Conditions for Noncollinear Instabilities of Ferromagnetic Materials

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Two criteria have been identified here which determine whether a magnetic metal orders in a collinear (e.g., ferromagnet) or noncollinear (e.g., spin-spiral) arrangement. These criteria involve the ratio between the strength of the exchange interaction and the width of the electron bands, as well as Fermi-surface nesting between spin-up and spin-down sheets of the Fermi surface. Based on our analysis we predict that even typical ferromagnetic materials (e.g., Fe, Co, and Ni) should be possible to stabilize in a noncollinear magnetic order in, e.g., high pressure experiments.

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The nature of the magnetic ordering in solids is, despite decades of research, not understood on a microscopic level. In particular, it is not known why one in nature most often observes collinear magnets (all spins are parallel or antiparallel) and only in few cases noncollinear magnetic ordering (that is neither parallel nor antiparallel). As a result of intense experimental [1–3] and theoretical [4–6] efforts certain trends regarding the magnetic ordering have evolved. For instance, it stands clear that Mn based materials, both in the fcc [4] and bcc [7] structure, often are observed in a noncollinear magnetic state. Likewise fcc Fe, and Fe based compounds where Fe is in the so-called intermediate or low spin state are noncollinear [4], as are the fcc Fe_xNi_{1-x} Invar alloys [8,9]. Recently, evidence has been found that suggests that Fe, that is a ferromagnet at ambient conditions in the bcc structure, would develop a noncollinear magnetic order in the hcp phase under pressure. Mazin *et al.* [10] have discussed the role that noncollinear magnetism plays on the appearance of superconductivity in Fe at the pressures of the earth inner core. Here we show, under more general conditions, how the ferromagnetic state can be unstable towards noncollinear spin-spiral states.

The most common theoretical explanations for noncollinear magnetic ordering involve either magnetic frustration in materials with crystal structures that have antiferromagnetic exchange interactions [4,11] or nearest neighbor ferromagnetic interactions that are of similar size to next nearest neighbor antiferromagnetic interactions [12]. For the late rare-earths the RKKY interaction has also been argued to cause noncollinear states [13].

The analysis of noncollinear magnetic states presented here builds on the symmetry of the electron wave function [4–6,14]. In a noncollinear scheme, the wave function can be described as a two component spinor instead of the usual one-electron wave function. The generalized Bloch spinor states [14] are then written as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \begin{pmatrix} e^{i(\mathbf{k}-\mathbf{q}/2)\cdot\mathbf{r}}\alpha_{\mathbf{k}}(\mathbf{r}) \\ e^{i(\mathbf{k}+\mathbf{q}/2)\cdot\mathbf{r}}\beta_{\mathbf{k}}(\mathbf{r}) \end{pmatrix}, \quad (1)$$

where $\mathbf{q}$ is the wave vector of the spin spiral, $\alpha(r)$ and $\beta(r)$ are periodic functions for the spin-up and spin-down components, respectively, and $\mathbf{k}$ is a wave vector in the Brillouin zone. The secular matrix formulated from these states is in general not block diagonal, and the two spin components are allowed to hybridize. The construction of the noncollinear wave function in Eq. (1) allows for a stabilization of a spin-spiral magnetic structure via the mechanisms displayed in Fig. 1. In this figure we present two schematic energy band structures. For a ferromagnetic configuration the spin-up and spin-down states are orthogonal to one another and cannot hybridize (they are represented by the straight blue and red lines in Fig. 1). However, for a noncollinear magnetic coupling, such as in a spin-spiral state, the two spin channels are allowed to hybridize. As a consequence a hybridization gap occurs

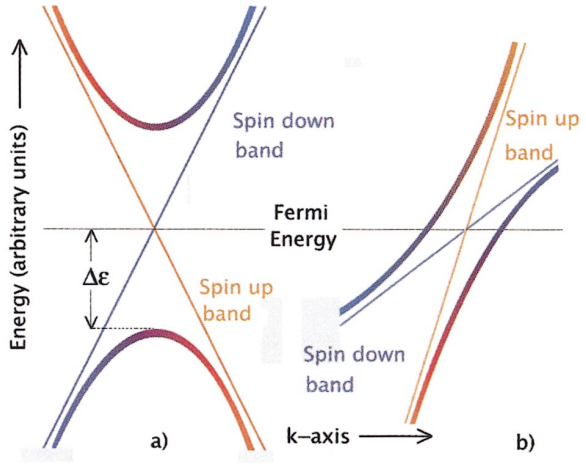

FIG. 1 (color). Schematic energy band structures of a hypothetical element. The straight red and blue lines stand for two orthogonal spin-up and spin-down bands, respectively, in the ferromagnetic state. The presence of a noncollinear coupling permits the hybridization of the two spin channels and the hybridized bands become the gradient-colored, curved lines. The horizontal line represents the Fermi energy. Two different possibilities are shown in (a) and (b).

with one band being pushed down in energy and one being pushed up. If the hybridization gap is located at the Fermi energy, as is drawn in Fig. 1(a), the state that becomes pushed up in energy is unoccupied and hence does not influence the total energy, whereas the band that is pushed down in energy lowers the total energy. In Fig. 1(b) a similar situation is presented, where a lowering of the band energy due to spin-spiral formation also occurs, however, the mechanism is not as efficient as in Fig. 1(a).

