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2008 J. Phys.: Condens. Matter 20 172201

(http://iopscience.iop.org/0953-8984/20/17/172201)

IOP Publishing JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **20** (2008) 172201 (6pp) doi:10.1088/0953-8984/20/17/172201

FAST TRACK COMMUNICATION

A new crossover in Fe_3O_4 magnetite under pressure near 6 GPa: modification to ‘ideal’ inverse cubic spinel?

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Received 6 February 2008, in final form 19 February 2008
Published 1 April 2008
Online at stacks.iop.org/JPhysCM/20/172201

Abstract
The results of the first study on the thermoelectric power (Seebeck effect) of single crystals of Fe_3O_4 magnetite at high pressure P up to 20 GPa and room temperature are reported. The electrical resistance and a sample’s contraction (relative compressibility) were also investigated over a P range of 0–20 GPa. A smooth bend (crossover) in the pressure dependence of the thermopower was firmly established near 6 GPa. This feature was attributed to a modification of Fe_3O_4 to an ‘ideal’ inverse configuration, the case where equivalent amounts of charges (the Fe^{2+} ions) and vacancies (the Fe^{3+} ions) at the octahedral sites provide nearly metallic polaron hopping conductivity via the octahedral network. The origin of this transformation might lie in (i) a P-tuning ‘perfection’ of the electronic transport in the inverse spinel, and/or in (ii) a transfer of a minor group of the charges from the tetrahedral sites to the octahedral ones, i.e. a normal → inverse configuration transition. Opportunities for the opposite valence transition in magnetite, from the inverse spinel to the normal (direct) one, are also discussed. At ambient pressure the samples of Fe_3O_4 were probed by Raman spectroscopy and using the electrical resistivity across the Verwey transition.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Fe_3O_4 magnetite is a constitutive mineral kindred to FeO wustite and Fe_2O_3 haematite and maghemite. As a model for $(M, Fe)_3O_4$ (M—metal) minerals, magnetite has important implications for the Earth’s interior and especially for the upper mantle. At ambient conditions magnetite, $Fe_2^{3+}Fe^{2+}O_4$, adopts a cubic spinel structure (space group $Fd\bar{3}m$) with the inverse configuration $[Fe^{3+}]_A[Fe^{2+} + Fe^{3+}]_BO_4$ [1, 2], where A and B mean respectively the tetrahedral and the octahedral sites in the spinel structure, AB_2O_4. By the way, the equivalence of the octahedral sites in Fe_3O_4 is a point at issue [3]. Starting above $P \sim 20$–25 GPa (at room temperature T) and up to $P \sim 60$ GPa, magnetite is gradually transforming to the high-pressure polymorph [4–8] with either the $CaTi_2O_4$-type structure (space group $Bbmm$) [6, 9, 10] or the $CaMn_2O_4$ one (space group $Pbcm$) [5].

Recently, one more characteristic feature was proposed for magnetite—a sluggish valence transition from the inverse state ($[Fe^{3+}]_A[Fe^{2+} + Fe^{3+}]_BO_4$) to the normal (direct) one ($[Fe^{2+}]_A[Fe^{3+} + Fe^{3+}]_BO_4$) around ∼7–15 GPa (at room T)

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without any change in the lattice symmetry [11–13]. This transformation should lead to an increase in the magnetic moment of the unit volume by 50% [13]. Besides a direct measurement of the magnetic moments at the A and B sites, for example, by neutron experiments (recent studies did not support this transition [14, 15]), the alternative methods which nowadays are being applied in the search for this valence transition are as follows: (i) investigation of a pressure dependence of the oxygen atomic coordinate [13, 16, 17] ($u \sim 0.2547$ and ~ 0.260, respectively for the inverse and the normal spinel structures [1, 13]), and (ii) a thorough study of the compressibility (the normal spinel structure was calculated to have the larger unit cell $a \sim 8.467$ Å versus $a \sim 8.395$ Å in the inverse spinel [18]). Earlier, at low temperatures, a transition around $P \sim 6$–8 GPa was actually established through electrical resistivity and x-ray diffraction [19–21]. However, careful experiments at room T to 20–22 GPa did not find any drastic changes in the properties [18, 22, 23]. Only one work [24] reported tiny anomalies noticed at room T near $\sim$7 GPa and attributed them to a discontinuous change of the Fe–O bond length. At lower P some effects in $\mathrm{Fe_3O_4}$ were also noticed [25, 26].

