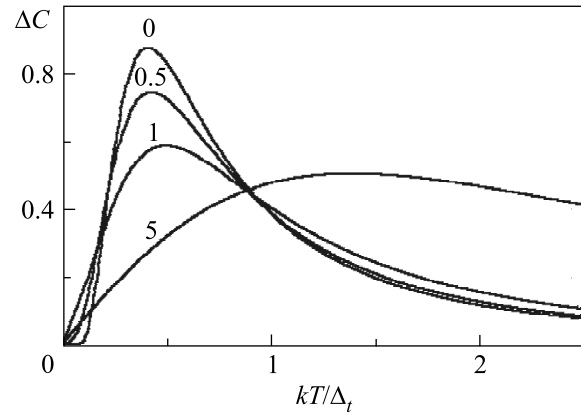


Fig.2. Temperature dependences of ΔC (relative units); The curves are labeled by the Γ/Δ values

contributions (3), proportional to the protons content in oxide, can be large and drastically change the low-temperature ($k_B T \leq \Delta_t$) properties of the considered systems.

The effect of random crystal fields. The low-temperature properties can change even more radically when allowing for the effect of the random crystal fields on the DDC states [10]. It is due to the possibility of bringing closer and even crossing of the main singlet and the lower of the splitted doublet DDC state under the influence of these fields. Let us illustrate it for the heat capacity ΔC , elastic modulus ΔC_{66} and dielectric susceptibility $\Delta \epsilon_{\alpha\alpha}$. To be short we will restrict ourselves here to the case of the random fields of the h_2 type. It allows us to describe qualitatively the effect of random

fields and to obtain the following simple expressions for the calculated values:

$$\begin{aligned}\Delta C &= \frac{2N_0 k_B}{\sqrt{\pi}} \int_{-\infty}^{\infty} \left(\frac{u}{\cosh(u)} \right)^2 \exp\{-x^2\} dx, \\ \Delta \epsilon_{\alpha\alpha} &= \frac{2N_0}{3k_B T \sqrt{\pi}} p^2 \int_{-\infty}^{\infty} \left[\frac{1}{u} \tanh(u) \right] \exp\{-x^2\} dx, \\ \Delta C_{66} &= -\frac{N_0}{24k_B T \sqrt{\pi}} \int_{-\infty}^{\infty} \left(V_2^2 \cosh^{-2}(u) + \right. \\ &\quad \left. + 2V_{3,4}^2 \frac{\tanh(u)}{u} \right) \exp\{-x^2\} dx,\end{aligned}\quad (4)$$

where $u = (x\Gamma + \Delta)/2k_B T$.

The normal distribution with dispersion Γ has been used here for random crystal fields. The typical temperature dependences of ΔC are shown in Fig.2.

It is seen in Fig.2 that the effect of random crystal fields results in the distinctive qualitative change in the thermodynamic parameters behavior at the temperatures $k_B T \leq \Gamma$. In this case in the temperature region $k_B T \leq \Gamma^2/\Delta_t^i$ for the ΔC , ΔC_{66} and $\Delta \epsilon_{\alpha\alpha}$ we obtain:

$$\begin{aligned}\Delta C &= N_0 k_B \exp\left\{-\left(\frac{\Delta_t}{\Gamma}\right)^2\right\} \frac{k_B T}{\Gamma} \frac{2\pi^{3/2}}{3}, \\ \Delta \epsilon_{\alpha\alpha} &= N_0 \frac{p^2}{\Gamma} \exp\left\{-\left(\frac{\Delta_t}{\Gamma}\right)^2\right\} \ln\left(\frac{\Gamma}{k_B T}\right) \frac{4}{3\sqrt{\pi}}, \\ \Delta C_{66} &= -N_0 \frac{V_2^2}{\Gamma} \exp\left\{-\left(\frac{\Delta_t}{\Gamma}\right)^2\right\} \left[1 + \right. \\ &\quad \left. + 2\left(\frac{V_{3,4}}{V_2}\right)^2 \ln\left(\frac{\Gamma}{k_B T}\right)\right] \frac{1}{6\sqrt{\pi}}.\end{aligned}\quad (5)$$

Thus at low temperatures the DDC contribution to the heat capacity varies linearly with temperature. The maximum slope in the $\Delta C(T)$ dependence occurs at $\Gamma/\Delta_t = \sqrt{2}$. The susceptibility is featured by the weak, logarithmic, increase with the temperature lowering in the region $k_B T \leq \Gamma^2/\Delta_t^i$. The behavior of the elastic modulus ΔC_{66} in the low-temperature region is the same (as that of $\Delta \epsilon_{\alpha\alpha}$) if $|V_2/V_{3,4}| \geq 1$; and if $|V_2/V_{3,4}| \ll 1$ the modulus ΔC_{66} is nearly independent of T .

