PHYSICAL REVIEW B VOLUME 60, NUMBER 14 1 OCTOBER 1999-II

Spiral spin-density-wave ground state of γ-Fe calculated with spin stiffness correction to the local-spin-density approximation

D. M. Bylander and Leonard Kleinman
Department of Physics, University of Texas, Austin, Texas 78712-1081
(Received 19 July 1999)

Our recently derived spin stiffness correction to the local-density approximation has enabled us to calculate spiral (S) spin-density wave (SDW) vs wave-vector curves for γ-Fe in significantly better agreement with experiment than heretofore possible. This enabled us to come to two conclusions: (i) The neutron-scattering peak at $\mathbf{q}=(2\pi/a)(1,0,0)$ is due to a local minimum in the energy and not an artifact arising from the overlap of the tails of nearby peaks. (ii) Neutron scattering cannot distinguish between a SSDW and multiple SDW's polarized in different transverse directions. We confirm that the ground state of γ-Fe is a SSDW.
[S0163-1829(99)50138-0]

Spin-density waves (SDW's) and spiral (S) SDW's are intrinsically different in that the former consist of out-of-phase spin-up and spin-down charge-density waves whereas the eigenfunctions comprising the latter are spinors. Cr is considered the prototypical itinerant SDW system and fcc iron (γ-Fe), which can be precipitated as small clusters, is considered the prototypical itinerant SSDW system. In fact, neutron-scattering experiments are unable to distinguish between a SSDW and SDW's with different transverse directions of polarization in different domains (or clusters). Cr is believed to have a transverse SDW between 122 and 312 K but only because below 122 K it has a longitudinal SDW.[1] In view of the fact that no previous SSDW calculations[2–5] of γ-Fe have even come close to finding the correct wave vector of the ground state, it is unclear why the γ-Fe ground state is believed to be a SSDW. In this paper, however, we will present computational evidence that such is the case.

Very small (up to 150 Å diameter) clusters of γ-Fe are precipitated out with the Cu lattice constant when a molten CuFe alloy solidifies. Larger clusters have a distorted lattice. With the addition of 3% Co to the Fe, the fcc lattice remains stable up to a 1000 Å diameter. Elastic neutron scattering[6] resulted in broad peaks at $\mathbf{q}=(2\pi/a)(1,\pm\gamma,0)$ with $\gamma=0$ and 0.1 for small clusters and in sharp peaks at $\gamma=0$ and 0.13 for the Co stabilized clusters. A very broad background scattering, probably arising from small clusters, accompanied the sharp peaks. The $(1,\pm 0.13,0)$ peaks were interpreted[6] as arising from SSDW's and the smaller (1,0,0) peak from the overlap of tails from the peaks at (1,0,0.13). It seems to us that the sharp peaks are much too sharp and the broad background much too broad to account for the (1,0,0) peak. We have believed that there might be a double minimum and either some fraction of the clusters got trapped in the metastable (1,0,0) minimum or that because of some parameter (Co concentration is one possibility) the (1,0,0) minimum is the ground state for that fraction of clusters. The present calculation supports the double minimum conjecture.

Two local-spin-density approximation (LSDA) calculations in the atomic sphere approximation[2,3] (ASA) found the SSDW ground state $\mathbf{q}=(2\pi/a)(\alpha,0,0)$ with $\alpha=0.6$ and a local minimum at $\mathbf{q}=(2\pi/a)(1,\frac{1}{2},0)$. A full potential LSDA calculation[4] was in close agreement but with $\alpha=0.55$. A generalized gradient approximation (GGA) calculation[3] in the ASA had the $(1,\frac{1}{2},0)$ minimum drop slightly below the $\alpha=0.6$ minimum whereas a full potential GGA calculation[5] found the absolute minimum at $\alpha=0.5$ but differed from all the other calculations in that the $\mathbf{q}=(2\pi/a)(1,0,0)$ SSDW lay above the ferromagnetic state at $\mathbf{q}=\mathbf{0}$. In every case, $\mathbf{q}=(2\pi/a)(1,0,0)$, which should be an energy minimum to account for the neutron-scattering peak, was a maximum. We attributed this failure to the fact that both the LSDA and GGA depend on the magnitude of the magnetization along the local axis of quantization and are oblivious to the fact that that axis is rotating.

