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Spin crossover and Mott–Hubbard transition under high pressure and high temperature in the low mantle of the Earth

S G Ovchinnikov[1], T M Ovchinnikova[2], V V Plotkin[3] and P G Dyad'kov[3]

[1] **Kirensky Institute of Physics of the Siberian Branch of the Russian Academy of Sciences, Akademgorodok 50 Bldg 38, Krasnoyarsk 660036, Russia**
[2] **Sukhachev Institute of Forest of the Siberian Branch of the Russian Academy of Sciences, Akademgorodok 50 Bldg 28, Krasnoyarsk 660036, Russia**
[3] **Trofimuk Institute of Petroleum-Gas Geology and Geophysics of the Siberian Branch of the Russian Academy of Sciences, Academician Koptyug Avenue 3, Novosibirsk 630090, Russia**

E-mail: sgo@iph.krasn.ru

Abstract. **E ect of high pressure induced spin crossover on the magnetic, electronic and structural properties of the minerals forming the Earth's low mantle is discussed. The low temperature P, T phase diagram of ferropericlase has the quantum phase transition point $P_c = 56$ GPa at $T = 0$ confirmed recently by the synchrotron Mössbauer spectroscopy. The LDA+GTB calculated phase diagram describes the experimental data. Its extension to the high temperature resulted earlier in prediction of the metallic properties of the Earth's mantle at the depth 1400 km $< h <$ 1800 km. Estimation of the electrical conductivity based on the percolation theory is given. We discuss also the thermodynamic properties and structural anomalies resulting from the spin crossover and metal–insulator transition and compare them with the experimental seismic and geomagnetic field data.**

1. Introduction

The lower mantle extends from 660 km to 2900 km with pressure increase from 24 GPa to 135 GPa and temperature increase from 2070 K to 2750 K [1,2]. The electrical conductivity is one of the important physical properties of the Earth's mantle [2]. The lower mantle consists of 79% Mg-perovskite $Mg_{0.9}Fe_{0.1}SiO_3$, 16% ferropericlase $Mg_{1-x}Fe_xO$ ($x = 0.17$–0.20), and 5% $CaSiO_3$ perovskite in volume, and the electrical conductivity occurs through iron-bearing phases. At normal conditions, all of them are insulators. At pressures of the lower mantle the Mott–Hubbard insulator-metal transition can be expected for the iron oxides [3]. The alternative and competing effect under high pressure is the spin crossover of each iron ion from the high spin (HS) to the low spin (LS) configuration [4]. Two main components of the low mantle are strongly different in the iron concentration. In the dominant Mg-perovskite it is below the percolation threshold (0.148 in three-dimensional materials [5]), while for the ferropericlase it is above the threshold. One may consider the ferropericlase as a random mixture of MgO and FeO, the metallic or magnetic state of the FeO component will be induced to the whole mixture according to the percolation theory when the FeO concentration is above the threshold. It is not

true for the Mg-perovskite. Indeed, the laboratory measurements of the electrical conductivity of the Mg-perovskite have revealed the quantitative change of the resistivity with stable insulator state under high pressure up to 143 GPa [6]. Moreover, the conducting or magnetic state of the ferropericlase will result in the conductivity and magnetism of the low mantle being the random mixture of the ferropericlase and the Mg-perovskite with the ferropericlase bulk concentration above the percolation threshold. Of course, any magnetic order cannot survive at typical for the low mantle temperature 2000 K, that is why we will discuss below only electrical properties. The Mott–Hubbard transition from insulator to metal for FeO under high pressure has been studied both theoretically and experimentally by many groups, see the review [4], the recent LDA+DMFT calculations [7] and the resistivity measurements [8]. The Mott–Hubbard transition results from competition of the intra-atomic Coulomb interaction U and the kinetic energy given by the electronic bandwidth $2W$. Under compression U is constant while W increasing. The insulator state at ambient pressure $P = 0$ with $U > W$ finally changes to the metallic one at critical pressure P_{MH} when $U = W(P_{MH})$. The HS/LS spin crossover under high-pressure results from competition between the intra-atomic Hund exchange interaction J and the crystal field $10Dq$ that increases with P. Thus the HS term (for Fe^{2+} in d^6 configuration it has $S = 2$) for individual atom and ion in a weak crystal field is changing to the LS term ($S = 0$) at pressure P_c when $10Dq(P_c) \sim J$, it has been shown long ago [9]. The spin crossover induces the pressure dependent effective Hubbard U [10]. It was found that $U_{eff}(P)$ dependence is not universal for different ionic configurations, it decreases for d^5 and increases for d^6 ions [11]. In ferropericlase the spin crossover under high pressure has been observed by X-ray emission spectroscopy [12]. Thus for ferropericlase the Mott–Hubbard transition may occur in the HS insulator state at $P = P_{MH}$ to the HS metal state that further transforms into the LS insulator state at $P = P_c$, $P_c > P_{MH}$ [13]. The geophysical consequence of these insulator–metal–insulator transitions is the metallization of the Earth's low mantle in the depth interval $\sim$ 1400–1800 km [14].

