GEOPHYSICAL RESEARCH LETTERS, VOL. 39, L06306, doi:10.1029/2012GL051046, 2012

Influence of hydrogen on the electronic states of olivine: Implications for electrical conductivity

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Received 20 January 2012; revised 23 February 2012; accepted 29 February 2012; published 28 March 2012.

[1] The influence of hydrogen on the electronic states in olivine was investigated by the first-principle calculations combined with the models of the mobility of electrons. We find that the dissolution of hydrogen modifies the electronic states when hydrogen is dissolved as charged defects but there is little modifications to the electronic structure when hydrogen is dissolved as a neutral defect such as two protons at M-site. In the former case an impurity state is created just above the valence band providing a mechanism of impurity conduction. The electrical conductivity calculated from this model using a model of the mobility appropriate for "polaron" mechanism of conduction shows a good agreement with the experimental observations on hydrated olivine. We conclude that the enhanced electrical conductivity in olivine by the dissolution of hydrogen may partly due to the enhancement of electronic conduction. Possible implications for high-temperature creep are also discussed. **Citation:** Wang, D., S. Karato, and Z. Liu (2012), Influence of hydrogen on the electronic states of olivine: Implications for electrical conductivity, *Geophys. Res. Lett.*, *39*, L06306, doi:10.1029/2012GL051046.

1. Introduction

[2] Even a small amount of hydrogen enhances some transport properties (electrical conductivity [*Huang et al.*, 2005; *Karato*, 1990; *Wang et al.*, 2006], plastic deformation: [*Karato and Jung*, 2003; *Karato et al.*, 1986; *Mei and Kohlstedt*, 2000]) and decreases melting temperature and change the composition of the melts [*Inoue*, 1994; *Kushiro et al.*, 1968]. Among these, the cause for enhanced melting is well known: the melting temperature is reduced essentially by the mixing entropy effects [e.g., *Carmichael et al.*, 1974]. In contrast, the mechanisms by which hydrogen enhances transport properties are still poorly understood.

[3] Through the development of well-characterized laboratory studies, atomistic mechanisms of hydrogen dissolution is now well understood for some materials [e.g., *Bolfan-Casanova*, 2005; *Kohlstedt et al.*, 1996], but the atomistic mechanisms of enhancement of transport properties are still controversial. In the previous studies, these processes are considered in terms of point defects at the level of atoms, i.e., vacancies, free protons etc. [e.g., *Karato*, 2006; *Kohlstedt*, 2006, 2009]. However, when hydrogen is dissolved in minerals, multiple species co-exist in a given mineral [*Nishihara et al.*, 2008], and in some cases electronic defects might be created. If indeed electronic defects are created by hydrogen-related impurities, then they will directly affect electrical conductivity but they may also affect high-temperature creep through the change in kink (or jog) density along the dislocation line [e.g., *Hobbs*, 1981; *Kohlstedt*, 2009]. In this paper, we will review the results of electronic density of state calculations for olivine containing hydrogen-related defects and discuss implications of these results on some transport properties of olivine including electrical conductivity and high-temperature creep.

2. Electronic Density of State of Hydrated Olivine

[4] We calculate the density of state (DoS) of electrons in both anhydrous and hydrous forsterite (Mg_2SiO_4) using the density functional approach. The generalized gradient approximation (GGA) was adapted to the exchange-correlation energy functional. The norm-conserving pseudo-potentials were used to describe the ionic cores. The details of the method are discussed in the previous study [*Wang et al.*, 2011] and only the essence is described here. For example, the atomic configurations associated with the introduction of hydrogen-related defects are calculated in this previous paper. Related studies on the electronic structure of hydrated minerals such as olivine are given by *Tsuchiya and Tsuchiya* [2009] and *Umemoto et al.* [2011]. Calculations for hydrous olivine were done on one unit cell (i.e., 28 atoms) containing two hydrogen atoms. The periodic boundary conditions are used. Applications of these results to a case with lower hydrogen content will be made through appropriate normalization as we describe later. Our calculations include not only the influence of a majority neutral defects but also minority charged defects. Figure 1 shows the electron density of states (DoS). The zero energy is defined to be the energy corresponding to the top of the valence band. At T = 0 K, electrons will occupy the states shown by the hatched regions. Figure 1a is the density of state of anhydrous olivine; Figure 1b is DoS for olivine with neutral defects $(2H)_M^\times$, Figure 1c for a case of charged defects, H'_M(M-site vacancy trapping one proton) and $H^\cdot$ (free hydrogen). It is noted that the addition of a neutral defect has no important effects on the electronic structure, whereas the addition of charged defects does. These results are in harmony with the known behavior of semi-conductors: addition of charged defects introduces impurity levels either as a donor or an acceptor depending on the sign of the charge [e.g., *Kittel*, 1986].

