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Electronic structure and magnetic properties of LaFeO_3 at high pressure

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The electronic ground state and magnetic properties of the wide-gapped antiferromagnetic insulator LaFeO_3 have been investigated by ^{57}Fe Mössbauer spectroscopy at pressures up to 63 GPa and temperatures of 7–300 K. Two separate magnetic-electronic phase transitions have been identified in the measured pressure range. At 300 K a new nonmagnetic phase begins to evolve at ~ 30 GPa and coexists in ever increasing abundance with the original magnetic phase at pressures up to ~ 45 GPa. In the range 45–55 GPa and 300 K the spectrum is comprised solely of a nonmagnetic phase having a single Fe site. Spectra recorded at 48 GPa and temperatures down to 7 K exhibit features of paramagnetic hyperfine structure. The results are consistent with a progressive transition from a magnetically ordered state to that of a spin-disordered state in the range 30–45 GPa. At 300 K and higher pressures of 55–63 GPa the nonmagnetic spectra show features of two sites with similar isomer shifts but different quadrupole splittings. Pressure evolution of the hyperfine interaction parameters and the magnetic transition at 30–45 GPa may be explained by a change of the original Fe high-spin state, namely, spin crossover to a low-spin configuration. The two sites at 55–63 GPa have been attributed to the coexistence of different charge states at crystallographically equivalent sites. These distinct charge states are supposed to represent both low-spin Fe(III) and Fe(II) as a result of fluctuations across a ligand-to-metal charge-transfer gap $\Delta \sim k_B T$ that has been reduced under high pressure.

INTRODUCTION

The AMO_3 ($A = \text{Sr, Ca}$ or a rare earth; $M =$ transition-metal) perovskite series have a variety of interesting physical properties. Some compounds are strongly covalent antiferromagnetic metals, others are metallic with an enhanced Pauli paramagnetism and many are magnetic insulators. A systematic study in recent years has shown that the A atoms influence the physical properties mainly through steric effects whereas the transition-metal (TM) atom plays a crucial role by way of its electronic ground state (valence and spin) and the concomitant magnetic properties.

These compounds are a subset of a broader class of 3d TM oxides, most of which have partially filled 3d bands and yet are magnetic insulators. In these insulators a “Coulomb” gap is manifested in the partially filled narrow 3d band because of strong on-site Coulomb repulsion which is not mitigated by the restricted range of kinetic energies available to a narrow-band system. The insulating gap may be either of the Mott-Hubbard intraband $d-d$ type or the charge-transfer (CT) interband $p-d$ type, depending on the constituent atoms that make up the solid.¹ Appropriate doping of these strongly correlated electron systems permit a variety of properties to be obtained. For example, insulator-metal transitions may be induced or magnetic transitions may occur, namely, antiferromagnetism \rightarrow ferromagnetism or antiferromag-

netism \rightarrow paramagnetism. High- T_c superconductivity is known to stem from doping appropriate copper oxide materials whose parent compounds are antiferromagnetic insulators (e.g., La_2CuO_4). Alternatively, pressure may be used to vary the interatomic spacing and consequently the band widths of the TM- d and ligand- p states. Thus pressure-tuning of the insulating gap is possible with associated consequences for the physical properties of the material. Examples² of the interesting, yet distinct, consequences of pressure and of doping have been delineated in studies on NiI_2 and V_2O_3 .

A recent example of the importance of electron-correlation effects in AMO_3 compounds has been aptly demonstrated in the series of rare-earth orthonickelates RNiO_3 ($R = \text{Pr, Nd, Eu, Sm}$). A new type of metal-insulator transition (MIT) has been discovered in these compounds by changing temperature alone.³ In PrNiO_3 and NdNiO_3 the MIT concurs with a magnetic-to-paramagnetic transition. In two other orthonickelates, EuNiO_3 and SmNiO_3 , the magnetic transition does not coincide with the drastic change in their transport properties. In all cases there is only a very small change in the unit-cell volume ($\sim 0.25\%$) at the MIT in contrast to the case of the classical V_2O_3 system. LaNiO_3 is metallic at ambient pressure and has an enhanced Pauli paramagnetism. The mechanism responsible for “temperature tuning” of the MIT in the orthonickelates is still the subject of considerable investigation.

