

Spin transition in a four-coordinate iron oxide

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Spin transition has attracted interests of researchers in various fields since early 1930's, with thousands of materials being realized including minerals and biomolecules. However, so far the metal centers in which it occurs have been almost always octahedral six-coordinate $3d^{4-7}$ metals, such as Fe(II). A five-coordination is only rarely seen. Here we report that $\text{SrFe}^{2+}\text{O}_2$, featuring a four-fold square-planar coordination, exhibits a high-spin ($S = 2$) to intermediate-spin ($S = 1$) transition on pressurization. A transition from antiferromagnetic insulator to ferromagnetic metal transition takes place at the same time. The ferromagnetic $S = 1$ state is found to be a half metal due to the inception of half-occupied spin-down (d_{xy} , d_{yz}) states. These results highlight the square-planar coordinated iron oxides as a new class of magnetic/electric materials.

Since the early 1930's the phenomenon of spin transition has attracted researchers of various fields, finding thousands of materials including minerals and biomolecules. In spite of all these efforts up to now, the metal centers, which undergo the spin transition, are nearly exclusively in an octahedral six-fold coordination such as Fe(II). A five-fold coordination is only rarely seen. Here we report that $\text{SrFe}^{2+}\text{O}_2$, featuring a four-fold square-planar coordination, exhibits a high-spin ($S = 2$) to intermediate-spin ($S = 1$) transition on pressurization. This transition is accompanied by a transition from antiferromagnetic insulating to a ferromagnetic so-called half-metallic states: only half of the spin-down (d_{xy} , d_{yz}) are filled. These results highlight square-planar coordinated iron oxides as new class of magnetic/electric materials.

Spin transition, or spin crossover, generally occurs in compounds of octahedrally coordinated $3d$ transition metal ions with d^4 , d^5 , d^6 and d^7 electronic configurations, and they are driven by the competition between the intra-atomic exchange energy and the crystal field energy. The former stabilizes a high-spin state, a spin state with a maximum spin multiplicity as for the free ion, while the latter stabilizes a low-spin state where the electrons occupy low energy orbitals only at the expense of increasing the exchange energy¹. This transition, which can be induced by external perturbations such as heating^{2, 3}, pressurization⁴⁻⁸, lightning⁹, magnetic field¹⁰, chemical substitution¹¹, and gas adsorption¹², were found in a wide range of materials like oxides (FeBO_3 , CaFeO_3)^{4, 5, 7, 10}, metal-organic complexes¹, porous materials¹²,

supramolecular systems³ as well as in human hemoglobin¹³. Some of these materials have found promising applications as sensors, or displaying and recording devices. Recent discoveries of the spin state transition in magnesiowüstite (Mg,Fe)O^{4, 5} and silicate perovskite (Mg,Fe)(Si,Al)O₃⁷ have provided renewed understanding on the seismic wave heterogeneity in Earth's lower mantle. Among the ions that exhibit spin state transition phenomena, the largest number of cases is found for the d^6 electronic configuration, of which divalent iron(II) represents the majority. The transition has been observed mostly between the high-spin ($S = 2$) and the low-spin ($S = 0$) states.

The crystal field energy depends on the particular geometrical arrangement of both metal ion and ligands, as well as on the metal-ligand distance. It also depends on properties such as substantial deviations from octahedral symmetry, packing effects in crystal lattices, the thermal contraction inherent to crystalline solids, and cooperative interactions. For example, it is known that a transition involving an intermediate spin state ($S = 1$ for d^6 and $S = 3/2$ for d^5) is feasible for five-fold coordinated compounds such as TbBaCo₂O₅ with a pyramidal coordination¹⁴ and the [Fe(P₄)Br]BPh₄·CH₂Cl₂ complex (P₄: hexapenyl-1,4,7,10-tetraphosphadecane, Ph: phenyl) with a trigonal-bipyramidal coordination¹⁵. To the authors' knowledge, however, up to now no spin transition is reported for compounds with a four or lesser coordinated metal ion.

A recently synthesized iron(II) oxide SrFeO₂, as prepared by the hydride reduction of SrFeO₃ at low temperatures, unprecedentedly has a square planar coordination of the high-spin iron(II) ion^{15, 16}. As shown in Fig. 1d, this material is built from two-dimensional FeO₂ layers intervened by Sr atoms, isomorphic with the so-called infinite layer structure as first found for (Ca,Sr)CuO₂. In spite of an apparent two-dimensional crystal structure, it undergoes an antiferromagnetic order at a remarkably high temperature (Néel temperature: $T_N = 473$ K) into a *G*-type spin structure, which is due to the strong hybridization between Fe $d_{x^2-y^2}^2$ and O p_σ orbitals as evidenced by a very low isomer shift in the Mössbauer spectrum.

Here we present investigations of pressurization on the spin and electronic state in SrFeO₂ by ⁵⁷Fe Mössbauer spectroscopy, electrical resistance, X-ray diffraction as well as by first-principles calculations. We found that SrFeO₂ is the first material with a four-fold coordinated metal ion which shows a spin state transition. The high-spin to intermediate-spin transition is accompanied by an insulator-to-metal transition as well as an antiferromagnetic-to-ferromagnetic transition.

Typical high-pressure ⁵⁷Fe Mössbauer spectra of SrFeO₂ at room temperature are shown in

Fig. 2a (see Supplementary Fig. 1 for details). Below ~ 30 GPa, no significant change was observed within the experimental uncertainties. The hyperfine field (H_{hf}) at 25 GPa, for example, is 42 T, which is nearly identical with that at ambient pressure¹⁵, indicating that the divalent iron ion remains in the high-spin state ($S = 2$), and that T_{N} remains high. The gradual and linear decrease in the isomer shift (IS) with pressure (see Supplementary Fig. 2) is in accordance with the trend observed in many iron compounds under high pressure^{1, 8} and can be interpreted in terms of gradually increased hybridization of Fe 3d orbitals with O 2p orbitals of the oxygen neighbors.

