SPIN TRANSITIONS IN IRON

Ctirad Matyska and Jakub Velímský

Department of Geophysics
Faculty of Mathematics and Physics
Charles University in Prague

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Outline

Quantum chemistry revisited (JV)

Iron in Lower Mantle Minerals (JV)

Fairy-tale I: What are the spin transitions? (CM)

Fairy-tale II: Changes of physical properties in the lower-mantle minerals? (CM)

Geodynamic story:
    Radiative transfer of heat at the bottom of the mantle? (CM)
    Other "asthenospheres" in the lower mantle? (CM)
    A viscosity hill in the lower mantle? (CM)
    A conductivity decrease in the lower mantle? (JV)

Hydrogen atom

- time-independent Schrödinger's equation

$$
\begin{aligned}
\hat{H}\psi(\boldsymbol{r}) &= E\psi(\boldsymbol{r}) \\
E_{nlm_s} &= \frac{-13.6\,\text{eV}}{n^2}\left[1 + \frac{\alpha}{n^2}\left(\frac{n}{l+m_s+\frac{1}{2}} - \frac{3}{4}\right)\right] \\
\psi_{nlm}(r,\vartheta,\varphi) &= N_{nl}\,\mathrm{e}^{-\frac{\rho}{2}}\rho^l L_{n-l-1}^{2l+1}(\rho)\,Y_{lm}(\vartheta,\varphi)
\end{aligned}
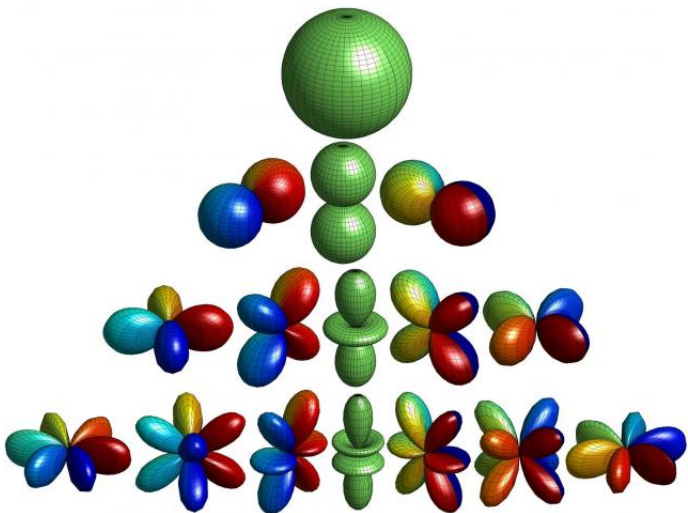$$

where quantum numbers are:
principal, $n = 1, 2, \ldots$
azimuthal, $l = 0, 1, \ldots, n-1 = s, p, d, f, \ldots$
magnetic, $m = -l, \ldots, l$
spin, $m_s = \pm\frac{1}{2}$

Hydrogen atom

http://zoi.utia.cas.cz/files/images/spherical_harmonics.preview.jpg
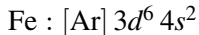
Electron configuration of atoms

- ▶ the Schrödinger equation is complicated by mutual interaction of electrons
- ▶ Pauli's exclusion principle: no two e^- can occupy the same quantum state simultaneously
- ▶ Hund's rule of maximum multiplicity: if two or more orbitals of equal energy are available, electrons will occupy them singly before filling them in pairs (eqv. greater total spin makes atom more stable)
- ▶ Madelung-Klechkovsky rule: orbits are filled in the order of increasing $(n + l, n)$
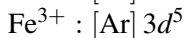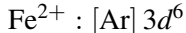

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f ...
6s 6p 6d ... ...
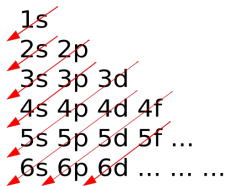
http://en.wikipedia.org/wiki/File:Klechkovski_rule.svg

Transition metals

- transition-metal ions have incomplete d-subshell:
  Fe : $[Ar]\, 3d^6\, 4s^2$
- during ionization, e^- are removed from the valence-shell s-orbitals before the d-orbitals
 Fe^{2+} : $[Ar]\, 3d^6$
  Fe^{3+} : $[Ar]\, 3d^5$
- transition metals usually have two or more oxidation states differing by 1