The scenario outlined above is quite analogous to the analysis of structural stabilities among the elements [15,16]. From this proposed mechanism two criteria stand clear as being critical for spin spirals to occur. First of all the Fermi energy (E_F) needs to cut through both spin-up and spin-down states. Hence, strong ferromagnets such as bcc Fe, hcp Co, and fcc Ni, where the spin-up band is filled, are not expected to form spiral magnetic structures, in contrast to fcc Fe, bcc Mn, and fcc Mn at ambient conditions. Second, the mechanism discussed in Fig. 1 is extra efficient if there exist nesting features between spin-up and spin-down states, which means that via a rigid shift in k space (with length q), large areas of the spin-up Fermi-surface can be made to coincide with the spin-down Fermi-surface. This guarantees that many k points are involved in the energy lowering process discussed above. One expects this to happen in all materials, provided that one can tune the exchange splitting and/or the band filling. Hence the stabilization of noncollinear magnetic ordering is not exclusive only for very specific and exotic compounds, as it has been discussed in the past, but instead likely for any element, alloy or compound.

A simple model calculation can be carried out to estimate the hybridization gap, which as discussed above, opens up as a result of the hybridization between the spin-up and spin-down states in the presence of noncollinear magnetism. The noncollinear component of the Hamiltonian, that gives rise to the hybridization corresponds, in a matrix representation, to the off-diagonal elements (denoted U) and will be considered for simplicity as a small perturbation to a ferromagnetic configuration of a material with free electron (FE) like band states. Hence we make use of perturbation theory for degenerate states, in order to estimate the size of $\Delta\varepsilon$ in Fig. 1. By using the wave function defined in Eq. (1), the resulting eigenvalue problem of our simple model can be written as [17]

$$\begin{bmatrix} \lambda_{\mathbf{k}-\mathbf{q}/2} - \varepsilon & U \\ U & \lambda_{\mathbf{k}+\mathbf{q}/2} - \varepsilon \end{bmatrix} \begin{bmatrix} e^{i(\mathbf{k}-\mathbf{q}/2)\cdot\mathbf{r}}\alpha_{\mathbf{k}} \\ e^{i(\mathbf{k}+\mathbf{q}/2)\cdot\mathbf{r}}\beta_{\mathbf{k}} \end{bmatrix} = 0, \quad (2)$$

where $\lambda_{\mathbf{k}} = k^2/2$ corresponds to the eigenvalue of the FE bands. In the FE model degeneracy occurs when $q = 2k_F$ and $k = 0$. As usual, a nonzero solution of Eq. (2) requires the determination of the roots of the secular determinant. Such a procedure, after some algebra, yields an expression for the two roots $\varepsilon_{\pm}$,

$$\varepsilon_{\pm} = \frac{1}{2}\left(k^2 + \frac{q^2}{4}\right) \pm \sqrt{\frac{1}{4}(\mathbf{k}\cdot\mathbf{q})^2 + U^2}. \quad (3)$$

Each root in Eq. (3) describes an energy band (e.g., as shown in Fig. 1). The solution $\varepsilon_{\pm}$ corresponds to the higher (lower) energy of the two bands. Consequently, the system can lower the total energy due to the hybridization gap with an amount

$$\Delta\varepsilon(\mathbf{k}) = \sqrt{\frac{1}{4}(\mathbf{k}\cdot\mathbf{q})^2 + U^2} - \frac{1}{2}\mathbf{k}\cdot\mathbf{q}. \quad (4)$$

It is clear that a larger gap causes a more significant effect in lowering the total energy and that this contribution to the energy stands in proportion to U. Hence, we have identified a mechanism that stabilizes the noncollinear configuration. It should be noted here that for a self-consistent calculation U becomes proportional to the non-diagonal component of the spin density matrix, hence it has an implicit $\mathbf{q}$ dependence. For a ferromagnetic solution to the crystal Hamiltonian U becomes zero and the solutions to Eq. (2) are instead $\lambda_{\mathbf{k}-\mathbf{q}/2}$ and $\lambda_{\mathbf{k}+\mathbf{q}/2}$.