In the papers [13,14] we have considered the multielectron ions with electronic/spin properties and neglected the lattice properties. Due to the large ionic radii difference for the HS and LS states (about 10%) the unit cell volume of these two states also differs. The importance of lattice degrees of freedom for the spin crossover has been discussed earlier [15,16]. In this paper, we discuss two topics: 1) the thermodynamic properties and volume anomalies resulting from the spin crossover; 2) the electrical conductivity value in the mantle close to the percolation threshold. We have shown that the anomaly of the bulk modulus is determined by the maximal change of the HS/LS concentration and takes place at the depth where the smooth metal–insulator and spin crossovers occur. At the same depth the anomalies of the seismic velocities and gradients have been revealed [17]. The increased conductivity in the metal layer of finite thickness is also important for many geophysical problems; one of them is the analysis of the geomagnetic field variations [18].

2. Spin crossover in ferropericlase at high pressure and temperature

At low temperature spin crossover results from the HS/LS energies equality $E_{HS} = E_{LS}$, that results from the crystal field growth under pressure [9]. At zero temperature spin crossover is the quantum phase transition with geometrical Berry-phase type order parameter [19]. We should mention here that there is also possible contribution from the intermediate spin state, nevertheless our estimation of its energy have shown that this level is about 1 eV higher than HS/LS levels at the crossover point [20]. At finite temperature, the entropy factor should be also considered. For the d^6 ion in an octahedral crystal field the HS state has magnetic degeneracy $g_{HS} = (2L + 1)(2S + 1) = 15$ with orbital $L = 1$ and spin $S = 2$ quantum numbers. For the LS with $L = S = 0$ $g_{LS} = 1$. From the free energy equality $F = E - TS$ of both states one can find the temperature dependent spin crossover pressure P_s that determines 50%–50% population of

the HS/LS states neglecting the lattice compressibility. For any given value of the high spin concentration n_{HS} (and LS concentration $n_{\mathrm{LS}} = 1 - n_{\mathrm{HS}}$) the corresponding pressure may be written like

$$P\left(n_{\mathrm{HS}}\right) = P_c + \frac{kT}{2\partial\varepsilon_s/\partial P}\,\ln\frac{n_{\mathrm{LS}}g_{\mathrm{HS}}}{n_{\mathrm{HS}}g_{\mathrm{LS}}}. \tag{1}$$

Here zero temperature spin crossover pressure $P_c = 56$ GPa for ferropericlase was found from the synchrotron Mössbauer measurements at helium temperature [20]. The linear temperature dependence from equation (1) has been also confirmed up to room temperature [20].