Crystal Field Theory Assumptions

- focuses on d-orbitals
- ionic bonding due to electrostatic interaction between metal and ligands (no covalent bond)
- ligands treated as negative point charges
- repulsion between the lone electron pair of the ligand and d-orbital electrons of the metal
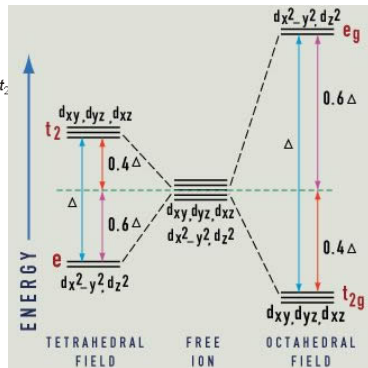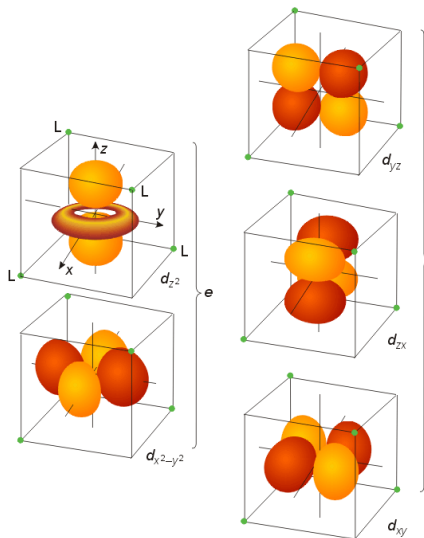
Crystal Field Theory for Octahedral Complexes

http://faculty.uml.edu/ndeluca/84.334/topics/topic6.htm
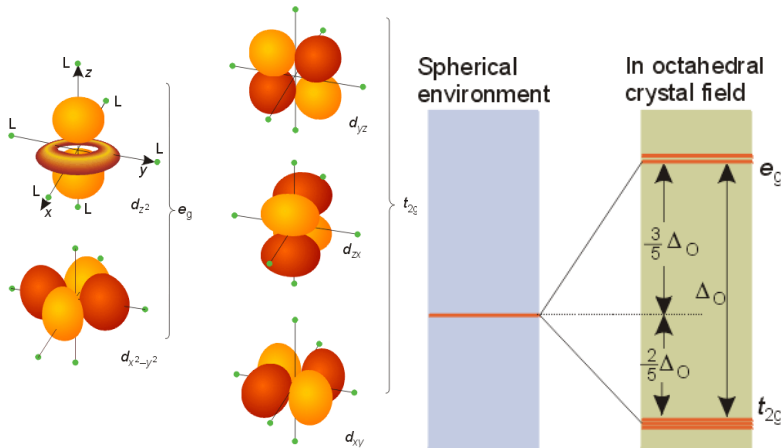
e_g: e — 2 orbitals, *gerade* — central symmetry
t_{2g}: t — 3 orbitals, *2* — asymmetry w.r.t. C_2 axis

Crystal Field Theory for Tetrahedral Complexes
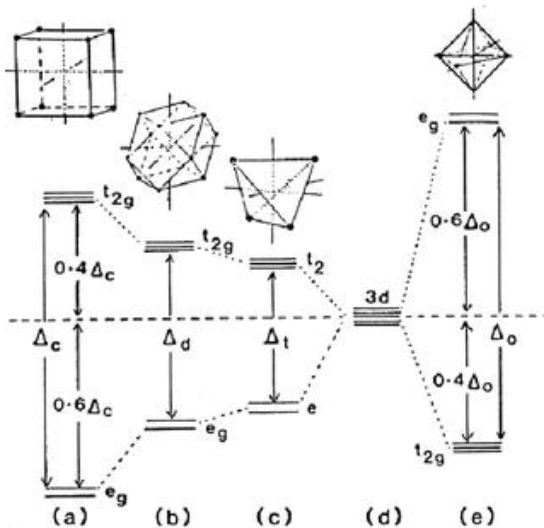

http://faculty.uml.edu/ndeluca/84.334/topics/topic6.htm,
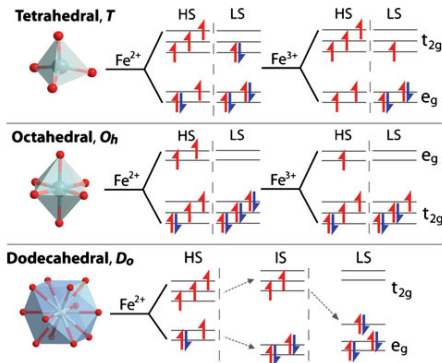http://www.webexhibits.org/causesofcolor/6AA.html

Crystal Field Theory — Summary

Ganguly (2008)

