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Predicting Anisotropic Electrical Conductivities of a Magnetic Insulator on the Basis of Its Magnetic Properties

Kee Hag Lee,*[†,‡] Rüdiger Dieckmann,[†]
Changhoon Lee,[§] and Myung-Hwan Whangbo*[,§]

Department of Materials Science and Engineering, Bard Hall, Cornell University, Ithaca, New York 14853-1501, Department of Chemistry, Research Institute of Basic Sciences, and BK21, Wonkwang University, Iksan 570-749, South Korea, and Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

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The electrical conductivity of an insulating crystalline oxide such as an olivine-type mineral is sensitive to subtle changes in point defect concentrations, which vary with the temperature, total pressure, and chemical potentials of the crystal components. Electrical conductivity and tracer diffusion measurements can provide useful insight into the transport properties and defect chemistry for many insulating minerals.[1−3] Olivines, $(Fe_{1-x}Mg_x)_2SiO_4$, constitute one of the most abundant minerals in the Earth's upper mantle and have been the subject of considerable interest in geophysics and mineral chemistry.[1−4] Studies on synthetic fayalite Fe_2SiO_4, the iron-rich end member of the olivine series, showed that it is a magnetic insulator.[5] The electrical conductivity of Fe_2SiO_4 measured at 1130 °C (i.e., at a geologically relevant temperature) as a function of the oxygen activity a_{O_2} exhibits a pronounced anisotropy.[6] The ratio of the electrical conductivities along the three crystallographic directions, $\sigma_b/\sigma_c/\sigma_a$, varies with oxygen activity. For example, at $a_{O_2} \approx 10^{-13}$, $\sigma_b/\sigma_c/\sigma_a \approx 1.00{:}0.93{:}0.49$ with $\sigma_b \approx 5.75 \times 10^{-2}$ S/cm, and at $a_{O_2} \approx 10^{-9.5}$, $\sigma_b/\sigma_c/\sigma_a \approx 1.00{:}0.89{:}0.64$ with $\sigma_b \approx 7.94 \times 10^{-2}$ S/cm (here the axes refer to the space group *Pnma*). As a_{O_2} is increased, the conductivities along all three directions increase gradually. At higher oxygen activities the electrical conduction of Fe_2SiO_4 arises largely from holes and is related to a trace amount of Fe^{3+} ions that provide electron hopping from their adjacent Fe^{2+} sites. The measured magnetic susceptibilities of Fe_2SiO_4 also exhibit pronounced anisotropy[7] and an antiferromagnetic ordering below 64.9 K.[8] The magnetic properties of a magnetic insulator are described in terms of spin exchange interactions, which in turn depend on hopping integrals t between adjacent spin sites.[9] The electrical conductivity arising from electron hopping also depends on hopping integrals between adjacent hopping sites.[10−12] Thus, it is of importance to explore whether or not the magnetic and electrical conductivity properties of a magnetic insulator are interrelated. We note that the poor conductivity of a magnetic insulator has been related to its superexchange.[13] In the present work we examine this relationship by considering fayalite Fe_2SiO_4 as an example.

When one type of charge carrier dominates, the electrical conductivity σ is proportional to the mobility μ of the carrier. At high temperature where the motions of the carriers can be modeled by a sequence of uncorrelated hops between adjacent sites, the mobility is proportional to the electron-transfer rate k_{ET} (i.e., $\mu \propto k_{ET}$).[10−12] In the weak coupling limit, which is valid for magnetic insulators, k_{ET} depends on the hopping integral t between adjacent sites and on the activation energy E_a as $k_{ET} \propto t^2 \exp(-E_a/k_BT)$.[10−12] Thus, for a system consisting of identical nearest neighbors, the electrical conductivity σ arising from electron hopping is related to t^2 and E_a as $\sigma \propto t^2 \exp(-E_a/k_BT)$. For a magnetic insulator, the spin exchange interaction between adjacent spin sites depends on the hopping integral as well. The spin exchange parameter J between adjacent spin sites[9] is written as $J = J_F + J_{AF}$ with $J_F = 2K$ and $J_{AF} = -(4t^2)/U_{eff}$, where K is the exchange integral between the magnetic orbitals describing the spin sites and U_{eff} is the effective on-site repulsion. Because K is a small positive number, spin exchange is ferromagnetic (i.e., $J > 0$) only when the antiferromagnetic term J_{AF} is very small in magnitude. Furthermore, for a given magnetic system consisting of identical magnetic ions, U_{eff} is constant.[9] For a system described by identical nearest-neighbor antiferromagnetic spin exchange J (<0), it is expected that $\sigma \propto t^2 \propto |J|$ if the activation energy E_a is identical for all nearest-neighbor hopping. This reasoning suggests that the electrical conductivities of a magnetic insulator are related to its spin exchange parameters. It should be noted that the spin exchange parameters J are small in magnitude because $U_{eff} \gg t^2$, and our use of J parameters is only to deduce the relative magnitudes of the t^2 values.

