Transport properties of Fe₃O₄ magnetite at high pressure up to 24 GPa: a search for crossovers

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Transport properties of Fe₃O₄ magnetite at high pressure up to 24 GPa: a search for crossovers

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The thermoelectric power (Seebeck effect) and the electrical resistivity of the cubic-spinel Fe₃O₄ magnetite were investigated under high pressures up to 24 GPa at room temperature. Comparative experiments were performed on several micro-samples cut from the same single-crystalline ingot of stoichiometric magnetite. The pressure dependencies of the thermopower, the resistivity, and a temperature difference along a sample (it is related to the thermal conductivity) demonstrated that a kink (bend) at 5–7 GPa is the only crossover that is reproduced in all the samples for all pressure cycles. In one of the samples studied, the beginning of some electronic transition was distinctly registered at 19.5–20 GPa. We discuss some hidden and probably optional electronic transition in Fe₃O₄ which occurs nearby the onset of the transformation to the high-pressure orthorhombic phase. The recently predicted two magnetic transitions in Fe₃O₄, namely, the valence transition from the inverse to the normal electron configuration and the spin transition of the Fe²⁺ ions, are analysed.

Keywords: magnetite; high pressure; thermopower; polaron hopping conductivity; octahedral network; valence transition; inverse and normal spinel

1. Introduction

Magnetite (Fe³⁺Fe²⁺O₄), the important iron oxide, is a model for (M,Fe)₃O₄ (M, metal) minerals and therefore has significant implications for the Earth’s interior. At ambient conditions it adopts a cubic spinel structure (space group, Fd3m) with the inverse electronic configuration [Fe³⁺]₄[Fe²⁺ + Fe³⁺]B⁴O₄ [1,2], where A and B are, respectively, the tetrahedral and the octahedral sites in the spinel structure, AB₂O₄; notice that the equivalency of the B sites is a point at issue [3]. Recently, two magnetic transitions were proclaimed for magnetite. The first was inferred from changes in Mössbauer spectra which are registered between ~7 and ~15 GPa (at room T) [4,5]. It was addressed to a sluggish valence transition from the inverse electronic configuration ([Fe³⁺]₄[Fe²⁺ + Fe³⁺]B⁴O₄) to the normal one ([Fe²⁺]₄[Fe³⁺ + Fe³⁺]B⁴O₄) that should increase the net magnetic moment by ~50% [5]. The second one, a spin transition of the Fe²⁺ ions at the B sites from the high-spin to the ‘intermediate’ state, was claimed on the basis of data of the X-ray
magnetic circular dichroism to occur at 12–16 GPa [6]; it was predicted to reduce the net magnetic moment by \( \sim 50\% \) [6]. The ‘classical’ model of the electrical conductivity in spinels [7,8] permitting the polaron hopping between the Fe\(^{2+}\) and Fe\(^{3+}\) ions only in the octahedral network suggests Fe\(_3\)O\(_4\) to be a good conductor when the electronic configuration is inverse, and an insulator if it is normal [4,5]. Spin transitions are known to reduce the population of the \( e_g \) electrons, which are responsible for the conductivity [6]; for instance, a high-spin to low-spin transition of the Fe\(^{2+}\) ions in Mg\(_{1-x}\)Fe\(_x\)O near \( \sim 50–60 \) GPa [9] was found to be concurrent with a distinct decrease in the conductivity [10]. Thus, both the predicted magnetic transitions may be effectively probed by transport techniques.

Very recent studies [11,12] did not support the proposed valence transition [4,5]. In our previous work [13] its groundlessness was also shown. In this work we present new data on the thermopower and the electrical resistivity of Fe\(_3\)O\(_4\) under pressures to 22–24 GPa and speculate about possible electronic transitions (\( \text{e.g.} \) the spin transition [6]) in the cubic spinel phase.

2. Experiments

A single-crystalline stoichiometric magnetite (Fe\(_3\)O\(_4\)) was synthesized by the floating zone method [14]. The electrical resistivity (\( \rho \)) and the concentration of electrons (\( n \)) in the ingot were determined, respectively, by the Montgomery [15] and Hall techniques. At room temperature they were found to be equal, respectively, to \( \rho = 4.3 \) m\( \Omega \) cm and \( n = 2.27 \times 0.10^{22} \) cm\(^{-3} \). The former corresponds to an earlier reported range of typical \( \rho \sim 4–15 \) m\( \Omega \) cm for single-crystalline Fe\(_3\)O\(_4\) [16], and furthermore evidences a high-quality of the ingot. A high pressure \( P \) was produced in the synthetic diamond anvil cells of the modified Bridgman type [17,18] (Figure 1). In order to get single-crystalline micro-samples of Fe\(_3\)O\(_4\) the ingot was shredded into tiny plates and those thought suitable were selected. The experiments were performed on several samples. Pressure dependencies of the resistivity and the thermopower were measured on an automated high-pressure setup [19] permitting simultaneous registration of several parameters of a sample under almost continuous alteration of \( P \). A displacement of the plungers during pressurization was measured by an electronic dilatometer with a sensitivity of \( \sim 7.5 \) Volts/mm. This method allows searching for volumetric anomalies of a sample under \( P \) [19].

