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Ab initio calculations of incommensurate antiferromagnetic spin fluctuations in hcp iron under pressure

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We present *ab initio* calculations of the static paramagnetic spin susceptibility for hcp iron at finite temperatures and for a range of pressures. The dominant magnetic fluctuations in hcp Fe are found to be incommensurate antiferromagnetic, characterized by the wave vector $\mathbf{q}_{inc}=(0.56,0.22,0)$. We show that $\mathbf{q}_{inc}$ is linked to a Fermi-surface nesting feature. For the lowest pressure $\sim$16 GPa at which hcp Fe forms, we find that these modes become unstable below a Néel temperature (T_N) of 69 K. T_N rapidly diminishes with increasing pressure. We therefore *predict* that hcp Fe will be found to have an incommensurate spin-density-wave-ordered state over a small pressure range starting with the onset of hcp phase. We note the coincidence with the superconductivity recently found in this material.

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At low temperatures, under sufficient pressure, iron swaps its body-centered-cubic (bcc) crystal structure in favor of a hexagonal-close-packed (hcp) arrangement with the loss of its ferromagnetic long range order. It also becomes superconducting[1] in a narrow range of pressures between 15 and 30 GPa. This recent observation of superconductivity has added the phase of a common element to the growing list of magnetic or nearly magnetic materials exhibiting a superconductivity in which magnetic fluctuations seem to play key role.[2–4] Prior to this finding the main interest in the magnetic properties of the high-pressure hexagonal phase of iron was motivated by their effect upon its structural and mechanical properties. As part of the study of the phase diagram of iron, this has a widespread relevance for subjects as disparate as, for example, the properties of steel and the structure of the Earth's inner core.[5]

The importance of magnetism upon the phase diagram of iron is well known. *Ab initio* density-functional theory (DFT) calculations have demonstrated that the formation of magnetic moments stabilizes the bcc phase of iron at low temperatures and normal pressures. Although stable only above the Curie temperature, fcc iron has been found to have an incommensurate spin-density wave (SDW) magnetic state at low temperature, following measurements on fcc Fe precipitates on copper[6] and *ab initio* calculations.[7–9]

The magnetic attributes of hexagonal iron have not been so well identified. To date, DFT calculations of the total energies of two possible antiferromagnetic (AFM) ordered states are lower than the nonmagnetic one for pressures up to 60 GPa.[10] The calculated elastic constants for such magnetic states were also shown to provide a better interpretation of experimental data than those from nonmagnetic states. On the other hand, *in situ* Mössbauer data from hcp iron[11–14] show no evidence of long-range magnetism although they do allow for it to possess strongly enhanced paramagnetism which diminishes with increasing pressure. In this paper we study the spin fluctuations (SF) in this material via calculations of the paramagnetic spin susceptibility as a function of both temperature and pressure.

The paramagnetic susceptibility of a metal can possess much structure in wave-vector **q** space. Indeed a peak at one temperature can evolve into a divergence at a lower one. This signifies the system's transition into a magnetically ordered state characterized by a static magnetization wave with a wave vector corresponding to that of the peak. The peaks of the paramagnetic susceptibility can be obtained by examining a wide range of wave vectors. Hence, we can identify the dominant SF and probe for many different possible magnetically ordered states. In hcp Fe we find the predominant modes to be incommensurate with the hexagonal lattice and set by nesting features of the Fermi surface. These fluctuations become unstable at low temperatures and at the lower pressures where hcp Fe is just stable, indicating an incommensurate SDW magnetic state.

Recently, Staunton *et al.*[15,16] developed an *ab initio*, all-electron scheme for calculating the wave vector, frequency, and temperature-dependent dynamic spin susceptibility. This linear response theory is based on DFT and uses a variational approach.[17] The application to Pd, Cr, and Cr alloys has produced results in good agreement with experimental data. We have utilized this scheme within the static limit to produce susceptibility results for hcp Fe, which are presented here. The details of the theoretical framework and computational scheme are provided elsewhere,[15,16] so here we present a brief summary only. After a lattice Fourier transform over lattice vectors $\{\mathbf{R}_i\}$ the full wave-vector **q**-dependent susceptibility $\chi(\mathbf{x}_l,\mathbf{x}'_{l'},\mathbf{q})$ becomes

$$\chi(\mathbf{x}_l,\mathbf{x}'_{l'},\mathbf{q})=\chi_o(\mathbf{x}_l,\mathbf{x}'_{l'},\mathbf{q})+\sum_{l''}^{N_s}\int \chi_o(\mathbf{x}_l,\mathbf{x}''_{l''},\mathbf{q}) \times I_{xc}(\mathbf{x}''_{l''})\chi(\mathbf{x}''_{l''},\mathbf{x}'_{l'},\mathbf{q})d\mathbf{x}''_{l''}, \quad (1)$$

where $I_{xc}(\mathbf{x}''_{l''})$ is the functional derivative of the effective exchange and correlation magnetic field within the local-density approximation[18] with respect to the induced magnetization density. For a general crystal lattice with N_s atoms

