Magnetic spiral induced by strong correlations in MnAu$_2$

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The compound MnAu$_2$ is one of the oldest known spin-spiral materials, yet the nature of the spiral state is still not clear. The spiral cannot be explained via relativistic effects due to the short pitch of the spiral and the weakness of the spin-orbit interaction in Mn, and another common mechanism, nesting, is ruled out as direct calculations show no features at the relevant wave vector. We propose that the spiral state is induced by a competition between the short-range antiferromagnetic exchange and a long-range interaction induced by the polarization of Au bands, similar to double exchange. We find that, contrary to earlier reports, the ground state in standard density functional theory is ferromagnetic, i.e., the latter interaction dominates. However, an accounting for Coulomb correlations via a Hubbard $U$ suppresses the Schrieffer-Wolff type $s-d$ magnetic interaction between Mn and Au faster than the superexchange interaction, favoring a spin-spiral state. For realistic values of $U$ the resulting spiral wave vector is in close agreement with experiment.

I. INTRODUCTION

The magnetic spiral is a type of noncollinear magnetic ordering in materials in which the localized moments form a screw-type pattern about an axis. Since the discovery of the first spin spiral in MnAu$_2$ in 1956 [1], the origins of such spirals have been subject of intensive research. A number of mechanisms have been discussed. In the local moment Heisenberg-exchange picture, a natural source of spirals is magnetic frustration of the nearest and next-nearest neighbor exchange parameters, for example, when $J_1 \neq 0$ (ferro- or antiferromagnetic) and $J_2 < 0$ (antiferromagnetic). If the next-nearest neighbor exchange is large enough, such that $|J_1| < 4|J_2|$, then the mean-field solution yields a spiral ground state [2,3]. This mechanism is applicable in both localized and itinerant electron systems, although in the latter one may expect long range interactions to play a role. For an itinerant system, the structure of the electronic response in reciprocal space captures the role of such interactions. If there is a maximum in the spin susceptibility at a particular wave vector $\mathbf{q}$, then this generates a spin density wave with the same wave vector, which can take the form of a spin spiral. In principle, a kink (as in the uniform 2D electron gas) or even a derivative singularity (as in the 3D electron gas) can induce an oscillatory interaction (Ruderman-Kittel-Kasuya-Yosida, or RKKY interaction) in real space, which can also encourage a spiral formation. Contrary to a common misconception, this effect does not require electron bands crossing the Fermi surface (the interaction is defined by the real, not imaginary, part of susceptibility), but it does become weaker as the excitation gap grows. Finally, geometric frustration can also encourage noncollinearity and helical ordering in materials.

The Dzyaloshinskii-Moriya (DM) interaction [4, 5], a relativistic effect that occurs in materials without an inversion center, has attracted a substantial amount of interest and can lead to moment canting or spiraling. This interaction becomes more important in materials with heavy elements, such as the rare earth series. Relativistic effects are important in such materials, although more than one mechanism is often in play. For example, the spiral phases of the heavy rare-earth metals Tb-Tm [6] are also understood to be due to nesting [7,9].

Spiral ordering is not restricted to materials with heavy magnetic ions. Spirals also form in lighter transition metal materials with an intriguing range of spiral vectors $\mathbf{q}$. The DM mechanism may be operative in some of these materials, but in such systems the weak relativistic effects induce spirals with long wavelengths as in MnSi [10–12]. Shorter wavelength spirals are also common, such as in the magnetically frustrated spinel chromites ZnCr$_2$Se$_4$ [13] and CdCr$_2$O$_4$ [14]. An interesting example is FeAs, featuring an incommensurate spiral with a period of 20 Fe layers [15,16]. This material is a good metal, so one may think that the conduction electrons mediate an oscillatory interaction via nesting or the classical 3D RKKY mechanism. However, the search for a nesting vector or features in the noninteracting susceptibility that match the spin spiral vector were unsuccessful [17]. But, as in the cited example of the 3D electron gas, oscillatory interactions may manifest themselves even without such peaks, and so one cannot rule out this mechanism in total without a full calculation of spin susceptibility in real space.