![Figure 1](Image). A high-pressure cell [20], general view (a), different types of anvils including: concaved anvils (toroidal geometry) (b), and ‘flat’ conventional anvils (c). 1, a sample; 2, a gasket; 3, anvil insets in high-pressure plungers; 4, supporting hard-alloy matrices (plungers) – they are usually made of tungsten carbide; 5, a special hard-durable part of a plunger (synthesized together with 3); 6, supporting rings. The arrows show external applied pressure. A ring-like bulge of the gasket 2 provides a supporting pressure, \( P_s \) (up to 10 GPa), around the tips of the anvils.
Pressure dependences of the electrical resistivity were measured by the sandwiching of a flat sample between two pairs of electrical probes. Two Pt–Ag ribbons of 5 μm in thickness were attached to a lower anvil, and the two other ribbons were put on an upper plane of a sample and were then pressured by an upper anvil (Figure 1). Since precise dimensions of a sample under pressure remained unknown, in the in situ measurements only a relative change of ρ under pressure could be determined. Then, the absolute values of ρ were calculated from the relative change.

In the measurements of the thermopower (S), the upper anvil was heated to create a temperature difference ΔT along the sample’s thickness. So, the anvils served both as electrical and thermal outputs to the sample [20]. Such an assembly (Figure 1) seems to be almost ideal for determination of S because (i) a uniform thermal flow goes exclusively through the bulk of the sample from the upper ‘hot’ plate to the lower ‘cold’ one, and (ii) a gasket of lithographic stone provides good thermal insulation [20]. S values were determined from simultaneous measurements of a thermoelectric voltage U and a temperature difference ΔT. More details are given in [19,20].

Pressure cycling was performed for verification of reversibility of pressure-induced changes. The uncertainties in determination of ρ and S were less than ~5% and ~10%, respectively.

3. Results and discussion

Figure 2 summarizes the main obtained results. The electrical conductivity mechanism in spinels was established to be the polaron hopping through the octahedral network of the Fe3+ (vacancy) and the Fe2+ (charge) ions [7,8,21]. Therefore, it strongly depends on the Fe2+/Fe3+ ratio at the B sites. Thus, according to theory [7], a value of the thermopower in Fe3O4 should be expressed as follows: 

\[ S = \left( k_0/e \right) \times \ln\left( 1 - c \right)/c \]

where \( k_0 \) is the Boltzmann’s constant, \( e \) is the electron charge, and \( c \) is the fraction of mobile charge carriers (polarons) per available equivalent sites in the unit cell. According to [2], Fe3O4 is characterized by a predominant but not exclusive inverse electronic configuration. Furthermore, a real number of the mobile polarons may be less than a number of the charges (the Fe2+ ions) at the B sites. In fact, ambient values of the thermopower in Fe3O4 were found to be equal to \( S \sim (−40–60) \mu V/K \) [13,22–24] (Figure 2), i.e. far from \( S \rightarrow 0 \), as would be expected for the ideal inverse electronic configuration with the equal amounts of the Fe2+ and Fe3+ ions at the B sites [7].

In some of the curves given in Figure 2, a bend (kink) near 5–7 GPa manifests in agreement with our previous work [13]. Figure 2b shows that up to 5–7 GPa, S normally changes from ~−40 to ~−(10–15) μV/K. In sample 5 (Figure 2c), pressure cycling permitted even achieving values of \( S \sim −5 \mu V/K \). Some of the curves of the sample’s contraction under pressure exhibit a tiny kink near 5–7 GPa, hinting at a change in the compressibility, while others do not show any anomalies (Figure 2d). A kink near 5–7 GPa is clearly seen in the dependencies of the temperature difference (ΔT) along a sample’s thickness for all the pressure cycles (Figure 2d); on the third and fourth cycles the measurements were carried out in a non-stationary regime, i.e. a ΔT value was a function of time (Figure 2c). At stationary thermal regime, ΔT may be expressed as follows: 

\[ ΔT = q \times h/λ \]

where \( q \) is the density of a thermal flow, \( h \) is the thickness of a sample, and \( λ \) is the thermal conductivity [19,20]. Therefore, the bend in the ΔT(P) curves (Figure 2d) should be related to a change in a pressure derivative of the thermal conductivity, \( dλ/dP \). Since the S(P) curves evidence that a number of charge carriers (polarons) significantly increase with P only to 5–7 GPa (Figure 2c), a growth in the electron contribution to \( λ \) is expected to become saturated to these P values.