We[7] then derived the exchange energy density functional for jellium with a SSDW, exact to second order in the magnetization. From this we obtained a term to be added to the LSDA exchange-correlation energy density functional,

$$E_{\mathrm{xc}}[\{\rho_{\alpha\beta}\}]=E_{\mathrm{LSDA}}[\rho_+,\rho_-]+\hat{E}_{\mathrm{xc}}[\{\rho_{\alpha\beta}\}], \tag{1}$$

where

$$\rho_{\alpha\beta}(\mathbf{r}_j)=\frac{1}{N}\sum_{k=1}^{N}\sum_{n}^{\mathrm{occ}}\psi_{\alpha n\mathbf{k}}(\mathbf{r}_j)\psi^*_{\beta n\mathbf{k}}(\mathbf{r}_j), \tag{2}$$

α and β are spin indices, n and $\mathbf{k}$ are band and wave vector indices, the $\mathbf{r}_j$ are the discrete points in the unit cell at which the ψ's are calculated,

$$\rho_\pm=\tfrac{1}{2}(\rho_{\uparrow\uparrow}+\rho_{\downarrow\downarrow})\pm\sqrt{\tfrac{1}{4}(\rho_{\uparrow\uparrow}-\rho_{\downarrow\downarrow})^2+\rho_{\uparrow\downarrow}\rho_{\downarrow\uparrow}}, \tag{3}$$

and

$$\hat{E}_{\mathrm{xc}}[\{\rho_{\alpha\beta}\}]=\int\hat{\epsilon}_{\mathrm{xc}}(\mathbf{r})d\mathbf{r}$$
$$=-A\int\frac{(\rho_{\uparrow\downarrow}\nabla\rho_{\downarrow\uparrow}-\rho_{\downarrow\uparrow}\nabla\rho_{\uparrow\downarrow})^2}{\rho^{4/3}\rho_{\uparrow\downarrow}\rho_{\downarrow\uparrow}}d\mathbf{r}, \tag{4}$$

where $\rho=\rho_{\uparrow\uparrow}+\rho_{\downarrow\downarrow}$. Note that in the present case $\rho_{\uparrow\uparrow}=\rho_{\downarrow\downarrow}$.

We call $\hat{E}_{\mathrm{xc}}[\{\rho_{\alpha\beta}\}]$ a magnetic stiffness correction to the LSDA because, noting that $\rho^*_{\uparrow\downarrow}=\rho_{\downarrow\uparrow}=|\rho_{\uparrow\downarrow}(\mathbf{r})|e^{i\varphi(\mathbf{r})}$ where

$\varphi(\mathbf{r})$ is the angle the rotating component of the magnetization (in γ-Fe that is the total magnetization) takes in the xy plane, we have

$$\hat{E}_{\rm xc}[\{\rho_{\alpha\beta}\}]=A\int [|\rho_{\uparrow\downarrow}|^2(\nabla\varphi)^2/\rho^{4/3}]d\mathbf{r}. \tag{5}$$

Thus we see that this correction to the energy density is proportional to the square of the rotating component of the magnetization and to the rate at which it rotates. A, whose value for jellium would not be expected to be appropriate for a transition metal, is a dimensionless parameter.

For wave vectors whose group contains the inversion operator, $\rho_{\uparrow\downarrow}$ is real and $\hat{E}_{\rm xc}[\{\rho_{\alpha\beta}\}]=0$. Thus it has no effect on SSDW's whose $\mathbf{q}$ is at the Γ, X, or L points in the fcc Brillouin zone and we had originally hoped that using different values of A we could make both the LSDA and GGA minima occur at or near X. However when we found the GGA ferromagnet at Γ lay below the SSDW at X that became impossible for the GGA. That the LSDA is correctable with the addition of a spin stiffness term while the GGA is not may be a consequence of the fact that, being local, at a given point the LSDA is independent of the direction of the magnetization at neighboring points whereas this must be included *ab initio* in deriving the GGA.

