Electrical conductivity of Iron under Earth core conditions using time-dependent density functional theory

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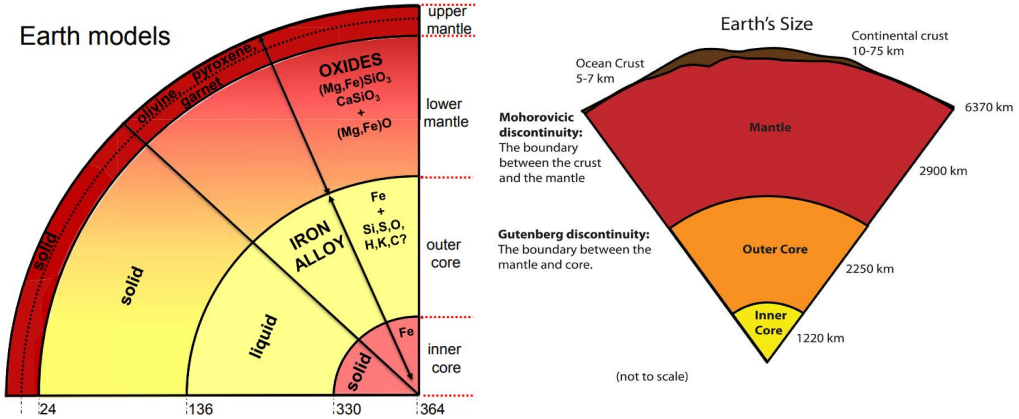
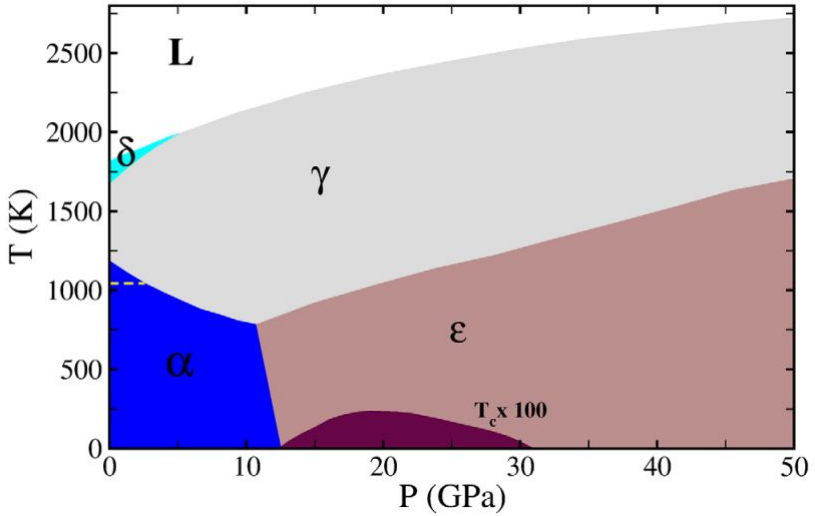
Earth core