A drastic change, however, arose in the Mössbauer spectrum at a pressure of 38 GPa. While it also consists of well-defined six peaks indicating the presence of magnetic order at ambient temperature, H_{hf} of 18 T is nearly a half only of that for the low-pressure phase, implying the occurrence of a spin-state transition into an intermediate spin ($S = 1$) state. This spectrum feature remains up to the maximum pressure of 70 GPa as applied in this study. In order to confirm the spin state transition, in other words to exclude the possibility that the reduction in H_{hf} is merely due to the reduction of T_{N} , we cooled down the sample to 7 K. The corresponding spectrum has an only slightly increased value of H_{hf} of 19 T, providing firm evidence that the iron ions in the high-pressure phase are in the intermediate spin state. The well-developed six-line pattern in the intermediate spin state indicates that the magnetic order temperature is still far above room temperature. Subsequently, Mössbauer spectroscopy of the high-pressure phase was conducted under a magnetic field, for which the incident γ -ray was set parallel to the applied magnetic field. As shown in Fig. 2 and in Supplementary Fig. 3, the intensities of the 2nd and 5th lines ($\Delta m = 0$) showed a remarkable decrease with increasing magnetic field and disappeared at 3 T. We thus conclude that the high-pressure phase is a ferromagnet. The quadrupole shift ($QS = S_1 - S_2$) changed suddenly from 1.53 mms^{-1} (25 GPa) to 0.70 mms^{-1} (38 GPa) after the transition. Both the initial and the new spectra coexist in the pressure range 27-37 GPa due to a pressure gradient within the sample. Yet, the analysis of the relative spectrum weight and the pressure gradient allowed a rough estimation of the critical pressure P_c of 33 ± 3 GPa.

To examine a possibility of structural change on the spin transition, we carried out *in situ* X-ray powder diffraction experiments in a diamond anvil cell at pressures up to 43 GPa. The diffraction data recorded (see Supplementary Fig. 4) are of high quality with a good signal-to-noise ratio, allowing accurate determination of the lattice parameters. All the peaks of the

diffraction pattern at each pressure could be assigned to tetragonal infinite-layer structure, and no additional reflections were detected within the resolution of the experiment. Though the measured range of the diffraction angles is not sufficient to make a final conclusion, it is likely that the transition is isostructural. At pressures below the spin transition, the pressure dependence of the volume can be fitted by the third order Birch-Murnaghan equation of state with the bulk modulus $K = 126$ GPa, which is slightly smaller than that estimated for the fully oxidized perovskite SrFeO_3 ($K = 146$ GPa)¹⁷. As displayed in Fig. 1a, the unit cell parameters a and c decrease smoothly with the application of pressure, but exhibit a significant drop at 33 ± 1 GPa, which agrees well with the pressure P_c as estimated from the Mössbauer study. Therefore, this anomaly might be associated with the claimed spin transition. A volume reduction of $\sim 3\%$ (Fig. 1b) is comparable with those for other compounds that exhibit high-spin to low-spin transitions¹.

First-principles calculations based on the hybrid density functional theory (PBE0) method^{18, 19} were carried out to examine the pressure dependence of the crystal and electronic structures. The antiferromagnetic $S = 2$ state is the ground state at atmospheric pressure and remains stable up to P_c , where the abrupt transition to the ferromagnetic $S = 1$ state occurs (Fig. 2b), verifying the experimental observations. The calculated P_c of 53 GPa is, however, rather high in comparison with the experimental P_c of 33 GPa. As shown in Fig. 2c, the calculated spin moment decreases from $3.5 \mu_B$ to $1.8 \mu_B$ (μ_B : bohr magneton) between the antiferromagnetic and ferromagnetic states, which is consistent with the change in H_{hf} from 42 T to 19 T. With respect to the a axis, both the theory and experiment indicated a drop of $\sim 2\%$, but concerning the c axis, the sign of change is opposite between the theory and experiment. However, in terms of the unit cell volume at P_c , the discrepancy between theory and experiment differs only by $\sim 3 \text{ \AA}^3$ (or 6%).

To understand the nature of the spin transition, we first focus on the antiferromagnetic $S = 2$ state. The local density-of-states of the Fe ion at atmospheric pressure is shown in Fig. 4a. Consistent with the results of previous “LDA+U” calculations^{20, 21}, the lone spin-down electron is found to occupy the d_z^2 orbital. The double occupation of d_z^2 allows a considerable reduction of the intra-atomic Coulomb repulsion^{20, 21}. The σ -bond formed between Fe $d_{x^2-y^2}$ and O $p_{x,y}$ is split into the bonding and antibonding states by ~ 7 eV owing to a strong in-layer Fe d and O p hybridization. For pressures less than P_c , both the bonding and antibonding states in the spin-up channel are occupied. In the antiferromagnetic $S = 2$ state, the d^6 state has the electronic configuration of $(d_z^2)^2 (d_{xz}, d_{yz})^2 (d_{xy})^1 (d_{x^2-y^2})^1$.