TABLE I. Parameters for hcp Fe at four volumes with $c/a=1.6$: a is lattice parameter (a_o), V is volume of unit cell (a_o^3), P is pressure (GPa) (Ref. 21), and $N(E_F)$ is DOS calculated at the Fermi energy (states/Ry cell), $\tilde{I}$ is Stoner parameter (Ry/cell).

a	4.5273	4.5773	4.6273	4.6773
V	128.98	133.30	137.72	142.23
P	45	26	21	16
$N(E_F)$	31.46	32.59	35.35	35.97
$\tilde{I}$	0.0189	0.0189	0.0190	0.0188
$1/(1-\tilde{I}N(E_F))$	2.34	2.49	2.89	2.95
$\tilde{I}N(E_F)$	0.60	0.62	0.67	0.68

located at positions $\mathbf{a}_l (l=1,\ldots,N_s)$ in each unit cell, the $\mathbf{x}_l$ are measured relative to the positions of atoms centered on $\mathbf{a}_l$. One-electron Greens functions for the unperturbed, paramagnetic system are employed to calculate the noninteracting susceptibility χ_o and are obtained via multiple-scattering [Korringa-Kohn-Rostoker KKR] theory.[19]

Equation (1) is solved using a direct method of matrix inversion.[16] The full Fourier transform is then generated,

$$\chi(\mathbf{q},\mathbf{q}) = (1/V)\sum_{l}\sum_{l'} e^{i\mathbf{q}\cdot(\mathbf{a}_l-\mathbf{a}'_{l'})}\int d\mathbf{x}_l \int d\mathbf{x}'_{l'} e^{i\mathbf{q}\cdot(\mathbf{x}_l-\mathbf{x}'_{l'})} \times \chi(\mathbf{x}_l,\mathbf{x}'_{l'},\mathbf{q}), \quad (2)$$

where V is the volume of the unit cell. The numerical methods used to evaluate Eqs. (1) and (2) can be found in Refs. 15,16, and 20.

Calculations of the susceptibility are described for four volumes in the range $(128a_0^3 < V < 143a_0^3)$, where a_0 is the Bohr radius. The largest volume we consider is $142.23a_0^3$, which corresponds to a pressure[21] of $P \sim 16$ GPa and the smallest volume is $128.98a_0^3$ with $P \sim 45$ GPa.[21] We use atomic sphere approximation, effective one-electron potentials, and charge densities. Calculations of the density of states (DOS) and electronic band structure compare well with full potential calculations.[4] A summary of the volumes and equivalent pressures together with the calculated density of states is contained in Table I. For all the volumes the axial ratio of the lattice constants is taken to be $c/a=1.6$, which is very close to the experimentally observed value over the pressure range considered here.[21,22] This value of c/a is lower than the ideal close-packed one ($c/a=\sqrt{8/3}=1.633$).

Table I shows the DOS at the Fermi energy [which is equal to $\chi_o(\mathbf{q}\approx 0)$] to decrease as pressure increases. The averaged Stoner parameters $\tilde{I}$, for the four volumes are also given. These $\tilde{I}$ are calculated by relating the susceptibility [from Eq. (1)] $\chi(\mathbf{q})$ to the noninteracting susceptibility $\chi_o(\mathbf{q})$, via the expression

$$\chi(\mathbf{q}) = \frac{\chi_o(\mathbf{q})}{1-\tilde{I}\chi_o(\mathbf{q})} \quad (3)$$

for $\mathbf{q}\simeq 0$. Within the temperature range 50 K$\leqslant T \leqslant$300 K, $\tilde{I}$ is found to be roughly constant. From Table I, we also find $\tilde{I}$ to be virtually pressure independent. The Stoner enhancement factor, $\chi/\chi_o = 1/[1-\tilde{I}N(E_F)]$ and therefore $1-\chi_o/\chi \equiv \tilde{I}N(E_F)$ decrease with increasing pressure. The values of $\tilde{I}$ compare very well with those of Mazin *et al.*[2] who calculated $\tilde{I}=0.0188$ (Ry/cell) at $V=146.53a_o^3$, using a fixed-spin-moment method. Note that even at the largest volume we find $\tilde{I}N(E_F)=0.68<1$, which indicates hcp Fe to be far from a ferromagnetic (FM) instability.