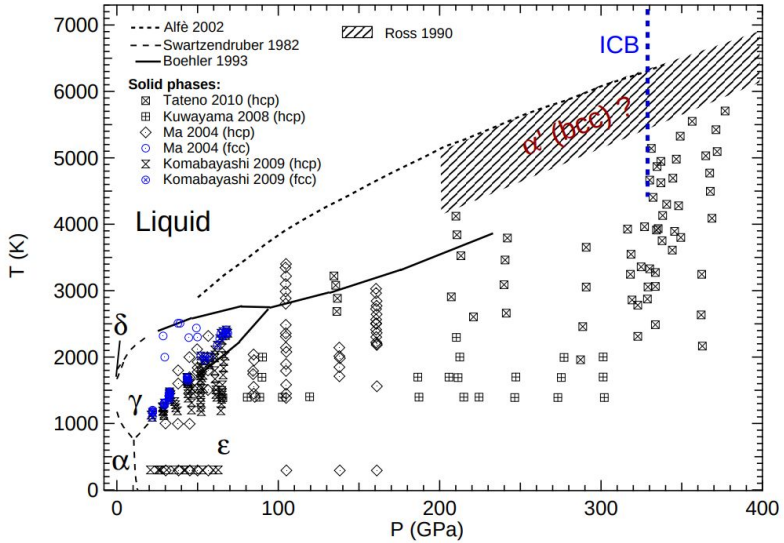


- The outer core, about 2200 kilometers thick, is mostly composed of liquid iron and nickel. The Ni-Fe alloy of the outer core is very hot, between 4800 and 5800 K.
- The inner core is a hot, dense ball of (mostly) iron. It has a radius of about 1220 kilometers. Temperature in the inner core is about 5500 K. The pressure is nearly 360 GPa.
- Earth's magnetic field is crucial to life on our planet. Although Earth's magnetic field is generally stable, it fluctuates constantly. As the liquid outer core moves, for instance, it can change the location of the magnetic north and south poles.
- Electrical and thermal conductivity calculations are of great importance for understanding the geophysical dynamics of the earth. This is important for the understanding of the heat flux in the earth's core and the production of magnetic field through the dynamo action.

Nationalgeographic.org; Simone Anzellini - PhD thesis, Université Pierre et Marie Curie; Labrosse et al. Physics of the Earth and Planetary Interiors 140, 127-143 (2003); Konôpkova et al. Nature 534, 95-98 (2016)

Iron phase diagram





- Geophysically relevant pressure-temperature regime of the Earth's inner core corresponding to the extreme pressure of 360 GPa combined with temperatures up to 6000 K.
- Phases: - α - BCC, ε - HCP, γ - FCC , δ - BCC, α' - BCC?, L - Liquid.

L. V. Pourovskii J. Phys.: Condens. Matter 31 373001 (2019); Simone Anzellini - PhD thesis, Université Pierre et Marie Curie

Linear response theory

- The linear response of the electronic system to an external, time-dependent perturbation *δv* is given in Fourier space by

$$n_{ind}(q,\omega) = \chi(q,\omega)\delta v(q,\omega)$$

- Compute density-density response function χ(q,ω). Frequently using Kubo-Greenwood formalism, lately using linear-response and real-time TDDFT

$$\frac{1}{\epsilon(q,\omega)} = 1 + \frac{4\pi}{q^2}\chi(q,\omega)$$

- Compute dynamical electrical conductivity

$$Re[\epsilon(\omega)] = 1 - \frac{1}{\epsilon_0\omega} Im[\sigma(\omega)]$$

$$Im[\epsilon(\omega)] = \frac{1}{\epsilon_0\omega} Re[\sigma(\omega)]$$

- Compute DC conductivity (ω=0) using Drude fit

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau}$$

Linear-response TDDFT

- Solving a set of Kohn-Sham equations for the KS orbitals

$$\left[-\frac{1}{2}\nabla_k^2 + V_{\rm S}(\boldsymbol{r})\right]\phi_k(\boldsymbol{r}) = \epsilon_k\phi_k(\boldsymbol{r})$$

- Evaluate Kohn-Sham density-density response function

$$\chi_{\mathcal{G}\mathcal{G}'}(\boldsymbol{q},\omega) = \frac{\chi^{KS}_{\mathcal{G}\mathcal{G}'}(\boldsymbol{q},\omega)}{1-\left[V(\boldsymbol{q}) + f_{\rm XC}(\boldsymbol{q},\omega)\right]\chi^{KS}_{\mathcal{G}\mathcal{G}'}(\boldsymbol{q},\omega)}$$

$$\chi^{KS}_{\mathcal{G}\mathcal{G}'}(\boldsymbol{q},\omega) = -\frac{1}{V}\lim_{\eta\to 0^+}\sum_{nm;\boldsymbol{k}}\left[f_{m;\boldsymbol{k}+\boldsymbol{q}}(T) - f_{n;\boldsymbol{k}}(T)\right] \times \frac{\langle\psi_{m;\boldsymbol{k}+\boldsymbol{q}}|e^{i(\boldsymbol{q}+\mathcal{G})\boldsymbol{r}}|\psi_{n;\boldsymbol{k}}\rangle\langle\psi_{n;\boldsymbol{k}}|e^{-i(\boldsymbol{q}+\mathcal{G}')\boldsymbol{r}'}|\psi_{m;\boldsymbol{k}+\boldsymbol{q}}\rangle}{\omega - \epsilon_{m;\boldsymbol{k}+\boldsymbol{q}} + \epsilon_{n;\boldsymbol{k}} + i\eta}$$