We find that the spin transition is attributed to the strong in-layer hybridization between Fe $d_{x^2-y^2} - O p_\sigma$ bonding states leading to electronic instability toward the depopulation of $d_{x^2-y^2} - O p_\sigma$ antibonding states. The depopulation of the Fe $d_{x^2-y^2}$ antibonding states can be seen in Fig. 4b showing the local density-of-states of Fe for the ferromagnetic $S = 1$ state. The Fe d electrons are increased to $d^{6.5}$ in total with the electronic configuration of $(d_z^2)^1 (d_{xz}, d_{yz})^2 (d_{xy})^1 (d_{x^2-y^2})^{0.25}$ for the spin-up channel and $(d_z^2)^1 (d_{xz}, d_{yz})^1 (d_{xy})^0 (d_{x^2-y^2})^{0.25}$ for the spin-down channel. Another point to be noted here is that the ferromagnetic $S = 1$ state is half-metallic. In the antiferromagnetic $S = 2$ state, the band gap decreases considerably with increasing pressure as shown in Fig. 3a, and then drops to naught at P_c .

The spin moment of the Fe $d_{x^2-y^2}$ bonding states is quenched due to the enhanced in-layer bonding between Fe d and O p . The double occupation of d_z^2 is maintained in the ferromagnetic $S = 1$ state just after the transition, but becomes energetically unfavorable due to the compression of the interlayer spacing. Therefore, the charge transfer from spin-down d_z^2 to spin-down d_{xy} has to occur, while the spin-down (d_{xz}, d_{yz}) states remain half-occupied (Fig. 4c). It follows that, as the pressure reaches $P \geq 70$ GPa, the spin-down states of d_{xy} and d_z^2 also become half-occupied in the ferromagnetic $S = 1$ state $(d_z^2)^{0.5} (d_{xz}, d_{yz})^1 (d_{xy})^{0.5} (d_{x^2-y^2})^{0.25}$ for the spin-down states, resulting in an increase of density-of-states at the Fermi level.

We conducted electrical resistance measurement on non-sintered powder sample under pressure, as summarized in Fig. 3. At ambient and low pressures, SrFeO₂ is a nonconductor or a semiconductor with an out-of-range resistance. The electrical resistance at room temperature became measurable above 17 GPa. Across the spin state transition, a drastic decrease of resistance occurs from kilohm at 27 GPa to ohm at 37 GPa, and to centiohm at 50 GPa. The temperature dependence of the electrical resistance $\Delta R/\Delta T$ becomes smaller, and finally its sign changes from negative to positive at ~ 60 GPa. Although $\Delta R/\Delta T$ turns negative at lower temperatures, this is possibly due to Anderson localization and the use of the non-sintered powder sample. In addition, the resistance measurements suffered from the pressure distribution in the sample as in the Mössbauer experiments, which must render the insulator-metal transition at P_c obscured to some extent. It is likely that the intermediate spin state is a metal as theoretically suggested.

Comparing with the ferromagnetic $S = 1$ state, the antiferromagnetic $S = 1$ state is much less stable above P_c . An examination of its electronic structure of the antiferromagnetic $S = 1$ state

(Fig. 4d) shows that, in addition to having a d_z^2 electron in the spin-down channel, the second spin-down electron actually prefers to occupy the d_{xy} orbital. The antiferromagnetic $S = 1$ state remains as an insulator. The sudden increase in the energy from antiferromagnetic $S = 2$ to antiferromagnetic $S = 1$ is due to the increase of Coulomb repulsion resulting from the double occupation of d_{xy} . We have also examined the possibility of spin transition induced by phonon instability at various pressures. More specifically, we considered the effects of Jahn-Teller lattice distortion and breathing phonon mode. The former could induce a spin state of $S = 1$, while the latter could result in a coexistence of the $S = 1$ and $S = 2$ states due to a charge disproportionation reaction. However, we find experimentally and theoretically that SrFeO_2 is stable against a cooperative oxygen displacement in either Jahn-Teller lattice distortion or breathing phonon mode in both antiferromagnetic and ferromagnetic states at all pressures. Therefore, the spin transition in SrFeO_2 is not due to these phonon instabilities.

The spin state transitions in $3d$ ions are routinely interpreted as due to the transfer of one or two electrons between d orbitals of opposite spin channels. The observed $S = 2$ to $S = 1$ transition in SrFeO_2 is distinctly different from the previously reported examples in two aspects: it involves the transfer of non-integer d electrons and the $p \rightarrow d$ charge transfer (see Supplementary Table 1).

A range of transition-metal oxides²³⁻²⁶ has now been found to exhibit half-metallic ferromagnetism – these are limited mostly to manganese and chromium oxides ($\text{La}_{1.3}\text{Sr}_{0.7}\text{Mn}_2\text{O}_7$, $\text{Tl}_2\text{Mn}_2\text{O}_7$, CrO_2 etc.). The double-perovskite oxide $\text{Sr}_2\text{FeMoO}_6$ is known as iron-based half-metallic ferromagnet, but it contains molybdenum which is rare in the earth crust. Since iron is the most abundant transition-metal, the discovery of half-metallic ferromagnetism in SrFeO_2 containing only iron is important in view of future application in industry related to magnetism and spin electronics, although P_c is still too high. Recent studies²⁷⁻²⁹ have demonstrated that the square planar coordination around iron in SrFeO_2 is not a mere fortuity but could be widely and universally available including serial spin-ladders $\text{Sr}_{n+1}\text{Fe}_n\text{O}_{2n+1}$ ($n = \text{integer}$), such as $n = 2$ $\text{Sr}_3\text{Fe}_2\text{O}_5$. One can also distort a square planar FeO_4 unit toward a tetrahedron as in CaFeO_2 . Although P_c in SrFeO_2 is yet still too high, it is desirable to reduce P_c in those related iron oxides while keeping the transition temperature far above room temperature.