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 (Neél temperature $T_N=740$ K at ambient pressure). Photoemission spectroscopy by Bocquet *et al.* has shown⁴ that it has a large ligand-to-metal CT gap $\Delta=2-3$ eV primarily because of the exchange stabilized electronic ground state of the TM (nominally Fe^{3+} , high-spin $3d^5$). Chainani, Mathew, and Sarma⁵ have shown that doped samples of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ retain their insulating behavior even up to Sr substitution as high as 40%.

This work reports on ^{57}Fe Mössbauer spectroscopy (MS) pressure studies of an Fe-based representative of the AMO_3 series, namely, LaFeO_3 . The capabilities of ^{57}Fe MS have only recently been extended to extreme conditions of high pressure and cryogenic temperatures,⁶ thus permitting an investigation of electronic and magnetic properties over a wide range of pressure (i.e., interatomic spacing). Studies were carried out at variable temperatures (7–300 K) and pressures up to 63 GPa, well beyond that of previous ^{57}Fe MS pressure studies on the orthoferrites where no drastic change in the electronic and magnetic properties were observed in the range 0–14 GPa.⁷

The orthoferrites crystallize in the space group $Pbnm$. The materials are orthorhombic distorted versions of AMO_3 cubic 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 Refs. 8 and 9.

EXPERIMENT

Sample preparation. Thoroughly mixed stoichiometric amounts of La_2O_3 and 25% ^{57}Fe -enriched Fe_2O_3 were heated at 1200°C for 6 h to produce ~ 45 mg of a dark-yellow colored compound. A quantitative analysis of the x-ray-diffraction pattern of the reacted product and comparison with literature values indicated that the main phase was LaFeO_3 perovskite and that the minority impurity contribution from unreacted La_2O_3 was less than 1% of the total crystalline phases present.

High-pressure ^{57}Fe Mössbauer methodology. Mössbauer spectroscopy pressure studies over an extended temperature range have been performed with a facility that has been described in detail in a separate publication.⁶ A 7 mCi $^{57}\text{Co}(\text{Rh})$ “point” source was used in conjunction with an end-window Ar-methane proportional flow counter. Static high pressures were generated in a new miniature piston-cylinder-type diamond-anvil cell (DAC) with backing plates consisting of a WC flat disk and a hemispherical rocker. Its compact dimensions (30×20 mm height and diameter, respectively) and light weight (50 g) permitted convenient use of the DAC at cryogenic temperatures. The anvils consisted of a matched pair of diamonds with culet flats of 400 μm beveled to 500 μm .

A sample cavity (160×40 μm) was punched/drilled in a preindented rhenium gasket. Small ruby chips were mixed with the LaFeO_3 and loaded into the cavity to permit pressure measurement by way of the ruby R_1 -line fluorescence line shift. No pressurizing medium was used. The pressure gradient was quantified to be $\sim 5\%$ of the average pressure by measuring a number of ruby chips distributed in the cavity. A spectrum of good quality for a reliable analysis to be made could be accumulated in 20–30 h. The hyperfine interaction parameters were obtained from theoretical least-squares fits to the spectra by using the appropriate Hamiltonians to obtain the nuclear transition energies and intensities.¹⁰

RESULTS AND ANALYSIS

In Fig. 1 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 splitting and single Fe site [Fig. 1(a)]. With increasing pressure in the range of 30–45 GPa—considered to be a second pressure regime—a new nonmagnetic component evolves in the central region of the spectrum. This is quite evident at 36 GPa [Fig. 1(b)]. In this range the high-pressure component coexists with the original low-pressure magnetic phase. Each spectrum at higher pressures in the third pressure regime, covering the range 48–51 GPa, are satisfactorily fitted with a single quadrupole doublet [Fig. 1(c)] to represent a new nonmagnetic high-pressure phase of LaFeO_3 at 300 K. The pressure dependence of the relative abundance of the magnetic phase, as derived from

