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SELECTED STUDIES OF MAGNETISM AT HIGH PRESSURE*

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ABSTRACT

Most previous studies of magnetism in various compounds under extreme conditions have been conducted over a wide pressure range at room temperature or over a wide a range of cryogenic temperatures at pressures below 20 GPa (200 kbar). We present some of the most recent studies of magnetism over an extended range of temperatures and pressures far beyond 20 GPa, *i.e.*, in regions of pressure-temperature (P-T) where magnetism has been largely unexplored. Recent techniques have permitted investigations of magnetism in selected 3d transition metal compounds in regions of P-T where physical properties may be drastically modified; related effects have often been seen in selected doping studies at ambient pressures. We present ⁵⁷Fe and ¹²⁹I Mössbauer studies covering the range 300 - 4 K to sub-megabar pressures in compounds such as Sr₂FeO₄, LaFeO₃ and FeI₂.

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representative of a broad class of $3d$ transition metal compounds. At ambient pressure the electronic structure of the transition metal atom in these antiferromagnetic insulators extends from $3d^4$ to $3d^6$ and has a distinct influence on the pressure evolution of their magnetic properties. Mössbauer studies of these compounds are considered in conjunction with available structural and electrical transport data at pressure.

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1. Introduction

In recent years compounds involving $3d$ transition metal (TM) elements have been the focus of intensive research in materials science because their electrical and magnetic properties may be substantially altered either by doping or by changing a physical parameter like pressure or temperature. Recent spectacular examples include high- T_C superconductivity in doped rare-earth copper-oxide materials [1], unusual magneto-resistance effects in doped manganese oxide materials [2], pressure-induced iso-structural I-M transition concurrent with a collapse of antiferromagnetism in TM halides [3], and temperature-tuning of an iso-structural insulator-to-metal (I-M) transition in rare-earth nickelate compounds [4]. The majority of these compounds are magnetic insulators under ambient conditions, counter to the conventional framework of the electronic band

structure in solids that those with partially filled $3d$ bands are expected always to be metallic. These magnetic insulators have a large optical gap (2-4 eV) and an optical absorption structure in the form of Frenkel excitons indicative of the d^n orbital multiplet that arises from crystal-field splittings. The local moments and energy band gap persist above the spin-ordering temperature. The magnetism is intimately linked to the TM electronic state. These magnetic compounds have generally been referred to as Mott insulators.

External pressure is a non-invasive, controlled means of varying the insulating gap in these systems; for example, gap-closure may occur as a result of bandwidth broadening associated with decreased lattice dimensions. This is in contrast to doping narrow band systems where the complications of electronic and structural disorder lead to effects that may not occur with pressure [5].

It should be noted that a rich variety of compounds containing the ^{57}Fe Mössbauer isotopes are Mott insulators. They are structural and electronic analogues of compounds in which high- T_C superconductivity, unusual magneto-resistance effects and temperature-driven I-M transitions occur. Major constituents of the Earth's interior are Fe-bearing magnetic insulators (oxides and sulfides), and investigating their magnetic and electronic and properties under extreme P-T conditions is of great importance to geophysical and geochemical studies. It is important to emphasize that Mössbauer spectroscopy (MS) represents the only means to study magnetism over the wide pressure range available with the diamond anvil cell (DAC). Our recent studies of magnetism under extreme conditions have been focused on MS pressure studies of $3d$ TM compounds that are Mott insulators

at ambient pressure, recognizing their importance to both materials science and geosciences. If ^{57}Fe MS is used for the magnetic studies, then the pressure dependence of the TM electronic- and spin-state may be investigated directly, given the link between magnetism and electronic structure. Examples will be given below to illustrate the rich pressure response of magnetism and electronic structure for a variety of Mott insulators having Fe in different initial oxidation states. To help interpret the results of MS pressure studies, it is necessary to understand the origin of the insulating gap and its relation to the electronic structure of the constituent atoms of the solid at ambient pressure.

2. Electronic structure and insulating gaps in 3d transition metal compounds

It has been recognized that the localization of carriers and corresponding insulating behavior in the Mott insulator is a result of strong on-site Coulomb repulsion U , which is not mitigated by the restricted range of kinetic energies available to a narrow d -band system. An energy gap occurs in the narrow $3d$ band, splitting it into an upper and a lower Hubbard sub-band separated by an amount U which is greater than a critical value of the d -band dispersional width W , that is mainly determined by the crystal structure, i.e. lattice parameter (see fig. 1). Doping or external pressure may be used to vary U and W , respectively, whereupon there are marked changes in physical properties; for example, the compound may undergo an I-M transition because of band-filling/depletion or gap-closure. In view of the the origin of the "Coulomb" gap, it is anticipated that a pressure-induced gap-closure and its associated I-M transition does not necessarily involve a

structural change and should be accompanied by a collapse of the magnetic moment -- a process often called the Mott transition. MS may be used to track the evolution with pressure of magnetism in Mott insulators. ¹²⁹I MS was used to detect a Mott transition in NiI₂ [3] for the first time.