At the temperatures $k_B T > \Gamma$ the obtained expressions for ΔC , ΔC_{66} and $\Delta \epsilon_{\alpha\alpha}$ result in the behavior of these parameters qualitatively close to that given by the expressions (3).

H/D/T isotope effects for the DDC-caused properties. Finally, it is noteworthy that the H/D/T isotope effects for the properties under study can be pronounced enough. The studies of isotope effects are of particular interest for proton conducting oxides due to

their possible impact on the understanding of the state and dynamics of protons. The main references to the previous isotope studies and some new predictions for the abnormal behavior of thermodynamic isotope effect in proton conducting oxides can be found in [11].

For the properties considered above, H/D/T isotope effects are caused by the strong dependence of the tunnel splitting parameter Δ_t on the mass of tunneling particle (H, D or T). Making use of the quasiclassical approximation for the parameter Δ_t in the symmetric double-well potential $U(x)$ (see, eg. [12]), the ratio of the splittings for protons and D or T ions can be written as follows:

$$\begin{aligned}\frac{\Delta_t^i}{\Delta_t^H} &= \sqrt{\frac{m_H}{m_i}} \exp\left\{-\left[A\sqrt{\frac{m_i}{m_H}} - 1\right] J\right\}, \\ J &= \frac{1}{\hbar} \int_{-a}^a \sqrt{2m_H(U(x) - E_0)} dx,\end{aligned}\quad (6)$$

where a and $-a$ are the boundaries of the region of sub-barrier motion, i denotes H, D or T, E_0 is the ground state energy in the potential well, and the possible difference of the factor A from the unity (resulting from the different E_0 values for H, D and T) is inessential for our considerations. The estimations for the characteristic parameters for the oxides considered (barrier height ~ 0.2 eV, $E_0 \sim 0.05$ eV and $2a \sim 50$ to 70 pm) give the typical J values about 4.5 to 7 for protons.

Thus, one can expect significant isotope effects at low temperatures. For example, for the heat capacity of the system with relatively weak random crystal fields $\Gamma \ll \Delta_t^i$ we have:

$$\begin{aligned}\frac{\Delta C_D}{\Delta C_H} &\cong \left(\frac{\Delta_t^D}{\Delta_t^H}\right)^2 \exp\left\{\frac{\Delta_t^H - \Delta_t^D}{k_B T}\right\} \gg 1, \quad k_B T \ll \Delta_t^i, \\ \frac{\Delta C_D}{\Delta C_H} &\cong \left(\frac{\Delta_t^D}{\Delta_t^H}\right)^2 \ll 1, \quad k_B T \gg \Delta_t^i.\end{aligned}\quad (7)$$

It is seen that the isotope effect can be exponentially large, it can change the character (from the magnitude more than one to less than one), and the type of temperature dependence. The temperature dependence of the ratio $\Delta C_D/\Delta C_H$ and the change of the character of isotope effect are illustrated in Fig.3.

The appreciable random fields $\Gamma \geq \Delta_t^i$ cause the significant reduction of the isotope effect $\Delta C_D/\Delta C_H$ in the temperature range $k_B T \ll \Delta_t^i$

$$\frac{\Delta C_D}{\Delta C_H} \cong \exp\left\{\frac{(\Delta_t^H)^2 - (\Delta_t^D)^2}{\Gamma^2}\right\} \geq 1. \quad (8)$$

But they comparatively weakly affect the ratio $\Delta C_D/\Delta C_H$ at temperatures $k_B T \gg \Delta_t^i$, Γ , where the