Metallization of the FeO_2 sheet would provide us a hope that further pressurization could lead to superconductivity in analogy with the layered cuprates. It is also interesting to compare the present compound with a recently discovered iron oxypnictide superconductors³⁰ since in

both cases the iron atoms form two-dimensional square lattice and are coordinated by four anions. Furthermore, preliminary calculations at higher pressures suggest a transition from the $S = 1$ state to a 2nd intermediate spin ($S = 1/2$) state before it finally falls onto the $S = 0$ state. It is interesting to check these points experimentally.

METHODS

The powder sample of SrFeO_2 was synthesized by the reducing reaction with CaH_2 of a slightly oxygen deficient perovskite $\text{SrFeO}_{2.875}$. The precursor $\text{SrFeO}_{2.875}$ was prepared by a high-temperature ceramic method from SrCO_3 (99.99 %) and Fe_2O_3 (99.99 %). $\text{SrFeO}_{2.875}$ and a two-molar excess of CaH_2 were mixed, finely ground in an Ar-filled drybox, sealed in an evacuated Pyrex tube, and reacted at 553 K for two days. The residual CaH_2 and the CaO byproduct were removed from SrFeO_2 by washing them out with a NH_4Cl /methanol solution. For details, please refer to the literature¹⁵.

The high-pressure ^{57}Fe Mössbauer measurements were performed up to 70 GPa using a Bassett-type diamond-anvil cell³¹. The ^{57}Fe -enriched SrFeO_2 powder and small ruby chips were enclosed in the hole of a Re gasket. Two types of pressure-transmitting media, a 4:1 methanol:ethanol solution and Daphne7373, were used. A point γ -ray source of ^{57}Co in a Rh matrix of 370 MBq and another one of 925 MBq having active areas of 1 mm and 4 mm in diameter, respectively, were used. The pressure was determined by means of ruby fluorescence manometry. To estimate the pressure distribution along the sample, several ruby chips were placed inside the hole at different distances from the center of the hole. It was found that the pressure gradient at the sample was not more than 8 GPa at maximal pressures. The γ -ray source could not be narrowed more because the high-pressure Mössbauer study allows only a limited sample and a long exposure time as long as a week was required to accumulate fairly reasonable spectral statistics. The magnetic field was produced by a superconducting solenoid operating in the persistent mode up to 3 T. ^{57}Fe Mössbauer experiments under the external magnetic field were carried out with the magnetic field applied along the γ -ray propagation direction. The velocity scale of the spectrum was relative to α -Fe at room temperature. Electrical resistance was measured with a standard dc four-probe method between 5 K and 300 K up to 67 GPa. Fine alumina powder and NaCl were pressed onto the gasket surface for electrical insulation and pressure-transmitting medium, respectively, on which sample powder and Pt electrodes were

placed together. Applied pressure was measured by means of fluorescence manometry on ruby chips placed around the sample. In this electrical resistance measurement the sectional area and the distance between probes were about $60\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ and $50\text{ }\mu\text{m}$, respectively.

Powder X-ray diffraction profiles at high pressures up to 43 GPa were recorded using Mo- K_α radiation from a 5.4 kW Rigaku rotating anode generator equipped with a $100\text{ }\mu\text{m}$ collimator. Powder sample of SrFeO_2 was loaded in a $300\text{ }\mu\text{m}$ hole of preindented stainless-steel gasket of the diamond-anvil cell. A 4:1 methanol:ethanol mixture was used as the pressure-transmitting medium. The shift of ruby fluorescence was used for the determination of pressure. To estimate the pressure distribution along the sample, several ruby chips were placed inside the hole at different distances from the center of the hole. It was found that the pressure gradient at the sample was not more than 0.5 GPa at maximal pressures. The diffracted X-ray was collected with an image plate. More details of the experimental setup are reported elsewhere³². Four diffraction peaks, 110, 011, 020, and 121 were used to calculate the cell parameters.

The first-principles calculations were performed using the Vienna *ab initio* Simulation Package (VASP)³³ with the ion-electron interaction described by the projector augmented wave potential (PAW)³⁴ (see Supplementary Information for details). We employed the hybrid density functional theory (PBE0) method^{18,35}, as implemented in VASP^{19,36}, to treat the localized Fe^{2+} states in SrFeO_2 . The exchange energy in PBE0 mixes the energies of exact Hartree-Fock (HF) exchange and PBE exchange from the local density functional approximation^{19,36}. The long-range part of the HF exchange interaction is included in PBE0. The weight of HF exchange in the mixing is general less than 25%. We find that the weights between 10% - 20% of HF exchange provide the most consistent results and describe the experimental findings reasonably well for SrFeO_2 . The results reported in this paper were done by using 15% HF with 85% of PBE for the exchange energy. We find that the spin transition pressure from the antiferromagnetic ($S = 2$) state to the ferromagnetic state is insensitive to the weights of mixing. It is the stable ranges of the $S = 2$ and $S = 1$ states within the ferromagnetic ordering that shows an increased sensitivity to the weights of HF mixing in PBE0.

In our calculations, the semicore states (the $3p$ and $4s$ states of Sr and the $3p$ state of Fe) were treated as valence states. An energy cutoff of 500 eV was chosen for the plane wave expansion. Full relaxation of atomic positions and lattice parameters at each pressure was achieved by minimizing forces and stress tensor components. Forces were minimized down to

10^{-5} eV \AA^{-1} and the difference in the total energies between two successive electronic iterations was required to be less than 10^{-7} eV. The angular momentum projected local density of states and magnetic moments of Fe were calculated within a sphere (i.e., the Wigner-Seitz radius) of 1.164 \AA .