3. Implications for Electrical Conductivity

[5] The electronic structure calculations described above provide an estimate of the density of states of electrons and the energy gaps between various energy bands. Among various electronic states, a particularly important one is an impurity state created just above the valence band. Such an impurity state is analogous to the state created by the addition of ferric

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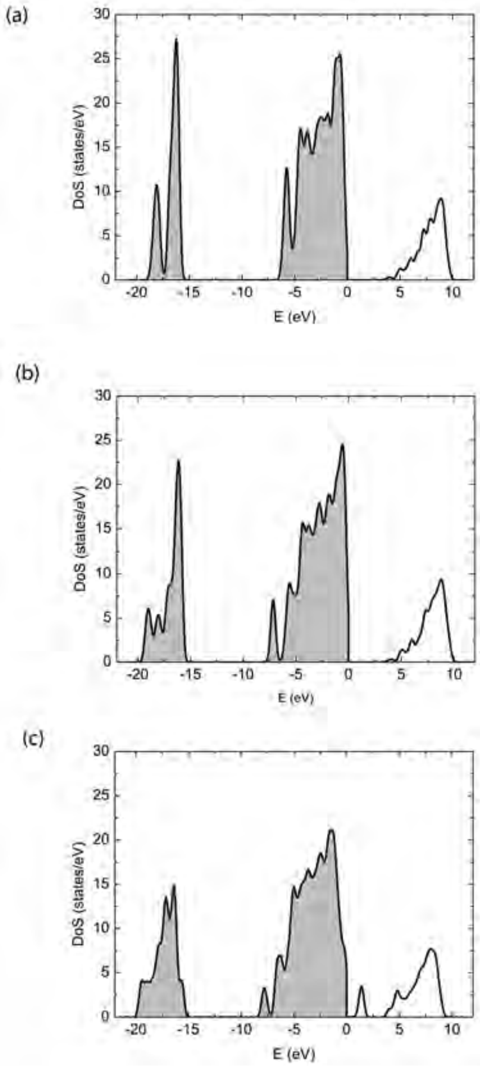

Figure 1. Electron densities of states (DoS). (a) DoS of state of anhydrous olivine; (b) DoS for olivine with neutral defects, $(2H)_M^{\times}$; (c) DoS for olivine containing charged defects, H'_M (M-site vacancy trapping one proton) and $H^{\cdot}$ (free hydrogen).

iron to olivine. Given those states, electrons can be accepted at these defects leaving electron holes in the valence band. From the density of state and the band gap corresponding to the impurity state, we can calculate the number density of charge carrier. Consequently, we can calculate electrical conductivity if we know the mobility.

[6] We use the relation

$$\sigma = |q| n \mu \tag{1}$$

to calculate the electrical conductivity due to electronic defects from the results of calculation of density of states of electrons. Because the charged hydrogen defects create an acceptor level, electron holes are created whose number density, n, is given by,

$$n = n_0 \exp\left(-\frac{E_a^*}{RT}\right) \tag{2}$$

where n_0 is the total number of the impurity states (per unit volume) and E_a^* is the energy difference between the energy of impurity level and the top of the valence band. These two quantities are known from the calculation of electronic state.

[7] The total number of impurity states (n_0) of olivine with two hydrogen atoms in the unit cell was calculated from the integrated area of the impurity level in the region of the gap within one unit cell. In order to calculate electrical conductivity for a smaller amount of water, we calculate the number of charge carrier of olivine in the following way. First, we use the fact that the number of impurity state created by the addition of hydrogen is proportional to the hydrogen-related defect. Second, the number of hydrogen-related defect depends on the fugacity of water that is in turn related to the total water content. Third, the majority of the hydrogen-related defect is a neutral defect, $(2H)_M^{\times}$, for which $C_W \propto f_{H2O}$ where C_W is the water content ($\sim[(2H)_M^{\times}]$). Under these assumptions, we have

$$\frac{n_0}{n_{00}} = \left(\frac{C_W}{C_{W0}}\right)^r \tag{3}$$

where n_0 is the number of impurity state for water content of C_W, and n_{00} is the number of impurity state for the reference water content, C_{W0}, and r is a parameter that depends on the nature of hydrogen-related defect. Based on the experimental result, we assume $r = 0.62$ for olivine [*Wang et al.*, 2006]. The choice of C_{W0} is tricky because not all hydrogen atoms assume the same species. Two hydrogen atoms in a unit cell would correspond to the water content of 3.2 wt%, but considering the fact that only a fraction of hydrogen atoms that assumes charged state ($H^{\cdot}$ and H'_M), we modify equation (3) to $\frac{n_0}{n_{00}} = \left(\frac{\beta C_W}{C_{W0}}\right)^r$ with $r = 0.62$ where C_W is the total water content in wt%, C_{W0} is the wt% of hydrogen that are in the charged state in our calculation (=3.2 wt%) and a parameter β ($0 < \beta < 1$) represents a fraction of hydrogen assuming free proton. The results are shown in Figure 2.

