Iron Under Pressure: "Kohn Tweezers" and Remnant Magnetism

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In this work we investigate the magnetic and structural properties of bulk Fe and Fe nanoparticles under pressure with x-ray absorption and emission spectroscopies providing answers to two fundamental questions: (a) the chicken-or-egg problem for the magnetic and structural transitions and (b) magnetism in the high pressure hcp phase. The two transitions, inextricably linked in the bulk, are clearly decoupled in the nanoparticles, with the magnetic collapse preceding the structural transition. Ultrafast x-ray emission spectroscopy detects remnant magnetism, probably antiferromagnetic fluctuations, up to pressures of about 40 GPa in the hcp phase. This could be of direct relevance to the superconductivity in ϵ-Fe [K. Shimizu *et al.*, Nature (London) **412**, 316 (2001)] through the existence of a quantum critical point and associated magnetic fluctuations.

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The high pressure magnetism of Fe is a key to the understanding of electronic, magnetic, and structural properties of $3d$ electrons and of the geophysics of Earth's interior. Experimentally it is well established that the high pressure α (bcc) to ϵ (hcp) transition is simultaneously accompanied by a magnetic transition from ferromagnetic to purportedly nonmagnetic states, extensively studied by Mössbauer spectroscopy [1–3], by x-ray emission spectroscopy (XES) [4], and x-ray magnetic circular dichroism (XMCD) [5]. However, the possibility of weak remnant magnetism in the hcp phase [4,6] has been invoked through indirect measurements of structural variation [7] or Raman mode splitting [8,9]. Theoretically, both the ambient pressure bcc ferromagnetic ground state and the structural and magnetic transitions are predicted though the accuracy in terms of the pressure domain of their existence is variable [6,7,10–13]. Practically all theoretical studies are consistent in predicting magnetism, more often antiferromagnetic ordering or fluctuations in the hcp phase as exemplified in [6]. These fluctuations could in fact mediate Cooper pair formation in Fe, as also proposed in other superconductors which have ferromagnetic phases [14]. Alternatively, they could just kill superconductivity originating through more conventional phonon pairing mechanisms. All these conjectures are subject to experimental detection of this remnant magnetism which has to date remained a vain hope.

We first address the coincidence of the structural transition and the magnetic collapse. K-edge XMCD spectroscopy shows that both transitions go strictly hand in hand though a case has been made [5] for a slight precedence of the magnetic transition. Theoretically it has been argued that it is the magnetic collapse that precedes the structural phase transition [10,11,13]. Magnetic states are characterized by unpaired electrons and aligned spins, which occupy different orbitals as opposed to paired electrons occupying the same orbital. The magnetic state thus tends to increase cell volume and is more compressible than the nonmagnetic state. A collapse of magnetism can open the way for a structural transition. But is it possible to decouple the structural and the magnetic transitions so as to clearly establish the precedence of one over the other? This chicken-or-egg question resurges when two phase transitions, for example, structural and electronic, occur simultaneously. Many years ago, Kohn, while discussing charge density wave transitions [15], proposed that in principle one could establish a hierarchy. He evoked "tweezers" which could permit the experimentalist to block the atomic structure at the transition, and hypothesized that in certain cases the electronic deformation would nevertheless occur, followed at a certain point by the structural deformation if the tweezers were then released. In nanocrystalline matter it is known that structure tends to be more stable, with a shift of structural phase transitions to higher pressure with respect to the bulk form [16]. The surface contribution of the free energy (which is important for the nanoparticle) implies a greater pressure before the transition becomes thermodynamically favorable with respect to the bulk value. Furthermore, often a kinetic barrier needs to be overcome which also can generate hysteresis between the increasing and decreasing pressure transitions [17,18]. In our experiment we use these barriers as "Kohn tweezers" to solve this chicken-or-egg problem. Our second aim in this work is the detection of any magnetism in the high

pressure regime. We use two different synchrotron based methods using high-energy x rays for compatibility with the high pressure environment. The first is Fe K-edge XMCD which [19,20], while lacking a formal link to the magnetic moment, has been shown to be a reliable marker of magnetism as a function of pressure [5,21]. XMCD, however, cannot detect antiferromagnetism, the total projected moment being zero. To overcome this limitation we use x-ray emission spectroscopy [22,23]. In particular, the $K\beta$ line shape depends on the spin state through the multiplet structure and the interplay between the crystal field and the exchange interaction. The variation of this line shape can again be reliably used to follow magnetic transitions [24]. The femtosecond time scale of the experiment is determined by the 1s core hole lifetime and so it is ideal for detecting eventually fluctuating moments. For precise structural information separate extended x-ray-absorption fine structure spectroscopy (EXAFS) measurements were made which permitted a standard structural adjustment.