- $f_{XC}(\mathbf{q}, \omega)$ is the exchange-correlation kernel: Adiabatic LDA (ALDA) commonly used

$$f_{\rm XC}(\boldsymbol{q},\omega) = \chi^{KS^{-1}}(\boldsymbol{q},\omega) - \chi^{-1}(\mathbf{q},\omega) - v(\boldsymbol{q})$$

Kubo-Greenwood formula

- The summation over the matrix elements of the Kohn-Sham orbitals with the velocity operator weighted with the difference of the Fermi occupation numbers is performed over all ***N*** bands and ***k***-points.

$$\Re\left[\sigma(\omega)\right] = \frac{2\pi e^2}{3\omega\Omega}\sum_{i,j}^{N}(f_i - f_j)|\langle i|\hat{v}|j\rangle|^2\delta(\epsilon_j - \epsilon_i - \hbar\omega)$$

Ramakrishna et al. PRB 103, 125118 (2021); Graziani et al. Frontiers and challenges in warm dense matter Springer (2014)

Baczewski et al. PRL 116, 115004 (2016); Andrade et al. Eur. Phys. J. B (2018) 91: 229

Real-time TDDFT

- Apply an external electric field ***E***(t) and follow the response of the system with the time evolution of the current density ***j***(t)

$$\vec{j}(\omega) = \sigma(\omega)\vec{E}(\omega) \qquad \mathbf{j}(\mathbf{r},t) = \Im\left[\sum_i^N \phi_i^*(\mathbf{r},t)\nabla\phi_i(\mathbf{r},t)\right] + \frac{1}{c}n(\mathbf{r},t)\,A_{KS}(\mathbf{r},t) \qquad A_{KS}(\mathbf{r},t) = A_{ext}(\mathbf{r},t) + A_{em}(\mathbf{r},t) + A_{xc}(\mathbf{r},t)$$

- LR-TDDFT requires matrix diagonalization of occupied and unoccupied orbitals, RT-TDDFT stems from the direct propagation of the occupied states and is computationally faster.

- Solve Time-dependent Kohn-Sham equation

$$\hat{H}(r,t) = \tfrac{1}{2}\left(-i\nabla + \tfrac{1}{c}A(t)\right)^2 + V_{KS}(r,t)$$

$$\hat{H}(r,t)\phi_{n,k}(r,t) = i\frac{\partial}{\partial t}\phi_{n,k}(r,t)$$

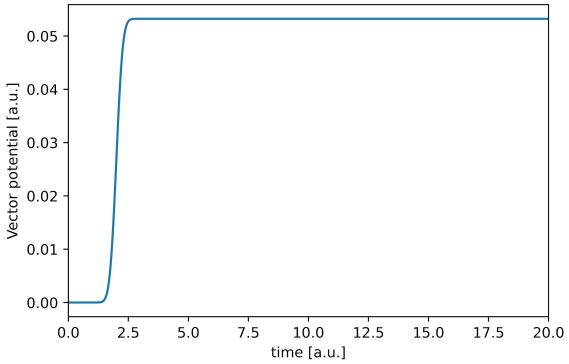
- Fourier transform to obtain the frequency dependent conductivity tensor

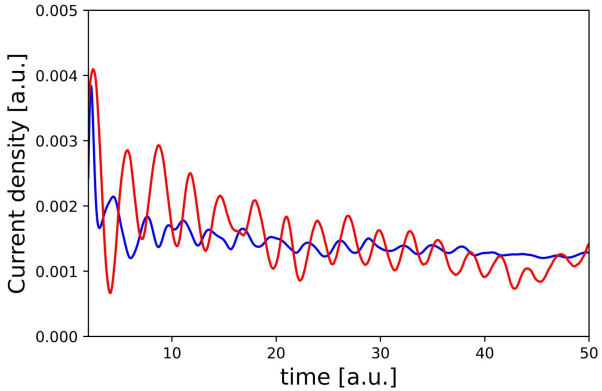
$$\sigma_{ab}(\omega) = \frac{\int \vec{j}_a(t)e^{i\omega t}dt}{\int \vec{E}_b(t)e^{i\omega t}dt} = \frac{\vec{j}_a(\omega)}{\vec{E}_b(\omega)}$$

Takimoto et al. JCP 127, 154114 (2007)

Real-time TDDFT - Ambient Iron

- Sigmoidal pulse in the Z direction of vector amplitude 0.1 a.u. with a time step=0.02 a.u. (1 a.u. = 24.19 Attoseconds) for a total simulation time up to 100 a.u. giving an energy resolution ~0.3 eV. Calculations are performed with a modified implementation of the Elk code.
- 24x24x24 *k*-points, 60 bands per atom.
- Comparison with a recently implemented feature by the developers of the Exciting (plane wave code similar to Elk). Instead, a delta kick is applied in the Z direction with an amplitude 0.1 a.u., time step=0.02 a.u.