References

- [1] Gütlich, P. & Goodwin, H. A. *Spin crossover in transition metal compounds I-III*, vol. 233-235, Springer-Verlag Heidelberg (2004).
- [2] Kröber, J., Coddjovi, E., Kahn, O., Crolière, F. & Jay, C. A spin transition system with a thermal hysteresis at room temperature. *J. Am. Chem. Soc.* **115**, 9810-9811 (1993).
- [3] Real, J. A., Andés, E., Muñoz, M. C., Julve, M., Granier, T., Bousseksou, A. & Varret, F. Spin crossover in a catenane supramolecular system. *Science* **267**, 265-267 (1995).
- [4] Badro, J., Fiquet, G., Guyot, F., Ruett, J.-P., Struzhkin, V. V., Vankó, G. & Monaco, G. Iron partitioning in earth's mantle: toward a deep lower mantle discontinuity. *Science* **300**, 789-791 (2003).
- [5] Lin, J.-F., Struzhkin, V. V., Jacobsen, S. D., Hu, M. Y., Chow, P., Kung, J., Liu, H., Mao, H.-K. & Hemley, R. J. Spin transition of iron in magnesiowüstite in the earth's lower mantle. *Nature* **436**, 377-380 (2005).
- [6] Rueff, J.-P., Kao, C.-C., Struzhkin, V. V., Bardo, J., Shu, J., Hemley, R. J. & Mao, H. K. Pressure-induced high-spin to low-spin transition in FeS evidenced by X-ray emission spectroscopy. *Phys. Rev. Lett.* **82**, 3284-3287 (1999).
- [7] Li, J., Struzhkin, V. V., Mao, H.-K., Shu, J., Jemley, R. J., Fei, Y., Mysen, B., Dera, P., Prakapenka, V. & Shen, G. Electronic spin state of iron in lower mantle perovskite. *Proc. Natl. Acad. Sci. U.S.A.* **101**, 14027-14030 (2004).
- [8] Takano, M., Nasu, S., Abe, T., Yamamoto, K., Endo, S., Takeda, Y. & Goodenough, J. B. Pressure-induced high-spin to low-spin transition in CaFeO_3 . *Phys. Rev. Lett.* **67**, 3267-3270 (1991).
- [9] Decurtins, S., Gütlich, P., Köhler, C. P., Spiering, H. & Hauser, A. Light-induced excited spin state trapping in a transition-metal complex: the hexa-1-propyltetrazole-iron (II) tetrafluoroborate spin-crossover system. *Chem. Phys. Lett.* **105**, 1-4 (1984).
- [10] Qi, Y., Müller, E. W., Spiering, H. & Gütlich, P. The effect of a magnetic field on the high-

- spin \leftrightarrow low-spin transition in $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. *Chem. Phys. Lett.* **101**, 505-505 (1983).
- [11] Ikeue, T., Ohgo, Y., Yamaguchi, T., Takahashi, M., Takeda, M. & Nakamura, M. Saddle-shaped six-coordinate iron(III) porphyrin complexes showing a novel spin crossover between $S = 1/2$ and $S = 3/2$ spin state. *Angew. Chem Int. Ed.* **40**, 2617-2620 (2001).
- [12] Halder, G. J., Kepert, C. J., Moubaraki, B., Murray, K. S. & Cashion, J. D. Guest-dependent spin crossover in a nanoporous molecular framework material. *Science* **298**, 1762-1765 (2002).
- [13] Nakano, N., Nakano, K. & Tasaki, A. A magnetic study of aciditic ferric hemoglobin. *Biochem. Biophys. Acta.* **251**, 301-313 (1971).
- [14] Moritomo, Y., Akimoto, T., Takeo, M., Machida, A., Nishibori, E., Takata, M., Sakata, M., Ohoyama, K. & Nakamura, A. Metal-insulator transition induced by a spin-state transition in $\text{TbBaCo}_2\text{O}_{5+\delta}$ ($\delta = 0.5$), *Phys. Rev. B.* **61**, R13325-13328 (2000).
- [15] Tsujimoto, Y., Tassel, C., Hayashi, N., Watanabe, T., Kageyama, H., Yoshimura, K., Takano, M., Ceretti, M., Ritter, C. & Paulus, W. Infinite-layer iron oxide with a square-planar coordination. *Nature* **450**, 1062-1065 (2007).
- [16] Köhler, J. Square-planar coordinated iron in the layered oxoferrate (II) SrFeO_2 . *Angew. Chem. Int. Ed.* **47**, 4470-4472 (2008).
- [17] Kawakami, T., Nasu, S., Kuzushita, K., Sasaki, T., Morimoto, S., Yamada, T., Endo, S., Kawasaki, S. & Takano, M. High-Pressure Mössbauer and X-Ray Powder Diffraction Studies of SrFeO_3 . *J. Phys. Soc. Jpn.* **72**, 33-36 (2003).
- [18] Perdew, M., Ernzerhof, M & Bruke, A. Rationale for mixing exact exchange with density functional approximations. *J. Chem. Phys.* **105**, 9982-9985 (1996).
- [19] Paier, J., Marsman, M., Hummer, K., Kresse, G., Gerbert, I. C & Ángyán, J. G. Screened hybrid density functionals applied to solids. *J. Chem. Phys.* **124**, 154709 (2006).
- [20] Xiang, H. J., Wei, Su-Huai & Whangbo, M.-H. Origin of the Structural and Magnetic Anomalies of the Layered Compound SrFeO_2 : A Density Functional Investigation. *Phys. Rev. Lett.* **100**, 167207 (2008).
- [21] Pruneda, J. M., Iniguez, J., Canadell, E., Kageyama, H. & Takano, M. Understanding the Unique Structural and Electronic Properties of SrFeO_2 . *Phys. Rev. B* **78**, 115101 (2008).
- [22] Hwang, H. Y. & Cheong, S.-W. Enhanced intergrain tunneling magnetoresistance in half-metallic CrO_2 films. *Science* **278**, 1607-1609 (1997).

