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Lattice-assisted proton hopping in oxides at low temperatures

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ABSTRACT

Stimulated diffusion of protons in oxides such as ABO_3 crystals and rutile TiO_2 is discussed in the context of quantum Brownian motion. A self-consistent lattice-assisted proton hopping (LAPH) model is developed by going from white noise (characteristic of the standard stochastic theory of superionic conduction) to colored noise in the Markovian limit. This model differs from the commonly used ion jump models in that the hydrogen diffusion rate prefactor is identified as a quantity proportional to the frequency of phonon assistance. Application of the quantum fluctuation–dissipation theorem suggests that the dynamic activation energy for diffusion is a function of a bath-mode frequency. The LAPH model can predict enhanced rates of barrier jumping at room temperature compared to thermally activated proton diffusion. This indicates that low-temperature solid oxide devices are potential candidates for use in hydrogen energy research. The LAPH model offers a valid explanation for the mechanism of high protonic mobility recently observed for TiO_2 in a picosecond transient pump-probe experiment. This unexpected dominant lattice relaxation channel must be considered as a new classical-like (but low-temperature) proton transfer mechanism. For vibration-assisted protonic jumps to occur at low temperature, the phonon assistance must be classified as a low-frequency vibration specific to each lattice.

1. Introduction

The current view of transport in superionic conductors (SICs), including high-temperature protonic conductors (HTPCs) of ABO_3-type [1,2] and rutile TiO_2 [3–5] (the librational motion of OH peculiar to the latter is an important point for discussion of proton mobility [6]), is far from complete. A decrease in operating temperature is challenging for solid oxide proton-conducting devices for two reasons: the rate of activated diffusion rapidly decreases with temperature and the dominant low-temperature (LT) transfer mechanism is expected to be tunneling and not hopping. We normally think of proton hopping phenomena in HTPCs as thermally activated processes, implying that high mobility can be obtained only at elevated temperature. However, efficient LT jumping migration of protons in crystals involving special channels for easy diffusion must be considered a real possibility. A considerable body of data suggests that external stimulation can break O–H bonds inside the lattice. Proton diffusion in rutile at ordinary temperatures can be induced by electron irradiation [7]. This can be studied using the Arrhenius equation for the diffusion coefficient

$$D = D_0 \exp(-E_a/k_B T), \tag{1}$$

where E_a is the activation energy for a barrier height of V_* located at $x = x_*$, k_B is Boltzmann′s constant, and x is the position in space. A general question arises as to whether an LT hopping process is a classical-like stochastic process, much as high-temperature (HT) mobility is a result of the classical fluctuation–dissipation theorem (FDT) directly related to Einstein′s Brownian motion theory.

For ionic transport, vastly different approaches have been used. Microscopic theory is not far enough advanced to give a physical insight into the principles underlying ion hopping. In the absence of detailed knowledge of the paths taken by mobile ions, models of superionic behavior are based on either hypothetical conduction paths or general considerations such as hopping times or demand consistency with structural information [8]. Unlike electrons, ions in a solid can be constrained to flow through a confining network of voids and channels [9]. The concept of a vibration mode is of use in understanding what factors dominate the behavior of conducting ions in a number of SICs [2]. The role of a low-energy optical phonon was considered to enhance the phonon amplitude and assist the jumping of mobile ions [10]. We proposed an alternative mechanism whereby a diffusing proton polarizes the environmental lattice in some perovskite oxides, and hence proton–phonon coupling may be conceived as a proton polaron [11]. A dispersionless phonon mode was attributed to Na motion in β-alumina [12]. A low-frequency mode in β-alumina was implicated in excitation from oscillation to diffusion in a picosecond transient [13]. There has been recent interest in picosecond pump-probe transient techniques because they can trigger fast LT proton transport along the *c*-channel in TiO_2 [14]. This intriguing and unexpected classical-type effect is qualitatively different from the radiation-induced diffusion of hydrogen observed, say, in MgO [15], and has a quantum nature [4].

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A suitable approach for optically stimulated migration of protons can be introduced using general observations for hopping times. We now discuss this in the context of vibrational lifetimes and related laser pulse widths. In a previous paper, we proposed a model for lattice-assisted proton hopping (LAPH) in HTPCs by drawing a simple analogy with polaron behavior [16]. In that case, we were able to interpret D_0 in Eq. (1) as being proportional to the frequency ω of a hypothetical mode taken as phonon assistance (associated, say, with oxygen octhaedra) in certain circumstances. The energy transfer per collision can be incorporated into Eq. (1) in a semi-classical approach based on the energy diffusion equation expressed in terms of a classical probability density function (PDF) for particle trapping [17,18]. A further analysis involving quantum PDF, such as the Wigner quantum distribution function (W) [19], will be required to understand the hopping rate τ^{-1} behavior at low enough temperature. To implement this we consider an LT extension of the usual FDT-based stochastic description of ion transfer through an interface, implying that the Markovian limit is valid. The obvious approach is to search for a set of diffusion-like equations that are counterparts to those for classical diffusion, with the difference that the Boltzmann distribution is replaced by W. A basic principle required here is quantum Brownian motion with colored noise [19,20]. We recently addressed this concept for an LT extension of the LAPH model, but the features of this fundamentally new transfer mechanism were outlined only very briefly [4].