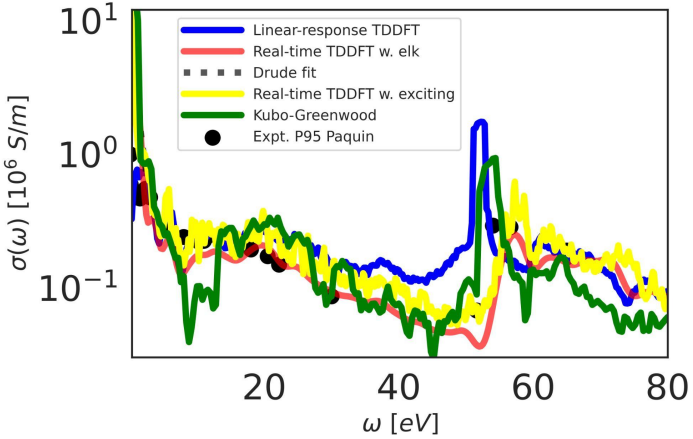


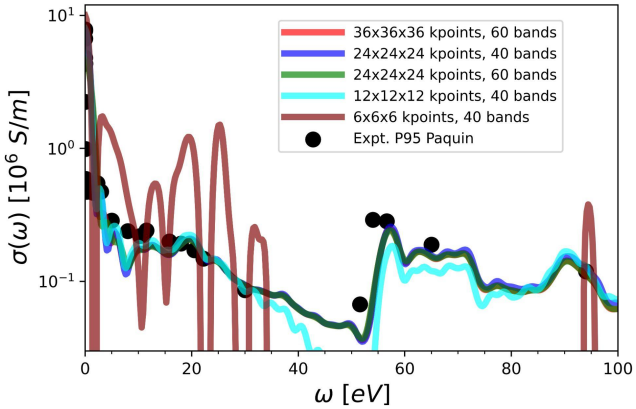


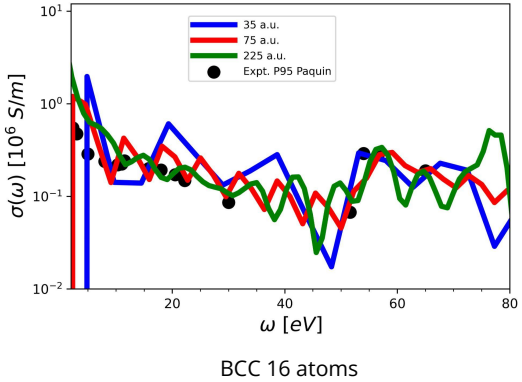
J.K. Dewhurst et al. ELK FP-LAPW code (2021); Pela et al. arXiv:2102.02630 (2021)

Real-time TDDFT - Ambient Iron

- In comparison with experimental results, RT-TDDFT is in good agreement. Additionally LR-TDDFT and Kubo-Greenwood are also compared.
- Due to the BCC symmetry, it is sufficient to evaluate the conductivity tensor by applying an electric field in a specific direction (in this case along Z) and thereby evaluating the conductivity tensor σ_{zz}.
- Convergence is achieved with sufficient number of *k*-points, bands and duration of the time-propagation.





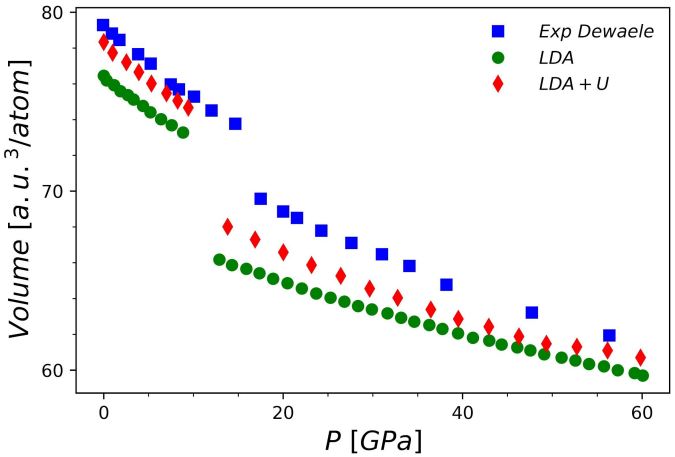


BCC 16 atoms

J.K. Dewhurst et al. ELK FP-LAPW code (2021); Pela et al. arXiv:2102.02630 (2021); R. A. Paquin - Handbook of optics, Volume II (1995)