[8] The mobility of electrons (or holes) in an ionic semiconductor is controlled by the electron-phonon interaction involving optical phonons. In a case where electron velocity

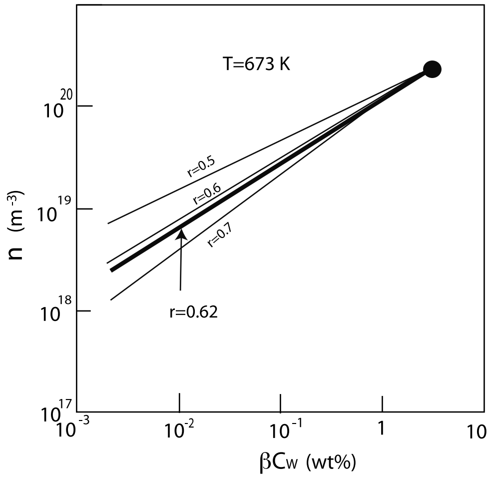

Figure 2. The number density of charger carrier of olivine with various water content at 673 K. A black circle is the number density calculated from the density of state shown in Figure 1 where two protons are inserted in the unit cell. Solid lines show the number density at lower water content. β is a fraction of water that assumes the charged states ($H^{\cdot}$ and H'_M), and C_W is the water content.

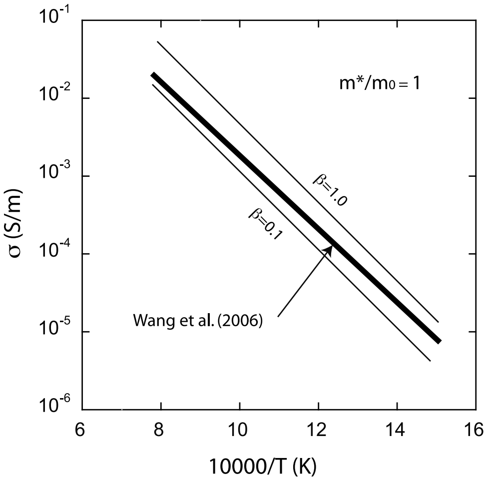

Figure 3. The comparisons of the calculated electrical conductivity results and the experimental observations with 0.01 wt% water in the cases of $m^*/m_0 = 1$. The experimental data can be explained a combination of parameters β and m^*/m_0.

is low, a moving electron polarizes the surrounding lattice that in turn modifies the resistance for electron motion (such a mode of electron conduction is referred to as "polaron" conduction). Consequently, the mobility is controlled by the difference in the lattice polarization for the low frequency (relaxed) and for the infinite frequency (unrelaxed), viz. [e.g, *Ziman*, 1960],

$$\mu = \frac{3}{2^{\frac{5}{2}}\pi^{\frac{3}{2}}} \frac{h^2}{em^{*\frac{3}{2}}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right)} \frac{1}{(kT)^{\frac{1}{2}}} \tag{4}$$

where e is the electric charge of an electron, m* is the effective mass of electron (or hole), k is the Boltzmann constant, h is the Planck constant, ε_∞ is the dielectric constant for the infinite frequency, ε is the static dielectric constant. The values of dielectric constants in olivine were determined by *Cygan and Lasaga* [1986] ($\varepsilon_\infty = 10\varepsilon_0$ and $\varepsilon = 2.5\varepsilon_0$ ($\varepsilon_0 = 8.854 \times 10^{-12}$ F/m)). Given equations (4), the only unknown parameter in the mobility is the effective mass of electrons (or holes).

[9] In this model, there are two unknown parameters, β (for the number density of charge carriers) and m^* (for the mobility). We calculated the electrical conductivity of olivine with 0.01 wt% water leaving the effective mass m^* and β (the fraction of hydrogen assuming charged state), and compared the results with the experimental results by *Wang et al.* [2006]. Figure 3 shows the calculated electrical conductivity as well as the experimental observations with 0.01 wt% water. The relationship between β and m^*/m_0 (m_0: mass of the free electron) that explains the experimental observations are shown in Figure 4.

[10] Figure 4 shows that for a plausible range of β (0.1–0.5), the effective mass will be $m^*/m_0 = 0.7$–1.5. The effective mass can be interpreted in terms of the electron-phonon interaction. The effective mass of the polaron, m*, is given by [*Kittel*, 1986]

$$m^* = m_0^* \frac{1 - 0.0008\alpha^2}{1 - \frac{1}{6}\alpha + 0.0034\alpha^2} \tag{5}$$

where m_0^* is the effective mass of electron in the conduction band and α is a non-dimensional constant representing the electron-phonon coupling. Given, $m_0^*/m_0 = 0.3$–0.5 for ionic solids [*Kittel*, 1986], $\alpha = 2$–5 will be consistent with the observations for $r = 0.62$. These values of α are representative of strongly ionic crystals [*Kittel*, 1986]. Therefore we conclude that the formation of electronic defects introduced by the dissolution of charged hydrogen-related defects is a plausible mechanism of enhancement of electrical conductivity in addition to the conduction by free hydrogen atoms.