The details of the calculation are given in Refs. 4 and 5. Here we only give the additional terms in the potential obtained from

$$\hat{v}_{\alpha\beta}=\delta\hat{E}_{\rm xc}/\delta\rho_{\beta\alpha}. \tag{6}$$

We find

$$\hat{v}_{\uparrow\uparrow}(\mathbf{r}_j)=\hat{v}_{\downarrow\downarrow}(\mathbf{r}_j)=-\tfrac{4}{3}\hat{\epsilon}_{\rm xc}(\mathbf{r}_j)/\rho(\mathbf{r}_j) \tag{7}$$

and

$$\begin{aligned}\hat{v}_{\downarrow\uparrow}(\mathbf{r}_j)&=\hat{v}^*_{\uparrow\downarrow}(\mathbf{r}_j)\\&=-2A\sum_{\mathbf{r}_i}\frac{\rho_{\uparrow\downarrow}(\mathbf{r}_i)\nabla\rho_{\downarrow\uparrow}(\mathbf{r}_i)-\rho_{\downarrow\uparrow}(\mathbf{r}_i)\nabla\rho_{\uparrow\downarrow}(\mathbf{r}_i)}{\rho^{4/3}(\mathbf{r}_i)\rho_{\uparrow\downarrow}(\mathbf{r}_i)\rho_{\downarrow\uparrow}(\mathbf{r}_i)}\\&\quad\times\left[\nabla\rho_{\downarrow\uparrow}(\mathbf{r}_i)\,\delta(\mathbf{r}_j-\mathbf{r}_i)-\rho_{\downarrow\uparrow}(\mathbf{r}_i)\frac{\partial\nabla\rho_{\uparrow\downarrow}(\mathbf{r}_i)}{\partial\rho_{\uparrow\downarrow}(\mathbf{r}_j)}\right]\\&\quad-\frac{\hat{\epsilon}_{\rm xc}(\mathbf{r}_j)}{\rho_{\uparrow\downarrow}(\mathbf{r}_j)},\end{aligned} \tag{8}$$

where

$$\frac{\partial\nabla\rho_{\uparrow\downarrow}(\mathbf{r}_i)}{\partial\rho_{\uparrow\downarrow}(\mathbf{r}_j)}=-i\mathbf{q}\delta(\mathbf{r}_i-\mathbf{r}_j)+\sum_{\mathbf{G}} i\mathbf{G}e^{i(-\mathbf{q}+\mathbf{G})\cdot(\mathbf{r}_i-\mathbf{r}_j)}, \tag{9}$$

and the last sum is over all reciprocal lattice vectors used in the calculation. Note that where $\rho_{\uparrow\downarrow}\to 0$, $\hat{v}_{\uparrow\downarrow}\to\infty$; this made the iteration to self-consistency much more tedious than in previous calculations.[4,5]

Choosing $A=0.350$ (when the units of $\hat{v}_{\alpha\beta}$ are Ry) we obtained the energy per atom (relative to the paramagnetic state) vs wave-vector curve displayed in Fig. 1 for $\mathbf{q}=(2\pi/a)(\alpha,0,0)$ and $(2\pi/a)(1,\gamma,0)$. The high-field ferromagnetic ground state increases in energy much more rapidly as $\mathbf{q}$ departs from zero than it did in Ref. 4 where we followed it out until it disappeared beyond $\alpha=0.19$. We made no attempt here to follow it beyond $\alpha=0.10$. There are three minima in the curve. That near $\alpha=0.6$ is the remnant of the deep LSDA minimum near $\alpha=0.55$. The minimum near $\gamma=0.19$ and the absolute minimum at X are new. For perfect agreement with the neutron data we would like the $\alpha\approx 0.6$ minimum to be somewhat higher or not to exist at all and the $\gamma\approx 0.19$ minimum to be at $\gamma=0.13$ and to be slightly lower so that it lay just barely below the minimum at X. Nevertheless Fig. 1 is close enough to ideal to be convincing that the neutron-scattering peak at X is due to a local energy minimum at X lying just above the absolute minima at $(1,\pm\gamma,0)$ and $(1,0,\pm\gamma)$ and not due to overlapping tails from those minima. Note that the SSDW at X is commensurate with the crystal lattice and therefore is an antiferromagnet with up and down spins alternating between [1,0,0] atomic planes.[8] In Ref. 4 we found a second [1,0,0] antiferromagnetic state which is almost certainly[9] the $\mathbf{q}=(2\pi/a)(1,0,0)$ SDW. This state has a different spin density than the SSDW and was found[4] to lie 1.29 mRy above the SSDW at X. This is large compared to the energy differences between the minima in Fig. 1. Therefore, now that our SSDW results are in good agreement with experiment, this energy difference is a strong confirmation of the experimentalists' assertion[6] that the ground state of γ-Fe is a SSDW and not a SDW.