Electrical properties of the inverse and the normal spinels should drastically differ. For the inverse spinel $\mathrm{Fe_3O_4}$ the mechanism of electrical conductivity was established to be the polaron hopping through the octahedral sites of the Fe^{2+} and Fe^{3+} ions [27]. However, there is no opportunity for charge exchange between the Fe^{2+} and Fe^{3+} ions at the equivalent sites in the pure normal spinel ($[\mathrm{Fe}^{2+}]_{\mathrm{A}}[\mathrm{Fe}^{3+} + \mathrm{Fe}^{3+}]_{\mathrm{B}}\mathrm{O}_4$), since all the tetrahedral sites are occupied by the Fe^{2+} ions and all the octahedral sites by the Fe^{3+} ones. In absolute value, the room T electrical resistivity ρ of the inverse spinel $\mathrm{Fe_3O_4}$ is around 4 mΩ cm [27], and, for example, $\rho \sim 10^7$ Ω cm for normal spinel zinc ferrite, $\mathrm{Zn}^{2+}\mathrm{Fe}_2^{3+}\mathrm{O}_4$ [28] (the ion radii for the Zn ions are quite similar to those for the Fe ions and a substitution of Fe^{2+} by Zn^{2+} gradually leads to the normal configuration, $[\mathrm{Zn}_x^{2+} + \mathrm{Fe}_{1-x}^{3+}]_{\mathrm{A}}[\mathrm{Fe}_{1-x}^{2+} + \mathrm{Fe}_{1+x}^{3+}]_{\mathrm{B}}\mathrm{O}_4^{2-}$ [29]). However, if a transition to the normal spinel is not complete, but only predominant and sluggish, it seems difficult to detect it through the electrical resistivity, as both the tetrahedral and the octahedral sites will contain Fe^{2+} and Fe^{3+} ions, and hence the conductivity may retain a high value. Thus, although the majority of models of conductivity in spinels consider only the octahedral networks [27, 30], the real situation may be more complex. Therefore, a dropping of ρ with P to 20 GPa at room T found in [8, 31] is not sufficient proof of the non-existence of the inverse → normal configuration transition in $\mathrm{Fe_3O_4}$ in this P–T range [13], and a more sensitive examination technique is required.

Thus, the goal of the present study was to search for possible crossovers in $\mathrm{Fe_3O_4}$ in a pressure range from 0 up to 20 GPa at room T with the assistance of the thermopower [32].

2. Experiments

A high-quality single-crystalline stoichiometric magnetite ($\mathrm{Fe_3O_4}$) was synthesized by the floating zone method [19]. At ambient P the ingot was characterized by means of Raman scattering, x-ray diffraction, and electrical resistivity. The Raman spectra for magnetite were collected using a Renishaw Ramascope under excitation with the 541.5 Å line of an Ar laser. Our spectra (figure 1) confirmed both the phonon assignment suggested in [33], and the laser-induced thermal and oxidation effects on the spectra (under laser heating of a surface above 250 °C, haematite is formed) [34, 35]. The wavenumbers of the phonons slightly decreased with the laser power because of the thermal expansion of the lattice (figure 1). The electrical resistivity ρ of the ingot was measured by the conventional Montgomery method, and at ambient T it was $\rho = 4.3$ mΩ cm.