Real-time TDDFT - Compressed Iron

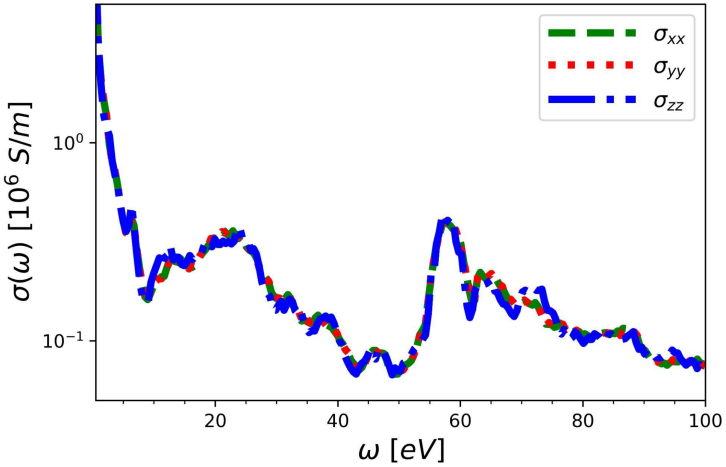
- Phase change around 10-20 GPa from α (bcc) to ε (hcp) phase.
- Electronic correlations in ε phase could be important for pressure range up to 60 GPa and at geophysically relevant region of pressure about 360 GPa and temperature of about 6000 K.
- DFT+U as on-site Coulomb interactions are particularly strong for localized *d* electrons. Fixed U=4.3 eV, J_H=1 eV for ε iron improves the Equation of state (EOS). Expensive to evaluate U systematically for independent configurations.

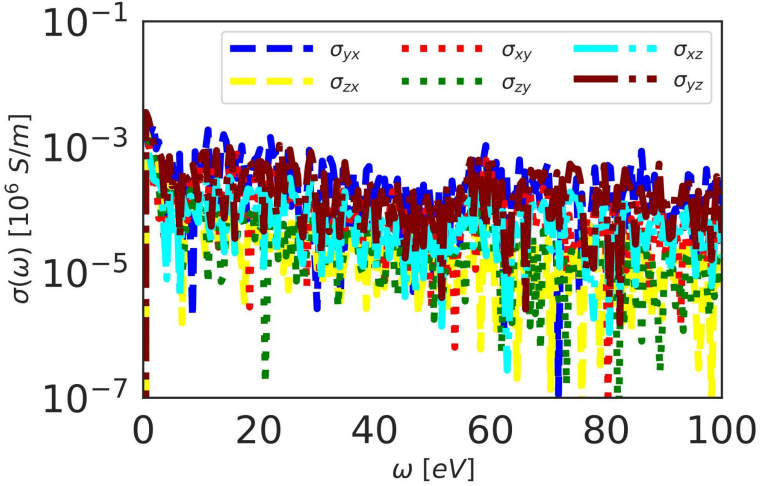


L. V Pourovskii J. Phys.: Condens. Matter 31 373001 (2019); Miyake et al. PRB 80, 155134 (2009); L. V. Pourovskii et al. PRB 87, 115130 (2013); Dewaele et al. PRL 97, 215504 (2006)