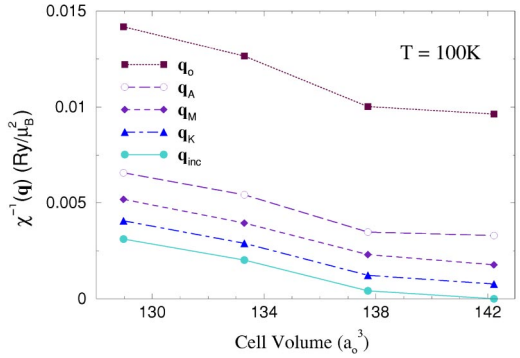

FIG. 1. The inverse susceptibility of hcp Fe at $T=100$ K for various wave vectors [$\mathbf{q}_o \simeq 0$, the nesting vector $\mathbf{q}_{inc} = 2\pi/a(0.56,0.22,0)$ and at the special points A,M, and K] for four unit-cell volumes.

From calculations of the susceptibility $\chi(\mathbf{q})$ [from Eqs. (1) and (2)] at many wave vectors in the Brillouin zone, a thorough search is made for dominant spin fluctuations and potential magnetically ordered states. The important ones are shown in Fig. 1. The temperature range for such calculations is 50 K$\leqslant T \leqslant$300 K. According to the full potential DFT calculations of Steinle-Neumann *et al.*,[10] two AFM configurations (termed AFM-I and AFM-II) are more stable than nonmagnetic or FM configurations for pressures up to $\sim$60 GPa at $T=0$ K. AFM-I has magnetization alternating in orientation in *ab* planes stacked along the *c* axis, while AFM-II has magnetization with opposite orientation on each layer aligned with the *c* axis and perpendicular to the *x* axis. If AFM-I is the lowest energy magnetic configuration, then for temperatures above the Nèel temperature, T_N, we should see a peak in the susceptibility at the special point wave vector $\mathbf{q}_A=(0,0,a/2c)$, (in units of $2\pi/a$). Similarly if AFM-II is the lowest-energy configuration, then we expect to see the peak in $\chi(\mathbf{q})$ at the special point $\mathbf{q}_M=(1/\sqrt{3},0,0)$. For all four volumes, however, we find the maximal peak in $\chi(\mathbf{q})$ to be at an *incommensurate* wave vector lying in the basal plane of $\mathbf{q}_{inc}=(0.56,0.22,0)$.

Figure 1 shows how $\chi^{-1}(\mathbf{q})$ varies with unit-cell volume for salient wave vectors at $T=100$ K. We see that $\chi(\mathbf{q}_{inc}) > \chi(\mathbf{q}_K) > \chi(\mathbf{q}_M) > \chi(\mathbf{q}_A) > \chi(\mathbf{q}_o \simeq (0,0,0))$ for all four volumes. Apparently, hcp Fe is the furthest away from forming a ferromagnetically ordered state as shown by the relatively high value of $\chi^{-1}(\mathbf{q}_o)$. This is followed by AFM-I ($\mathbf{q}_A$) and then AFM-II ($\mathbf{q}_M$). In agreement with Steinle-Neumann *et al.*,[10] we find the AFM-II to be a more stable configuration than AFM-I. But we also find a third special-point antiferromagnetic structure, AFM-III, characterized by $\mathbf{q}_K=(1/\sqrt{3},1/3,0)$, to be more stable than either of these. This