Our experiments benefited from the availability of high quality monodispersed Fe nanoparticles in the unoxidized, bcc phase at ambient pressures prepared according to a published procedure using the reduction of $\{Fe[N(SiMe_3)_2]_2\}_2$ in an environment of palmitic acid and hexadecylamine [25]. Tuning acid concentration and growth time allows control both on the shape (cubic for dimensions of 10 nm or more) and on the size of the nanoparticles. The size dispersion of our nanoparticle samples is of the order of 1.5 nm. The magnetization of nanoparticles at ambient conditions is equal to that of bulk Fe (2.2 μB). XMCD and EXAFS measurements were performed at SOLEIL (ODE beam line, Figs. 1 and 2) on bulk Fe and nanoparticles of a mean size of 11.9 nm. A 1.3 T magnetic field was used for XMCD measured over an energy range of 7060–7300 eV with a focal spot of 30×50 μm (FWHM). $K\beta$ XES was measured at ESRF (ID16 beam line, Fig. 3) as a function of pressure for bulk Fe as well as nanoparticles of a mean size of 10 nm. We used a 1 m spherically bent Si(531) crystal analyzer as energy filter for measuring the $K\beta$ line in transmission geometry through the pressure cell diamonds at a scattering angle of 20°. The beam size (50×110 μm FWHM) is comparable to the sample size ensuring optimum throughput of the emitted x rays. We loaded nanoparticles in diamond anvil cells under argon atmosphere of a glovebox to avoid oxidation. Rhenium gaskets were used with silicone oil as transmitting medium to prevent coalescence of nanoparticles. Identical conditions were used for the bulk foil sample. The medium is not fully hydrostatic especially for pressures exceeding 20 GPa, and we have measured the upper limit of the pressure gradient to be about 10%. Unless mentioned, all experiments are at 300 K. In Figs. 1(a) and 1(b) we show the structural transitions as obtained from the variation of the distance in the 1st and 2nd shell (nearest neighbor distances) in the EXAFS

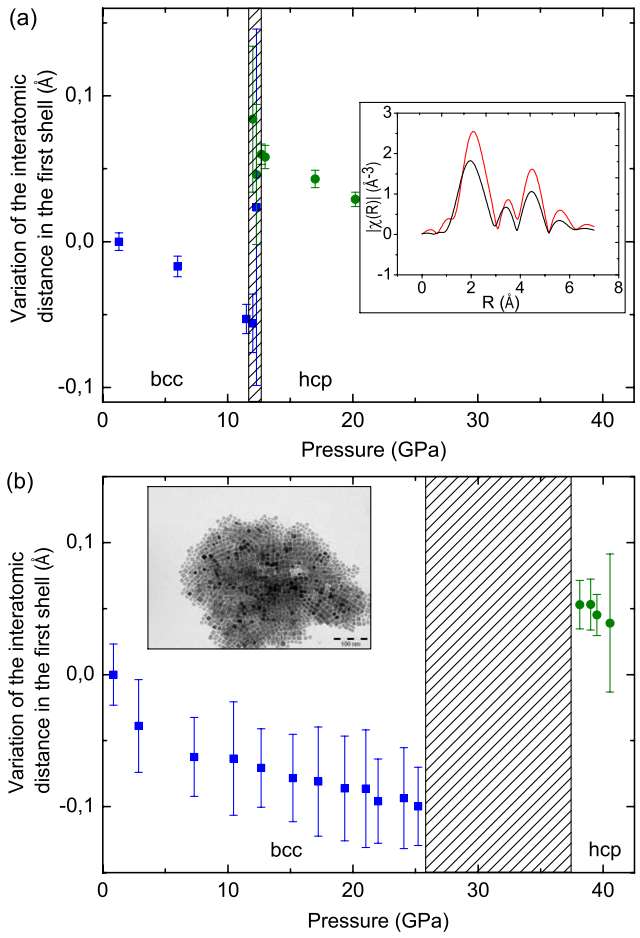

FIG. 1 (color online). Variation of the interatomic distance in the first shell for bulk (a) and nanoparticles (b) versus pressure. The interatomic distance was computed by fitting the radial distribution with a bcc (blue square) or a hcp (green circle) model. The inset of (a) represents the radial distribution of the first five shells for bulk [gray (red) curve] and nanoparticles (black curve) versus the interatomic distance. The inset of (b) is a transmission electron microscopy picture of the 11.9 nm nanoparticles.

