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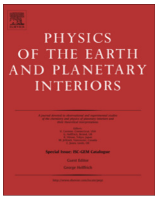

Letter

Some notes on hydrogen-related point defects and their role in the isotope exchange and electrical conductivity in olivine

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ABSTRACT

Nominally anhydrous minerals such as olivine dissolve hydrogen in a variety of forms including free (or interstitial) proton ($H^{\bullet}$) and two protons trapped at the M-site ($(2H)_M^{\times}$). The strength of chemical bonding between protons and the surrounding atoms are different among different species, and consequently protons belonging to different species likely have different mobility (diffusion coefficients). I discuss the role of diffusion of protons in different species in the isotope exchange and hydrogen-assisted electrical conductivity adding a few notes to the previous work by Karato (2013) including a new way to test the model. I conclude that in the case of isotope exchange, the interaction among these species is strong because diffusion is heterogeneous, whereas there is no strong interaction among different species in electrical conduction where diffusion is homogeneous (in an infinite crystal). Consequently, the slowest diffusing species controls the rate of isotope exchange, whereas the fastest diffusing species controls electrical conductivity leading to a different temperature dependence of activation energy and anisotropy.

This model explains the differences in the activation energy and anisotropy between isotope diffusion and electrical conductivity, and predicts that the mechanism of electrical conductivity changes with temperature providing an explanation for most of the discrepancies among different experimental observations at different temperatures except for those by Poe et al. (2010) who reported anomalously high water content dependence and highly anisotropic activation energy. When the results obtained at high temperatures are used, most of the geophysically observed high and highly anisotropic electrical conductivity in the asthenosphere can be explained without invoking partial melting.

1. Introduction

Since the first suggestion by Karato (1990) of the enhancement of electrical conductivity by hydrogen in olivine, a number of experimental studies have been conducted on the role of hydrogen in electrical conductivity in olivine and other minerals. The importance of hydrogen in electrical conductivity is now well established for most minerals (e.g., (Karato and Wang, 2013; Yoshino and Katsura, 2013)). However, there are some discrepancies among the published experimental results and the degree to which hydrogen-enhanced conductivity explains the geophysical observations is still controversial (see above reviews). This is partly caused by the subtleties in the experimental studies on electrical conductivity of materials containing hydrogen as impurities (i.e., impedance spectroscopy versus one-frequency measurement, the evaluation of hydrogen loss/gain during the measurements; see (Karato and Dai, 2009 and Karato and Wang, 2013) for discussions of experimental studies), but also due to the complications in the manner in which hydrogen-related defects are incorporated and migrate in a mineral.

In this note, I will focus on the latter, i.e., the theoretical aspect and provide some additional discussions on the nature of hydrogen-related defects and their migration in olivine. Karato (2013) proposed a theoretical model of hydrogen–deuterium isotope exchange by diffusion in order to explain two major puzzles: (i) the discrepancies between diffusion and conductivity (largely different activation energy and anisotropy) and (ii) the discrepancies among different experimental studies conducted at different temperatures. The predictions of this model were tested by Dai and Karato (2014) where they showed that the mechanisms of electrical conduction change with temperature, and at high temperatures, average conductivity is higher than those extrapolated from the previous low temperature results and anisotropy is substantially higher than that at lower temperatures. These results provide an explanation for the discrepancy among different experimental studies and imply that a majority of geophysical

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observations of electrical conductivity of the asthenosphere can be explained by the presence of geochemically reasonable amounts of hydrogen if the results at high-temperature are used. However, the model proposed by Karato (2013) involves subtle physics of point defects that is not familiar to a majority of mineral physicists and geophysicists. My discussions with fellow scientists motivated me to write this note to provide a more detailed explanation of the model and its implications.

2. Diffusion-conductivity discrepancies

The hypothesis of hydrogen-assisted conductivity was proposed based on the Nernst–Einstein relationship, viz.,

$$\sigma = f\frac{Dcq^2}{RT} \tag{1}$$

where σ is electrical conductivity, f is the formation factor (a non-dimensional factor ~1), D is the diffusion coefficient of charge carrying species, c is the concentration of that species, q is the electric charge of that species, R is the gas constant and T is temperature. The Nernst–Einstein relationship implies that, for fixed water content, the activation energy and the anisotropy must be approximately the same for both hydrogen diffusion and hydrogen-assisted electrical conductivity.

However, a number of experimental studies on hydrogen-assisted electrical conductivity and hydrogen diffusion showed that the activation energy for hydrogen diffusion in olivine and wadsleyite (120–140 kJ/mol) are substantially higher than that of hydrogen-assisted electrical conductivity at relatively low temperatures (70–90 kJ/mol) (e.g., olivine: (Du Frane and Tyburczy, 2012; Kohlstedt and Mackwell, 1998; Wang et al., 2006), wadsleyite: (Dai and Karato, 2009; Hae et al., 2006; Huang et al., 2005)). In addition, although anisotropy in hydrogen diffusion in olivine single crystals is very large (a factor of 10–100; (Du Frane and Tyburczy, 2012; Kohlstedt and Mackwell, 1998)), hydrogen-assisted electrical conductivity in olivine measured at relatively low temperatures is nearly isotropic (Yang, 2012) (Poe et al. (2010) reported the results showing some anisotropy but the degree of anisotropy determined under their experimental conditions is much smaller than the degree of anisotropy of hydrogen diffusion: see a note on their work in the later part of this paper). Although the uncertainties in the measurements of diffusion coefficients are large, these discrepancies are so large that I believe that it is important to explain the cause of these discrepancies.