- [23] Kimura, T., Tomioka, Y., Kuwahara, H., Asamitsu, A., Tamura, M. & Tokura, Y. Interplane Tunneling Magnetoresistance in a layered manganite crystal. *Science* **274**, 1698-1701 (1996).
- [24] Okimoto, Y., Katsufuji, T., Ishikawa, T., Urushibara, A., Arima, T. & Tokura, Y. Anomalous variation of optical spectra with spin polarization in double-exchange ferromagnet: $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. *Phys. Rev. Lett.* **75**, 109-112 (1995).
- [25] Shimakawa, Y., Kubo, Y. & Manako, T. Giant magnetoresistance in $\text{Tl}_2\text{Mn}_2\text{O}_7$ with the pyrochlore structure. *Nature* **379**, 53-55 (1996).
- [26] Park, J.-H., Vescova, E., Kim, H.-J., Kwon, C., Ramesh, R. & Ventakesan, T. Direct evidence for a half-metallic ferromagnet. *Nature* **794**, 794-796 (1998).
- [27] Kageyama, H., Watanabe, T., Tsujimoto, Y., Kitada, A., Sumida, Y., Kanamori, K., Yoshimura, K., Hayashi, N., Muranaka, S., Takano, M., Ceretti, M., Paulus, W., Ritter, C. & André, G. Spin-ladder iron oxide $\text{Sr}_3\text{Fe}_2\text{O}_5$. *Angew. Chem. Int. Ed.* **47**, 5740-5745 (2008).
- [28] Tassel, C., Watanabe, T., Tsujimoto, Y., Hayashi, N., Kitada, A., Sumida, Y., Yamamoto, T., Kageyama, H., Takano, M. & Yoshimura, K. Stability of the infinite layer structure with iron square planar coordination. *J. Am. Chem. Soc.* **130**, 3764-3765 (2008).
- [29] Tassel, C., Pruneda, J. M., Hayashi, N., Watanabe, T., Kitada, A., Tsujimoto, Y., Kageyama, H., Yoshimura, K., Takano, M., Nishi, M., Ohoyama, K., Mizumaki, M., Kawamura, N., Íñiguez, J. & Canadell, E. CaFeO_2 : a new type of layered structure with iron in a distorted square planar coordination. *J. Am. Chem. Soc.* **130**, 214410-214419 (2008).
- [30] Kamihara, Y., Watanabe, T., Hirano, M., Hosono, H. Iron-based layered superconductor $\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$ ($x = 0.05-0.12$) with $T_c = 26$ K. *J. Am. Chem. Soc.* **130**, 3296-3297 (2008).
- [31] Bassett, W. A., Takahashi, T. & Stook, P. W. X-Ray Diffraction and Optical Observations on Crystalline Solids up to 300 kbar. *Rev. Sci. Instrum.* **38**, 37-42 (1967).
- [32] Arora, A. K., Yagi, T., Miyajima, N., Mary, T. A. Amorphization and decomposition of scandium molybdate at high pressure. *J. Appl. Phys.* **97**, 013508 (2005).
- [33] Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15-50 (1996).
- [34] Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758-1775 (1999).
- [35] Perdew J. P., Burke K., Ernzerhof M., Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* **77**, 3865-3868 (1996).

- [36] Paier, J., Hirschl, R., Marsman, M. & Kresse, G. The Perdew–Burke–Ernzerhof exchange–correlation functional applied to the G2-1 test set using a plane-wave basis set. *J. Chem. Phys.* **122**, 234102 (2005).

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Author contributions

H.K designed and coordinated the overall study seeking advice from M.T (experiment) and C.L.F (theory). N.H conceived high-pressure Mössbauer study, while X-Q.C conceived theoretical studies. Y.T synthesized the material. T.K, S.S, K.H, Y.S and Y.M conducted high-pressure Mössbauer and electrical resistivity experiments, and T.K analyzed the data with the help of M.T and S.N. Y.T, C.T, A.K, T.O and T.Y performed high-pressure X-ray diffraction experiments, and Y.T and C.T analyzed the data. X-Q.C, C.L.F and R.P performed the theoretical work and analysis. H.K and T.K co-wrote the experimental part and C.L.F and X-Q.C

co-wrote the theoretical part with comments from R.P. All contributed to the discussion of the results.