As to the predicted spin transition of the Fe2+ ions to occur between 12 and 16 GPa [6], all the data gathered for several samples (Figure 2) do not support it. Thus, the electrical resistivity (Figure 2a) does not show any anomalies which might potentially be addressed to this transition.
Figure 2. The pressure ($P$) dependencies of the electrical resistivity ($\rho$), the thermopower ($S$), the temperature difference along the sample’s thickness ($\Delta T$), and the sample’s contraction ($\Delta x$) of Fe$_3$O$_4$ at 293 K. The labels #1–#6 mark different samples cut from the same ingot. The thin arrows point the directions of $P$ variation. (a) The inset shows the temperature ($T$) dependence of $\rho$ of the ingot across the Verwey transition at $T_v \sim 120–125$ K; (b) the bulk arrow points to the onset of electronic transition; (c) the inset shows determination of $S$ values from linear slopes of curves of a thermoelectric voltage ($\Delta U$) versus $\Delta T$; those for the first cycle were both given at $\sim 0$ GPa and at maximal $P$ achieved in this cycle, while the others only at maximal $P$.

If the population of the $e_g$ electrons of the Fe$^{2+}$ ions is reduced by even a few percent [6], a corresponding variation in the thermopower value should be of several $\mu$V/K, but this is not the case (Figure 2b, and c). Notice that the seemingly tiny anomalies seen in the $S(P)$ curves given in Figure 2b appear to be owing to an ‘instrument quantization’ of the microvolt’s values of a thermoelectric voltage from the sample. Near and above 12–16 GPa, the $\Delta T(P)$ curves (Figure 2d) do not find a change in the thermal conductivity; likewise, the $\Delta x(P)$ curves (Figure 2d) show no change in the compressibility. The latter agrees with data in [5] suggesting no change in the compressibility up to $\sim 20$ GPa. Other experimental and theoretical studies also do not find this spin transition to 20 GPa [5,25–27].

However, vagueness in behavior of Fe$_3$O$_4$ near the beginning of a sluggish pressure-driven structural transformation to an orthorhombic phase above 20–25 GPa [28] still persists. While, a metallic type of the electrical conductivity of the orthorhombic phase has been firmly established.
in [28], the beginning of this transition was found to be concurrent with a significant growth in the electrical resistivity [29,21], suggesting either semiconducting [21] or insulating [29] properties of the high-pressure phase. In one sample investigated, we repeatedly registered the onset of a transition at 19.5–20 GPa (Figure 2b). The decompression cycles did not exhibit a hysteresis in the transition pressure, hinting at the electronic nature of this transition. Thus, a ‘hidden’ electronic transition in fact would occur near the beginning of the structural transformation [28]. A moderate growth in \( \rho \) registered above 18 GPa in [21] is consistent with the hypothesis of the spin transition [6], while a drastic jump in \( \rho \) near 20 GPa established in [29] could support the hypothesis of the transition to the normal electronic configuration [5]. Hence, these two suppositional magnetic transitions [5,6] could help in the search for the real origin of the puzzling behavior of Fe\(_3\)O\(_4\) around and beyond 20 GPa. To clarify the situation, sample #5 was compressed up to \( P \) as high as \( \sim 24 \) GPa, but no transition at 19–20 GPa was detected (Figure 2c). Likewise, no transition was found by the electrical resistivity to 22 GPa (Figure 2a). Thus, the existence of some ‘hidden’ electron transition remains a question to be clarified.

4. Conclusion

A thorough search for possible pressure-driven crossovers in the spinel phase of Fe\(_3\)O\(_4\) has been carried out with an assistance of techniques of thermopower and electrical resistivity. We have established that the bend (kink) appearing in the curves near 6 GPa is the only feature that is reproduced in all the samples investigated. In one sample we found an abrupt growth in \( |S| \) at 19.5–20 GPa. However, in others compressed to 22–24 GPa, this peculiarity was not reproduced. The data gathered do not support the hypothesis of the spin transition in Fe\(_3\)O\(_4\) to occur between 12 and 16 GPa [6].

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