Iron in Lower Mantle Minerals

Fig. 3 Crystal field splitting diagrams for iron in tetrahedral, octahedral, and dodecahedral sites in the lower-mantle minerals. Iron is shown as a (2+) or (3+) cation in high-spin, intermediate-spin (dodecahedral site), and low-spin electronic configurations. The crystal field splitting energy (CFSE) can be altered by pressure, temperature, and/or composition. The energy of the e_g orbitals (those which are oriented towards the ligands) is heightened by increased repulsion due to shortened e_g orbital-ligand distance during pressure-induced unit cell distortion, resulting in an overall larger CFSE. When the CFSE surpasses the spin-pairing energy, the spin-pairing transition of $3d$ electrons is more favorable than jumping the energy gap to achieve aligned spins. For example, the low-spin state with all six $3d$ electrons paired ($S = 0$) in Fe^{2+} occurs at high pressures in the lower-mantle ferropericlase

Lin & Wheat (2011)

Effect of Spin Transition on Electrical Conductivity

Electrical conductivity of the lower-mantle ferropericlase across the electronic spin transition

Jung-Fu Lin,[1] Samuel T. Weir,[1] Damon D. Jackson,[1] William J. Evans,[1] Yogesh K. Vohra,[2] Wei Qiu,[2] and Choong-Shik Yoo[1]

[1] Electrical conductivity of the lower-mantle ferropericlase-$(Mg_{0.75},Fe_{0.25})O$ has been studied using designer diamond anvils to pressures over one megabar and temperatures up to 500 K. The electrical conductivity of $(Mg_{0.75},Fe_{0.25})O$ gradually rises by an order of magnitude up to 50 GPa but decreases by a factor of approximately three between 50 to 70 GPa. This decrease in the electrical conductivity is attributed to the isosymmetric high-spin to low-spin transition of iron in ferropericlase. That is, the electronic spin transition of iron results in a decrease in the mobility and/or density of the charge transfer carriers in the low-spin ferropericlase. The activation energy of the low-spin ferropericlase is 0.27 eV at 101 GPa, consistent with the small polaron conduction (electronic hopping, charge transfer). Our results indicate that low-spin ferropericlase exhibits lower electrical conductivity than high-spin ferropericlase, which needs to be considered in future geomagnetic models for the lower mantle.

Citation: Lin, J.-F., S. T. Weir, D. D. Jackson, W. J. Evans, Y. K. Vohra, W. Qiu, and C.-S. Yoo (2007), Electrical conductivity of the lower-mantle ferropericlase across the electronic spin transition, *Geophys. Res. Lett.*, *34*, L16305, doi:10.1029/

Brodholt, 2000a]. These studies showed that the electrical conductivity of ferropericlase is very sensitive to the iron content, ferrous to ferric iron ratio, and point defects. However, the electrical conductivity of the low-spin ferropericlase has not been measured and the potential effect of the recently observed pressure-induced electronic spin-pairing transition of iron on the electrical conductivity of ferropericlase is still unknown [e.g., *Badro et al.*, 2003; *Lin et al.*, 2005, 2006a, 2006b, 2007; *Speziale et al.*, 2005; *Goncharov et al.*, 2006; *Persson et al.*, 2006; *Tsuchiya et al.*, 2006; *Keppler et al.*, 2007].

[4] Ferropericlase is a solid solution between periclase (MgO), a wide band gap insulator, and wüstite (FeO), a classical Mott insulator and an important member of the highly correlated transition metal monoxide (TMO) group [*Mott*, 1990; *Cohen et al.*, 1997]. The Mott insulator-metal transition results from the closure of the Mott-Hubbard *d-d* band gap or of the charge-transfer *p-d* gap, and has been theoretically and/or experimentally reported to occur in transition metal oxides such as FeO [*Cohen et al.*, 1997; *Knittle and Jeanloz*, 1986], MnO [*Patterson et al.*, 2004; *Yoo et al.*, 2005], and Fe_2O_3 [*Pasternak et al.*, 1999]. In this

Effect of Spin Transition on Electrical Conductivity
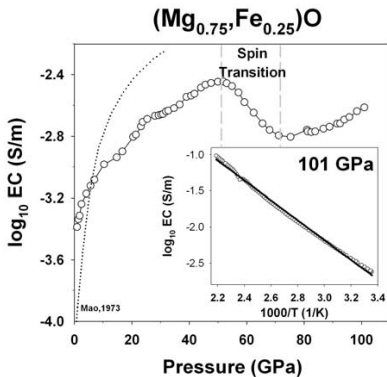
Figure 2. Electrical conductivities of $(Mg_{0.75},Fe_{0.25})O$ as a function of pressure obtained from a six-probe designer anvil cell. The conductivity increases by an order of magnitude up to 50 GPa but drops by a factor of approximately three from 50 to 70 GPa. Dotted line: electrical conductivities of $(Mg_{0.78},Fe_{0.22})O$ at high pressures [*Mao*, 1973]. Insert, electrical conductivities of $(Mg_{0.75},Fe_{0.25})O$ plotted against absolute reciprocal temperature at 101 GPa. Open circles: experimental data; solid line: fit to the Ahrenius equation.