To investigate the above suggested scenario we have carried out first principles theoretical calculations [18] for several transition metals. In passing we note that such calculations are extremely accurate in reproducing experimental data for the magnetic moment, magnetic order, and critical temperature [4,19]. The tuning of the exchange splitting was made either by modifying the volume or by using the so-called fixed spin moment method [20,21]. In this Letter we have for simplicity only investigated noncollinear magnetic structures that have a spin-spiral geometry but our arguments are appli-

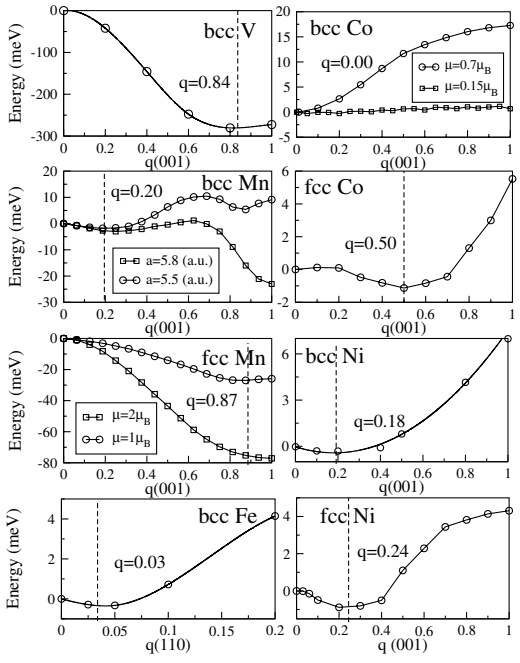

FIG. 2. Calculated energies as a function of $\mathbf{q}$ value for several elements, Ni, Fe, Co, Mn, and V, in the bcc and fcc crystal structures. The wave vector $\mathbf{q}$ was considered for simplicity along the (001) except in the case of bcc Fe, where the (110) direction was considered.

cable also for other more complex noncollinear structures (e.g., the 3**q** structure [4]). All elements that have been investigated, bcc V, bcc and fcc Mn, bcc Fe, bcc, and fcc Co, as well as bcc and fcc Ni, are either nonmagnetic or adopt a collinear magnetic structure, at normal conditions. However, we find that they all favor a noncollinear state after tuning the exchange splitting so that the mechanism illustrated in Fig. 1 becomes operative.

We illustrate our findings in Fig. 2, where we show the energy versus the wave vector $\mathbf{q} = (0, 0, q)$, that describes the spin-spiral structure along the (001) direction. In our notation, $q = 0$ stands for ferromagnetic and $q = 1$ for antiferromagnetic ordering, whereas all other energy minima correspond to a noncollinear magnetic structure. At the equilibrium volume fcc Ni is known to be a ferromagnet. However, fixing the spin to be $0.2\mu_B$/atom, the fcc Ni ground state results in a spin-spiral structure with $\mathbf{q} = (0, 0, 0.24)$ (Fig. 2). Under the same condition we find that bcc Ni also develops a spin-spiral structure, with $\mathbf{q} = (0, 0, 0.18)$. A similar behavior can be observed in bcc Fe, at a compressed volume ($V/V_0 \sim 0.6$) the ground state becomes a spin-spiral structure with $\mathbf{q} = (0.03, 0.03, 0)$. Calculated data for fcc Fe have not been included in Fig. 2 since this material has been studied extensively in the literature [22–24], and is known to possess a noncollinear magnetic state in the low spin configuration and a collinear antiferromagnetic state in the high spin configuration. In the case of bcc Co, we fixed the moment to be 0.7 and $0.15\mu_B$. In the former case a ferromagnetic state has the lowest total energy, while an almost flat curve with several local minima, is observed for the latter case. The variations observed in this curve are smaller than the accuracy of the calculations, and it is difficult to conclude if one **q** vector is more stable than the other. However, one can conclude that there is a competition between noncollinear and collinear-interactions that are of almost the same size. For fcc Co a spin moment fixed to a value of 0.8 μ_B stabilizes a spin spiral with $\mathbf{q} = (0, 0, 0.5)$. We also show in Fig. 2 how by enhancing the volume of vanadium ($V/V0 = 1.82$), which is nonmagnetic at the equilibrium volume, it is possible to find a stable spin-spiral structure with $\mathbf{q} = (0, 0, 0.84)$. Our two last examples concern fcc and bcc Mn. We find that when fixing the magnetic moment of fcc Mn to be $2\mu_B$ a collinear, antiferromagnetic state is stabilized and when decreasing the magnetic moment to $1\mu_B$ a spin spiral with $\mathbf{q} = (0, 0, 0.87)$ is the most stable state. The same effect can be achieved in bcc Mn by modifying its volume. We find that an antiferromagnetic state is stabilized when the lattice constant is ~5.8(a.u.). However, decreasing the lattice constant to ~ 5.5 (a.u.) produces a spin spiral with $\mathbf{q} = (0, 0, 0.20)$.