The material MnAu$_2$, as stated above, is one of the earliest examples of magnetic spiraling [1,18,19] and may provide better clues than FeAs as to how short-period spirals can form. The spiral has an even shorter period than FeAs, the material is a metal, and, unlike FeAs, Mn $d$-states are removed from the Fermi level, so the system may be a better representation of a model with localized moments and an interaction transferred via itinerant electrons of a different nature. The magnetic structure consists of ferromagnetic Mn planes (local moments are
in-plane) stacked along the crystallographic c axis, with the in-plane magnetization direction rotating from plane to plane. The rotation angle varies with temperature, from 60° at 5 K to 40° at 250 K [20]. The Néel temperature is \( T_N = 363 \text{ K} \) [1] and the material transitions from the spiral to a ferrimagnetic fan-like structure at room temperature upon application of a \( \sim 10 \text{ kOe} \) magnetic field [1, 18, 21], which gives rise to a giant magnetoresistance effect [21].

The crystal structure itself is also interesting. The Au atoms, which have 5 neighbors each, have much larger atomic radii when compared with Mn, and so they form the framework that holds the structure together, with the Mn atoms fitting into the center of cubic Au cages throughout the lattice. Such an arrangement has implications for the electronic structure, which we will discuss later.

The common explanation for the \( \text{MnAu}_2 \) spiral is magnetic frustration, where \( |J_1| < 4|J_2| \) [2, 3]. In this notation, \( J_1 \) is the exchange between nearest neighbor planes and \( J_2 \) is the exchange between 2nd nearest neighbor planes. This interpretation was supported by density functional (DFT) calculations [22], in which the exchange constants were calculated using a relativistic extension [23] of the torque method [24] within the screened Korringa-Kohn-Rostoker formalism [25], and it was reported that \( |J_1| < 4|J_2| \) was satisfied. However, the presence of highly itinerant carriers casts doubt on the idea of fully describing the magnetism in this system using a \( J_1 - J_2 \) Heisenberg model. It is possible that the standard Heisenberg model can even fail to give a qualitative description of the magnetic state, as in the case of the Fe-based superconductors where such a description is dramatically inadequate, see Refs. [26, 27]. Furthermore, while computational estimates for \( J_{1,2} \) seem to satisfy the spiral criterion, direct calculations (not performed in Ref. [23]) show that the true DFT ground state is a uniform ferromagnet and not a spiral.

We are not aware of any other first-principles studies of the magnetic interactions and the ground state of \( \text{MnAu}_2 \). Overall, first-principles calculations of \( \text{MnAu}_2 \) have been sparse, aside from the above reference and a pair of reports with calculations of the density of states [28, 29]. It is worth revisiting this problem using modern, full potential DFT calculations with noncollinear spin configurations and extracting the exchange parameters from total energy calculations, rather than by the torque perturbation theory with spherically-symmetrized potentials [22]. Given the good separation between the Mn and Au electrons, one may hope to elucidate microscopic reasons for the spiral ordering.

The paper is organized as follows. In Section II we will detail our computational methods for calculating the electronic structure and total energy and extracting the exchange constants. We then follow in section III with a report of our results and a subsequent discussion. Our main result is that, contrary to Ref. [22], a “vanilla” density functional theory does not account for the spirals in \( \text{MnAu}_2 \). However, upon accounting for on-site Coulomb correlations by applying an LSDA+U correction to the Mn d orbital, we see that spiral solutions appear for reasonable values of \( U \) and agree with the helical angle from experiment. This is an unexpected result, as the Hubbard \( U \) enhances localization and suppresses itinerant effects. Here, however, the correlated electrons forming local moments are different from the itinerant electrons mediating the magnetic interaction, and so a typical analysis using superexchange fails in such materials. Instead, the magnetism needs to be reanalyzed in a way similar to dilute magnetic semiconductors and Kondo lattices. We show, in particular, that the main effect of the application of \( U \) is to reduce hybridization between Mn bands and Au electrons forming the Fermi surface. While the nearest neighbor superexchange is suppressed as \( 1/U \), the transferred RKKY-type interaction goes as \( 1/U^2 \), introducing partial cancellation between the antiferromagnetic superexchange and ferromagnetic transferred interaction between the neighboring layer, which, in turn, enhances the \( |J_2/J_1| \) ratio. We describe our conclusions in section IV.

II. COMPUTATIONAL METHODS

We employed density functional theory (DFT) in three different implementations to study spin spirals in \( \text{MnAu}_2 \). We used PAW potentials as implemented in VASP [30, 51] and full potential linear augmented planewaves as implemented in ELK [32] and WIRE2K [33]. The Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) [34] was used for the exchange-correlation functional in all three codes and the local spin-density approximation (LSDA) [35] was also used in ELK. Correlation effects were considered in \( \text{MnAu}_2 \) using the DFT+U method in the fully localized limit [36], in which an empirical Hubbard \( U \) is introduced on the \( d \) orbitals of the Mn and/or Au atoms. Also, for a better comparison with the atomic sphere approximation (ASA) calculations of Ref. [22], which were not a full potential treatment, we have performed selected calculations in the ASA using a linear muffin-tin orbitals (LMTO) code [37].