It is evident from fig. 1 that the insulating gap may be of the so-called Mott-Hubbard (M-H) *d-d* type or so-called charge-transfer (C-T) *p-d* type with gap energy Δ , depending on whether the TM-*d* or anion-*p* band is the highest occupied band. Other possible gaps include those of TM *d*-TM 4*s* or even anion *p* - TM 4*s* character, depending on the relative magnitudes of U and Δ and the position of the 4*s* band-edge. The nature of the insulating gap depends on the crystal structure and the constituent ions that make up the solid; for example, Δ is directly related to the electronegativity of the anion and the Madelung potential [6]. It also determines the mode of carrier delocalization in the metallic state upon closure of the gap. Charge fluctuations involving TM ions only, $d^n + d^n \rightarrow d^{n-1} + d^{n+1}$ (d^n : electronic configuration of TM site) are expected for a M-H intra-band gap closure. Whereas ligand-to-metal charge transfer, $d^n \rightarrow d^{n+1} \underline{L}$ ($\underline{L}$: ligand hole) is expected for a C-T inter-band gap closure.

It should be noted that the *d* states of a TM ion consist of an orbital multiplet split by crystal-field effects; for example, in cubic symmetry the *d* states split into two-fold e_g and three-fold t_{2g} orbitals broadened into bands due to translational symmetry. Therefore, in a more detailed picture of fig. 1, the gap U would be present in both e_g and t_{2g} sub-bands. With increasing formal valence of the metal element, Δ systematically decreases and

becomes very small or even negative for compounds involving unusually high valences such as Fe^{4+} . This is a case where there is strong hybridization (i.e. charge transfer) between p and d states resulting in a $d^n \underline{L}$ hybridized valence band that is primarily of anion- p character. The result of strong hybridization is to split-off a $d^n \underline{L}$ discrete state, effectively introducing a gap into the valence band; carrier delocalization occurs by ligand-to-ligand charge transfer, $d^n \underline{L} + d^n \underline{L} \rightarrow d^n + d^n \underline{L}^2$ upon closure of the gap [7].

The origin and nature of the insulating gaps depicted in fig. 1 emerged from a theory developed by Zaanen, Sawatzky and Allen (ZSA) [8] in an attempt to understand the nature of the gaps in TM halides, oxides and sulfides and to interpret photoelectron spectra of these compounds. It is now well-established that the physical properties of TM compounds may be drastically modified in the regimes of both the pressure-temperature or the composition-temperature phase diagrams near to the I-M transition (where the ZSA framework is not necessarily applicable and where there is a dearth of alternative theories). Suitable theories should be formulated in terms of parameters involving U , Δ and the bandwidths. Experiments in which these parameters are varied, e.g. pressure experiments, represent a crucial test of any theory and provide incentives for the development of an appropriate alternative theory to help understand the effect of perturbations on the gapped state in narrow band systems, especially near the I-M transition.

3. High-pressure Mössbauer methodology

The diamond-anvil cells (DACs) for Mössbauer pressure studies have already been reviewed in ref. [9]. For the specific case of ^{57}Fe MS in a DAC there are severe constraints resulting from the high attenuation (70-80 %) of the 14.4-keV radiation by the pair of anvils of typical 0.3 C diamonds and the minute dimensions of the sample cavity of $\sim 10^{-3} \text{ cm}^2$. To reduce these deleterious effects we have utilized an optimized tight geometrical arrangement consisting of a $^{57}\text{Co}(\text{Rh})$ "point" source of high specific activity with source strength is in the range 3-7 mCi, optimal isotopically enriched absorbers loaded in the DAC, and high-efficiency proportional counters (end-window type, gas-flow Ar-CH_4 or Kr-CO_2). An example of this arrangement and its application at cryogenic temperatures has been published in ref. [10]. The gasket material usually consists of the high-Z alloy $\text{Ta}_{90}\text{W}_{10}$ for experiments below 35 GPa; a much harder Rhenium gasket is used for studies at higher pressure. A small central hole in the prepressed gasket forms the sample cavity. Both materials are iron-free effective collimators of 14.4-keV source-radiation for typical dimensions of the sample cavity that may range from a starting thickness of 40 μm to a final thickness of 10 μm at high pressure. Fine ruby chips in the cavity permit pressure measurements through the R_1 -line fluorescence line-shift [9]. Liquid argon is normally loaded as a pressure-transmitting medium. The pressure gradient, which is normally quantified by measuring a number of ruby chips distributed in the cavity, is typically $\sim 5\%$ of the average pressure. The pressure change with temperature in our DACs has been measured to be similarly small.

4. MS pressure studies of magnetism

4.1 Sr_2FeO_4

The Fe-based perovskites CaFeO_3 and SrFeO_3 have Fe in the unusually high oxidation state of 4^+ ($3d^4$). These compounds have already been investigated quite extensively by Mössbauer spectroscopy in separate experiments at cryogenic temperatures and at high pressure [11].