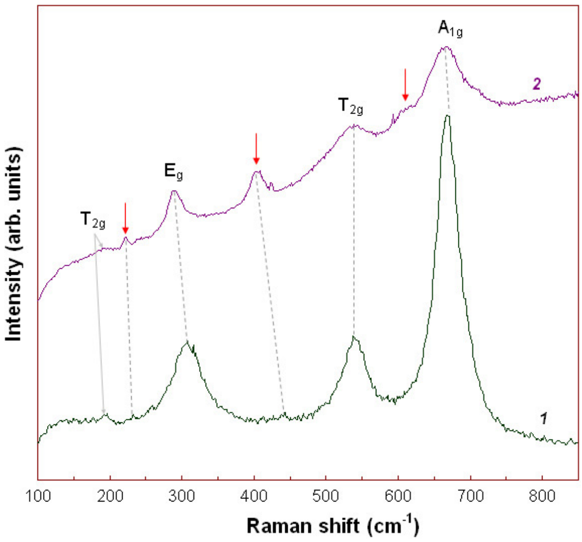

Figure 1. The ambient non-polarized Raman spectra of single-crystalline $\mathrm{Fe_3O_4}$ magnetite. The spectrum **1** is the 'own' one and exhibits wavenumbers at 194, 307, 540, and 668 cm^{-1} [33]. In the spectrum **2** (collected at an elevated laser power) besides the 'own' phonons ($\sim$190, 298, 538, and 665 cm^{-1}), those of haematite ($\mathrm{Fe_2O_3}$) are seen at 222, 405, and $\sim$620 cm^{-1} (marked by the vertical arrows) [34]. The contribution of $\mathrm{Fe_2O_3}$ at $\sim$405 cm^{-1} manifested in a number of previous studies confused the phonon assignment of $\mathrm{Fe_3O_4}$ [34, 35].

The high-pressure experiments were performed on four samples cut from different places in the same ingot; the samples were numbered 1–4 for convenience. Since the high-pressure behaviours of all the samples were quite similar, we show data only for two of them. A high pressure P was produced in synthetic diamond anvil cells of the modified Bridgman type [32, 36]. The working diameters of the diamond tips were within the 0.6–0.8 mm range. Pressure dependences of the thermopower and the electrical resistance were measured using an automated high-pressure set-up [37] permitting simultaneous registration of several parameters of a sample under almost continuous alteration of P. Values of the thermopower S were determined in three regimes as follows: (i) at fixed temperature difference ΔT (or density of thermal flow) along a sample under gradual alteration of P, (ii) at fixed P under gradual variation in ΔT (S values are determined from a linear dependence of a thermoelectric voltage on ΔT [37]), and (iii) under monotonic alteration of both P and ΔT. The electrical resistance R was measured by a two-probe method.

The anvils were characterized by a high electrical conductivity and were used both as electrical outputs to a sample and as a heater–cooler pair [32, 36, 37]. Possible contributions to S from the anvils themselves were checked for by measurement for Pb ($S \approx -1.27\ \mu\text{V K}^{-1}$). Errors in the determination of R and S values were less 5 and 10%, respectively. A technique of registration of the contraction Δx of a sample was described in [38].

3. Experimental results and discussion

3.1. Behaviour of the transport properties under pressure up to 20 GPa

The ambient thermopower values determined in our experiments (figure 2(a)) are close to those previously reported, $S \sim -(40\text{–}60)\ \mu\text{V K}^{-1}$ [39, 40]. We establish that $|S|$ firstly drastically diminishes with P and then becomes a weak function of P (figure 2(a)). A bend in the $S(P)$ curves that we register near ~5–7 GPa correlates with those in the P dependences of a sample's contraction, Δx, and a temperature difference along a sample, ΔT (figure 2(c)). The kink in the $\Delta x(P)$ curves is an indicator of a possible change in the compressibility, which is consistent with data from several studies on the equation of state of a powdery sample, summarized in [13]. Structural works performed on single-crystalline Fe_3O_4 did not confirm a change in the compressibility [17, 18, 41, 42]. However, as these works [17, 18, 41, 42] used only a few points of the equation of state, such an inference is not robust. Since in the stationary thermal regime, $\Delta T = qh/\lambda$, where q is the density of thermal flow, h is the thickness of a sample, and λ is the thermal conductivity [37, 38], the bend in the $\Delta T(P)$ curves (figure 2(c), inset) may be related to an alteration in both the compressibility and the thermal conductivity. The decompression cycles demonstrate the absence of a hysteresis loop below 5–7 GPa, suggesting an electronic nature of the crossover (figure 2(a), inset). To the present, the only research group that predicted the inverse → normal spinel valence transition (near 6–7 GPa at room T) [11] reported on its experimental observation [12, 13]. However, results of other groups provide strong evidence against this valence transition [14, 15, 18, 43]. Therefore, an alternative attribution should be considered.