Here we analyze the LT limit of LAPH in some detail and illustrate the main properties of phonon assistance. The remainder of the paper is organized as follows. In Section 2 we discuss the basis for the model. In Section 3 we briefly analyze the transport aspects required in studying the relation between HT and LT diffusion rates. Section 4 describes the main theory. We begin with an analogy to the known stochastic description of ion transport in terms of classical FDT. In Section 4.2 we discuss an equation that LT current obeys. We then focus on calculation of the characteristics in Section 5 and a discussion of the results in Section 6. Section 7 concludes with a summary.

2. Definitions of the LAPH model

In the absolute rate theory (ART) framework, the prefactor in Eq. (1) is taken as a constant

$$D_0 = \frac{1}{2}\nu_a d^2, \tag{2}$$

where d is the jump distance and ν_a (constant) is the attempt frequency, which follows from classical FDT. By analogy, we might expect that the quantum FDT can yield the diffusion coefficient for protons interacting with an LT thermostat. In our model, species participating in a transfer step may act by affecting the potential barrier. The generalized activation energy $E_a{}^{(d)} = E_a{}^{(d)}(|u|,\omega,T)$ becomes a dynamic quantity, where the frequency is identified by a single oscillator frequency $\omega = \omega_0$ from FDT and $|u|$ (constant) is the coupling strength between protons and a harmonic phonon bath. We take the LT diffusion coefficient in the classical form

$$D_{\mathrm{LT}} = D_0^{(d)} \exp(-E_a^{(d)}/k_B T) \tag{3}$$

for consistency with the over-the-barrier regime. Elementary transfer can be visualized as reservoir-mediated barrier crossing relative to the effective potential $V(q)$ along a newly appearing reaction coordinate q. This result allowed determination of the apparent activation energy barrier as $E_a{}^{(d)} \approx V(q_*)$ along the unique mode-related coordinate q at a point q_* such that the bare potential barrier is $V(x_*) > V(q_*)$. If the quantum system evolves along the q-coordinate, it will appear to an observer as if a stream of protons moves parallel to the c-axis. This raises the question as to what is the ion attempt frequency that determines the dynamic prefactor $D_0{}^{(d)}$. Clearly, straightforward application of Eq. (1) at LT using

$$\tau^{-1(\mathrm{ART})} = \nu_a \exp(-V_\bullet/k_B T) \tag{4}$$

is incorrect. We previously showed that $D_0{}^{(d)}$ is proportional to ω at HT in a polaron-like picture [16] under the condition

$$\hbar\omega \sim k_B T, \tag{5}$$

where, however, ω is interpreted in terms of certain well-defined vibrational modes.

Here we re-examine the meaning of ν_a, in that the hopping mechanism is not the one normally expected for thermal activation. Approximation (5) holds because the general LAPH mechanism is assumed to be satisfactory over a wide temperature range. However, the resulting phonon assistance is a low-frequency vibration due to LT. We must determine how such a vibrational motion fits with the accepted picture of parallel transport to the q-direction. Experimental evidence points to the fact that vibrational relaxation in rutile single crystals after exposure to ultrafast resonant infrared light radiation does not occur via a multiphonon process, and that the unstable oscillator couples quickly to another oscillatory motion that can be a contributory factor in long-range proton migration [14]. It is not unreasonable to believe that the promoting mode in rutile shows up as merely skeletal motion (i.e., associated with the vibrational sublattice in the immediate vicinity of the c-axis), much as the motion of a proton in ABO_3 oxides would be affected by oxygen octhaedra. Assignment of the coupling constants is a problem. To distinguish a low-frequency phonon spectrum from that of a simple harmonic oscillator, it should be expressed as

$$\omega_0 = k_0 \Omega \tag{6}$$

when required (where k_0 is a constant specified later). In the LT case, the development of additional solutions with relations Ω/ω_0 other than unity is not ruled out (the case $\Omega = \omega = \omega_0$ is the simplest possibility). The proton follows a phonon-activated walk with a hopping probability of $w = w_{mm'}$ between neighboring points m and m'. A key point of the model is that $w = w(\omega)$, while varying, is in essence characterized by the reciprocal of the time t_0 between proton jumps taken as an observable. We solve the problem of low-frequency phonon assistance by identifying Ω with an effective cycle frequency due to combined interaction effects. The proposed phenomenological approach does not imply a one-to-one correspondence between the unique mode and a single clearly-seen vibration. As we see later, t_0 can be understood, in light of LT measurement methods, in terms of the lifetime T_1 of excited modes (defined in the literature as $T_1 = 1/(2\pi c_l \Gamma)$, where Γ is the line width and c_l is the speed of light), implying that the coupling parameters chosen are quite arbitrary, depending on the operating temperature. This is why we use the term lattice-assisted instead of vibration-assisted. However, from what has been said, the possibility of identifying Ω with a real mode should not be ruled out and deserves further study. In principle, the current view leaves room for a wide range of vibrational behaviors, including phonon assistance of a complex nature (mixing phonon modes). The presence of phonon-assisted proton transitions in response to external conditions (e.g., resonant light) can be verified in independent experiments of various types. Eq. (3) implies the functional relationship

$$t_0^{-1} = A\,\omega \exp(-E_a^{(d)}/k_B T), \tag{7}$$

where A is a phenomenological parameter, previously measured for TiO_2 [14]. It may appear that the classical character of motion (over-the-barrier jumps) conflicts with essentially quantum (LT)