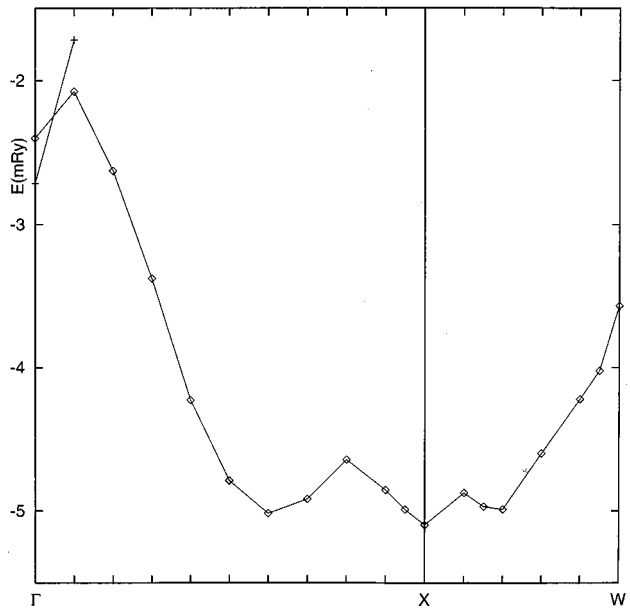

FIG. 1. Energy of the spiral spin-density wave for wave vectors along the $\Gamma(0,0,0)$ to $X(1,0,0)$ line and X to $W(1,\frac{1}{2},0)$ line relative to that of nonmagnetic fcc Fe at the same lattice constant of 6.822 bohrs. The short line beginning at Γ is the high-field state.

In Fig. 2 the integrated vector magnetization and its integrated magnitude over the Wigner-Seitz cell are plotted vs wave vector. For reasons to be explained, except at $\mathbf{q}=\mathbf{0}$ the two curves are much more nearly identical than they were without[4,5] the spin stiffness correction. It is interesting to note the $\mathbf{q}=(2\pi/a)(1,0.1,0)$ point has a sharp minimum in magnetization to go with its local maximum in energy but from that point to W the magnetization increases while the energy after a small but important dip becomes less negative; this is just the reverse of the behavior without the stiffness correction.

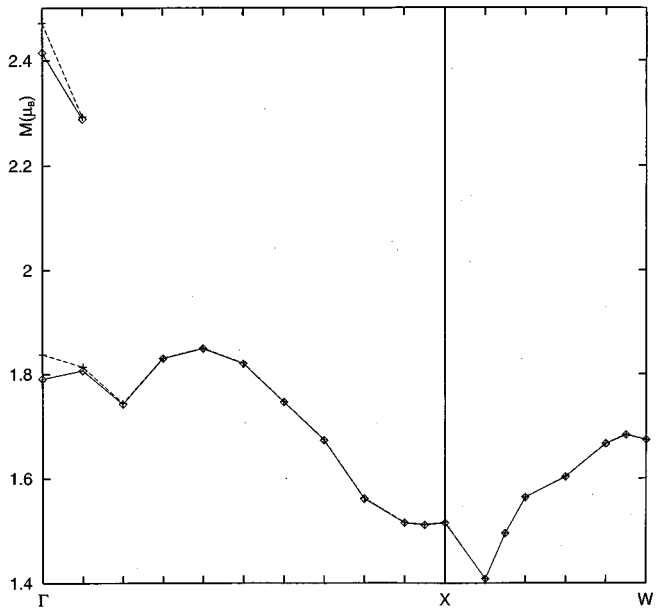

FIG. 2. Integral of the magnitude of the magnetic moment over the Wigner-Seitz cell (dashed line) and of the vector magnetic moment (solid line) for spiral spin-density waves with **q** along the ΓX and XW lines. The short line beginning at Γ is the high-field state.