3.2. Analysis of the conductivity under pressure

A mechanism of electrical conductivity in Fe_3O_4 was established to be the polaron hopping through the octahedral sites of the Fe^{3+} and Fe^{2+} ions [27, 30, 31]. According to [27], an equation for the thermopower S of Fe_3O_4 is as follows:

$$S = \frac{k_0}{e} \ln\left(\frac{1-c}{c}\right). \qquad (1)$$

where k_0 is Boltzmann's constant, e is the electron charge, and c is the fraction of mobile charge carriers (polarons) per available equivalent site in the unit cell. For magnetite, a number of Fe^{3+} and Fe^{2+} ions at available equivalent sites (octahedral) is supposed to be equal, since the ambient configuration is believed to be exclusively inverse—$[Fe^{3+}]_A[Fe^{2+} + Fe^{3+}]_BO_4$ [2, 13]. Therefore, the parameter

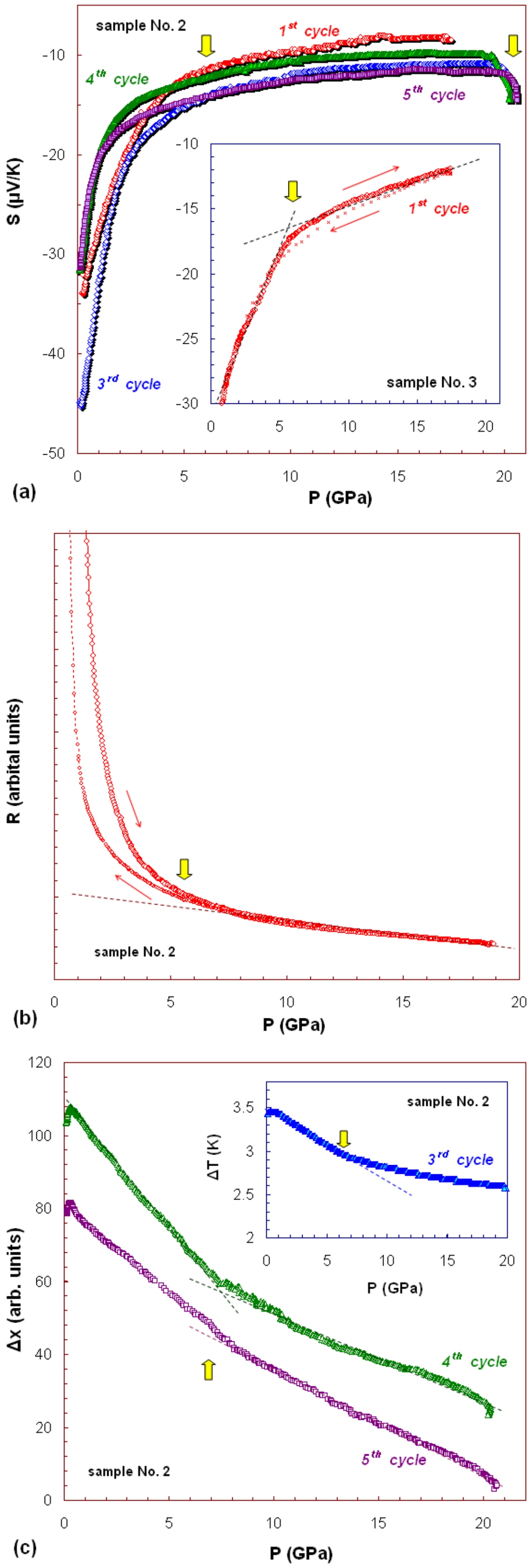

Figure 2. The pressure P dependences of the thermopower S (a), the electrical resistance R (b), and a sample's contraction Δx (c) for single-crystalline Fe_3O_4 magnetite at $T = 293$ K. (a) The features near 5–7 and ~19.5–20 GPa marked by the bulk arrows are discussed in the text. In the inset the thin arrows point in the directions of P variation. (b) The thin arrows point in the directions of P variation. (c) The inset shows the dependence of a temperature difference along a sample ΔT on P.