Recently, another tetravalent Fe-based compound, Sr_2FeO_4 , has been the subject of considerable investigation. The compound is an antiferromagnetic semiconductor having a Néel temperature $T_N \approx 60$ K. It is an iso-structural analogue of the antiferromagnetic insulator La_2CuO_4 , the parent compound of the original Sr-doped high- T_C materials discovered by Bednorz and Müller [1]. Sr_2FeO_4 crystallizes in the tetragonal space group $I4/mmm$ K_2NiF_4 structure. It has a 2-D type structure comprised of sheets of FeO_6 octahedra perpendicular to the c -axis with each Fe^{4+} ion in D_{4h} symmetry. ^{57}Fe MS at ambient pressure shows that the single Fe site quadrupole doublet at room temperature evolves to a complicated magnetic spectrum consisting of at least four sites having H_{hf} in the range 25-33 T [12]. This has been attributed to a spiral-spin structure, and from neutron diffraction studies on the same sample, there is no evidence of a crystallographic change down to 4 K.

Raman and optical spectroscopy pressure studies to 20 and 38 GPa have recently been performed on this compound [13]. An oxygen-derived Raman mode disappears at about 5.5 GPa. The optical reflectivity increases substantially in the near-infrared region as the pressure rises above 6 GPa; at $P > 13$ GPa it saturates at a considerably higher value

compared to ambient pressure. From this behavior, it has been speculated that the semiconductor gap narrows under pressure to culminate in a semiconductor-metal transition. We have performed ^{57}Fe Mössbauer, X-ray diffraction and electrical-resistance pressure studies on Sr_2FeO_4 to complement the previous Raman and optical studies.

Sample preparation : The material has been prepared according to the method described by Adler [14]. Even after repeated attempts in which synthesis conditions were slightly varied a small amount of Fe_2O_3 was always evident in addition to the main phase K_2NiF_4 -type Sr_2FeO_4 . Mössbauer pressure studies were therefore performed on pure samples of natural isotopic abundance whose ambient-pressure parameters conformed closely to literature values. Temperature dependent Mössbauer studies of the sample at ambient pressure gave both $\text{IS} = 0.00(1)$ mm/s (relative to $\alpha\text{-Fe}$) and $\Delta E_Q \approx 0.42(2)$ mm/s at room-temperature, an onset of magnetic ordering at $T_N \approx 60$ K, and a complex magnetic spectrum at 33 K. This behavior is typical of Fe in a high formal oxidation state within the K_2NiF_4 - type crystal structure [12,14].

The sample was loaded into a Merrill-Basset-type miniature DAC, initial sample cavity dimensions were 350- μm diameter and 40- μm thickness. The thermal scan method or a temperature dependent study have been used to estimate T_N at 9 GPa and 19 GPa ; magnetic spectra at these pressures were recorded at $T \ll T_N$. Each magnetic spectrum was recorded over several days to obtain sufficient statistics for comparison with the data at ambient pressure.

Pressure experiments : Examples of spectra as well as Mössbauer parameters at room temperature as a function of pressure is plotted in fig. 2. The isomer shift decreases linearly in the measured pressure range with no indication of discontinuous changes, consistent with an increase in density and preliminary measurements performed at the CHESS synchrotron X-ray facility (Cornell Univ.) that reports no structural change at pressures to 27 GPa. However ΔE_Q tends towards a minimum value at ~ 5.5 GPa, see fig. 2. The spectrum at 5.5 GPa may be fitted with a single Lorentzian doublet to obtain a $\Delta E_Q \approx 0.24$ mm/s. For $P > 5.5$ GPa ΔE_Q increases monotonically.

Low temperature measurements (see fig. 3(a)) indicate that the material is magnetic at 9 GPa having sharper features compared to the spectrum at ambient pressure and T_N in the range 60-70 K. The quality of the spectrum does not permit a detailed analysis to be made. The magnetic spectrum at 19 GPa has sharpened or simplified considerably compared to magnetic spectra at lower pressures. The maximum value of H_{hf} is estimated to be ~ 25 T and there is a substantial quadrupole shift.

Temperature dependent resistance $R(T)$ measurements in a DAC set-up were performed at pressures to $P \sim 20$ GPa and show that a semiconductor-metal transition occurs at 17(1) GPa. Resistance-temperature data at two selected pressures have been plotted in fig. 3 (b), metallic behavior is clearly evident at 19 GPa.

Discussion : The Fe local environment is a slightly elongated octahedron (Fe-O bond distances are 4×1.932 and 2×1.950 , [13]) under ambient conditions. With pressure increase we observe a cycle where the c/a ratio of the tetragonal unit cell decreases,

reaching a minimum value where Fe-O bond lengths almost equal to each other. At this point and the electric-field-gradient (EFG) is expected to attain its minimum value, see fig. 2 (b). With further pressure increase the c/a will decrease below the "cubic" value resulting in an increase in the crystal-field splitting and consequently in the EFG. An oxygen-derived Raman mode disappears at $P \sim 5.5$ GPa [14] possibly because it is no longer Raman-active in a tetragonal unit cell having regular FeO_6 octahedral units.