measurements for bulk Fe and the 11.9 nm nanoparticles. In the inset of Fig. 1(a) are shown the radial distributions up to the 5th successive shell obtained from near ambient pressure data showing a unit cell contraction in the nanoparticles with respect to the bulk. This phenomenon, observed in some metallic nanoparticles, is attributed to the consequent reduction of surface energy even though a price is paid in terms of elastic energy [16,26]. The structural transition appears by fitting the data with a bcc (hcp) model and we can formally exclude oxidation and affirm that the data are completely compatible with the expected phases. The transition region, where both phases coexist, is shown hatched, and for the nanoparticles fits in this region were not significant. The transition in the bulk is very sharp and occurs at 12 GPa with a width less than 1 GPa. In the nanoparticles the transition is shifted to remarkably higher pressures and, despite the initial lattice contraction, starts

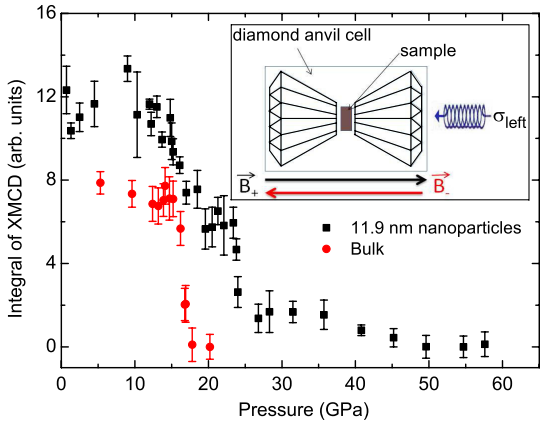

FIG. 2 (color online). Variation of the integrated XMCD signal at the Fe K edge for bulk Fe (red circles) and 11.9 nm Fe nanoparticles (black squares) showing the shifting of the magnetic transition to lower pressures and a broadening in the nanoparticles.

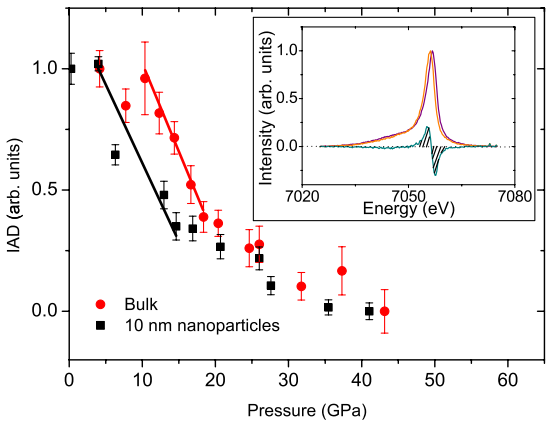

FIG. 3 (color online). Integrated absolute difference (hatched area shown in the inset) between the Fe $K\beta$ fluorescence measured at a given pressure with respect to a reference for bulk Fe (red circles) and 10 nm Fe nanoparticles (black squares), used to follow the magnetic transition with pressure. The solid lines are guides for the eye. The nanoparticles are seen to transit at lower pressure with respect to the bulk. The signal continues to diminish after the sharp transition indicating remnant magnetism both in the bulk and in the nanoparticles in the high pressure hcp phase.

at 25 GPa and terminates at 38 GPa. Nonhydrostaticity and size dispersion, which can contribute to broadening, are estimated to introduce a maximum width of the order of 1–3 GPa. We propose that the very large transition width observed is an intrinsic feature in an ensemble of nanoparticles due to the limited size of the individual nanoparticle. In bulk samples such a transition usually nucleates at grain boundaries as well as defects. These should be present in strongly unequal and, in general, very small numbers in nanoparticles of this size, thus provoking a large overall distribution.