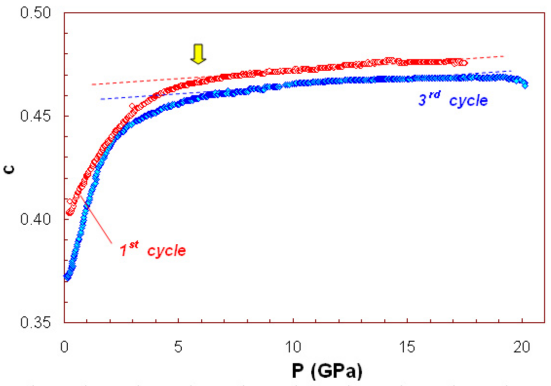

Figure 3. The typical pressure P dependences of a fraction of mobile polarons c per available site in the unit cell of the cubic spinel Fe_3O_4 at $T = 293$ K. The $c(P)$ curves were calculated using equation (1), using the thermopower data for sample No. 2 (figure 2(a)). The smooth bend near 5–7 GPa marked by the bulk arrow is discussed in the text.

c should be equal to 1/2 (one polaron versus two available octahedral sites in the unit cell), and hence the thermopower is expected to be close to zero, $S \approx 0$ (equation (1)). However, this inference drastically contradicts the ambient thermopower values established in experiments, $S \sim -(40–60)\ \mu\mathrm{V\ K^{-1}}$ ([39, 40] and figure 2(a)). Thus, this discrepancy suggests a lower number of mobile polarons, which may be estimated using equation (1) as $c \approx 0.37$ [27, 30] for average $S \approx -50\ \mu\mathrm{V\ K^{-1}}$. Since the possibility of polaron hopping on the octahedral sites depends on the activation energy E_a, using an expression $c = 1/2 \cdot \exp(-E_a/(k_0T))$ for the parameter $c \approx 0.37$, one can estimate $E_a \sim 0.008$ eV at ambient P.

Using the $S(P)$ curves (figure 2(a)) one can calculate with the assistance of equation (1) the pressure dependence of a fraction of mobile polarons c (figure 3). So, above 6 GPa $c \approx 0.47$ (nearly 1/2) and $E_a \sim 0.002$ eV. The latter is much less than k_0T ($\approx$0.025 eV). The estimated values of E_a are much less than those found from $\rho(T)$ curves in [31]. Besides, the $\rho(T)$ curve of Fe_3O_4 depends on the sample and its preparation method [8, 19, 20, 31, 44]; the divergence in the estimates of E_a may be owing to the circumstance that the fitting with the exponential dependence is based on too short T ranges [31]. For correct determination of E_a one should ascertain the exponential character of the $\rho(T)$ curve; hence, the alteration in ρ with T should exceed $e \approx 2.73$. But heating above 250 °C already leads to the formation of Fe_2O_3 ([33] and figure 1) and confuses the situation. Thus, the state beyond 6 GPa at ambient T is indeed close to metallic conductivity. From figure 3 we can infer that above 6 GPa magnetite exhibits the parameter c close to 1/2, hinting at an 'ideal' inverse configuration $[Fe^{3+}]_A[Fe^{2+} + Fe^{3+}]_BO_4$ [1, 27]. Notice that to 6 GPa the electrical resistivity of Fe_3O_4 drops by approximately one order [31] and becomes less than that of liquid mercury ($\rho \sim 1$ mΩ cm), which is considered as the border between semiconductors and metals. Hg also shows $S \approx -8.8\ \mu\mathrm{V\ K^{-1}}$ [27], close to that for Fe_3O_4 above 6 GPa (figure 2(a)).

During the proposed inverse → normal spinel transition [13], the electrical charges (Fe^{2+}) should redistribute between the octahedral and tetrahedral sites (by a charge transfer or by a rearrangement of O atoms around the Fe ions) [13]. In an intermediate configuration ($[Fe^{2+}_x + Fe^{3+}_{1-x}]_A[Fe^{2+}_{1-x} + Fe^{3+}_{1+x}]_BO_4^{2-}$), the Fe^{2+} and Fe^{3+} ions locate both in the octahedral and the tetrahedral sites which opens up more possibilities for charge exchange. A charge exchange between the ions with the equivalent valency (Fe^{3+} and Fe^{3+} or Fe^{2+} and Fe^{2+}) seems to be strongly energetically unprofitable, as is confirmed by the very low electrical conductivity in normal cubic spinels [28].