The main conclusions derived from the MS experiments at pressure are : (1) in the metallic state the compound is still magnetic having $T_N \sim 130$ K, (2) the original magnetic structure -- deduced to be spiral-spin-type in the 2-D structure at ambient pressure -- changes considerably under pressure, (3) there is no evidence of charge disproportionation of the type $2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$, (4) electronic and magnetic properties are similar to the cubic perovskite SrFeO_3 that is metallic and magnetic ($T_N \approx 131$ K) at ambient pressure [11].

Carrier delocalization in the metallic state of compounds having the TM atom in an unusually high oxidation state is supposed to occur by ligand-to-ligand charge transfer, $d^{n+1} \underline{L} + d^{n+1} \underline{L} \rightarrow d^{n+1} + d^{n+1} \underline{L}^2$ [7]. This may barely influence the magnetic moment of the Fe atom in Sr_2FeO_4 thus explaining the persistence of magnetism even within the metallic state at 19 GPa.

4.2 FeI_2

Previous ^{129}I Mössbauer pressure studies of the transferred hyperfine field in NiI_2 and CoI_2 showed that the magnetic moment collapses at the I-M transition of ~ 20 GPa and ~ 12.5 GPa, respectively [4]. X-ray measurements show that NiI_2 remains iso-structural across the transition. These pressure studies have now been extended to the case of FeI_2 in which the TM site may be directly probed by ^{57}Fe MS. This is further complemented by ^{129}I Mössbauer studies of the anion site. FeI_2 , similar to the other TM halides, is a layered antiferromagnetic insulator at ambient pressure ($T_N = 9$ K) that crystallizes in hexagonal-type CdI_2 ($P \bar{3}m$) structure [15]. Each ferrous ion in the $\text{I} - \text{Fe}^{2+} - \text{I}$ sandwiched layer is surrounded by an octahedral arrangement of anions and has D_{3d} (trigonal) site symmetry. The Fe^{2+} spins within any layer align ferromagnetically along the trigonal c -axis and successive layers that are weakly coupled have an antiparallel arrangement of spins.

Sample preparation : Samples were prepared for both ^{57}Fe and ^{129}I Mössbauer pressure studies by solid-vapor reaction of the elements in an evacuated quartz tube. The isotopic enrichment for ^{57}Fe Mössbauer studies on a number samples ranged from 20-30 % and a separate sample fully enriched in ^{129}I was synthesized for the ^{129}I Mössbauer studies. The crimson-red flakes were loaded into the DAC under exceptionally dry conditions in a glove-box because FeI_2 is extremely hygroscopic. The typical initial sample cavity dimensions in the $\text{Ta}_{90}\text{W}_{10}$ gasket was $250 \times 35 \mu\text{m}$. ^{57}Fe MS experiments both on the original material in the quartz tube and after loading in the DAC sealed to a pressure of 1 GPa showed no sign of hydrate impurity phases. In the temperature interval 300 - 90 K, the quadrupole doublet of the hydrate (impurity) phases has characteristically large ΔE_Q values of 2-3 mm/s compared with anhydrous FeI_2 that has ΔE_Q in the range 0.6 - 0.8

mm/s [16]. However ^{129}I Mössbauer studies of the ^{129}I -enriched sample showed an Iodine-based impurity contribution of ~15% of the total crystalline phase content -- this is thought to originate from the starting materials used in the synthesis process.

Pressure experiments : Examples of ^{57}Fe paramagnetic and magnetic spectra recorded at $P < 20$ GPa are shown in fig. 4 (a). A single Fe site has been used in a fit of the data. Each magnetic spectrum at low temperatures has a combined magnetic/quadrupole interaction of comparable magnitude and the absorption envelope extends over a range of ~ 5 mm/s. These are typical features of a static magnetic hyperfine field in a high-spin ferrous compound. Discrepancies in the fit to the magnetic spectrum are due to thickness effects and texturing both of which have not been accounted for. Up to $P \sim 20$ GPa the saturation magnetic field H_{hf} at the Fe site increases monotonically from 7 to 12 T and T_N , obtained from a temperature dependent study at each pressure, exhibits a more than ten-fold increase from 9 to 125 K (see fig. 5 (a)). At room temperature the IS decreases monotonically and ΔE_Q reaches a broad maximum at ~12 GPa (see fig. 5 (b)).