The data in Fig. 2 show that fulfilling the conditions for noncollinear order discussed in Fig. 1 is equally well accomplished by changing the lattice constant as by fixing the magnetic moment. In all the cases presented in Fig. 2 we have found that noncollinear states appear when the Fermi level cuts through both spin-up and spin-down bands, and our first principles results are consistent with the analysis of Fig. 1.

The discussion presented above suggests that there should be a notable modification in the Fermi-surface topology associated with the transition from a collinear magnetic state to a noncollinear state. In order to illustrate this we show in Fig. 3 the Fermi-surface for a ferromagnetic state [25] of fcc Co (with a spin moment fixed to be $0.8\mu_B$/atom) as well as for the noncollinear magnetic state corresponding to the energy minimum in Fig. 2. Note that we show only the contribution from two bands in the ferromagnetic case, that merge to one band in the noncollinear state.

According to the discussion of Fig. 1, there are large modifications in the Fermi surface due to the noncollinearity. Some of them come from the fact that the spin-up and spin-down ferromagnetic bands in Fig. 3 merge to one hybridized noncollinear band, whereas some other changes arise from the mixing of spin-up and spin-down Fermi-surface sheets, which come from bands that (due to space limitation) are not displayed in Fig. 3. An example of this is the conspicuous protrusion that is located along the z direction of the collinear Fermi-surface (see Fig. 3). This large topological change in the Fermi-surface comes from mixing of a spin-down sheet (not shown) that overlaps heavily with the (red) spin-up sheet shown in Fig. 3. In addition some sheets of the ferromagnetic Fermi-surface vanish when the spin-spiral state develops (data

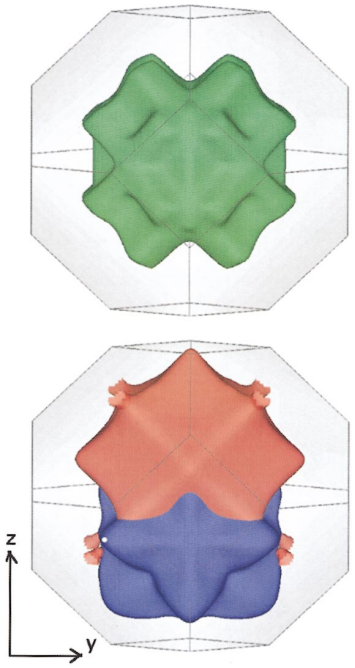

FIG. 3 (color). Calculated Fermi surface of fcc Co, in the ferromagnetic state (lower part) and for the spin-spiral state (upper part). The spin-up sheets are shown in red and the spin-down in blue, whereas the noncollinear Fermi surface is shown in green.

not shown), in agreement with the energy band drawn in Fig. 1(a).

Our analysis shows that a noncollinear state can be stabilized in any element or compound provided the band filling and exchange splitting are tuned correctly. This conclusion holds irrespective of the chemical composition of the material or the nature of the crystal structure. This means that complex magnetic structures may indeed be found even though the crystal geometry in itself does not give rise to magnetic frustration. It should be noted that the opening of band gaps in noncollinear configurations has been analyzed in special cases [4,19], but a general analysis as presented here, with the identification of specific criteria for when to expect noncollinear magnetic ordering has not been discussed before. We also point out that our findings do not overthrow the well established fact that antiferromagnetic interactions on a frustrated lattice produces a noncollinear magnetic state [11]. Instead we show that noncollinear magnetic ordering should be viewed as a general phenomenon and that collinear ordering (ferromagnetism, ferrimagnetism and antiferromagnetism) should be viewed as special cases when the exchange splitting is sufficiently large to disable the mechanism discussed in Fig. 1.

We point out that if the spin-spin correlations, calculated here in k space, would be formulated in a real space representation, one would end up with competing ferromagnetic and antiferromagnetic interactions. A general conclusion may be reached from our finding, namely, that ferromagnetic magnetic systems (elements, alloys, or compounds) when being compressed will not necessarily simply undergo a transition from ferromagnetic to nonmagnetic, as discussed in the past [26]. Instead it is most likely that for second order phase transitions one should observe a sequence of transitions from ferromagnetic via noncollinear to nonmagnetic. We also point out that Fe, an element currently discussed at a length in connection to geophysical sciences, quite likely may be a noncollinear magnet within a pressure range corresponding to the earth inner core [27].

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