After the first models explained the high electrical conductivity of magnetite through polaron hopping between the Fe^{2+} and Fe^{3+} ions in the octahedral network [27, 30, 39], the following models for spinels were basically limited to this proposed mechanism. The maximum of the electrical conductivity is achieved when the amounts of Fe^{2+} and Fe^{3+} ions at the octahedral sites are equivalent [27]. Then, according to this 'classical' approach [27], the electrical resistivity is expected to show exponential-like growth with a degree of coordination transformation to the normal spinel. In other less common models of conductivity of spinels—for example, in one described in [29]—the possibility of charge exchange between M^{2+} and Fe^{3+} ions at the tetrahedral sites is also considered. Reference [29] experimentally demonstrated that the maximum of the electrical conductivity of 'intermediate' iron spinels is observed when the amounts of M^{2+} and Fe^{3+} ions at the tetrahedral sites are almost equal. Such models hint at both a non-monotonic behaviour of $S(P)$ and $R(P)$ curves during the coordination transition, and a significant growth in R and S to completion. Our $S(P)$ and $R(P)$ curves (figure 2) provide evidence against both cases, and hence against the valence transition [13].

3.3. *Explanation of the crossover near 6 GPa*

Thus, we may conclude that the smooth kink that we register near 6 GPa (figure 2) is not a track of any structural transformation. Beyond 5–7 GPa the electron transport in magnetite is consistent with an 'ideal' inverse configuration [27], hinting at two possibilities as follows.

(i) P-tuning 'perfection' of the electronic transport in the inverse cubic spinel towards to an 'ideal' case.

(ii) At ambient P–T, Fe_3O_4 has not exclusive but a dominant inverse spinel configuration, and P 'moves' a minor group of charges from the A sites to the B ones; i.e. a transition goes from the normal to the inverse spinel, opposite to the prediction [11–13].

The first variant could remove the discrepancies between experimental data and theoretical predictions for Fe_3O_4 [27]. One can surmise two possible reasons leading to the 'perfection' of the electron transport. The first one consists in that at ambient P not all polarons in Fe_3O_4 are mobile and applied P stimulates them to participate in the conductivity; so, the crossover corresponds a situation where almost all the polarons become mobile. The second reason is a volumetric effect, i.e. a passing of some threshold value in the distances between the Fe ions and O in the octahedral network owing to a reduction in the unit volume, $\Delta V/V_0 \sim 3\%$, to 6 GPa [13, 18]. The latter, with accounting that beyond 6 GPa the conductivity in Fe_3O_4 is nearly metallic ($E_a \sim 0.002$ eV), correlates with a predicted 'half-metal → metal' electronic transition in Fe_3O_4 when the shortest distance between the Fe ions at the B sites and a neighbouring oxygen atom (Fe^{oct}–O) decreases to some critical value [45]. However, [45] finds that the transition happens when the Fe^{oct}–O distance reduces from 2.06 to 1.99 Å, which corresponds to $\Delta V/V_0 \sim 11$ %, i.e. $P \sim 25$ GPa [6]. Recently, the non-equivalence (in magnetic moments, charges, etc) of the B sites in Fe_3O_4 was theoretically predicted [3]. Assuming that the conductivity mechanism in Fe_3O_4 is the polaron hopping by the B sites [27, 30], this non-equivalence [3] in principle also could be a reason for a divergence between 'real' and 'expected' ('ideal') transport properties at ambient P [27]. Probably, P-tuning can influence this. Meanwhile, the above reasons do not explain the kink in the sample's compressibility (figure 2(c) and [6, 7, 13]).

The second variant could explain this kink in the compressibility (figure 2(c) and [6, 7, 13]), assuming different lattice parameters of the normal and the inverse cubic spinels, respectively $a \sim 8.467$ Å and $a = 8.395$ Å [18]. Assigning this feature to effects of non-hydrostaticity of P [18] is not convincing. Thus, in [18] it was demonstrated for single-crystalline Fe_3O_4 that above 8 GPa non-hydrostaticity leads to an increase in the compressibility in accordance with expectations, while the effect observed is opposite (figure 2(c) and [6, 7, 13]). Direct measurements of an average charge difference between the A and B sites in Fe_3O_4 find at ambient conditions values lower than $0.5e$. For example, [2] reported $0.46e$, suggesting for the inverse and the normal configurations, respectively, ~96% and ~4% fractions. Experimentally, at ambient P–T the magnetic moment of the cubic unit cell was found to be 34 μ_B (μ_B—the Bohr magneton), i.e. higher than expected (32 μ_B) [27]; this also hints at the existence of a normal fraction (~1/8) at ambient conditions[4].