In the vicinity of 20 GPa both IS and ΔE_Q exhibit a discontinuous decrease. At this pressure drastic changes occur in features of the ^{57}Fe spectra recorded at low temperatures. Spectra at 20 GPa and low temperatures show a pronounced sagging base-line [17]. A central resonance is evident with weaker resonance dips located on either side which gradually diminish in intensity as the temperature is raised. Evidence of the sagging base-line, central doublet near to zero velocity and resonance dips in the wings of the spectrum persist in the spectra up to $P \sim 27$ GPa, see fig. 6 (a). The sagging base-line

occurs over an extended temperature range of at least 60 K down to 20 K. Spectra in the range 20-27 GPa may be fitted with a central doublet and a sextet to obtain an estimate of $H_{\text{hf}} \sim 30$ T at the lowest temperatures. The ^{57}Fe hyperfine interaction parameters thus indicate that an important change in the electronic structure of the material first occurs at $P \sim 20$ GPa; however a magnetic moment on the TM is still present to pressures of ~ 27 GPa from evidence provided by MS data at low temperatures. A transferred hyperfine field measured by ^{129}I MS is still evident at 22 GPa although substantially smaller than H_{hf} in the spectrum at 16 GPa (see fig. 4 (b)).

^{57}Fe MS measurements above 30 GPa show that ΔE_Q is almost independent of pressure, in contrast to the behavior at lower pressures. Furthermore at 35 GPa a quadrupole doublet is prominent down to the lowest temperature of 15 K (see fig. 6 (a)) and resonance dips in the wings of the spectrum are weak or absent compared with the spectrum at 27 GPa.

Temperature-dependent resistance behavior at selected pressures from experiments conducted on a sample in a separate DAC are displayed in fig. 6 (b). The compound is semiconducting at 23 GPa and there are indications of metallic behavior at 28 GPa. Quite substantial pressure gradients developed at high pressure in this sample cavity because no pressure transmitting medium was used. Therefore the upturn in resistance at low temperatures at 28 GPa is attributed to a semiconducting volume fraction of the phase-mixture in the cavity. Preliminary X-ray diffraction measurements to pressures of 26 GPa show no evidence of a structural change.

Discussion : At pressures to ~ 20 GPa FeI_2 is fully insulating and displays magnetic behavior anticipated for a covalent ferrous material. The increase of the hyperfine field from 7 T to 12 T in this range may be attributed to changes in the orbital contribution -- a volume-dependent term that is proportional to the average of the $3d$ charge density distribution $\langle r^{-3} \rangle$ [4,18]. The behavior of H_{hf} and the more than ten-fold increase in T_N is very similar to the magnetic behavior of CoI_2 up to the I-M transition at 12.5 GPa. By contrast the transferred H_{hf} in NiI_2 remains constant up to 13 GPa after which it slightly decreases to eventually vanish at the I-M transition of ~ 19 GPa ; T_N shows only a four-fold increase over this pressure range [4]. The orbital contribution to the magnetic moment from the lower-lying t_{2g} band in both Co^{2+} (d^7) and Fe^{2+} (d^6) is not completely quenched, in contrast to the case of Ni^{2+} (d^8). This possibly explains the similarity of the magnetic behavior of CoI_2 and FeI_2 as opposed to the magnetic behavior of NiI_2 .

Unusual behavior is evident in FeI_2 in a second pressure regime of 20-28 GPa where a magnetic moment still persists at the TM site. There is a considerably enhanced internal magnetic field compared to the values at $P < 20$ GPa, see fig. 5 (a). The existence of a magnetic moment and values of the ^{57}Fe IS and ΔE_Q at room temperature (fig. 5 (b)) suggest that the original high-spin state has not changed. The combination of spectral features at 20-27 GPa and low-temperatures (sagging base-line etc.) are reminiscent of **paramagnetic** hyperfine structure from electron spin relaxation effects [19]. The spectra at low temperatures are supposed to represent a regime of intermediate relaxation where the nuclear-spin Larmor precession frequency ω_L is comparable to the electron spin-flip frequency ω_S ; fast relaxation, $\omega_S \gg \omega_L$, occurs at 300 K. There is evidence of

semiconducting behavior indicative of a material with a small band gap in this pressure range (fig. 6 (b)). The pressure dependence of the ^{57}Fe IS and ΔE_Q values at room temperature indicate that a new electronic state develops in a third regime at pressures beyond ~ 28 GPa, consistent with resistance studies which indicate metallic behavior at 28 GPa. At pressures beyond ~ 28 GPa, Mössbauer studies at low temperatures in conjunction with the behavior of ΔE_Q at room temperature suggests that magnetism is conceivably absent. The sequence of transitions that occur upon pressurization are : magnetic-insulator (0-20 GPa) $\rightarrow$ high-spin paramagnetic-semiconductor (20-28 GPa) $\rightarrow$ nonmagnetic-metal (> 28 GPa). The transitional phase at 20-28 GPa in FeI_2 was not evident in previous studies on CoI_2 and NiI_2 where magnetic properties as a function of pressure were deduced from the transferred H_{hf} at the ^{129}I site [4].

