Nature of the High-Pressure Transition in Fe$_2$O$_3$ Hematite

James Badro* and Guillaume Fiquet

Laboratoire de Minéralogie-Cristallographie de Paris (UMR 7590), CNRS Case 115,
4 Place Jussieu, 75252 Paris CEDEX 05, France

Viktor V. Struzhkin, Maddury Somayazulu, and Ho-kwang Mao

Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, D.C. 20015

Guoyin Shen

GSECARS, University of Chicago, 5640 South Ellis, Chicago, Illinois 60637

Tristan Le Bihan

ESRF, BP 220, 38043 Grenoble CEDEX, France

We present a new method to separate the crystallographic and electronic phase transitions in hematite using x-ray emission spectroscopy and x-ray diffraction. Our observations, based on the behavior of a metastable high-pressure phase in the stability domain of the low-pressure phase, show that the electronic transition is preempted by the crystallographic transition. The former occurs only afterwards in the high-pressure phase, possibly as a result of a Mott transition. The idea that the electronic transition drives the transition in hematite is therefore invalidated. Such methods should help elucidate the mechanics and the driving forces behind a number of first-order high-pressure phase transitions.

It is often in high-pressure phase transitions that modifications are observed in several basic properties of a material, such as crystal structure, electronic structure, elastic, dielectric, thermodynamical, and transport properties, and so on. It is, in general, impossible to separate the effect of these modifications, and therefore to pinpoint the unique property which drives the transition; that is, the property for which the free energy of the high-pressure (HP) phase is *necessarily* lower than that of the low-pressure (LP) phase.

The case of hematite is typical. Indeed, at a pressure of roughly 50 GPa, hematite, a rhombohedrally structured antiferromagnetic insulator [1], undergoes a transition to a phase which has a totally different crystal structure [2–5] which is still unknown; different electronic [spin transition from iron in a high-spin state (HS) to iron in a low-spin state (LS)] [6] and magnetic properties, vanishing of magnetic ordering [3,7–9], and radically opposite transport properties; the sample undergoes an insulator-metal transition [10]. Several studies dealing with the phase transition and the properties of the high-pressure phase briefly address the question of its exact nature, not so much by proof or direct observation, but rather by intellectual affinity towards one or the other of the plausible explanations.

In order to unambiguously separate the crystallographic transition from the electronic transition, one has to be able to produce an *intermediate* state—that is, neither the LP phase or the HP phase, but something in between—where one finds either of the crystal structures

(LP or HP) present with the opposite characteristic from an electronic point of view; e.g., either a rhombohedral structured compound with low-spin iron or a sample with the HP crystal structure and iron in the high-spin state. In this case, it becomes obviously possible to separate the effect of the driving force (the property that is modified in the intermediate state) from that of any other physical property (which remain identical in the intermediate state), which then become instead consequences of the transition. It is, of course, not always straightforward, if ever possible at all, to obtain such a state. Yet, with the scheme described below, it was possible to obtain this intermediate state in hematite.

One way to obtain such a state is to allow the system to relax in a metastable domain of the phase diagram, and to observe changes—or relaxation—of the properties in that domain. In order to understand the states produced in the experiment, one has to recall what happens to hematite at high pressure. Hematite undergoes a transition at 50 GPa, and it is of importance to note that, close to that pressure, the transition is favored (either due to kinetics or to the slope of the phase line) when temperature is slightly increased. One has to be careful though, as a large increase in temperature will end up in forming a new high-pressure high-temperature phase [11]. Using that property, one can start with a system in the stable LP phase at or very close to the transition, heat the sample to drive the transition (i.e., cross the phase boundary) to the stable HP phase, and cool it down again to the starting point where the HP phase is now *metastable* as this is the

stability domain of the LP phase, and allow the system to relax (Fig. 1). During that relaxation process, if a reverse phase transition were to occur towards the initial LP phase, then the problem could not be solved, as one would not be able to separate the phenomena. On the other hand, if only one of the properties (crystal or electronic structure) is affected but not the other, then the separation is immediate and the driving force can be determined.

In order to probe the physical properties that have to be separated, we combined two bulk-sensitive techniques: x-ray diffraction for structural information, and x-ray emission spectroscopy which is sensitive to the spin state of iron as a probe of electronic structure. The sensitivity of the latter technique to local magnetic moment has been well established by many x-ray-emission spectroscopy studies of TM elements and their compounds [12–15], and has been recently applied to the study of pressure-induced HS to LS transitions [6,16]. In this case, the emission spectrum of HS Fe is characterized by a main peak $K\beta_{1,3}$ with an energy of 7058 eV, and a satellite peak $K\beta'$ located at lower energy appearing as a result of the $3p$ core-hole $3d$ exchange interaction in the final state of the emission process. Since the LS state of Fe^{3+} (d^5 configuration) is characterized by a total magnetic moment 5 times smaller than that of HS Fe^{3+}, the eventual collapse of the $3d$ magnetic moment as a consequence of an electronic transition is signaled by the strong reduction of the low energy satellite's intensity, as shown in [6].

