Nuclear and magnetic structure of magnetite under pressure to 5.3 GPa and at low temperatures to 130 K by neutron scattering

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Neutron powder diffraction data are reported on well-characterized samples of magnetite under hydrostatic pressure between 0 and 5.3 GPa and in the temperature range 130–300 K. We find that the inverse spinel structure is stable under these conditions, that there is no change in the long-range ferrimagnetic order, and that the refined structural coordinates related to it (oxygen internal coordinate and magnetic moments) are pressure and temperature independent in the P/T range considered.

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Magnetite (Fe_3O_4) is the earliest known magnet and undoubtedly one of the most fascinating minerals. Academic interest in Fe_3O_4 is largely a result of Verwey's discovery¹ of a discontinuous change in the resistance at $T_V=122$ K. Magnetite crystallizes at ambient temperature in the inverse spinel structure ($Fd\bar{3}m$, $Z=8$) in which Fe^{3+} occupies the tetrahedral (A) sites, whereas both Fe^{2+} and Fe^{3+} occupy the twice as abundant octahedral (B) sites. Verwey and others speculated that above T_V , the iron on the B sites is in a mixed-valent state $[\text{Fe}^{3+}]_A[\text{Fe}^{2.5+}\text{Fe}^{2.5+}]_B$, causing the metallic character through charge delocalization. Below T_V the charges in the respective ions would localize to $[\text{Fe}^{3+}]_A[\text{Fe}^{2+}\text{Fe}^{3+}]_B$ and hence produce the experimentally observed insulating state. It was only recently that this picture has been considerably refined.^{2,3} In fact, the Verwey transition is accompanied by a structural transition from $Fd\bar{3}m$ to a monoclinic superstructure with space group $P2_1/c$, very close to the orthorhombic $Pmca$ structure proposed before by Iizumi *et al.*⁴ In this structure there are two inequivalent Fe positions on the tetrahedral A sites and 6 inequivalent Fe positions on the octahedral B sites. The diffraction data^{2,3} indicate that charge ordering occurs at B sites along the c axis, though the charge disproportioning is weak: $[\text{Fe}^{2.4+}\text{Fe}^{2.6+}]_B$. First-principles band structure calculations^{5,6} confirm this picture.

Most of the detailed structural work so far reported on Fe_3O_4 concentrated either on ambient-pressure and low-temperature properties, in view of the interest related to the Verwey transition, or on high-temperature aspects owing to the geophysical implications of magnetite, the latter exclusively carried out by x-ray diffraction.^{7–9} Very recently, x-ray diffraction up to 20 GPa was reported for $T < 130$ K which confirmed that the structural distortion follows closely the $T_V(P)$ line derived from transport data.¹⁰ Here we present a neutron diffraction study under pressure in the 0–6 GPa range, between 300 K and T_V . Our interest in this subject arose out of recent reports of anomalies in Mössbauer spectra which were interpreted as an inverse to normal spinel transition in this pressure-temperature range.^{11,12} This might be correlated with an abrupt increase of the magnetic dichroic x-ray absorption observed at 7–8 GPa.¹³

In view of the presence of magnetic order in Fe_3O_4 (magnetite is ferrimagnetic below 851 K) neutron diffraction is the technique of choice to detect changes in both the nuclear and magnetic structure. A sample of Fe_3O_4 was obtained by grinding a part of a large (1 cm³) perfect single crystal purchased from NEYCO. Before grinding to a fine powder in acetone, the heat capacity of a small piece of the sample was measured using a physical properties measurement system (PPMS) from Quantum Design. A sharp and unambiguous Verwey temperature with an onset of 120 K was detected (Fig. 1) from which we conclude¹⁴ that the sample is almost perfectly stoichiometric ($\delta=0.001$) in $\text{Fe}_{3(1-\delta)}\text{O}_4$. Interestingly, a measurement on commercially obtained powder of Fe_3O_4 from Aldrich (99.99%) showed only a weak and very broad signal, although both the x-ray and neutron diffraction patterns of the two samples were almost identical. About 50 mg of the sample was loaded into the Paris-Edinburgh

FIG. 1. Main figure: specific heat measured on cooling of the Fe_3O_4 sample used in the diffraction measurements showing the onset of the Verwey transition at 120 K. Inset: sequence of diffraction measurements with corresponding pressure-temperature conditions. The dotted line indicates the proposed transition line from the inverse to the normal spinel structure (Refs. 11 and 12).