4.3 LaFeO_3

The orthoferrite LaFeO_3 has a similar structure to that of LaNiO_3 , namely, a simple rhombohedrally distorted perovskite. In contrast to its nickelate counterpart it is an antiferromagnetic insulator (Néel temperature $T_N = 740$ K at ambient pressure). LaNiO_3 is metallic at ambient pressure, the Ni^{3+} ions are in the low-spin state and the compound has an unusually enhanced Pauli paramagnetism [19]. Photoemission spectroscopy on LaFeO_3 by Bôcquet *et al* [20] has shown that it has a large ligand-to-metal C-T gap $\Delta = 2\text{-}3$ eV primarily because of the exchange stabilized electronic ground state of the TM ion (nominally Fe^{3+} , high spin $3d^5$).

The orthoferrites crystallize in the space group $Pbnm$ and are orthorhombic distorted versions of cubic AMO_3 perovskites (e.g. $SrFeO_3$) as a result of steric adjustments when smaller rare-earth elements are substituted at the A sites. The Fe atoms have an octahedral local environment and the distortion is manifested as a tilting of the octahedra off the c -axis direction. The degree of tilting is dependent on the size of the A atom and this determines the deviation of the Fe-O-Fe superexchange angle from 180° . Details of the crystal and magnetic structure may be found in ref. [21].

Sample Preparation : Thoroughly mixed stoichiometric amounts of La_2O_3 and 25% ^{57}Fe -enriched Fe_2O_3 were heated at $1200^\circ C$ for six hours to produce ~ 45 mg of a dark-yellow colored compound. A qualitative phase analysis from an X-ray diffraction study indicated that the main phase was $LaFeO_3$ perovskite with unreacted La_2O_3 as an impurity contribution of less than 1% of the total crystalline phases present. Static high pressures were generated in a new miniature piston-cylinder-type DAC. The anvils consisted of a matched pair of diamonds with culet flats of $400\ \mu m$ beveled to $500\ \mu m$. A sample cavity ($160 \times 40\ \mu m$) was punched/drilled in a pre-indented rhenium gasket.

Pressure Studies : In fig. 7 (a) we depict Mössbauer spectra recorded at 300 K typical of different pressure regimes covered in the present study. In the first pressure regime, up to $P \sim 30$ GPa, the compound is magnetic; the Mössbauer spectra are each characteristic of a simple magnetic hyperfine interaction with a small quadrupole interaction and single Fe site. In the range 30 - 45 GPa -- considered to be a second pressure regime -- a new non-magnetic component coexists with the original magnetic phase. Each spectrum at

higher pressures in the third regime, covering the range 48 - 51 GPa, may satisfactorily be fitted with a single quadrupole doublet to represent a new non-magnetic high pressure phase of LaFeO_3 at 300 K. The pressure dependence of the relative abundance of the magnetic phase, as derived from the absorption intensities of the MS spectra, is shown in fig. 7 (b). It is also evident from fig. 7 (b) that the maximum variation in H_{hf} is less than 5% up to 42 GPa. Since H_{hf} is proportional to the magnetic moment of Fe^{3+} we may conclude that the $3d$ band does not broaden substantially in this pressure range.

Mössbauer spectra at 48 GPa were recorded as a function of temperature down to 7 K to further elucidate the electronic state and magnetic properties of LaFeO_3 in the third pressure regime, see fig. 8 (a). At ~85 K the base-line exhibits "sagging" and resonance absorption peaks begin to occur in the wings of the spectrum. The sagging base-line persists down to 7 K; distinct resonance dips are evident in the wings of the spectrum at 40 and 7 K. The sagging baseline in the spectra at low-temperatures in fig. 8 (a) is indicative of a relaxation process from spin fluctuations. It is noteworthy that the fluctuation effects persist over a wide temperature range of 85 K down to 7 K. This should be contrasted with the relaxation effects normally manifested in a rather narrow temperature interval, ~ 5 K, as a precursor effect to the onset of magnetic ordering at the Néel temperature [22]. We suggest that the internal magnetic field sensed by the nucleus at 48 GPa is derived from a dynamic single-ion effect (paramagnetic hyperfine structure), in contrast to the long-range cooperative exchange processes that lead to magnetic ordering at $P < 30$ GPa [23]. At 48 GPa and low temperatures $\omega_L \approx \omega_S$ and this represents a regime of intermediate relaxation; the fast relaxation regime in which $\omega_S \gg$

ω_L occurs at 300 K. Pronounced "sagging" still present at 7 K is an indication that magnetic ordering probably does not occur to well below this temperature.

Beyond the third pressure regime a second non-magnetic site evolves in the range 55-63 GPa at 300 K (see fig. 8 (b)). Optimal fits to each spectrum in this high pressure regime were obtained by using two quadrupole doublets.