Fe_2SiO_4 has an orthorhombic crystal structure (space group *Pnma*) with two crystallographically nonequivalent iron

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[†] Cornell University.
[‡] Wonkwang University.
[§] North Carolina State University.

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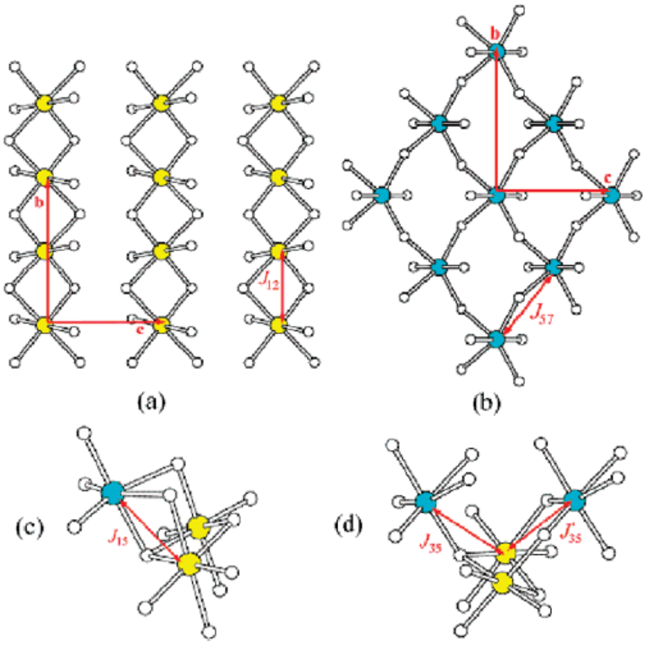

Figure 1. Spin exchange paths of Fe_2SiO_4: (a) J_{12} in the layer of edge-sharing $Fe(1)O_6$ octahedra. (b) J_{57} in the layer of corner-sharing $Fe(2)O_6$ octahedra. (c) J_{15} between edge-sharing $Fe(1)O_6$ and $Fe(2)O_6$ octahedra. (d) J_{35} and J'_{35} between corner-sharing $Fe(1)O_6$ and $Fe(2)O_6$ octahedra. The Fe(1) and Fe(2) atoms are represented by yellow and cyan circles, respectively.

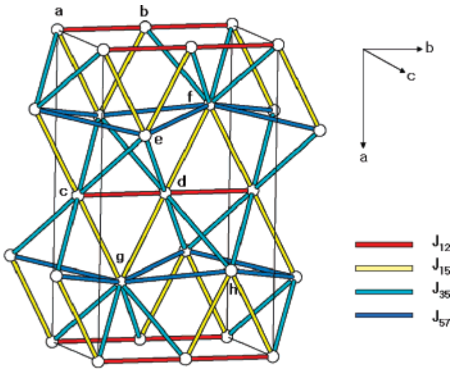

Figure 2. Three-dimensional arrangements of the Fe sites and the spin exchange paths J_{57}, J_{12}, J_{15}, and J_{35} in Fe_2SiO_4.

atoms, Fe(1) and Fe(2).[14] In the three-dimensional structure of Fe_2SiO_4, layers of chains made up of edge-sharing $Fe(1)O_6$ octahedra (Figure 1a) alternate with layers of corner-sharing $Fe(2)O_6$ octahedra (Figure 1b). The magnetic properties of Fe_2SiO_4 below room temperature have been described in terms of four superexchange parameters:[7] J_{12}, the spin exchange between two edge-sharing $Fe(1)O_6$ octahedra; J_{57}, the spin exchange between two corner-sharing $Fe(2)O_6$ octahedra; J_{15}, the spin exchange between edge-sharing $Fe(1)O_6$ and $Fe(2)O_6$ octahedra (Figure 1c); and J_{35} and J'_{35}, the spin exchanges between corner-sharing $Fe(1)O_6$ and $Fe(2)O_6$ octahedra (Figure 1d). (For simplicity, $J_{35} = J'_{35}$ will be assumed, as in ref 7.) Then, the three-dimensional arrangement of the four spin exchange paths in Fe_2SiO_4 is schematically depicted in Figure 2.