Taking into account the different volumes for the HS and LS unit cell and its pressure dependence one should compare not the free energies but the Gibbs potentials $G = F + PV$. The general thermodynamics of the mixed spin state is given in the paper [16]. We have calculated the HS and LS unit cell volumes from the Birch–Murnagan equation of states with $B' = 4$ and different modulus $B_{\mathrm{HS}} = 210$ GPA, $B_{\mathrm{LS}} = 161$ GPA [21]. The average volume in a mixed state was calculated as

$$V(P) = V_{\mathrm{HS}}(P)\,n_{\mathrm{HS}}(P) + V_{\mathrm{LS}}(P)\,n_{\mathrm{LS}}(P). \tag{2}$$

Here the HS/LS concentration is determined by the HS/LS enthalpy $H = E + PV$

$$n_{\mathrm{HS}}\left(P, T\right) = \frac{1}{1 + \frac{g_{\mathrm{LS}}}{g_{\mathrm{HS}}}\exp\left(\frac{H_{\mathrm{HS}} - H_{\mathrm{LS}}}{kT}\right)}. \tag{3}$$

Effect of lattice compressibility on the pressure dependence of HS concentration is not large, see figure 1.
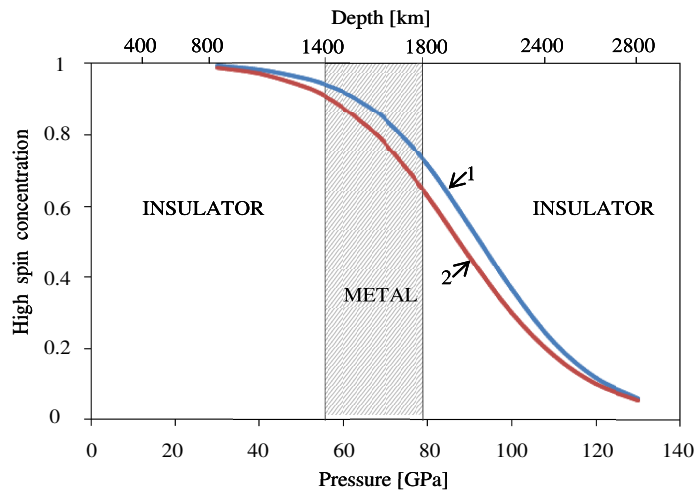

Figure 1. Concentration of high spin state of the Fe^{3+} ion as function of pressure and depth at $T = 2200$ K. Curve 1 (2) calculated without (with) lattice compressibility.

A shadow region in figure 1 corresponds to the metal state with the Mott–Hubbard transition at $P_{\mathrm{MH}} = 56$ GPa according to the LDA+DMFT calculation for FeO [7]. The right border of the metal region is determined by spin crossover induced metal to insulator transition due to sharp increase of the U_{eff} at the spin crossover point P_c [13]. At high temperature, both transitions are smooth due to electric carrier excitations over small insulator gap. In the Earth geotherm both pressure and temperature increases with depth, the temperature change for the depth 1400–2000 km is rather small, ~ 100 K. That is why we fixed it for simplicity as $T = 2200$ K. Equation 2 allows calculating the pressure dependence of the unit cell volume and the bulk modulus $1/K = -1/V(dV/dP)$, that is shown in figure 2a. The deviation of $K(P)$ dependence from linear in the interval of depths 1200–2400 km results from the HS/LS mixed state as clear from figure 2b, where the LS concentration and its baric derivative is shown. The
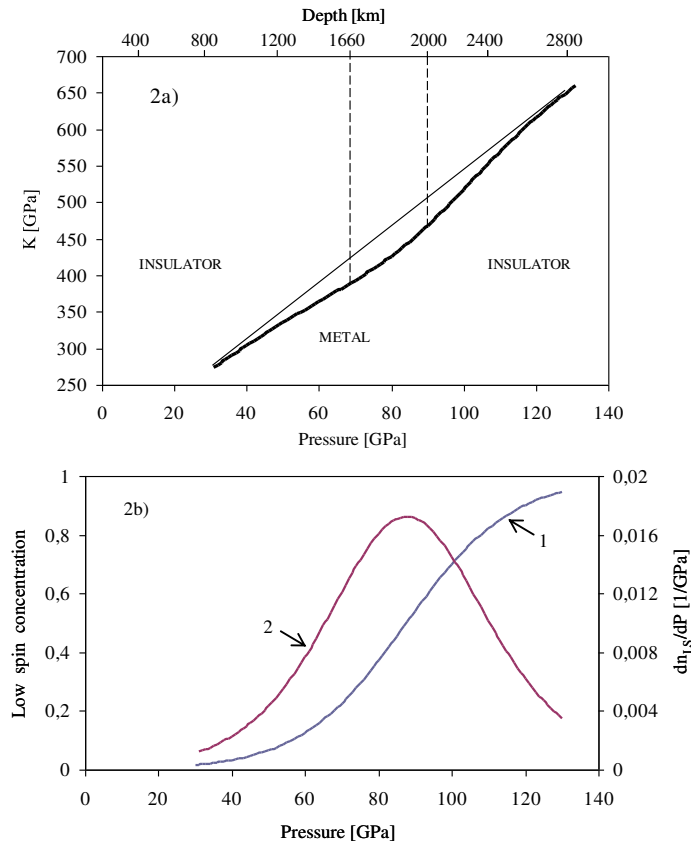
Figure 2.   2a) Adiabatic bulk modulus K as function of pressure and depth for ferropericlase.   2b) Pressure dependence of the low spin concentration (1) and its baric derivative (2) at $T = 2200$ K.