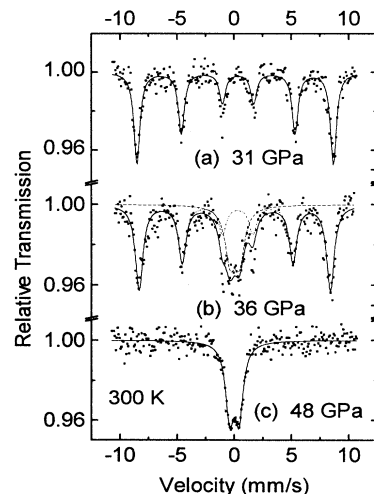


FIG. 1. Pressure evolution of Mössbauer spectra at 300 K in the range 0–50 GPa. Solid lines are theoretical fits: (a) is a magnetically split spectrum with a small quadrupole interaction characteristic of the range 0–30 GPa, (c) corresponds to a pure quadrupole splitting typical of $P > 45$ GPa, assuming a single Fe site in both cases. (b) corresponds to the “mixed-phase” regime 35–45 GPa.

the absorption intensities of the MS spectra, is shown in Fig. 2.

To help unravel details of the Mössbauer spectra at pressures above 35 GPa, additional measurements were made over a smaller velocity range (see Fig. 3). Fitting the nonmagnetic component with a single quadrupole-split doublet produces discrepancies even after accounting for the innermost lines of the sextet which are evident at 36–42 GPa in Fig. 3. In this pressure range the nonmagnetic and magnetic contributions are probably best represented by a distribution of quadrupole splittings and magnetic hyperfine fields, respectively.

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. At ~ 85 K the baseline exhibits “sagging” and resonance absorption peaks begin to occur in the wings of the spectrum (Fig. 4). The sagging baseline 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. 4 is indicative of a relaxation process from spin fluctuations on a time-scale of $1/\omega_L$, where ω_L is the Larmor precession frequency of the ^{57}Fe nucleus. It is noteworthy that the fluctuation effects persist over a wide range of temperature of 85 K down to 7 K. This should be contrasted with the relaxation effects associated with three-dimensional magnetic ordering that develops from, for example, cooperative superexchange processes in crystalline TM oxides. These relaxation effects are normally manifested in a rather narrow temperature interval, ~ 5 K, as a precursor effect to the onset of magnetic ordering at the Néel temperature. A prime example is the behavior near T_N in the orthoferrites at ambient pressure.¹¹ Therefore the magnetic hyperfine interaction evident at $P < 30$ GPa in LaFeO_3 is supposed to be radically different in origin from that observed at low temperatures and high pressure ($P > 45$ GPa). 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.^{12,13} AT 48 GPa and low temperatures $\omega_L \approx \omega_s$,

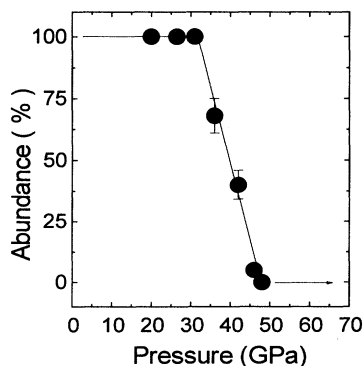


FIG. 2. Pressure dependence of the relative abundance of the magnetic component.

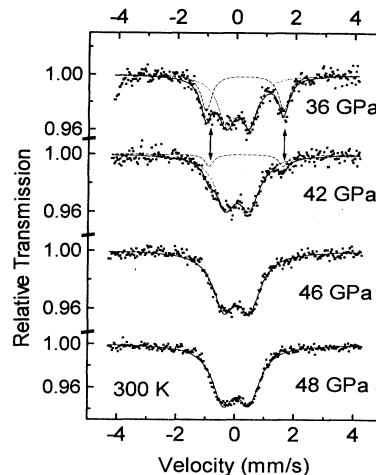


FIG. 3. Higher resolution scan of the central region of the spectra for the range 35–50 GPa at 300 K. The innermost lines of the magnetic component are indicated by arrows at the lowest pressure.

where ω_s is the spin-flip frequency, and this represents a regime of intermediate relaxation; the fast relaxation regime in which $\omega_s \gg \omega_L$ 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 nonmagnetic site evolves in the range 55–63 GPa at 300 K (see Fig. 5). Optimal fits to each spectrum in this high-pressure regime were obtained by using two quadrupole doublets.