3.4. Are there any opportunities for the inverse → normal spinel transition?

The present work finds no transition from the inverse to the normal configuration in Fe_3O_4 at ambient T to 20 GPa, and thereby infers that the P–T diagram proposed in [13] is not correct. The Mössbauer spectra of magnetite in the Verwey phase, below 120 K and above 20 GPa, clearly exhibit differences from the ambient ones [11–13, 46]. While in [11–13] these spectra were repeatedly found to be consistent with the normal spinel, [46] related the spectra of the Verwey phase to a doubling of a lattice parameter of the unit cell, which was confirmed in direct structural studies [47, 48]. Alternative interpretations are also possible [43]. As regards the Verwey phase, the existing data for the Verwey phase provide evidence against the normal configuration. Nevertheless, some facts remain puzzling. For example, although the theory strongly suggests the inverse spinel Fe_3O_4 to be exclusively an n-type conductor ([27] and equation (1)), [39] finds a sign inversion in the $S(T)$ curves followed by a drop of S from ~ -50 μV K^{-1} down to ~ -100 μV K^{-1} below 120 K; this hints at hole conductivity.

The existing data in the literature concerning the high-pressure orthorhombic phase of Fe_3O_4 are incompatible. Thus, in [9] a metallic conductivity in this phase was theoretically predicted and experimentally verified, while an abrupt jump in an $R(P)$ curve by two orders above 20 GPa at room T was found in [8], concurrent with the beginning of the structural transition, hinting at the opening of an energy gap. Then, we can infer two possibilities.

(i) If we assume that the high-pressure orthorhombic phase is a metal as suggested in [9], the growth in $R(P)$ above 20 GPa [8] should be owing to some processes or transitions in the cubic spinel; for instance, *hypothetically* it could be related to the transition to the normal configuration (since the normal spinel has a larger a than the inverse one [18], the 'inverse → normal' transition under P looks hardly thermodynamically possible, while it could happen concurrently with the transformation to the high-pressure phase).

(ii) Otherwise, if the growth in R beyond 20 GPa [8] is a track of the high-pressure phase, the latter may not be a metal. Thus, for example, an orthorhombic high-pressure phase of PbTe exhibits a metal-like behaviour of $\rho(T)$ and for a long time was believed to be a metal. Later, it was found to be a narrow-gap semiconductor, that is, metallizing in the next cubic CsCl-structured phase [49].

In the present work for one sample of the four investigated we repeatedly detected a drastic increase in $|S|$ at $P \sim 19.5$–20 GPa (figure 2(a)) for several pressurization cycles. On decompression, this peculiarity showed no hysteresis in the P value that is typical for electronic transitions. However, these data are not sufficient for issuing an exact conclusion and thereby for clarifying the situation. Thermopower measurements to higher pressures seem to be an effective method for resolving discrepancies; however, a number of experimental difficulties restrict them.

4. Conclusion

Using the thermopower technique we clearly established a new crossover in magnetite at ambient T and pressure $P \sim 6 \pm 1$ GPa. This peculiarity was explained by P-driven 'perfection' of the electronic transport in the inverse spinel configuration of Fe_3O_4 towards an almost 'ideal' case, while also hinting at a possibility of transfer of a minor group of the electrical charges (the Fe^{2+} ions) from the tetrahedral sites to the octahedral ones.

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[4] Considering a model of 24 iron ions in the unit cell of Fe_3O_4 (8 of them are at the tetrahedral sites and 16 at the octahedral ones), $[Fe^{2+}_x + Fe^{3+}_{1-x}]_A[Fe^{2+}_{1-x} + Fe^{3+}_{1+x}]_B O^{2-}_4$, and assuming that (i) magnetic moments at the A and B sites are antiparallel, and (ii) Hund's rule predicts the Fe^{3+} and Fe^{2+} ions having respectively 5 μ_B and 4 μ_B, the total moment (34 μ_B) may be obtained as a difference between the moments at the B and A sites, $[8 \times 4 \times (1-x) + 8 \times 5 \times (1+x)] - [8 \times 4 \times (x) + 8 \times 5 \times (1-x)]$ if we take $x = 1/8$.

Acknowledgments

The authors are grateful to Dr A E Karkin (IMP), Dr Y Yuasa, and Professor T Suemoto (ISSP) for assistance with the characterization of the samples. The work was partly supported by the RFBR, #07-08-00338. SVO also thanks the JSPS and the ISSP for the financial support.

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