Figure Legends

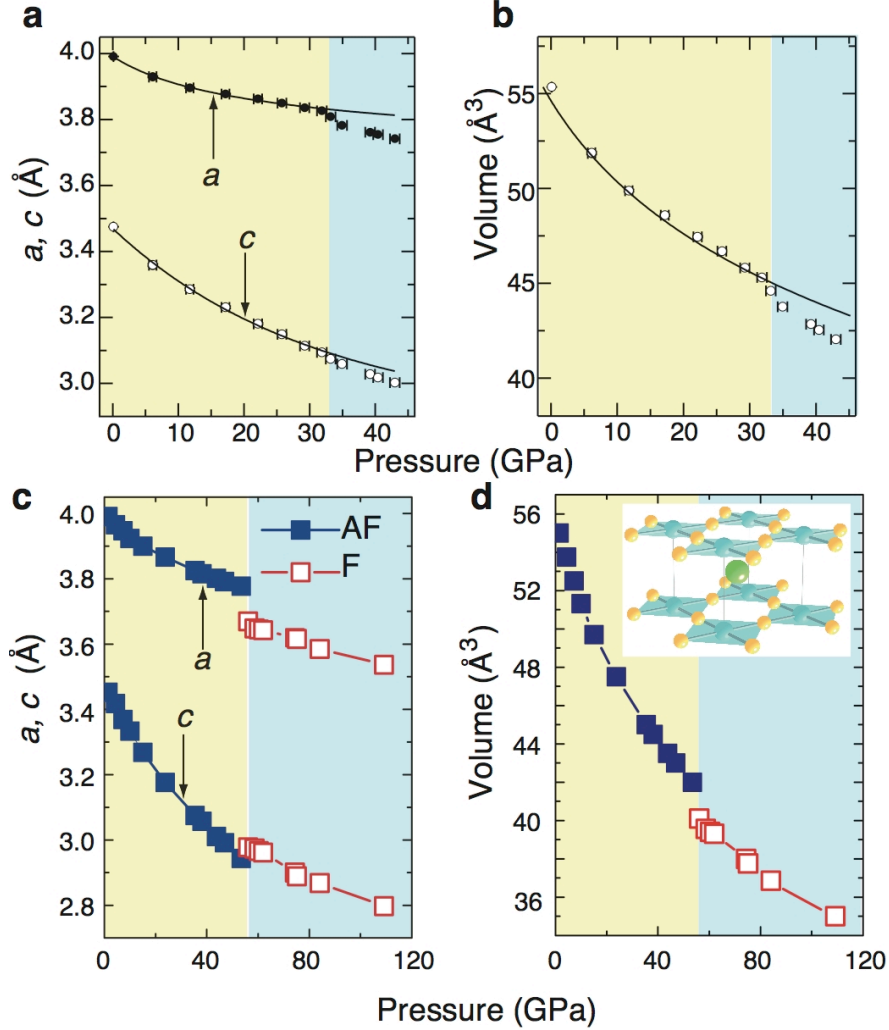


Fig. 1. **Lattice anomaly at the spin state transition.** The lattice parameters a , c (**a**) and the volume V (**b**) as a function of pressure. The errors bars are s.d. determined by the least-squares fitting, and are within the size of the symbols. The solid lines in **a** are the guide to the eyes and that in **b** is the fit to the third order Birch-Murnaghan in the low-pressure phase. **c**, **d** Calculated cell parameters and volume for the $S = 2$ antiferromagnetic (AF) state and the $S = 1$ ferromagnetic (F) state. Inset of **d** is the crystal structure of SrFeO_2 , where blue, green and yellow balls represent Fe, Sr and O atoms, respectively.

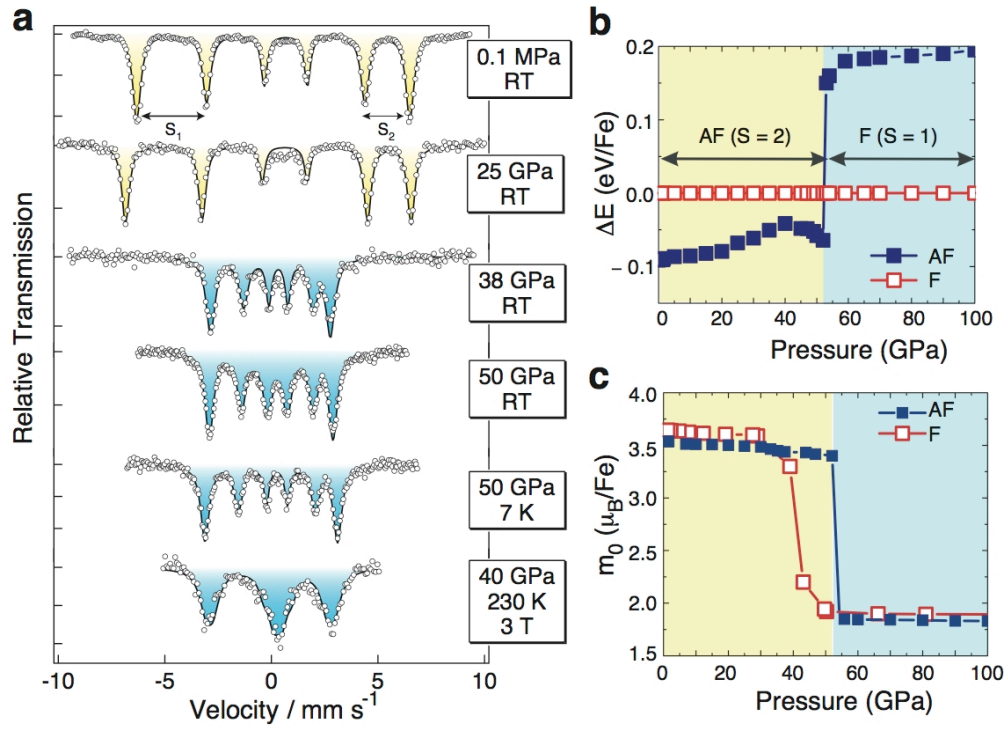


Fig. 2. **High-spin-to-intermediate-spin transition in SrFeO_2 under high pressure.** **a**, Typical high-pressure ^{57}Fe Mössbauer spectra obtained from SrFeO_2 (see Supporting Fig. 1 for detail). The yellow spectra correspond to the $S = 2$ state, while the blue to the $S = 1$ state. The solid lines represent the fitted curves. Velocity scale is relative to $\alpha\text{-Fe}$ at room temperature. **b**, Calculated energy difference (ΔE) between the $S = 2$ antiferromagnetic (AF) state and the $S = 1$ ferromagnetic (F) state. **c**, Calculated spin moment (m_0) for the $S = 2$ antiferromagnetic (AF) state and the $S = 1$ ferromagnetic (F) state.