The pressure dependence of the hyperfine interaction parameters associated with these spectra will be discussed next. The pressure evolution of the isomer shift (IS) and

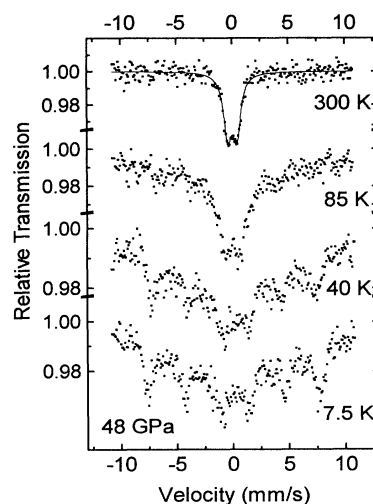


FIG. 4. Temperature evolution of Mössbauer spectra at 48 GPa. Note the “sagging” baseline that extends over a range of 85–7 K; a quantitative fit would require a more complicated fitting procedure than was used, but the data clearly show the appearance of magnetic ordering.

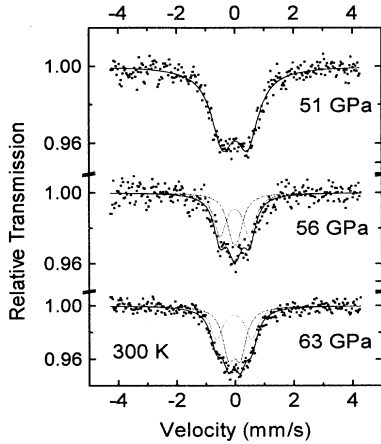


FIG. 5. Mössbauer spectra at 300 K and $P > 50$ GPa in the nonmagnetic state. Solid lines are theoretical fits. Spectra at 56 and 63 GPa have each been fitted with two quadrupole doublets.

quadrupole shift/splitting (E_Q) at 300 K are depicted in Figs. 6(a) and 6(b).¹⁴

The magnetic hyperfine field (H_{hyp}). In the first two pressure regimes extending up to ~ 45 GPa, H_{hyp} increase monotonically from 52.5 T at ambient pressure to reach a maximum of ~ 54 T at 20 GPa after which there is a monotonic decrease to an average value of 52.2 T at 42 GPa. Since H_{hyp} is proportional to the magnetic moment of Fe^{3+} and its maximum variation is less than 5% up to 42 GPa, we may conclude that there is no substantial broadening of the $3d$ band in this pressure range.

Isomer shift. The IS of the magnetic component in the first regime (0–30 GPa) decreases linearly by about $4.4 \times 10^{-3} \text{ mm s}^{-1}/\text{GPa}$. Being negatively proportional to the s -electron density at the nucleus, this decrease in IS

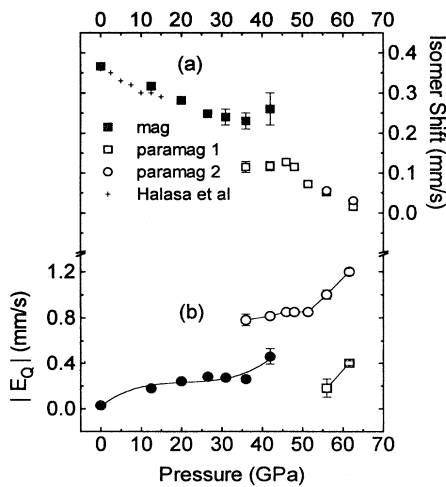


FIG. 6. Pressure dependence of the hyperfine interaction parameters at 300 K. Solid symbols refer to the magnetic phase and open symbols to the nonmagnetic phase: (a) Isomer shift values relative to α -Fe and linear least-squares fits of the data (dashed lines); (b) absolute value of the quadrupole shift/splitting. Lines are a guide to the eye.

is merely indicative of a gradual decrease in volume with increasing pressure. Previous results of Mössbauer measurements by Halasa, DePasquali, and Drickamer⁷ in the range of 0–14 GPa quantitatively agree with our results and have been included in Fig. 6(a) for comparison.