The experiments were conducted on the undulator beam line at Sector 13, Consortium for Advanced Radiation Sources of the Advanced Photon Source at Argonne National Laboratory and beam line ID30 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. X-ray emission spectra were obtained using white undulator radiation. The undulator gap was set so that the first harmonic energy was at 12 KeV to optimize the combined effect of the sample absorption cross section and x-ray absorption in the diamond window. The x-ray beam size was focused down to 10×5 μm using a pair of rhodium-coated Kirkpatrick-Baez mirrors [17,18]. The measurements were made using a 870 mm diameter Rowland circle spectrometer arranged in the vertical plane, which leaves place for the diffraction and laser-heating setup in the horizontal plane. A spherically bent Si(440) single crystal analyzer was used. At the $K\beta$ emission line energy, the associated Bragg angle is equal to 66.20°. The angle between the incident x-ray beam and the sample-analyzer direction was set to 90° to reduce elastic scattering background, with the emitted x-rays going through a beryllium gasket (incoming x-rays go through one of the diamond anvils). X-ray diffraction was collected at 29.2 keV on image plates.

High purity Fe_2O_3 (99.998%) powder was used in the experiment; nanocrystalline Al_2O_3 was used as a thermal insulator between the sample and the diamond in order to reduce thermal leakage during laser heating and to cancel any risk of chemical reaction of the oxide with carbon. The gasket was a high-strength beryllium disk 5 mm in diameter and 1 mm initial thickness. Pressure was measured using the ruby fluorescence technique.

Hematite was compressed in a diamond anvil cell to 46 GPa; x-ray diffraction and emission spectra were recorded, and showed no crystallographic or spin (electronic) transition indicating the sample has not undergone any transformation (Fig. 2). At that point, the sample was slightly (below 1500 K) laser heated using a Nd:YAG laser. In these conditions, the HP phase nucleated, and was then quenched in temperature. Immediately after heating, the sample is in the LP phase stability domain but has the structure of the HP phase (metastability) as shown by x-ray diffraction (a new crystal-structure) and x-ray emission (a collapse of the magnetic moment) (Fig. 2). The x-ray diffraction spectra are in agreement with those obtained on cold compression of hematite at 60 GPa reported in Fig. 2, and indicates that the heating process was delicate enough not to induce a transition to the high-pressure high-temperature phase [11]. Pressure was remeasured using ruby fluorescence to make sure thermal expansion of the sample and modifications in the sample chamber during laser heating did not change the pressure after heating. We then allowed the metastable system to relax (46 GPa and 300 K) for ten hours, and another measurement was made. X-ray diffraction showed the same crystal structure as obtained after laser heating (HP crystal structure), whereas the x-ray emission spectrum reverted to the high-spin state of the LP phase (Fig. 2). During these ten hours of relaxation, the
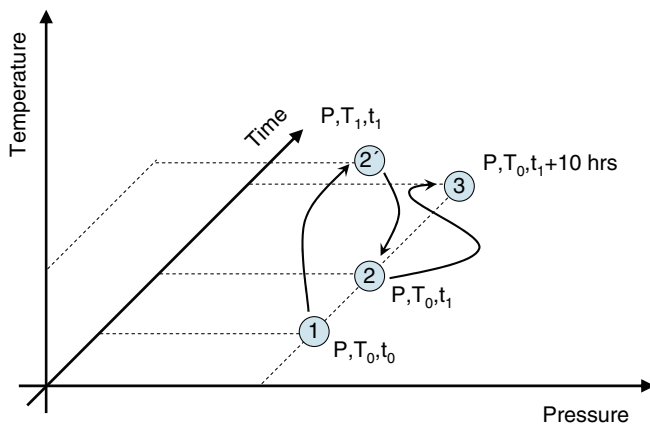

