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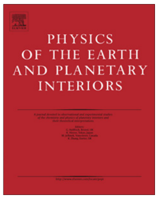

Theory of isotope diffusion in a material with multiple species and its implications for hydrogen-enhanced electrical conductivity in olivine

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ABSTRACT

The relationship between isotope diffusion coefficient and electrical conductivity is examined for a material where a dominant charge-carrying atomic species (e.g., hydrogen) is present as various forms with different diffusion coefficients (e.g., two protons trapped at M-site vacancy, one proton trapped at M-site vacancy etc.). It is shown that the isotopic diffusion occurs keeping the concentration ratio of each species fixed as determined by the thermo-chemical environment. Consequently, the isotope diffusion coefficient is the harmonic average of diffusion coefficients of individual species and is dominated by the slowest diffusing species. In contrast, when electric current is carried by charged species, the concentrations of individual species do not change. Therefore, electrical conductivity is related to the arithmetic average of individual diffusion coefficients dominated by the fastest diffusing species. The difference between these two cases can be large when different species have largely different diffusion coefficients. This model provides an explanation for the observed differences between experimental observations on isotopic diffusion (of H-D) and hydrogen-enhanced electrical conductivity and supports a hybrid model of hydrogen-enhanced electrical conduction where electrical conductivity is dominated by the fast moving hydrogen-related species. The species with the largest mobility may change with temperature leading to a change in anisotropy of conductivity. The degree of enhancement of electrical conductivity by hydrogen is high enough to explain most of the geophysically observed electrical conductivity of Earth's upper mantle.

1. Introduction

Following the suggestion by Karato (1990) that hydrogen may enhance electrical conductivity in olivine, a number of experimental studies have been performed in the last several years to test this hypothesis. These studies have largely confirmed the original hypothesis, but details are still debated including the magnitude of this effect and the atomic mechanisms by which hydrogen enhances electrical conductivity (for review see Karato and Wang (2013); Yoshino (2010)).

In the first paper where the important role of hydrogen in electrical conductivity was suggested, Karato (1990) used the chemical diffusion coefficient determined by Mackwell and Kohlstedt (1990) and calculated electrical conductivity for a range of hydrogen content. Chemical diffusion of hydrogen involves diffusion of hydrogen together with the diffusion of another charge-compensating species, and hence this method would be valid only when the diffusion of charge-compensating species is faster than the intrinsic diffusion coefficient of hydrogen (Kohlstedt and Mackwell, 1998). The charge-compensating diffusing species is either M-site vacancies or electron holes, both of which have high diffusion coefficients and hence this assumption is likely justified (Kohlstedt and Mackwell, 1998).

However, already in the early studies such as (Wang et al., 2006), it was recognized that the electrical conductivity calculated from the diffusion coefficients of hydrogen gives systematically smaller values than actually measured conductivity. Also the activation energy of hydrogen-assisted conductivity (~70–90 kJ/mol) is much smaller than that of diffusion (~140–150 kJ/mol) (Dai and Karato, 2009b; Hae et al., 2006; Yoshino, 2010). Such differences have been confirmed by the recent study of isotope diffusion of hydrogen and deuterium in olivine (Du Frane and Tyburczy, 2012) (Fig. 1). The discrepancy includes not only the discrepancy in the magnitude of conductivity and activation enthalpy (Fig. 1a) but also the nature and magnitude of anisotropy (Fig. 1b).

Any viable model of hydrogen-enhanced electrical conductivity must explain these major discrepancies. Based on these observations as well as the observed dependence of conductivity on water content (water fugacity), (Karato, 2006) concluded that a simple model assuming a single hydrogen-related species is not appropriate and proposed a hybrid model where the role of multiple hydrogen-related species is emphasized. In contrast, from the same observation,

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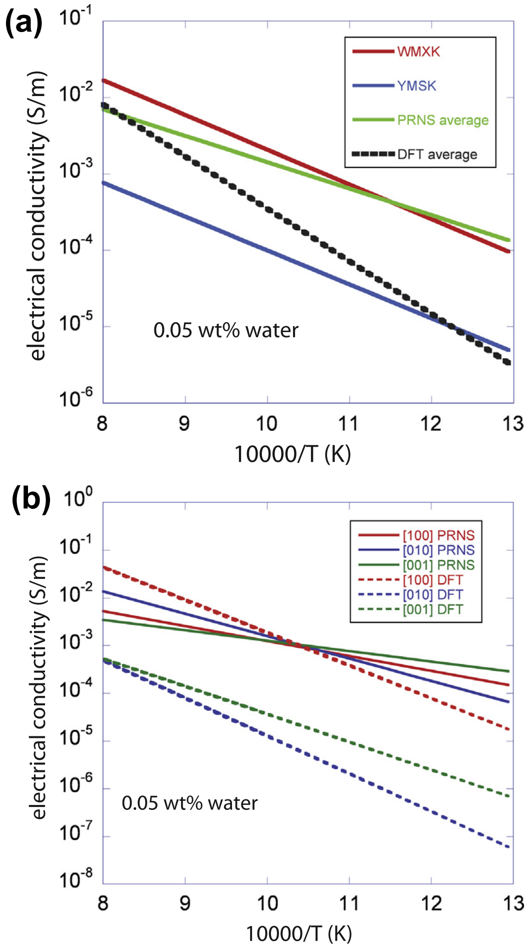