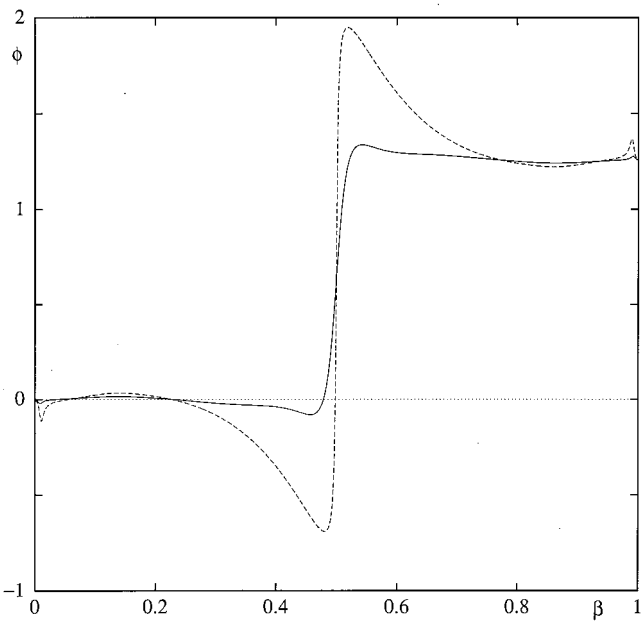

FIG. 3. Phase of the spiral spin-density waves $\varphi(\mathbf{r})$ for $\mathbf{q}=(2\pi/a)(0.4,0,0)$ and $\mathbf{r}=\beta(a/2,\pm a/2,0)$ or $\beta(a/2,0,\pm a/2)$ with (solid curve) and without (dashed curve) the spin stiffness correction added to the LSDA.

Figure 3 is a comparison of $\varphi(\mathbf{r})$ for $\alpha=0.4$ with and without the spin stiffness correction along a line from an atom at $(0,0,0)$ to one at $(a/2,\pm a/2,0)$ or $(a/2,0,\pm a/2)$. With the correction φ changes by $\alpha\pi$ from one neighbor to the other for any α whereas without the correction the change was $\alpha\pi$ only for $\alpha<0.5$ and was $\alpha\pi-2\pi$ for $\alpha \geqslant 0.5$. We see that the stiffness correction causes the magnetization direction to be nearly constant in each Wigner-Seitz cell, with almost all the change occurring at the edge of the cell where the magnetization is very small. This explains why the SSDW magnetizations and their magnitudes integrated over the cell are nearly identical in Fig. 2. Note that $\varphi(\mathbf{r})$ is both the direction of the magnetization and the phase of $\rho_{\downarrow\uparrow}(\mathbf{r})$; when this phase is constant except where $\rho_{\downarrow\uparrow}(\mathbf{r})$ is small, $\tilde{E}_{\mathrm{xc}}[\{\rho_{\alpha\beta}\}]/A$ is small. Thus as A is made larger, its effect saturates and further increases of A cause little change in the energy of the SSDW's.

In conclusion, using a very simple exchange-correlation energy density functional consisting of the usual LSDA term plus a spin stiffness term we have been able to calculate SSDW vs wave vector curves for γ-Fe in close enough agreement with experiment to enable us to draw two important conclusions. These are that the ground state is indeed a SSDW and not a SDW and that the two different neutron-scattering peaks arise from a double minimum in the curve. Further improvements in the density functional may be difficult to obtain. They will require some sort of GGA in which the electronic wave functions are assumed to be spinors from the beginning. Unlike our stiffness correction, it will contain gradients of the diagonal elements of the spin-density matrix as well as the off-diagonal.

These calculations were performed at the Texas Advanced Computing Center of the University of Texas at Austin and were supported by the University and NPACI. The research was supported by the Welch Foundation (Houston, TX) and the NSF under Grant No. DMR-9614040.

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[8] In Ref. 4 we mistakenly said the spin density at X vanishes everywhere on the planes midway between [1,0,0] atomic planes. It vanishes at those points on the plane which are midway between nearest-neighbor atoms. It is, however, quantized along a fixed direction.

[9] For reasons explained in Ref. 4, noncommensurate SSDW states are relatively easy to compute whereas noncommensurate SDW states are not. Therefore we have not proven that this antiferromagnetic state is the commensurate limit of a SDW but it is extremely unlikely that three different [1,0,0] antiferromagnetic states could exist.