3. Extension of model of isotope exchange

The main purpose of my paper (Karato, 2013) was to solve this puzzle by extending the theory of isotope exchange to a case where multiple species are involved. The key concepts in my theory are (i) there are multiple H (hydrogen)- (and D (deuterium)-) bearing point defects in minerals such as olivine, (ii) different H- (or D-) bearing species have different diffusion coefficients (different mobility), and (iii) the concentration ratio of these defects maintains the local equilibrium defined by the free energy of these species $\frac{C_i}{C_j} = \exp(-\frac{\Delta G_i - \Delta G_j}{RT})$ (C_i: concentration of the i-th species, ΔG_i: free energy of the i-the species relative to the ground state (perfect crystal); Fig. 1).

The first point was clearly demonstrated in wadsleyite by Nishihara et al. (2008) based on infrared spectroscopy studies of samples prepared at a range of chemical conditions, but the presence of multiple hydrogen-bearing defects was also suggested in olivine from the experimental data of electrical conductivity (Karato, 2006; Wang et al., 2006) (see also a review by Karato and Wang (2013)). A free proton $H^{\bullet}$(could be considered as an interstitial proton, $H_I^{\bullet}$) and two protons at M-site vacancy $(2H)_M^{\times}$ likely have different diffusion coefficients because protons in $(2H)_M^{\times}$ are strongly trapped at the crystallographic site (M-site) while free proton is not strongly bonded to any site (I use the Kröger–Vink notation for point defects; see caption of Fig. 1).

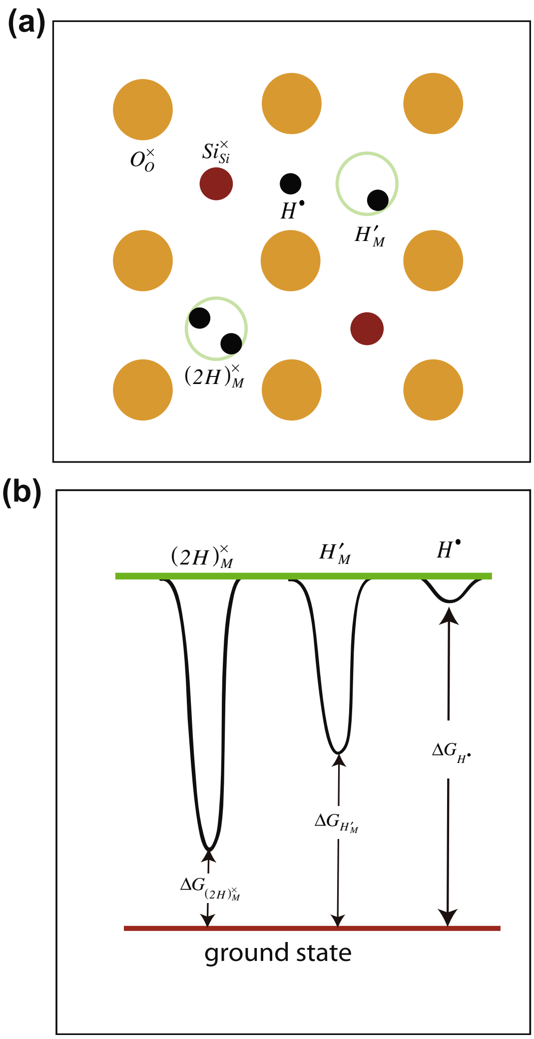

Fig. 1. (a) A schematic diagram showing various H-bearing species in olivine. The Kröger–Vink notation of defects is used: X_Y^Z where X: species, Y: site, Z: effective charge relative to the perfect lattice (×: neutral, •: +e, ′: −e). (b) A schematic diagram showing the energy levels and the strength of binding for each hydrogen-bearing species. Hydrogen in $(2H)_M^{\times}$ is trapped in the deep potential well and their mobility is low (and likely crystallographically controlled, i.e., anisotropic). Free proton (or proton in the interstitial site), $H^{\bullet}$, is only loosely bonded and hence is highly mobile and its diffusion coefficient is not strongly anisotropic. The concentration of each defect is determined their free energy relative to the ground state, ΔG_i. ΔG_i is the smallest for $(2H)_M^{\times}$, and it has the highest concentration (concentration also changes with chemical conditions; (Nishihara et al., 2008)).

In case of isotope exchange, the driving force is $-\frac{\partial c_i}{\partial x}$, and consequently diffusion itself will modify the concentrations of each species as a function of position. To illustrate this point, let us consider isotope exchange between two crystals in a case where diffusion coefficient of different species has the following order: $D_{H^{\bullet},D^{\bullet}} > D_{H'_M,D'_M} > D_{(2H)_M^{\times},(2D)_M^{\times}}$ (D_X: diffusion coefficient of X). In this case, the concentration ratio of various species would be out of equilibrium, if these species diffused independently (Fig. 2). It can also be shown that the charge balance condition is not satisfied as far as the properties of H-bearing and D-bearing defects are not exactly identical (e.g., the diffusion coefficient depends on the