Fig. 1. A comparison of measured electrical conductivity with the conductivity calculated from isotope diffusion coefficients. The comparison is made for the water content of 0.05 wt.% to minimize the influence of extrapolation (most of measurements in the literature were made at or near this water content). Data source, DFT: (Du Frane and Tyburczy, 2012), PRNS: (Poe et al., 2010), WMXK: (Wang et al., 2006), YMSK: (Yoshino et al., 2009)). The water content for each measurement corresponds to those determined by SIMS (when FTIR with (Paterson, 1982) calibration is used, a correction factor of 3 was applied). (a) A comparison of average conductivity. All conductivity data show much lower activation energy than that of isotope diffusion. The results by WMXK agree well with those by PRNS. The results by YMSK show much lower conductivity than these. (b) A comparison of conductivity including anisotropy. Anisotropy of conductivity reported by Poe et al. (2010) changes with temperature and is markedly different from anisotropy calculated from the isotope diffusion data reported by Du Frane and Tyburczy (2012).

Du Frane and Tyburczy (2012) concluded that the degree to which hydrogen enhances electrical conductivity is not as large as (Wang et al., 2006) and (Dai and Karato, 2009a) showed, and they argued that a hybrid model presented by Karato (2006) is inconsistent with their observation.

Problems with a simple single-species model have been discussed in several previous papers where a hybrid model of conductivity was presented to explain such discrepancies (Karato, 2006; Karato and Wang, 2013). However, atomistic mechanisms to cause these differences were not explained very clearly in the previous studies. Given the new experimental work by Du Frane and Tyburczy (2012) that clearly demonstrated the discrepancies between isotope diffusion and conductivity measurements, and given their discussion against a hybrid model of electrical conductivity, it seems appropriate to provide a theoretical analysis of isotope diffusion to understand the causes of these discrepancies. In this paper, I will examine the microscopic physics of isotope exchange between two materials where a given atomic species (e.g., hydrogen) occurs in a multiple forms. I will show that direct correlation between isotope diffusion coefficient and electrical conductivity is broken down in such a case if a given atomic species in different forms have largely different diffusion coefficients. Consequently, the direct comparison of electrical conductivity calculated from isotope diffusion coefficients and actual electrical conductivity is not justified in these materials.

2. Theory

When electric current is carried by charged species, electrical conductivity is related to the diffusion coefficients of relevant species. Such a relation is given by the Nernst–Einstein relationship (e.g., Mott and Gurney, 1940), viz.,

$$\boldsymbol{\sigma} = \frac{1}{RT}\sum\nolimits_i f_i q_i^2 D_i C_i \tag{1}$$

where $\boldsymbol{\sigma}$ is electrical conductivity, f_i is a non-dimensional factor of order unity, q_i is the electrical charge (relative to the vacuum), D_i is the diffusion coefficient, C_i is the concentration of the i-th species, and RT has usual meaning. This relation would imply that once one knows the concentration and (self) diffusion coefficient of all relevant species, one can calculate electrical conductivity.

The relation (1) is valid only when summation over i is made for all relevant species. When a given atomic species, say hydrogen, occurs in several different forms (e.g., two protons at M-site, one proton at M-site, free proton etc.) then summation must be made for all of these species. As I will show in this paper, in a material where a given species (e.g., hydrogen) occurs in various forms, the isotope exchange involves strong interaction of various species and consequently, isotope diffusion coefficient does not directly represent the self diffusion coefficient of any atomic species but rather corresponds to some average of individual diffusion coefficients. Consequently the relation between individual diffusion coefficients and isotopic diffusion coefficient needs to be known in order to understand the relationship between isotopic diffusion coefficient and electrical conductivity.

3. Theory

Experimental observations summarized by Karato (2006); Karato and Wang (2013); Nishihara et al. (2008) suggest that hydrogen in these materials ($(\mathrm{Mg,Fe})_2\mathrm{SiO}_4$) is dissolved in multiple forms including $(2H)_M^\times$ (two protons at M-site vacancy), H'_M (one proton at M-site vacancy) and $H^{\cdot}$ ("free" proton) (for deuterium, $(2D)_M^\times$, D'_M, $D^{\cdot}$). Hydrogen in each of these species has different chemical bonding with its surroundings, and therefore likely has different mobility. These species are created by the ionization reaction,

$$(2H,2D)_M^\times \leftrightarrow (H,D)'_M + (H,D)^{\cdot}. \tag{2}$$

The concentrations of these defects may also be affected by the presence of other charged defects such as the M-site vacancy, V''_M (Karato, 2008). At equilibrium, the concentration ratio of each species is determined by the physico-chemical environment (temperature, pressure, the fugacity of water and of oxygen, and oxide activity) (Nishihara et al., 2008).

In an isotope exchange experiment, one brings two crystals with different isotopic compositions (H/D ratios) into contact (Fig. 2). When multiple species are present, concentration gradient must be present for each species that varies as a function of position. Consequently, each species will diffuse driven by the concentration gradient, and the diffusion flux should be proportional to the diffusion coefficient of each species.