In the second pressure regime where magnetic and paramagnetic phases coexist, the IS appears to undergo a discontinuous change of $\sim 0.1 \text{ mm/s}$. Beyond the second pressure regime, $P > 45$ GPa, the IS decreases linearly by $6.2 \times 10^{-3} \text{ mm s}^{-1}/\text{GPa}$ reaching a value close to 0 mm/s at 63 GPa. The IS values of the two doublets in the range 55–63 GPa are almost identical to each other [see Fig. 6(a)].

The quadrupole shift/splitting. When the quadrupole interaction is much smaller than the magnetic interaction in a magnetically split spectrum the shift in line positions due to the quadrupole interaction is given by

$$E_Q = \frac{1}{2} e^2 q Q \frac{(3 \cos^2 \theta - 1)}{2}, \quad (1)$$

where Q is the nuclear quadrupole moment, e is the charge of the proton, $eq = V_{ZZ}$ is the maximum value of the electric-field gradient (EFG) in the principal axis system appropriate to the octahedral local environment of the TM atom, and θ is the angle between V_{ZZ} and the direction of H_{hyp} at the iron site. In Fig. 6(b) we depict the pressure variation of the absolute value of E_Q . X-ray and neutron-diffraction studies at ambient pressure^{8,9} have shown that the Fe-O-Fe superexchange angle is $\sim 157^\circ$ and that the magnetic moments at the Fe^{3+} sites are aligned along the c axis of the unit cell, respectively. At ambient pressure E_Q is almost equal to its maximum value of $e^2 q Q / 2$. This is a result of H_{hyp} being collinear with the direction of the magnetic moments and assuming V_{ZZ} is along the major axis [010] of the FeO_6 octahedron that is slightly tilted off the c -axis direction by $\sim 12^\circ$ due to the deviation of the superexchange angle from 180° . 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 E_Q to vary monotonically from 0 to about -0.28 mm/s as a consequence of variations of the magnitude of the EFG,¹⁴ changes in θ or a combination of both effects.

In the second pressure regime and beyond, at $P > 31$ GPa, $E_Q = e^2 q Q / 2$ for the nonmagnetic phase and varies from $\sim 0.8 \text{ mm/s}$ to $\sim 1.2 \text{ mm/s}$ 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 $\sim 0.25 \text{ mm/s}$ was assigned to one of the components [see Fig. 6(b)].

DISCUSSION

In an attempt to interpret the pressure evolution of the hyperfine interaction parameters it is necessary to highlight the following experimental results:

- (1) There is an incipient collapse of the magnetic state at ~ 30 GPa and the onset of a new paramagnetic regime occurs possibly having T_N less than 7 K;
- (2) The new paramagnetic phase at high pressure has a

rather large value of E_Q which is not typical of trivalent iron with the high-spin electronic configuration;

(3) There is a discontinuous change in the IS at the magnetic transition;

(4) Two iron sites with disparate E_Q values and almost identical IS values occur at $P > 55$ GPa.

The collapse of the magnetically ordered state at 300 K (see Fig. 2) and the implication, from relaxation effects over a wide range of low temperatures at $P \sim 48$ GPa (see Fig. 4), 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. High-pressure x-ray-diffraction studies are required to check whether a crystallographic transition is responsible for this magnetic transition.¹⁵

A substantial change in electronic structure may originate from a Mott-type MIT involving correlation-gap closure and the accompanying electron/hole delocalization or from a spin-state transition involving changes in the crystal-field splitting and an accompanying high-spin (HS) \rightarrow low-spin (LS) crossover. In what follows we provide evidence from the Mössbauer data in favor of a spin crossover electronic transition to account for the magnetic transition and the nature of the new paramagnetic phase of LaFeO₃ at high pressure.