Table 1. Definitions of the Six Ordered Spin Arrangements of Fe_2SiO_4 Employed for the Evaluation of Its Spin Exchange Parameters J_{57}, J_{12}, J_{15}, and J_{35}[a]

	spins at the Fe sites							
state	a	b	c	d	e	f	g	h
FM	↑	↑	↑	↑	↑	↑	↑	↑
AF1	↑	↑	↑	↑	↑	↓	↑	↓
AF2	↑	↓	↑	↓	↑	↑	↑	↑
AF3	↑	↓	↑	↓	↑	↓	↑	↓
AF4	↑	↑	↓	↓	↑	↓	↓	↑
AF5	↑	↑	↓	↓	↓	↑	↑	↓

[a] See Figure 2 for the definition of the Fe sites a−h.

To evaluate the spin exchange parameters J_{57}, J_{12}, J_{15}, and J_{35}, we carried out first principles spin-polarized density functional theory calculations for six ordered magnetic states (FM, AF1, AF2, AF2, AF3, AF4, and AF5) for the room-temperature structure of Fe_2SiO_4 (Table 1). Our calculations employed the frozen-core projector augmented wave method[15,16] encoded in the Vienna ab initio simulation package[17] with the generalized-gradient approximation (GGA),[18] the plane-wave cutoff energy of 400 eV, and 32 *k*-points for the irreducible Brillouin zone. To properly describe the strong electron correlation in the 3d transition-metal oxide, the GGA plus on-site repulsion U method[19] was employed with $U = 4.5$ eV and $J = 0.90$ eV. In terms of the four spin exchange parameters, the total spin exchange interaction energies of the six ordered spin states are expressed as

$$\text{FM:}\quad N^2(-8J_{57} - 4J_{12} - 16J_{35} - 8J_{15})/4$$

$$\text{AF1:}\quad N^2(+8J_{57} - 4J_{12})/4$$

$$\text{AF2:}\quad N^2(-8J_{57} + 4J_{12})/4$$

$$\text{AF3:}\quad N^2(+8J_{57} + 4J_{12})/4$$

$$\text{AF4:}\quad N^2(+8J_{57} - 4J_{12} + 16J_{35} - 8J_{15})/4$$

$$\text{AF5:}\quad N^2(+8J_{57} - 4J_{12} - 16J_{35} + 8J_{15})/4$$

where N is the number of unpaired spins at each Fe^{2+} site of Fe_2SiO_4 (i.e., $N = 4$).[9,20] Thus, by equating the electronic energy differences between these states to the corresponding differences in the total spin exchange interaction energies, we obtain $J_{57} = -1.13$ meV, $J_{12} = -0.79$ meV, $J_{15} = +0.05$ meV, and $J_{35} = -0.67$ meV. In general, first principles density functional theory calculations overestimate the magnitude of a spin exchange parameter by a factor of approximately three.[9] If we take this tendency into consideration, the J_{57} and J_{12} values are in reasonable agreement, but the J_{15} and J_{35} values are not, with those deduced from the simulation of the canted moments of the Fe(1) and Fe(2) sites (i.e., $J_{57} = -0.40$ meV, $J_{12} = -0.24$ meV, $J_{15} = -0.17$ meV, $J_{35} = -0.53$ meV).[7] Nevertheless, our discus-

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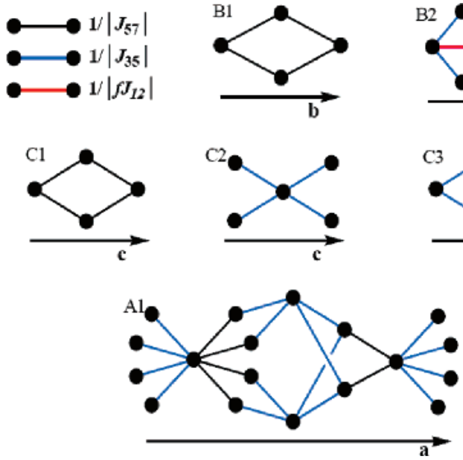