The pressure evolution of the isomer shift (IS) and quadrupole shift/splitting (ΔE_Q) at 300 K are depicted in fig. 9. In the second pressure regime where magnetic and paramagnetic phases coexist, the IS appears to undergo a **discontinuous** change of ~ 0.1 mm/s. Small pressure-induced distortions of the FeO_6 octahedron and progressive changes of the crystallographic c/a ratio in the magnetically ordered state (0-30 GPa) cause ΔE_Q to vary monotonically from 0 to about -0.28 mm/s. This may be due to variations in the magnitude of the EFG in θ (the angle between the maximum value of the EFG, $eq = V_{ZZ}$, and the direction of H_{hf}), or a combination of both effects. In the second pressure regime and beyond, at $P > 31$ GPa, $\Delta E_Q = e^2qQ/2$ for the non-magnetic phase and varies from ~ 0.8 mm/s to ~ 1.2 mm/s as derived from the pure quadrupole split doublets. It should be noted that where two doublets have been used to obtain optimal fits at $P > 55$ GPa a much smaller value of ~ 0.25 mm/s was assigned to one of the components (see fig. 8 (b)). The IS values of the two doublets are almost identical to each other.

Discussion : The collapse of the magnetically ordered state at 300 K (fig. 7) and the implication, from relaxation effects over a wide range of low temperatures at $P \sim 48$ GPa (fig. 8 (a)), that $T_N < 7$ K in the paramagnetic phase, are compelling indications that the

magnetic transition is associated with a substantial change in the electronic structure of the TM atom. High pressure X-ray diffraction studies are required to check whether a crystallographic transition drives this magnetic transition or vice versa.

A spin-state electronic transition may account for the magnetic transition and the nature of the new paramagnetic phase of LaFeO_3 at high pressure. Spin-crossover may be anticipated from progressive pressure-induced distortions of the FeO_6 octahedron that will increase the crystal-field splitting until it is comparable to the electron spin-pairing energy. In the mean-field theory the magnetic ordering temperature is related to the atomic spin S by $k_B T_N \sim J S^2$, where J is the exchange integral and k_B is the Boltzmann constant. If the magnetic phase transition were to involve spin crossover, that is, a spin-state change of high-spin (HS) $\rightarrow$ low-spin (LS), $S=3/2 \rightarrow S=1/2$, then a considerable reduction in T_N would ensue. Spin equilibrium and fluctuations between the two spin states ($\text{HS} \leftrightarrow \text{LS}$) may explain the coexistence of magnetic and non-magnetic phases at 300 K in the range 30-45 GPa. The discontinuous change in IS in the second pressure regime of 35-45 GPa in LaFeO_3 may be a consequence of a lattice contraction accompanying the pressure-induced spin conversion to a LS state [24].

The magnetic hyperfine field at 48 GPa and low temperatures (fig. 8 (a)) is estimated to be $H_{\text{hf}} \sim 48$ T from the positions of the resonance dips in the wings of the spectrum. The rather large field of 48 T for an $S=1/2$ LS state is supposed to originate from orbital and dipolar contributions to H_{hf} , in addition to the contact term. The former two contributions are absent in HS Fe(III). An Fe LS state is also consistent with the rather

large value of $\Delta E_Q \geq 0.85 \text{ mm/s}$ derived for trivalent iron at high pressure (see fig. 9). By comparison, HoFeO_3 which is more distorted than LaFeO_3 under ambient conditions has $\Delta E_Q \sim 0.3 \text{ mm/s}$ in the paramagnetic state at 700 K [25].

The two non-magnetic Fe sites at 55-63 GPa are characterized by identical IS and quite different ΔE_Q values (see fig. 9). Assuming that the model of spin crossover is correct, it may be deduced that the spectra in this range display features of C-T charge fluctuations, perhaps as a precursor to closure of the ligand-to-metal inter-band gap. That is, fluctuations of the type $d^n \rightarrow d^{n+1} \underline{L}$ occur, where $n=5$ and $\underline{L}$ is a hole in the oxygen p -band. These fluctuations would correspond to Fe sites having the d^5 and d^6 electronic configuration. The former is LS ferric-like having a relatively small ΔE_Q and the latter is LS ferrous-like having a relatively large ΔE_Q . This regime of "valence equilibrium" may be anticipated in a compound having a small C-T gap $\Delta \approx k_B T$ that has been reduced under pressure due to bandwidth broadening. A reduction of the Fe-O interatomic distance or changes in the superexchange angle are likely to influence both the O-2p and Fe-3d (Hubbard) bandwidths.

5. Concluding remarks

The pressure evolution of magnetism and related electronic properties has been investigated in a selected number of transition metal compounds with a variety of cation oxidation states and crystal structures at ambient pressure, namely, Sr_2FeO_4 (Fe^{4+} ; d^4), FeI_2 (Fe^{2+} ; d^6) and LaFeO_3 (Fe^{3+} ; d^5). ^{57}Fe MS show evidence of unusual pressure-induced magnetic-electronic transitions in each of these compounds. The 2-D

antiferromagnetic semiconductor Sr_2FeO_4 transforms to a magnetic metallic state at ~ 18 GPa. FeI_2 evolves from a layered antiferromagnet insulator to a paramagnetic semiconductor at ~ 20 GPa and then becomes a non-magnetic metal beyond 30 GPa. Antiferromagnetic insulating LaFeO_3 undergoes a progressive transition to a spin-disordered state in the range 30-45 GPa ; this has been rationalized in terms of a spin cross-over transition. Preliminary pressure-dependent structural data on these compounds indicate that no drastic structural changes are involved at the magnetic-electronic transitions, but a detailed structural investigation as a function of pressure would be an important complement to these Mössbauer studies.