4. Discussions and Conclusions

[11] The experimental results on the electrical conductivity in hydrated nominally anhydrous minerals show that the conductivity is not always linearly proportional to the water content [e.g., *Dai and Karato*, 2009; *Wang et al.*, 2006] that suggests that the neutral, majority of hydrogen-related defects ($(2H)_M^\times$) do not carry much of the electric current [*Karato*, 2006]. Our present study also showed that if hydrogen is added as a neutral defect such as $(2H)_M^\times$, then the dissolution of hydrogen has little effects on electronic states. However, we also showed that if hydrogen is dissolved as charged defects, then the dissolution of hydrogen has an important modification to the electronic state, similar to the case of impurities such as ferric iron.

[12] The details of the mobility of electrons (holes) in a semiconductor is not well understood, and formulae other than equation (4) can be found in the literature [e.g., *Bosman and van Daal*, 1970]. For instance, *Constable and Roberts* [1997] used electrical conductivity and thermo-power observations on dry (hydrogen-free) olivine to conclude that the mobility is exponentially dependent on temperature. In the model that we used in this paper, the mobility is not dependent on temperature exponentially, and the activation energy of electrical conductivity corresponds mainly to the temperature dependence of the concentration of charged defects (equation (2)). Distinguishing these two models is not possible with currently available data, but if one has additional data sets such as the thermopower or the Hall coefficient for hydrated olivine, further insights into the conduction mechanisms will be obtained.

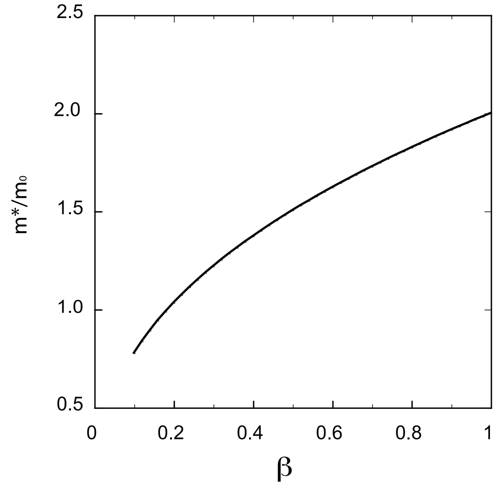

Figure 4. The relationship between m^*/m_0 and β that explains the experimental observations on electrical conductivity.

Our study showed that the formula (4) is consistent with the experimentally determined activation enthalpy, and it also explains the acceptable mobility corresponding to the plausible range of the electron-phonon interaction in an ionic crystal. Therefore we conclude that in addition to the direct contribution to conductivity through the migration of free proton ($H^{\cdot}$) [e.g., *Karato*, 2006], the dissolution of hydrogen enhances electronic conduction through the creation of an impurity level in the band gap.

[13] A possible implication of this model is that the anisotropy of electrical conductivity is different among these possible models. Studies on anisotropy in conductivity in comparison to the anisotropy of hydrogen diffusion [e.g., *Du Frane and Tyburczy*, 2012] will provide an additional clue as to the mechanisms of electrical conduction [e.g., *Poe et al.*, 2010; *Yoshino et al.*, 2006].

[14] The presence of impurity level produced by water-bearing defects may also influence the high-temperature creep through the change in kink (or jog) density along the dislocation line [e.g., *Hobbs*, 1981; *Kohlstedt*, 2009]. In these cases, the density of kinks (or jogs) depends on the concentration of charged point defects and the velocity of dislocations is sensitive to the chemical environment [e.g., *Karato*, 2008]. Increased kink (or jog) density by the addition of charged hydrogen-related defects may enhance the rate of plastic deformation.

[15] In summary, the present study shows that the addition of water (hydrogen) to olivine modifies the physical properties of olivine including electrical conductivity through the modifications to the electronic properties of olivine. The change inn the electronic structure could also affect high-temperature creep through the change in the kink (or jog) density along the dislocation lines. However, such a modification occurs only when charged defects are introduced by the dissolution of water.

[16] **Acknowledgments.** This work is partially supported by and important field program of Knowledge innovation Program (KZCX2-YW-QN608) and National Natural Science Foundation of China (NSFC, 40774036 and 41074063) and NSF of USA (EAR-0911465).The Editor thanks the two anonymous reviewers for their assistance in evaluating this paper.

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