The material \( \text{MnAu}_2 \) belongs to the space group \( I4/mmm \) with Wyckoff positions 2a for Mn and 4e for Au, which yields planes of Mn and Au atoms (2 layers of Au between each Mn layer). We set the lattice parameters to \( a = 3.37013 \text{ Å} \) and \( c = 8.75894 \text{ Å} \) and the internal parameter for Au to \( z_{\text{Au}} = 0.34 \). The experimental ground state of \( \text{MnAu}_2 \) is a spin spiral, where ferromagnetic Mn planes (local moments are oriented in-plane) rotate about the \( c \)-axis with a noncollinear pitch vector close to the incommensurate \( \pi/2c \). To simulate the magnetic state, we consider spin spirals in \( \text{MnAu}_2 \) with two different methods. The first is to construct explicit spirals in supercells using noncollinear moments in the \( xy \)-plane commensurate with \( q = \{0, 0, \pi/2c\} \), which is done using the GGA functional in both VASP and ELK.
The second approach is to use a spin spiral method to simulate spirals in a primitive cell with one Mn atom, which is done using the LSDA functional in ELK alone.

We fit the energy calculations using the above methods to the one-dimensional Hamiltonian,

$$ H = \text{const.} + \sum_i J_i \cos (i\theta), \quad (1) $$

where the sum is taken over the layers of Mn atoms. Our primary interest is in the ratio $|J_2/J_1|$, so at a minimum we kept the first two terms in the sum with constants $J_1$ and $J_2$, and then we varied the number of layers in the sum to evaluate the robustness of the fit and the extracted parameters.

III. DISCUSSION

We calculated the band structure and density of states (DOS) of ferromagnetic MnAu$_2$ using the LSDA functional, shown in Figs. 1(a) and 2(a). The Mn $d$-bands are fully spin-split, corresponding to the ionic configuration of Mn($d^5$) and the formal Mn valency of 5+. The total moment of the system is 3.93 $\mu_B$/Mn, and the reduction of the moment from the ideal 5 $\mu_B$ is due to the hybridization of Mn with Au. The bands crossing the Fermi energy consist of both Mn and Au character that is spin-dependent: the minority bands have $\sim 1.6$ times more Mn weight than the majority bands, while the majority bands have $\sim 1.5$ times more Au weight than the minority bands. We note that while the Au bands are polarized at the Fermi energy, the net moment on the Au ions is zero.

The crystal structure of MnAu$_2$, as mentioned earlier, consists of Mn atoms placed in cubic Au cages. The band structure and DOS suggest that the electronic structure at the Fermi level is mostly determined by the Au atoms, therefore we calculated the band structure of a hypothetical Au system where the Mn atoms have been removed, shown in Fig. 1(b). In the real system there is a charge transfer of one electron per Au ion, so the Fermi level is chosen to reflect an ionic charge of Au$^{1-}$. Comparing panels (a) and (b) shows the remarkable similarity between the two band structures, indicating that much of the electronic structure is due to the Au atoms only. The spin majority band crossing the Fermi energy in panel (a) is the same Au band in panel (b), while the spin minority band originates from the Mn atoms when they are placed into the structure, shifting the Au bands upwards in energy.

We next calculated the energy as a function of the spiral’s helical angle $\theta$ using the spin spiral method of ELK and explicit spirals in supercells in both ELK and VASP. For the spin spiral method we used the LSDA functional [38] and for the supercell calculations we used the GGA functional. We then computed the difference of $E(\theta) - E(0)$, comparing the energy of the spiral state with the energy of the ferromagnetic configuration. The results are summarized in Fig. 3(a). We consistently find in all cases that there is a preference for the ferromagnetic ground state. The qualitative trend across codes and functionals is the same. They differ with respect to the energy of the antiferromagnetic configuration, with the LSDA spiral method yielding the highest energy and the GGA VASP calculation yielding the lowest energy. Overall, this shows that DFT does not support a stable spin spiral, which is in disagreement with KKR calculations from Ref. [22].