Real-time TDDFT - Compressed Iron

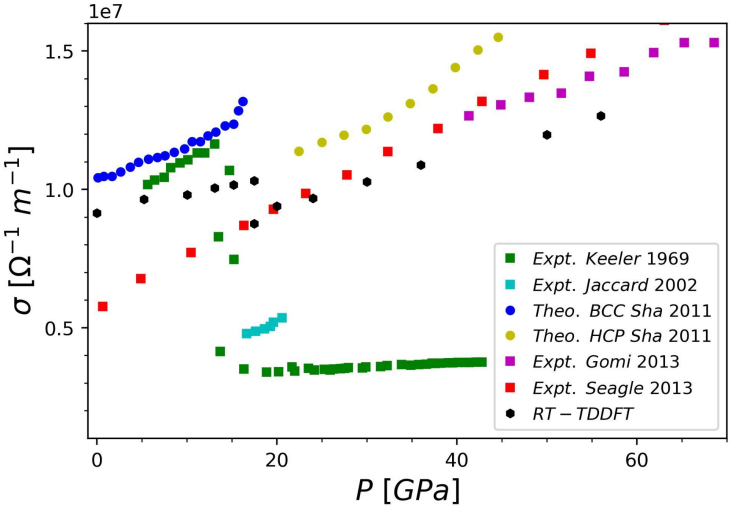
- For an HCP lattice (a=b≠c), only the diagonal conductivity tensor components are considered and the rest can be ignored.





Real-time TDDFT - Compressed Iron

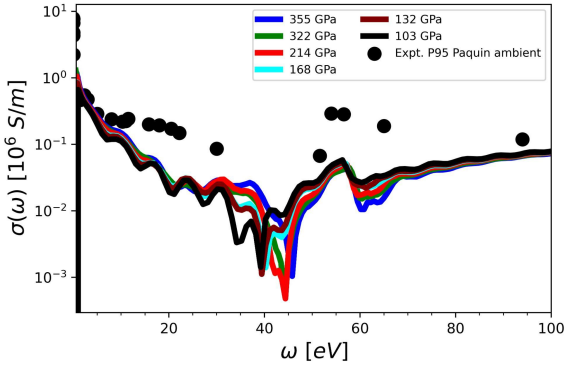
- Drop in DC conductivity during the phase transition from α (bcc) to ε (hcp) phase.

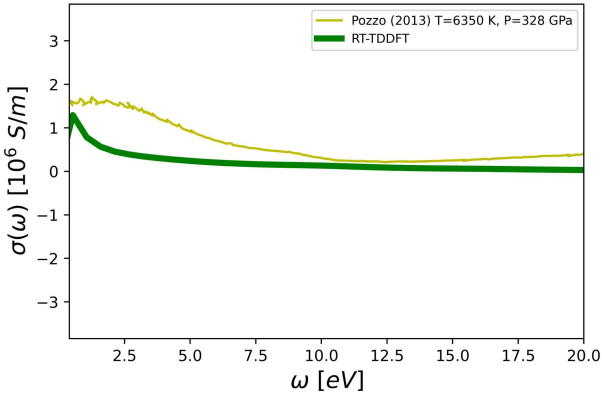


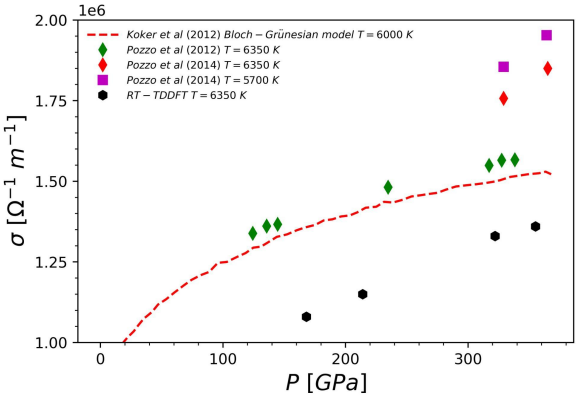
Sha - J. Phys.: Condens. Matter 23 075401 (2011), Keeler- Solid state communications 7, 271-274 (1969), Gomi - Physics of the Earth and Planetary Interiors 224 88-103 (2013), Seagle - Geo. Research Letters 40 5777-5381 (2013), Jaccard - Phys. Letters A 299 282-286 (2002)

Real-time TDDFT - Inner core boundary conditions

- Results at T=6350 K show DC conductivity increases with pressure.
- Comparison only possible with other theoretical data obtained using Kubo-Greenwood at these conditions. The electrical conductivity is in the range previously reported by Pozzo and Koker et al. for similar conditions.







Pozzo et al. PRB 87, 014110 (2013); Koker et al PNAS 109, 4070 (2012)

Summary

- The knowledge of the phase diagram and melting curve of iron up to the inner core boundary conditions are of fundamental importance in geophysics and planetary science.

- Real-time TDDFT is capable of describing the natural decay of current in metals, and obtain the frequency dependent conductivity along with the DC value.

- Computationally inexpensive compared to LR-TDDFT and is a suitable alternative to other *ab-initio* methods.