maximum of the derivative determines the maximal lattice softening at pressure about 85 GPa that corresponds to the depth 1900 km. Two dashed vertical lines in figure 2a at 1660 km and 2000 km indicate the region of depths where the anomalies of the seismic velocities and gradients have been revealed [17]. One can see from figure 2 that the maximal lattice softening occurs near the smooth metal–insulator transition. Thus, we conclude that electronic, magnetic and elastic properties of the ferropericlase in the conditions of the Earth's low mantle are strongly interconnected.

3. Electrical conductivity estimation

Previously we have estimated the conductivity of metallic ferropericlase at the 1800 km to be $\sigma_0 = 250$ Sm/m. The mixture of Mg-perovskite and ferropericlase is also metallic as it was discussed in the Introduction because the ferropericlase concentration is above the percolation threshold. The conductivity value in the mixture of nonmetallic perovskite and metallic ferropericlase is smaller, it is estimated in this chapter. In the percolation theory [5] the dependence of the conductivity on the metal component concentration x is given by $\sigma(x) \sim (x - x_c)^{1.5}$ above the threshold x_c and $\sigma(x)$ becomes linear far from x_c with the limit σ_0 at $x = 1$. For three-dimensional lattice $x_c = 0.148$ [5], thus we can estimate $\sigma(x) = 3.36$ Sm/m for $x = 0.18$ and $\sigma(x) = 6.93$ Sm/m for $x = 0.20$. These conductivity values are clearly underestimated because the conductivity of Mg-perovskite is neglected. According to the laboratory measurements [6] for the temperature ~ 2000 K and pressure 70–100 GPa its conductivity is about 0.1–1 Sm/m. The conductivity value 250 Sm/m of 100% ferropericlase is certainly overestimation. The conductivity of the Earth's low mantle may also be influenced by small amount of metallic Fe (1%) and another metal oxides (5%) that may be also metallic

at these pressures. Thus, very reliable estimation of the low mantle conductivity at the depths 1400–2000 km is still absent. Our opinion is that this value may be 10–50 Sm/m. One should keep in mind that it is the estimation of the conductivity of the whole Mantle as the mixture of metallic ferropericlase and insulating Mg-perovskite that of course is smaller than conductivity 250 Sm/m of ferropericlase itself. These data may be used for the modeling of the penetration of the electromagnetic field through the Earth interior. Global geomagnetic data have been inverted for detecting a high-conductivity layer at depths of 1500–2000 km to test the prediction of the metallic layer inside the lower mantle [22]. We received the results of processing of both synthetic and global data-average monthly values of the geomagnetic field from 1920 to 2009. The inverted global data are consistent with the possible existence of a high-conductivity layer.

Acknowledgments

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