As the FeO₆ octahedron is progressively distorted under pressure by way of changes in the Fe-O-Fe superexchange angle and the Fe-O interatomic distance, the crystal-field splitting energy (CF) gradually increases. When CF exceeds the average electron spin-pairing energy (SP) the HS configuration of trivalent Fe with five unpaired spins in the 3d-orbital multiplet ($t_{2g}^3 e_g^2$) undergoes spin crossover to an LS state, ($t_{2g}^5 e_g^0$), that has a single unpaired spin in the t_{2g} levels.¹³ Possible spin crossover in LaFeO₃ may lead to dramatic changes in the magnetic and electronic properties, as described below.

In the mean-field theory the ordering temperature is expressed as

$$k_B T_N = -2ZJS(S+1), \quad (2)$$

where $Z=6$ is the number of nearest neighbors, J is the exchange integral and S is the atomic spin. If the magnetic phase transition were to involve a spin crossover, that is, a spin-state change of $\frac{3}{2} \rightarrow \frac{1}{2}$, then a considerable reduction in T_N would ensue according to Eq. (2). When the relative difference between the crystal-field splitting and the mean spin-pairing energy is $|CF-SP| \approx k_B T$ then HS and LS spin states may coexist in thermal equilibrium (HS \leftrightarrow LS). This regime of spin equilibrium and fluctuations between the two spin states may explain the coexistence of magnetic and nonmagnetic phases at 300 K in the range 30–45 GPa.

The paramagnetic high-pressure phase in the range 45–55 GPa has an EFG which is substantially larger than that of the magnetic phase at lower pressure. The value of $E_Q \sim 0.85$ mm/s is higher than anticipated for HS Fe³⁺ in an octahedral local environment where typical values of E_Q are usually less than 0.5 mm/s (Refs. 9 and 18) even for an appreciable distortion of the surrounding configuration of ligands. For example, HoFeO₃

which is more distorted than LaFeO₃, under ambient conditions has $E_Q \sim 0.3$ mm/s in the paramagnetic state at 700 K.¹⁸ In general the contributions to the EFG are from lattice (eq_{LATT}) and electronic (eq_{EL}) terms. In the ${}^5T_{2g}(O_h)$ Fe(III) HS state eq_{EL} is negligible compared with eq_{LATT} because of the spherically symmetric electron distribution. In the LS state, however, eq_{EL} is expected to be considerably enhanced due to the effect of the single unpaired electron (or hole) in the t_{2g} levels. Therefore a LS state of the TM in LaFeO₃ is consistent with the large value of $E_Q \geq 0.85$ mm/s derived for trivalent iron at high pressure.

The magnetic hyperfine field at 48 GPa and low temperatures (Fig. 4) is estimated to be $H_{hyp} \sim 48$ T from the positions of the resonance dips in the wings of the spectrum. The hyperfine field is composed of contact, orbital, and dipolar contributions:¹⁹

$$H_{hyp} = H_C + H_L + H_D. \quad (3)$$

High-spin Fe(III) has a spherical distribution of electric charge due to the orbital configuration $t_{2g}^3 e_g^2$ and therefore only H_C contributes to H_{hyp} (~ 11 T per unpaired electron in the 3d shell). However in LS Fe(III) both the orbital motion of the unpaired 3d electron in the t_{2g} levels and the dipolar field from the resultant aspherical distribution of electronic charge make a contribution as well. A wide range of values may then be possible for H_{hyp} depending on the relative contribution from each term in Eq. (3). The rather large field of 48 T for the $S = \frac{1}{2}$ LS state is supposed to originate from the additional contributions of H_L and H_D which are absent in HS Fe(III).