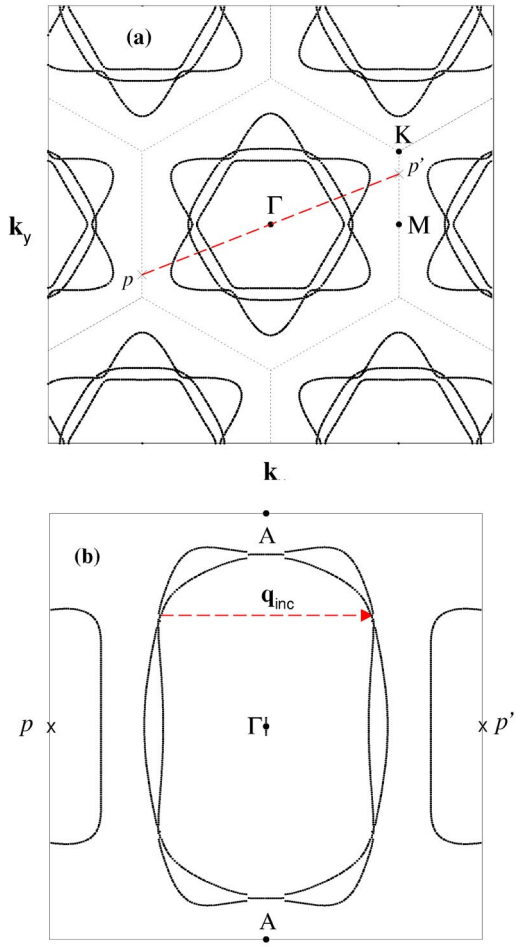

FIG. 2. Cross sections of the Fermi surface of hcp Fe at $V=137.72a_o^3$, where (a) is in the basal plane (extended zone) and (b) is the cross section of the Brillouin zone, where the x axis is along the direction of $\mathbf{q}_{inc}$ and the y axis is in the c axis (0,0,1), respectively.

structure would have the magnetization direction alternating in layers stacked along $\mathbf{q}_{\mathrm{K}}$. Although $\mathbf{q}_{\mathrm{K}}$ signifies a more stable AFM configuration than AFM-I and AFM-II, it is at the incommensurate vector ($\mathbf{q}_{inc}$) where we see the maximal peak in $\chi(\mathbf{q})$, which leads to the conclusion that the dominant spin fluctuation modes are incommensurate with wave vector $\mathbf{q}_{inc}=(0.56,0.22,0)$. At $T=100$ K, these enhanced incommensurate AF-SF are shown in Fig. 1 to decrease in strength as volume decreases with increasing pressure.

We can trace this wave vector $\mathbf{q}_{inc}$ to a nesting of the metal's Fermi surface as shown in Figs. 2(a) and 2(b). The Fermi surface is calculated using the fully relativistic KKR method[23,24] and is generated from three bands straddling the Fermi energy and is comprises of three sheets. Figure 2(a) shows a cross section of the Fermi surface in the basal plane, which is dominated by two hexagonal-like shapes centered on Γ. The dashed line connecting p and p' indicates the direction of vector $\mathbf{q}_{inc}$. This incommensurate vector $\mathbf{q}_{inc}=(0.56,0.22,0)$ nests two pieces of Fermi surface as shown in Fig. 2(b), which is a cross section where the x axis is along the direction of $\mathbf{q}_{inc}$ and the y axis is along the c axis. The nesting vector is indicated by the arrow in Fig. 2(b).

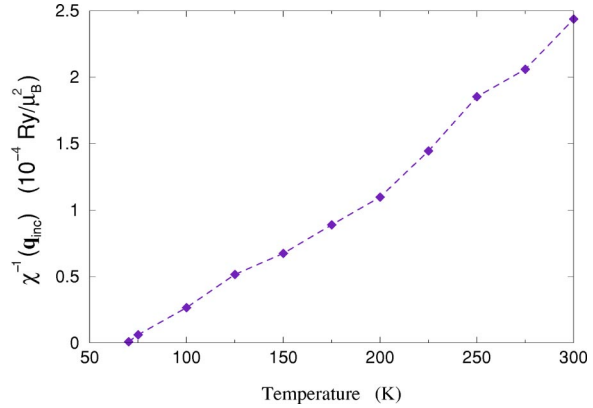

FIG. 3. The inverse of the enhanced susceptibility of hcp Fe for the unit-cell volume $142.23a_o^3$ and at the nesting vector $\mathbf{q}_{inc}=2\pi/a(0.56,0.22,0)$. The graph indicates a Néel temperature of 69 K.

Further investigations of the full spin susceptibility, Eq. (1), reveal that an instability arises at the nesting vector $\mathbf{q}_{inc}$ for hcp Fe for the larger volumes. We estimate a Néel temperature $T_N=69$ K for volume $V=142.23(a_0^3)$ and pressure $P\sim16$ GPa (the smallest volume at which hcp Fe is stable). This is shown in Fig. 3. T_N rapidly drops below 50 K (the lowest temperature we can consider accurately) as the volume is successively reduced. We therefore infer that hcp Fe has an incommensurate SDW magnetically ordered state in a small pressure range starting at a pressure where the hcp phase is stable.[12,14] As the pressure is increased, the Néel temperature swiftly decreases to zero.