FIG. 1 (color online). A schematic sketch of the states obtained. In the initial state (1), the system is in the low-pressure phase, very close to the transition, as shown by the x-ray measurements. The sample is then heated (2′) and cooled again (3), and ruby pressure measurement shows the pressure did not change (pressure probably increased slightly during heating due to thermal pressure, but this effect is not reproduced here for clarity), and x-ray measurements were performed. Then the sample was allowed to relax for 10 h, and pressure and x-ray measurements were performed one last time.
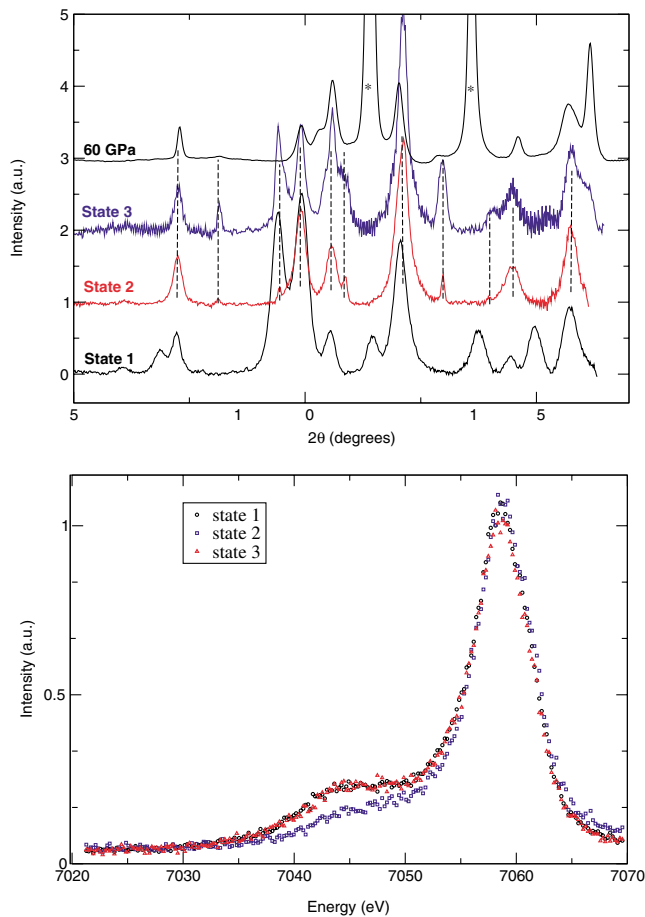
FIG. 2 (color online). The top figure shows integrated angular-dispersive powder diffraction spectra taken at the three stages of the experiment, as described in the text and in Fig. 1. A reference pattern of the high-pressure phase taken at 60 GPa on cold compression using neon pressure medium is also shown. The diffraction lines in the high-pressure phase were not indexed as the structure has not been determined, but dashed lines corresponding to the diffraction lines are drawn as a guide to the eye. In the 60 GPa pattern, the diffraction lines due to the pressure medium (neon) are represented with an asterisk. The figure below shows the x-ray $K\beta$ emission spectrum in those same conditions. In the first state, the system is in the low-pressure phase and, in the second state, the system is in the high-pressure phase. But in the third state, the system is in an intermediate state with the crystal symmetry of the high-pressure phase and the electronic structure on the low-pressure phase. It can be noted that there is a residual signature of finite spin in the high-pressure phase (see also Ref. [6]).

system underwent a reverse electronic transition from the state characterized by low-spin iron to that of high-spin iron. We interpret the fact that this intermediate state accommodates a high-spin state in the HP phase as a sign that the electronic transition is not *required* in order to obtain the HP phase. It is therefore only a consequence of the crystallographic transition, it occurs subsequently to the crystallographic transition in the HP phase, and is isostructural.

In general, one expects such electronic transitions as Mott transitions or HS-LS transitions to be isostructural. A Mott transition, as defined by Mott [19] himself, is an isostructural paramagnetic metal to paramagnetic insulator transition. A HS-LS transition does not have to be accompanied by a metal-insulator transition, but leads to a system with lower spin or atomic magnetic moment, due to a rearrangement of electrons in the outermost electronic orbitals. Their isostructural nature implies that no modification of crystal symmetry should be observed, but rather changes associated with modifications of the internal degrees of freedom in the unit cell, as a result of the change in chemical bonding between the anions and cations induced by such radical electronic transformations. This characteristic is confirmed by our diffraction measurements, as one may note that, although peaks neither appear nor disappear (isostructural) during the electronic transformation, their relative intensities vary somehow, and reflect these changes and the rearrangement in the internal coordinates of Fe and O in the HP structure. Also, the measurable $K\beta'$ satellite in the LS state (Fig. 2 and Ref. [6]) is the signature of a very small yet finite spin and atomic magnetic moment. This shows that this state which lacks magnetic ordering [9] is probably very weakly paramagnetic, and goes against the idea that magnetism has vanished in the compound at high pressure [9]. The high-pressure state could then be a paramagnetic metallic state; in this case, this transition could be a Mott transition, but we have not measured the electrical conductivity of the sample, and our data therefore does not allow us to address this issue. Whether the electronic transformation observed is the signature of a HS-LS transition, or a Mott transition, remains to be determined.

In conclusion, we provide a new scheme for separating the crystallographic and electronic transitions in the high-pressure phase of hematite. Our results show that the crystal-structure change drives the transition, and that the subsequent electronic transition is isostructural. The electronic transition to the low-spin high-pressure phase (which is a paramagnetic metallic state) occurs only afterwards in the high-pressure phase, possibly as a result of a Mott transition. The affirmation that the transition is driven by a magnetic collapse towards a nonmagnetic metallic state [9] is therefore invalidated. Although this new method is not guaranteed to work in all cases and for all phase transitions, it remains to be tested in other such typical cases where it could prove very helpful to understand the real nature of high-pressure phase transitions.

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*Electronic address: james.badro@ens-lyon.fr
URL: http://james.badro.free.fr

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