FIG. 2. Diffraction patterns of Fe_3O_4 at 300 K (top) and 130 K (bottom). The line through the data (dots) are results of a Rietveld fit; difference plots are given below. Tick marks designate positions of nuclear and magnetic reflections. The small peak marked as * is due to the anvils made of sintered diamond. Residuals: $\chi^2=2.86$, $R_{wp}=12.8\%$, $R_p=15.2\%$, $R_{exp}=7.22\%$ (top) and $\chi^2=2.59$, $R_{wp}=13.3\%$, $R_p=15.4\%$, $R_{exp}=8.25\%$ (bottom).

press¹⁵ using sintered diamond anvils and a 4:1 deuterated methanol-ethanol mixture as the pressure transmitting medium. It is known that this liquid provides hydrostatic conditions in the pressure range considered here (0–5.3 GPa), at least at 300 K. Since the pressures in our measurements were changed only at ambient temperature and the cooling under constant load on the cell is known to be essentially isochoric, the conditions are believed to be close to hydrostatic even at low temperatures. The lack of broadening of the Bragg peaks supports this assumption (Fig. 2). All diffraction data were collected at the PEARL/HiPr station of the UK spallation source ISIS at the Rutherford Appleton Laboratory. Typical data collection times per spectrum (Fig. 2) were 3–4 h. The inset of Fig. 1 shows the sequence of measurements in the P/T domain. Rietveld refinements were carried out using FULLPROF,¹⁶ refining a minimal set of variables—i.e., the lattice parameter, the internal oxygen coordinate u , and the magnitude of the magnetic moments on the A and B sites, as well as absorption, background, and two profile coefficients. Pressure values were obtained from the measured lattice parameter by a Birch-Murnaghan equation of state with values for the bulk modulus $B=186$ GPa and its pressure derivative $B'=4$ as proposed by Finger *et al.*¹⁷ Figure 2 shows data and corresponding refinements for spectra at 300 K/5.3 GPa as well as 130 K/4.6 GPa, the latter being obtained by cooling

TABLE I. Upper: refined structural parameters of Fe_3O_4 ($Fd\bar{3}m$). Pressure values were derived from the measured lattice parameter using a Birch-Murnaghan equation of state with $B=186$ GPa, $B'=4$ taken from Finger *et al.* (Ref. 17). Lower: ambient pressure neutron (n) and x-ray (x) data by Wright *et al.* (Ref. 3).

P (GPa)	T (K)	a (Å)	u	m_A (μ_B)	m_B (μ_B)
0	300	8.3918(33)	0.25487(13)	4.05(6)	−3.60(4)
0.7	300	8.3810(47)	0.25585(14)	4.49(9)	−3.65(6)
3.2	300	8.3453(37)	0.25578(16)	4.06(8)	−3.33(6)
4.6	130	8.3264(37)	0.25576(16)	4.05(8)	−3.57(6)
5.3	300	8.3167(37)	0.25597(17)	4.11(8)	−3.31(6)
0 (n)	130	8.3939(2)	0.25490(5)	4.20(3)	−3.97(2)
0 (x)	130	8.390405(3)	0.25521(3)		

the 300 K sample under constant load. Table I lists results of the fits which are plotted in Fig. 3.