Effect of Spin Transition on Electrical Conductivity

Electrical conductivities of pyrolitic mantle and MORB materials up to the lowermost mantle conditions

Kenji Ohta [a,*], Kei Hirose [a,b], Masahiro Ichiki [a], Katsuya Shimizu [c], Nagayoshi Sata [b], Yasuo Ohishi [d]

[a] Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, Tokyo 152-8551, Japan
[b] Institute for Research on Earth Evolution, Japan Agency for Marine-Earth Science and Technology, 2-15 Natsushima-cho, Yokosuka, Kanagawa 237-0061, Japan
[c] Center for Quantum Science and Technology under Extreme Conditions, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan
[d] Japan Synchrotron Radiation Research Institute, 1-1-1 Koto, Sayo, Hyogo 679-5198, Japan

A B S T R A C T

The electrical conductivities of natural pyrolitic mantle and MORB materials were measured at high pressure and temperature covering the entire lower mantle conditions up to 133 GPa and 2650 K. In contrast to the previous laboratory-based models, our data demonstrate that the conductivity of pyrolite does not increase monotonically but varies dramatically with depth in the lower mantle; it drops due to high-spin to low-spin transition of iron in both perovskite and ferropericlase in the mid-lower mantle and increases sharply across the perovskite to post-perovskite phase transition at the D″ layer. We also found that the MORB exhibits much higher conductivity than pyrolite. The depth–conductivity profile measured for pyrolite does not match the geomagnetic field data below about 1500-km depth, possibly suggesting the existence of large quantities of subducted MORB crust in the deep lower mantle. The observations of geomagnetic jerks suggest that the electrical conductivity may be laterally heterogeneous in the lowermost mantle with high anomaly underneath Africa and the Pacific, the same regions as large low shear-wave velocity provinces. Such conductivity and shear-wave speed anomalies are also possibly caused by the deep subduction and accumulation of dense MORB crust above the core–mantle boundary.
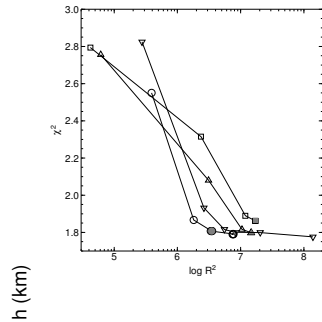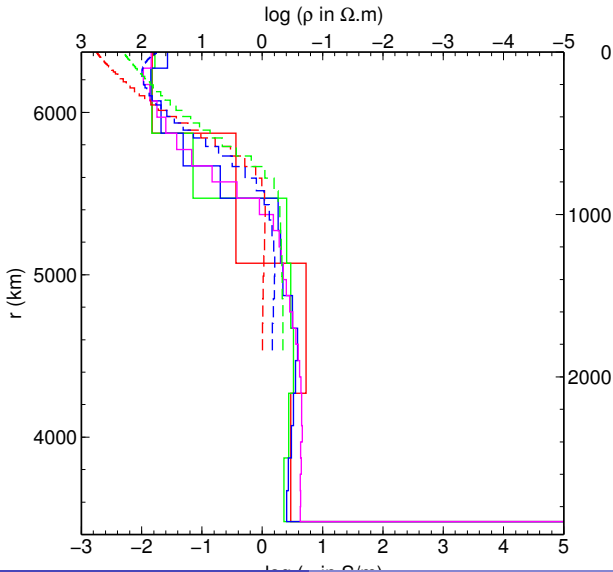
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Effect of Spin Transition on Electrical Conductivity
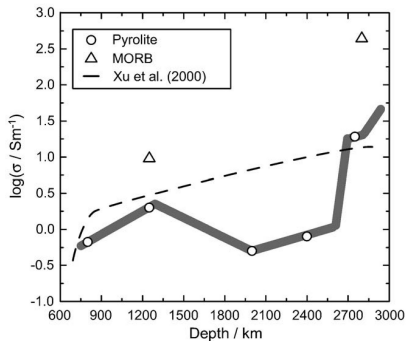
1-D inversion of CHAMP satellite data

Results

1-D inversion of CHAMP satellite data

Results