The recent discovery of superconductivity in hcp iron by Shimizu *et al.*[1] with a critical temperature up to $T_c=1.7$ K, has lead to conjecture as to whether the Cooper pairings are mediated by phonons or magnetic fluctuations (AFM or FM).[2–4] As yet, there is insufficient experimental data to clarify the nature of the superconductivity (e.g., conventional *s*-wave or unconventional *p* wave, *d* wave). Saxena and Littlewood[25] noted that conventional electron-phonon coupling is a strong likelihood, but that this mechanism would be suppressed by strong magnetic spin fluctuations. Mazin *et al.*,[2] estimated a sizeable electron-phonon coupling, but could not explain why the superconductivity disappears so rapidly with pressure. They found that the elastic properties in hcp Fe do not change fast enough to explain the disappearance of the superconductivity at ~30 GPa. Other theoretical works by Jarlborg[3] and Bose *et al.*[4] reinforce the difficulty of a phonon-mediated mechanism. Bose *et al.*[4] calculated *s*-wave superconductivity to be persistent far beyond pressures of 200 GPa. Our calculations indicate an incommensurate AFM ordered state below a temperature of 70 K and at a pressure ~16 GPa, which is very close to the start of the superconducting phase. The disappearance of this magnetic order with increasing pressure would appear to coincide with that of the superconductivity. This suggests that the superconductivity is unconventional and that the incommensurate AFM-SF play an important role in the pairing mechanism.

In summary, we find the dominant spin fluctuations in hcp Fe to be incommensurate AFM-SF, characterized by the wave vector $\mathbf{q}_{inc}=(0.56,0.22,0)$. For the unit-cell volume $142.23a_o^3$, where pressure is ~16 GPa, we find these modes to become unstable and calculate a Néel temperature of 69 K. T_N drops rapidly as the pressure is increased. We therefore *predict* that an incommensurate SDW ordered state will be found in this narrow pressure range starting with the onset of the hcp phase.

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[1] K. Shimizu *et al.*, Nature (London) **412**, 316 (2001).
[2] I.I. Mazin, D.A. Papaconstantopoulos, and M.J. Mehl, Phys. Rev. B **65**, 100511 (2002).
[3] T. Jarlborg, Phys. Lett. A **300**, 518 (2002).
[4] S.K. Bose, O.V. Dolgov, J. Kortus, O. Jepsen, and O.K. Andersen, cond-mat/0207318 (unpublished).
[5] S. Gilder and J. Glen, Science **279**, 72 (1998).
[6] Y. Tsunoda, Y. Nishioka, and R.M. Nicklow, J. Magn. Magn. Mater. **128**, 133 (1991).
[7] M. Uhl, L.M. Sandratskii, and J. Kübler, Phys. Rev. B **50**, 291 (1994).
[8] C.S. Wang, B.M. Klein, and H. Krakauer, Phys. Rev. Lett. **54**, 1852 (1985).
[9] F.J. Pinski, J.B. Staunton, B.L. Gyorffy, D.D. Johnson, and G.M. Stocks, Phys. Rev. Lett. **56**, 2096 (1986).
[10] G. Steinle-Neumann, L. Stixrude, and R.E. Cohen, Phys. Rev. B **60**, 791 (1999); cond-mat/0111487 (unpublished).
[11] M.F. Nicol and G. Jura, Science **141**, 1035 (1965).
[12] G. Cort, R.D. Taylor, and J.O. Willis, J. Appl. Phys. **53**, 2064 (1982).
[13] R.D. Taylor, G. Cort, and J.O. Willis, J. Appl. Phys. **53**, 8199 (1982).
[14] R.D. Taylor, M.P. Pasternak, and R. Jeanloz, J. Appl. Phys. **69**, 6126 (1991).
[15] J.B. Staunton, J. Poulter, B. Ginatempo, E. Bruno, and D.D. Johnson, Phys. Rev. Lett. **82**, 3340 (1999).
[16] J.B. Staunton, J. Poulter, B. Ginatempo, E. Bruno, and D.D. Johnson, Phys. Rev. B **62**, 1075 (2000).
[17] S.H. Vosko and J.P. Perdew, Can. J. Phys. **53**, 1385 (1975).
[18] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
[19] J.S. Faulkner and G.M. Stocks, Phys. Rev. B **21**, 3222 (1980).
[20] E. Bruno and B. Ginatempo, Phys. Rev. B **55**, 12 946 (1997).
[21] A.P. Jephcoat, H.K. Mao, and P.M. Bell, J. Geophys. Res., [Solid Earth Planets] **91**, 4677 (1986).
[22] W.A. Basset and E. Huang, Science **238**, 780 (1987).
[23] P. Strange, H. Ebert, J.B. Staunton, and B.L. Gyorffy, J. Phys.: Condens. Matter **1**, 2959 (1989).
[24] E. Bruno, B. Ginatempo, E.S. Giuliano, A.V. Ruban, and Yu.Kh. Vekilov, Phys. Rep. **249**, 353 (1994).
[25] S.S. Saxena and P.B. Littlewood, Nature (London) **412**, 290 (2001).