These data may be compared to the most accurate structural ambient pressure data available for the spinel phase of Fe_3O_4 . Our 0 GPa results on the oxygen internal atomic coordinate u obtained from data collected in a vanadium can are in excellent agreement with both the high-resolution neu-

FIG. 3. Fractional atomic coordinate of oxygen (upper) and magnetic moments (lower) of Fe_3O_4 at 300 K and 130 K. Ambient pressure neutron and x-ray data by Wright *et al.* (Ref. 3) are given for comparison. If not indicated otherwise, error bars are smaller than symbol size.

tron and x-ray data of Wright *et al.*³ The high-pressure refinements of the pattern in the pressure cell give u values larger by 0.001 (three estimated standard deviations). This is undoubtedly an artifact of the refinements, probably due to an incomplete correction of the anvil absorption, but will have no effect on the conclusions. Likewise, our refined magnetic moments on the A and B sites for 0 and 0.7 GPa (obtained in a vanadium can and in the high-pressure cell, respectively) compare very well with the ambient pressure values obtained by Wright *et al.*³ The overall conclusion of these measurements detailed in Fig. 3 is that, within experimental error, both the oxygen coordinate as well as both magnetic moments are pressure independent up to 6 GPa and 130 K. At 300 K, a similar conclusion was already drawn from x-ray data of Kuriki *et al.*,⁹ although the absolute value of u in this work appears to be unusually low. The most important data point in our work is the one at 130 K and 4.6 GPa since it lies below the proposed inverse to normal spinel transition as indicated by Mössbauer absorption measurements.^{11,12} In the spinel structure, the oxygen coordinate u is related to the Fe-O bond lengths d_A and d_B of the tetrahedral (A) and octahedral (B) sites by $d_A = \sqrt{3}a(u - 1/8)$ and $d_B = a(1/2 - u)$, where a stands for the lattice parameter. For $u = 0.2559$ (Fig. 3) we find hence $d_A = 1.90 - 1.88$ Å and $d_B = 2.048 - 2.031$ Å ($a = 8.392 - 8.326$ Å between 0 and 5.3 GPa) which correspond to values typical for Fe^{3+} in tetrahedral coordination and a mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ in octahedral coordination—i.e., the inverse spinel structure. In turn, Fe^{2+} and Fe^{3+} are known to adopt bond lengths of 1.990 Å and 2.016 Å in a tetrahedral and octahedral coordination, respectively.¹⁸ For a normal spinel structure $[\text{Fe}^{2+}]_A[\text{Fe}^{3+}\text{Fe}^{3+}]_B$ we would hence expect $u = 0.260 - 0.263$ —i.e., an increase of u by at least 0.004 if the inverse spinel converts to the normal spinel structure.

From the data shown in Fig. 3 this scenario can almost certainly be excluded. The precision of our measurement of u is at least one order of magnitude better than the expected change and the lack of significant difference between the structure at 300 K and 130 K is robust to details of the refinements. It should be noted that the concept of valence sums to derive oxidation states from bond lengths is, rigorously speaking, established only from ambient pressure

data.¹⁸ However, our observed pressure-induced variations of bond lengths are small (0.015 Å; see above), typically one order of magnitude smaller than the changes expected by valence changes; i.e., the above arguments still hold.

An inverse to normal spinel transition would also cause changes in the refined magnetic moments. Since the moments at the A (Fe^{3+}) and B ($\text{Fe}^{2.5+}$) sites differ by at least $0.2\mu_B$ (Fig. 3), such a transition would entail a drop of the moment at the A site by at least $0.4\mu_B$. This is not supported by our data. However, our results are consistent with band structure calculations by Zhang and Satpathy.¹⁹ These predict stable moments up to lattice compressions of 3.5% corresponding to pressures of 25 GPa.