A spin-state transition may be accompanied by a structural distortion in trivalent TM compounds. In some cases metal-ligand bond lengths have been shown to change by ~ 0.1 Å upon spin state conversion in Fe(III) complexes.²⁰ LaCoO₃ which is isomorphous to LaFeO₃ undergoes an anomalous thermal expansion associated with the thermal excitation of Co³⁺ ions from the LS to the HS state at ~ 90 K.²¹ In an analogous way, the discontinuous change in IS in the second pressure regime of 35–45 GPa in LaFeO₃ may be a consequence of a lattice contraction accompanying the pressure-induced spin conversion to a LS state.

The two nonmagnetic Fe sites at 55–63 GPa are characterized by identical IS and quite different E_Q values (see Fig. 6). Assuming that the model of spin crossover is correct, it may be deduced that the spectra in this range display features of CT charge fluctuations, perhaps as a precursor to closure of the ligand-to-metal interband 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 with the former being LS ferriclike and the latter being LS ferrouslike. This “valence equilibrium” situation is supposed to arise from a small CT gap $\Delta \approx k_B T$. A reduction of the CT gap is expected if there is an increase in both the O-2p and Fe-3d (Hubbard) bandwidths from, for example, a pressure-induced reduction of the Fe-O intera-

tomic distance or from changes in the superexchange angle. The large values of E_Q at 44–55 GPa are expected to prevail at higher pressures due to the LS d^5 state which has one unpaired electron in the t_{2g} levels. An LS d^6 site has no unpaired electrons, is diamagnetic and is also expected to contribute a small EFG and hence E_Q . The IS is usually quite sensitive to any difference in valence states for HS compounds at ambient pressure. However the range of IS values for LS Fe(III) and LS Fe(II) overlap considerably.¹⁰ In addition, the pressure dependence of IS for divalent and trivalent Fe differ and therefore their values may converge at high pressure. Thus the assignment of LS Fe(III) and Fe(II) to the two Fe components in each spectrum at $P > 55$ GPa is consistent with the distinct values of E_Q and yet similar values of the IS that have been derived from analysis of the spectra.

In conclusion it should be noted that the Ni^{3+} ions in $LaNiO_3$ at ambient pressure are known to have the LS electronic configuration. This compound is isomorphous to $LaFeO_3$ and is metallic with an anomalously enhanced Pauli paramagnetism.²² This is testimony that the LS electronic state of the TM may have a profound influence on the transport and magnetic properties in trivalent TM oxides. Both pressure x-ray-diffraction and resistivity studies on $LaFeO_3$ would represent an important complement to the Mössbauer studies of this work.

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¹³W. T. Oosterhuis, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman (Plenum, New York, 1966), Vol. 7, p. 97.

¹⁴The isomer shift IS characterizes the s -electron density at the nucleus. It is influenced by shielding effects of the d electrons. The quadrupole splitting E_Q is due to the electric-field

gradient (EFG) at the nucleus. The EFG arises from an aspherical or noncubic distribution of molecular orbitals and/or from surrounding charges (e.g., ligands) in a noncubic environment. See also Ref. 10.

¹⁵It is anticipated that quite a substantial structural adjustment would be necessary to reduce T_N from ~ 740 K to well below 300 K in the orthoferrites. Increasing pressure should decrease the Fe-O distance and lead to an increase in magnetic coupling and T_N . The ordering temperature decreases as the deviation of the Fe-O-Fe superexchange angle from 180° increases and varies from 740 K for $LaFeO_3$ ($\sim 156^\circ$) to 623 K for $LuFeO_3$ ($\sim 141^\circ$), see Ref. 16. In $Fe(OH)_3$ ($\sim 140^\circ$) which is isomorphous with the orthoferrites but with the rare earth absent, superexchange is mediated by OH^- anions and $T_N \sim 427$ K. This has been deduced from a Mössbauer study (Ref. 17).

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¹⁹The Fermi-contact term H_C arises from the imbalance of opposing s -electron spin density at the nucleus due to interaction of s with unpaired d electrons. A nonzero orbital magnetic moment contributes to H_L . The dipolar field H_D depends on the angular distribution of electrons in the $3d$ shell and thus on eq_{EL} . See also Ref. 10.

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