In Fig. 2 we show the variation of the integrated dichroic signal measured by K-edge XMCD. The bulk magnetic transition (at 15 GPa with a width of 2.6 GPa) is at a slightly higher pressure with respect to the structural one that we measure using EXAFS. This, however, is not conclusive since the measurements are not simultaneous and changes of a few GPa in transition pressures in varying experimental conditions have been observed. No magnetic signal is observed in the hcp phase. The integrated dichroic signal for the bulk at low pressures is weaker than in the nanoparticles. We have verified that this is due to the shape anisotropy of the foil bulk sample which the 1.3 T field used in these experiments is not strong enough to overcome. We find a weak magnetic signal in the high pressure hcp phase of the nanoparticles which vanishes at a pressure of about 50 GPa and could be compatible with a surface magnetic component related to a lower coordination of the surface Fe atoms and observed in Fe clusters or ultrathin layers ([27] and references therein).

The main conclusion, however, is that the change in the magnetism starts significantly earlier than the structural change, at a pressure of 10 GPa, and has a large width (nearly 15 GPa), which could be attributed in good part to the reasons invoked above. The structural and magnetic properties of nanoparticles are sufficiently far removed from the bulk to move the lines of the bulk Fe phase diagram as a function of the pressure. While the structural transition is retarded by our Kohn tweezers, the magnetic transition actually starts at lower pressures than in the bulk material because of the intrinsic unit cell contraction.

In Fig. 3, we show the variation of the integrated difference (see inset) between the measured $K\beta$ line at a given pressure and a nonmagnetic reference which is taken to be the highest pressure bulk Fe data. Since this is a relative measurement, the ambient pressure value is normalized to unity and the variation of this signal with pressure is used to follow the magnetic transition. The striking conclusion is that bulk Fe remains clearly magnetic for pressures greater than 20 GPa after the magnetic collapse accompanying the structural transition. The measured XES signal then decreases continuously to the last measured pressure point which is at 43 GPa. For the nanoparticles, as already seen by XMCD measurements, the magnetic collapse starts earlier but again magnetism persists well into the hcp phase. XES measurements exclude that the early collapse of magnetism in the nanoparticles could be due to a collapse of Curie temperature with pressure.

As mentioned earlier, we provide experimental confirmation of the findings of several theoretical studies. What of other experiments? Mössbauer experiments [1–3] have repeatedly failed to detect magnetism in the hcp phase. Interestingly, magnetism in the form of fluctuations would not be detected by the Mössbauer method due to the much slower time scale of the experiment. More recently, an x-ray diffraction study at high pressure on annealed Fe samples [7] indicates that hcp Fe is continuously compressible to a pressure of about 50 GPa

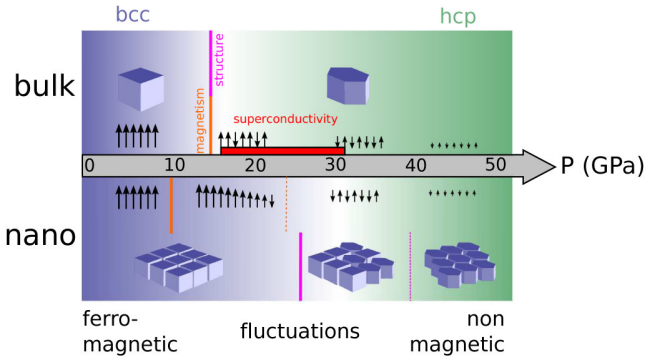

FIG. 4 (color online). A composite phase diagram based on our measurements for the structural transition (schematized by cubic or hexagonal blocks) and the magnetic transition (schematized by oriented spins) with pressure in Fe bulk and nanoparticles. The transition pressures are indicated by vertical lines. The main results of this work, the decoupling of these transitions and the direct measurement of remnant magnetism in the hcp phase, are shown.

after which the c/a ratio remains constant. In the absence of structural change, this is interpreted as arising due to changes in magnetism, notably persistent magnetism in hcp Fe up to roughly 50 GPa. We have then directly confirmed this hypothesis with our measurement.