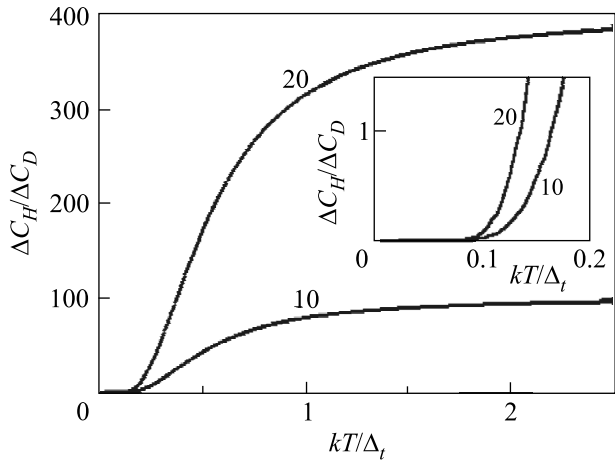


Fig.3. The ratio $\Delta C_H/\Delta C_D$ as a function of temperature at $\Gamma = 0$; The curves are labeled by the Δ_t^H/Δ_t^D values

respective asymptotic expression in (7) is still approximately valid.

The isotope effect for the DDC contributions to the elastic constants and to the dielectric susceptibility is not so pronounced. For example, in the case of relatively weak random crystal fields Γ the ratios $\Delta\epsilon_D/\Delta\epsilon_H$ and $\Delta C_{66(D)}/\Delta C_{66(H)}$ are about Δ_H/Δ_D at temperatures $k_B T \ll \Delta_t^i$ and at the high temperatures $k_B T \gg \Delta_t^i$ the isotope effect is small: the ratios mentioned are equal to $1 + O(\Delta_D/\Delta_H)^2$.

It is important to note, that the substitution of protons by deuterium or tritium ions can change the behavior of thermodynamic values not only quantitatively, but also qualitatively (because the ratio between the tunneling parameter and the dispersion of random crystal fields also changes with this substitution). For example, the exponential temperature dependence of the heat capacity, which is expected for protons at low temperatures and $\Gamma < \Delta_t^H$, can change into the linear one for deuterons and tritons, given $\Gamma > \Delta_t^{D,T}$ (Fig.4).

Conclusions. It is shown that DDCs significantly change the properties of oxides. In particular, the DDC contribution to the heat capacity can be significant at low temperatures and exhibits unusual temperature dependence: it has a Shottky anomaly and can linearly vary with T decrease. The temperature dependence of the DDC contribution to the elastic constants and dielectric susceptibility can also be unusual: in some cases it can increase as $\ln T$ at low temperatures. It is shown that isotopic substitution of protons could significantly change the DDC contribution magnitudes under appropriate conditions, and the temperature dependences of these isotope effects can be abnormal: up to the change of the effect character with temperature variation. Our

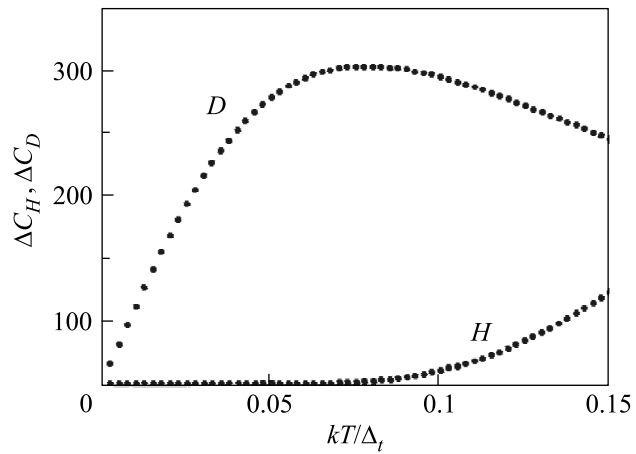


Fig.4. The temperature dependences of the proton (H) and deuteron (D) DDC contributions to the heat capacity (relative units) for the noticeable magnitude of random crystal field: $\Gamma/\Delta_t^H = 0.25$, $\Delta_t^H/\Delta_t^D = 10$

results demonstrate that the insight obtained from the low-temperature studies of the DDC-specified properties can provide essential information for understanding the nature of state and dynamics of protons in oxides.

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