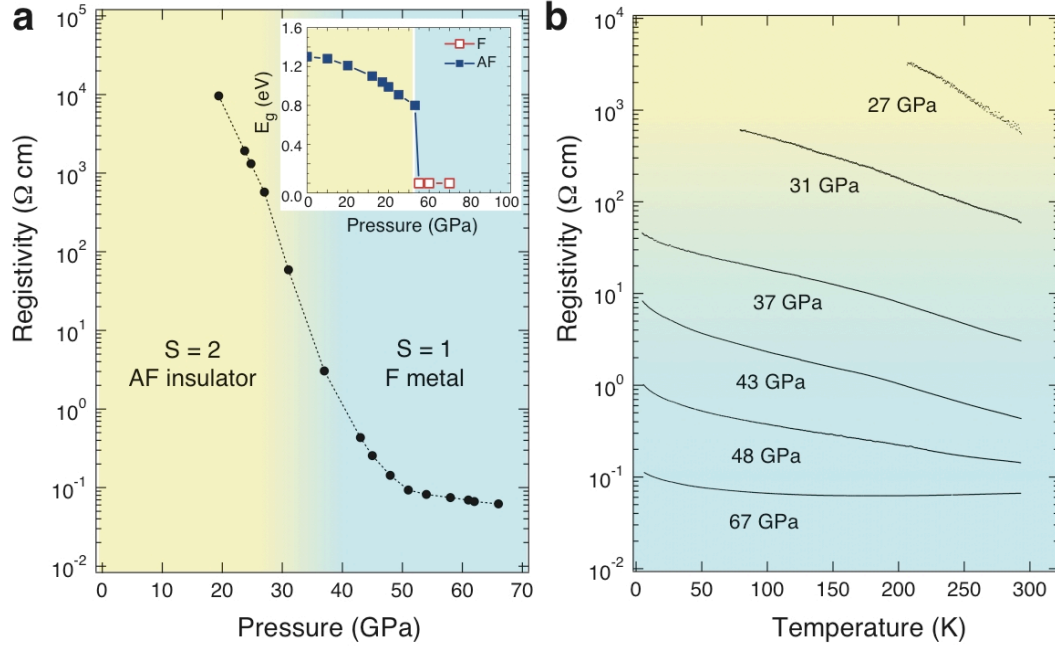


Fig. 3. Insulator metal transition at the spin transition. **a**, Room temperature electrical resistivity of SrFeO₂, demonstrating an insulating state for the low-pressure phase ($P < P_c$) and a metallic state for the high-pressure phase ($P > P_c$). The inset represents the calculated energy gap for the $S = 2$ antiferromagnetic (AF) state and the $S = 1$ ferromagnetic (F) state, in consistency with the experimental results. **b**, Temperature dependence of the electrical resistivity under pressure.

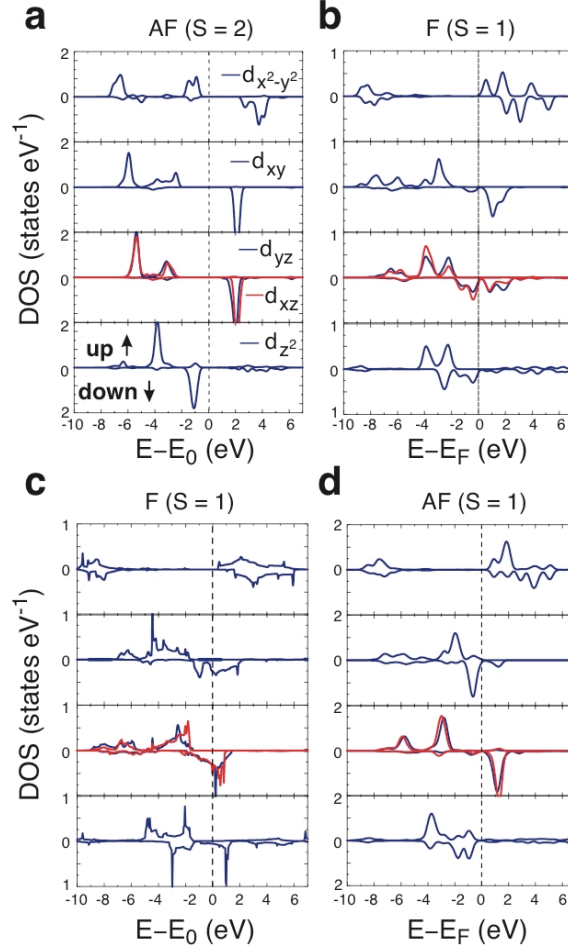


Fig. 4. **Calculated local density-of-states of Fe in SrFeO₂.** **a**, high-spin ($S = 2$) antiferromagnetic (AF) state at 0 GPa (insulating); **b**, intermediate-spin ($S = 1$) ferromagnetic (F) state at 53 GPa (metallic); **c**, intermediate-spin ($S = 1$) ferromagnetic (F) state at 70 GPa (metallic); **d**, unstable intermediate-spin ($S = 1$) antiferromagnetic (AF) state at 65 GPa (insulating). In the $S = 2$ antiferromagnetic state, the lone spin-down electron occupies the spin-down d_z^2 orbital. In the $S = 1$ ferromagnetic state, the $d_{x^2-y^2}$ antibonding states become unoccupied, which results in the charge transfer from $d_{x^2-y^2}$ to d_{yz} (or d_{xz}). The d_z^2 orbital maintains its double occupation through the spin state transition at 53 GPa. The energy zero (E_0) is set at the middle of the gap (**a** and **d**) and at the Fermi level (**b** and **c**).