We have noted that the compounds investigated in this work are electronic and structural analogues of a broad class of TM compounds in which the combined effects of a narrow $3d$ band and electron-electron Coulomb repulsion are pivotal in establishing their physical properties. Some of the oxides have been the focus of important recent discoveries of novel magnetic and electrical-transport properties in materials science. Mössbauer spectroscopy covering an extended temperature and pressure range is a unique powerful approach to "tune" and probe both magnetism and the electronic ground state of representative TM compounds. This is crucial for establishing the composition of the pressure-temperature phase diagram to determine the direction of future exploratory studies of these and other related materials.

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FIGURE CAPTIONS

FIGURE 1 : A schematic diagram of the insulating gaps that occur in the band structure of 3d TM compounds due to the on-site electron-electron Coulomb repulsion U . (a) The highest fully occupied anion p band and the 3- d band are shown on the left and right side of the vertical axis, respectively. The effect of U is to split the narrow 3 d band into an upper and lower sub-band. Shaded bands represent occupied states and unoccupied states are left unshaded. For simplicity the bandwidth W is assumed to be same for all three bands. (b) Representation of the most likely charge-fluctuations that occur in the metallic state of an ionic lattice consisting of TM ions and closed-shell anions, depending on the nature of the original gapped state (see text).

FIGURE 2 : (a) ^{57}Fe Mössbauer spectra of Sr_2FeO_4 recorded at room temperature and selected pressures. Solid lines are theoretical fits to the data by using Lorentzian profiles. (b) Pressure evolution at room temperature of the isomer shift (relative to $\alpha\text{-Fe}$) and quadrupole splitting ΔE_Q in Sr_2FeO_4 . Solid lines are to guide the eye.

FIGURE 3 : (a) Spectra of Sr_2FeO_4 at cryogenic temperatures and pressures ranging from ambient to 20 GPa. (b) Resistance as a function of temperature at two selected pressures. Semiconducting behaviour is evident at 12 GPa whereas the sample is metallic at 18.5 GPa.

FIGURE 4 : (a) ^{57}Fe Mössbauer spectra of FeI_2 at $P < 20$ GPa . (b) ^{129}I Mössbauer spectra at pressures to 22 GPa , an impurity phase is indicated by the asterisk “*”. Solid lines through the data in both panels are theoretical fits using Lorentzian lineshapes and the full Hamiltonian.

FIGURE 5 : (a) Pressure evolution of the Néel temperature T_N and of the TM saturation magnetic hyperfine field H_{hf} (at $T \ll T_N$). Open symbols are estimates of the magnetic hyperfine field from spectra displaying relaxation effects at 20-27 GPa . (b) Pressure dependence of both the isomer shift (relative to $\alpha\text{-Fe}$) and quadrupole splitting ΔE_Q from ^{57}Fe Mössbauer spectra of FeI_2 at room temperature.

FIGURE 6 : (a) ^{57}Fe Mössbauer spectra of FeI_2 at $P > 20$ GPa. (b) Temperature dependent resistance data at two selected pressures. Semiconducting behavior is evident at 23 GPa whereas metallic behavior occurs at 28 GPa.

FIGURE CAPTIONS contin ...

FIGURE 7 : (a) Pressure evolution of ^{57}Fe Mössbauer spectra at 300 K in the range 0-50 GPa for LaFeO_3 . Solid lines through the data are theoretical fits. (b) Pressure dependence of the magnetic hyperfine field H_{hf} and the abundance A of the magnetic phase at room temperature . Solid lines are to guide the eye.

FIGURE 8 : (a) Temperature evolution of Mössbauer spectra in LaFeO_3 at 48 GPa. The "sagging" base-line that extends over a range of 85-7 K is noteworthy . (b) Mössbauer spectra of LaFeO_3 at 300 K and $P > 50$ GPa in the non-magnetic state. Solid lines through the data are theoretical fits. Spectra at 56 and 63 GPa have each been fitted with two quadrupole doublets.

FIGURE 9 : Pressure dependence of the isomer shift IS (relative to $\alpha\text{-Fe}$) and the quadrupole interaction ΔE_Q at room temperature in LaFeO_3 . Solid symbols refer to the magnetic phase and open symbols to the non-magnetic phase . Solid lines are a guide to the eye .

FIGURE 1 : Hearne , Pasternak and Taylor

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FIGURE 8 : Hearne , Pasternak and Taylor

FIGURE 9 : Hearne , Pasternak and Taylor