We can exclude a ferromagnetic nature of this persistent magnetism as it is not visible by XMCD, and the Mössbauer measurements exclude static antiferromagnetism. Theoretical works do not favor a paramagnetic state [14], which leaves us with antiferromagnetic fluctuations, perfectly visible through the XES method. Our final word concerns the proximity of this magnetism in the Fe phase diagram (Fig. 4) with superconductivity in Fe. Several authors [6,14,28,29] have discussed this proximity as indicative of a possible exotic origin of superconducting pairing mediated by spin fluctuations which could be enhanced at very low temperatures. Current experimental limitations do not allow us to perform XES measurements at temperatures below 20 K and we did not find any change in the magnetism of Fe in the hcp phase (21 GPa) between 300 and 20 K.

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[1] G. Cort, R. Taylor, and J. Willis, J. Appl. Phys. **53**, 2064 (1982).
[2] S. Nasu, T. Sasaki, T. Kawakami, T. Tsutsui, and S. Endo, J. Phys. Condens. Matter **14**, 11 167 (2002).
[3] A. B. Papandrew *et al.*, Phys. Rev. Lett. **97**, 087202 (2006).
[4] J.-P. Rueff, M. Mezouar, and M. Acet, Phys. Rev. B **78**, 100405(R) (2008).
[5] O. Mathon *et al.*, Phys. Rev. Lett. **93**, 255503 (2004).
[6] G. Steinle-Neumann, L. Stixrude, and R. E. Cohen, Proc. Natl. Acad. Sci. U.S.A. **101**, 33 (2003).
[7] S. Ono, T. Kikegawa, and M. Kenji, Am. Mineral. **95**, 880 (2010).
[8] Y. Tsunoda, Y. Nishioka, and R. M. Nicklow, J. Magn. Magn. Mater. **128**, 133 (1993).
[9] S. Merkel, A. F. Goncharov, H.-K. Mao, P. Gillet, and R. J. Hemley, Science **288**, 1626 (2000).
[10] T. Asada and K. Terakura, Phys. Rev. B **46**, 13 599 (1992).
[11] M. Ekman, B. Sadigh, K. Einarsdotter, and P. Blaha, Phys. Rev. B **58**, 5296 (1998).
[12] K. J. Caspersen, A. Lew, M. Ortiz, and E. A. Carter, Phys. Rev. Lett. **93**, 115501 (2004).
[13] J. B. Liu and D. D. Johnson, Phys. Rev. B **79**, 134113 (2009).
[14] I. I. Mazin, D. A. Papaconstantopoulos, and M. J. Mehl, Phys. Rev. B **65**, 100511(R) (2002).
[15] D. Adler, Rev. Mod. Phys., **40**, 714 (1968), see Discussion section.
[16] Alfonso San-Miguel, Chem. Soc. Rev., **35**, 876 (2006).
[17] S. H. Tolbert and A. P. Alivisatos, J. Chem. Phys. **102**, 4642 (1995).
[18] B. J. Morgan and P. A. Madden, J. Phys. Chem. C **111**, 6724 (2007).
[19] H. Ebert, H. Freyer, A. Vernes, and G.-Y. Guo, Phys. Rev. B **53**, 7721 (1996).
[20] Ch. Brouder, M. Alouani, and K. H. Bennemann, Phys. Rev. B **54**, 7334 (1996).
[21] F. Baudelet *et al.*, Phys. Rev. B **82**, 140412(R) (2010).
[22] F. M. F. de Groot, A. Fontaine, C. C. Kao, and M. Krisch, J. Phys. Condens. Matter **6**, 6875 (1994).
[23] G. Peng, X. Wang, C. R. Randall, J. A. Moore, and S. P. Cramer, Appl. Phys. Lett. **65**, 2527 (1994).
[24] J.-P. Rueff and A. Shukla, Rev. Mod. Phys. **82**, 847 (2010).
[25] L.-M. Lacroix, S. Lachaize, A. Falqui, M. Respaud, and B. Chaudret, J. Am. Chem. Soc., **131**, 549 (2009).
[26] W. H. Qi and M. P. Wang, J. Nanopart. Res. **7**, 51 (2005).
[27] O. Sipr, M. Kosuth, and H. Ebert, Phys. Rev. B **70**, 174423 (2004).
[28] S. S. Saxena and P. B. Littlewood, Nature (London) **412**, 290 (2001).
[29] T. Jarlborg, Phys. Lett. A **300**, 518 (2002).