Figure 3. Series of electron-hopping paths (in a repeat unit cell) relevant for the electron conduction of Fe_2SiO_4 when the electric field is applied along the three crystallographic directions.

sion requires only the relative values of the spin exchange parameters (see below). Spin exchange parameters deduced experimentally depend on model Hamiltonians used for simulation analysis, so the resulting spin exchange parameters are not necessarily consistent with the electronic structure of a system under examination.[9] Thus, for the discussion of the anisotropic electrical conductivities of Fe_2SiO_4 at sufficiently high oxygen activities, the spin exchange parameters estimated from our calculations will be employed.

When the electric field is applied along a certain direction of a magnetic insulator, the hopping paths most relevant for the electrical conduction are those made up of the nearest-neighbor hopping paths that deviate least from the field direction. Thus, according to the spin exchange paths shown in Figure 2, the relevant hopping paths for the hopping electrical conduction along the *b*-, *c*-, and *a*-directions of Fe_2SiO_4 are those depicted in Figure 3, respectively. There are two B1 and two B2 paths per unit cell along the *b*-direction, two C1, two C2, and two C3 paths per unit cell along the *c*-direction, and one A1 path per unit cell along the *a*-direction. These hopping paths are different and nonuniform. In evaluating the contributions of these paths to electrical conductivity, it is reasonable to assume that each nearest-neighbor hopping path with antiferromagnetic spin exchange J gives rise to resistance that is proportional to $1/|J|$. Then, the total resistance R_i associated with a series of hopping paths i (i.e., i = B1, B2, C1, C2, C3, and A1 in Figure 3) covering one unit cell length can be estimated on the basis of Ohm's law[21] by using the antiferromagnetic spin exchange parameters J_{57}, J_{12}, and J_{35}. The spin exchange J_{15} can be neglected because it is ferromagnetic so that its contribution to electron hopping should be negligible. In the hopping path A1, there occur two Y-type loads consisting of one J_{57} and two J_{35} spin exchanges. In the evaluation of R_{A1}, it is necessary to first transform the Y-type loads into the corresponding Δ-type loads.[21] Let R_b, R_c, and R_a refer to the total resistance per unit cell along the *b*-, *c*-, and *a*-directions, respectively. Then, $1/R_b = 2/R_{B1} + 2/R_{B2}$, $1/R_c = 2/R_{C1} + 2/R_{C2} + 2/R_{C3}$, and $R_a = R_{A1}$.

Given that the structure of Fe_2SiO_4 is orthorhombic, the resistivity ratio along the three directions $\rho_b/\rho_c/\rho_a$ is given by (acR_b/b):(abR_c/c):(bcR_a/a) so that the conductivity ratio $\sigma_b/\sigma_c/\sigma_a$ is then related to R_b, R_c, and R_a as $\sigma_b/\sigma_c/\sigma_a = (b/acR_b)$:$(c/abR_c)$:$(a/bcR_a)$. In evaluating the relative R_b, R_c, and R_a values, it is important to note that the spin exchange J_{12} takes place through edge-sharing, whereas the spin exchanges J_{57} and J_{35} take place through corner-sharing. Thus, the vibrational modes associated with J_{12} would be stiffer than those associated with J_{57} and J_{35} so that the activation energy E_a for hopping should be greater for the path J_{12} than for the paths J_{57} and J_{35}. Therefore, we introduce a reduction factor f for the hopping path J_{12}. As a result of the exponential dependence of σ on E_a, that is, $E_a \propto \exp(-E_a/k_BT)$, the value of f can be very small. The calculated conductivity ratio $\sigma_b/\sigma_c/\sigma_a$ is 1.00:0.66:0.29 for $f = 1$, which deviates considerably from the experimental ratio 1.00:0.89:0.64 at $a_{O2} \approx 10^{-9.5}$ (at the highest oxygen activity investigated where hole conduction dominates). However, the calculated ratio becomes reasonably close to the experimental one for small f values, for example, 1.00:0.82:0.36 for $f = 1/10$ and 1.00:0.84:0.37 for $f = 1/100$. Our study shows that the anisotropic electrical conductivities of a magnetic insulator can be predicted reasonably well in terms of its spin exchange interactions.

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