For pressures beyond the range investigated in this study, structural changes are expected in the 10–30-GPa region. Ambient temperature x-ray data of Kuriki *et al.*⁹ up to 18 GPa find a significant continuous decrease of u beyond 10 GPa. More recent unpublished x-ray measurements²⁰ at 300 K under hydrostatic (He) conditions to 20 GPa indicate, on the contrary, an increase of u to reach $u \sim 0.26$ at 15 GPa, consistent with a normal spinel structure, as discussed above. In whatever case, the cubic structure seems to be stable up to 20–30 GPa, where a sluggish first-order transition to a structure with space group $Pbcm$ was reported at 24 GPa and 823 K.^{7,8} Interestingly, this is the pressure range where first-principles calculations¹⁹ predict a sharp drop of the B -site magnetic moment by a factor of 3. We therefore suspect that these structural changes are accompanied by significant changes in the magnetic moments at pressures around 20 GPa. This is currently being investigated by neutron scattering.

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¹E. J. Verwey, *Nature* (London) **144**, 327 (1939).

²J. P. Wright, J. P. Attfield, and P. G. Radaelli, *Phys. Rev. Lett.* **87**, 266401 (2001).

³J. P. Wright, J. P. Attfield, and P. G. Radaelli, *Phys. Rev. B* **66**, 214422 (2002).

⁴M. Iizumi, T. F. Koetzle, G. Shirane, S. Chikazumi, M. Matsui, and S. Todo, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **B38**, 2121 (1981).

⁵Horn-Tay Jeng, G. Y. Guo, and D. J. Huang, *Phys. Rev. Lett.* **93**, 156403 (2004).

⁶I. Leonov, A. N. Yaresko, V. N. Antonov, M. A. Korotin, and V. I. Anisimov, *Phys. Rev. Lett.* **93**, 146404 (2004).

⁷Y. Fei, D. J. Frost, H.-K. Mao, C. T. Prewitt, and D. Häusermann, *Am. Mineral.* **84**, 203 (1999).

⁸C. Haavik, S. Stølen, H. Fjellvag, M. Hanfland, and D. Häusermann, *Am. Mineral.* **85**, 514 (2000).

⁹A. Kuriki, Y. Moritomo, Y. Ohishi, K. Kato, E. Nishibori, M. Takata, M. Sakata, N. Hamada, S. Todo, N. Mori, O. Shimomura, and A. Nakamura, *J. Phys. Soc. Jpn.* **71**, 3092 (2002).

¹⁰G. Kh. Rozenberg, M. P. Pasternak, W. M. Xu, Y. Amiel, M. Hanfland, M. Amboage, R. D. Taylor, and R. Jeanloz, *Phys. Rev. Lett.* **96**, 045705 (2006).

- ¹¹M. P. Pasternak, W. M. Xu, G. Kh. Rozenberg, R. D. Taylor, and R. Jeanloz, *J. Magn. Magn. Mater.* **265**, L107 (2003).
- ¹²M. P. Pasternak, W. M. Xu, G. Kh. Rozenberg, R. D. Taylor, and R. Jeanloz, *J. Phys. Chem. Solids* **65**, 1531 (2004).
- ¹³O. Mathon, F. Baudelet, M. D'Astuto, J.-P. Itié, P.-Y. Plaçais, and S. Pascarelli, ESRF Exp. Report He1617, 2004 (unpublished).
- ¹⁴R. Aragon, P. M. Gehring, and S. M. Shapiro, *Phys. Rev. Lett.* **70**, 1635 (1993).
- ¹⁵J. M. Besson, R. J. Nelmes, G. Hamel, J. S. Loveday, G. Weill, and S. Hull, *Physica B* **180-181**, 907 (1992).
- ¹⁶J. Rodríguez-Carvajal, *Physica B* **192**, 55 (1993); <http://www-llb.cea.fr/fullweb/powder.htm>
- ¹⁷L. W. Finger, R. M. Hazen, and A. M. Hofmeister, *Phys. Chem. Miner.* **13**, 215 (1986).
- ¹⁸I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci.* **41**, 244 (1985).
- ¹⁹Z. Zhang and S. Satpathy, *Phys. Rev. B* **44**, 13319 (1991).
- ²⁰M. P. Pasternak (private communication).