The origin of this disagreement cannot be ascribed to using different density functionals, as we found the same
result with LSDA and GGA, nor in the approximations used to represent the crystal potential and electron (spin) density. We have verified, using a LMTO method that employs the same spherical approximation as the KKR method of Ref. [22], that the ground state is still ferromagnetic, see Fig. 3(a). An important difference may be that Ref. [22] uses the perturbative torque method to calculate the exchange constants, while we performed total energy calculations for explicit spin spiral configurations.

This results also hold when spin-orbit coupling (SOC) is turned on. The band structure of MnAu$_2$ with and without SOC is practically identical even though in principle Au is heavy enough to support non-negligible SOC effects. Importantly, the moment on Au is zero and therefore relativistic magnetic interactions of the DM type are excluded.

Although MnAu$_2$ is a good metal, the Mn $d$-states are quite localized and are subject to local Hubbard correlations, not accounted for in straight DFT. It is well known that other compounds with Mn$^{2+}$ require a Hubbard $U$ on the order of 3–5 eV to reproduce the correct positions of Mn bands. With this in mind, we employed the LSDA+$U$ method in combination with the spin spiral calculations in ELK to incorporate additional electronic correlations. We applied the Hubbard $U$ to the Mn 3d orbitals, using two plausible values for $U$, $U = 3.7$ eV and $U = 4.7$ eV. The parameter $J$ was set to $J = 0.7$ eV. In addition, we also checked if the application of $U = 3.7$ eV and $J = 0.7$ eV to the Au 5d orbitals affected the results. The results of these calculations are in Fig. 3(b).

We found that spirals form when $U$ is applied to Mn states, while adding an additional $U$ to Au had a negligible effect. For $U = 3.7$ eV, a shallow energy minimum of $\sim 3$ meV appears around $\theta = 30^\circ$, and for $U = 4.7$ eV a deeper well of $\sim 8$ meV/Mn appears around $\theta = 45^\circ$. Finally, we note that including $U$ compresses the overall energy scale compared with the results of Fig. 3(a).

This evolution can be understood if we picture the relevant magnetic interaction as a combination of the nearest-neighbor-plane antiferromagnetic superexchange, proportional to $t_\perp^2/\Delta_{\uparrow\downarrow}$, and the transferred magnetic interaction mediated by the Au electrons. Note that $t_\perp$ is the effective interplane hopping and $\Delta_{\uparrow\downarrow}$ is the energy cost of transferring a Mn $d$ electron to a neighboring site and flipping its spin. The transfer interaction can be visualized as the spin susceptibility of the Au subsys-

FIG. 2. The total and species-projected DOS of MnAu$_2$ calculated using the FLAPW code ELK. (a) The DOS using the LSDA functional. (b) The DOS using the LSDA+$U$ functional with $U = 4.7$ eV.

FIG. 3. The energy difference between a helical, in-plane spiral with angle $\theta$ and a ferromagnetic configuration in MnAu$_2$. (a) The energy dependence for LSDA and GGA functionals. The calculations are either spin spiral configurations or explicit supercell calculations using VASP, ELK, or LMTO, see the legend. (b) The energy dependence using LSDA+$U$, where the Hubbard $U$ is applied to Au and/or Mn $d$-states. See the legend for the values of $U$. 
TABLE I. The extracted exchange constants obtained by fitting the results of Fig. 3 to Eq. 1. For comparison, the calculated constants from Ref. [22] are also included. All constants are reported in units of meV.

| Const. | LSDA | LSDA+U | LSDA+Uudvardi et. al. |
|--------|------|--------|-----------------------|
| $J_1$  | -49.37 | -16.50 | -8.51 |
| $J_2$  | 8.17  | 6.43   | 6.30 |

tem multiplied by the square of the Mn-Au interaction vertex. In our case this vertex is, to a first approximation, the Schrieffer-Wolff interaction [30, 40], which is proportional to $\tau^2/\Delta_{sd}$, where $\tau$ is the Mn-Au hopping amplitude and $\Delta_{sd}$ measures how removed the occupied Mn $d$-states are from the Fermi level. For a Fermi energy that falls roughly in the middle of the lower and upper Mn Hubbard bands, $\Delta_{sd} \approx \Delta_{\uparrow\downarrow}/2$. Furthermore, in the LSDA+U calculations $\Delta_{\uparrow\downarrow} \approx \Delta_{ex} + U$, where $\Delta_{ex}$ is the LSDA (Stoner) exchange splitting.

The transferred interaction is distance dependent and is allowed to change sign, in contrast to the superexchange interaction. In particular, our calculations are consistent with a ferromagnetic nearest-neighbor interaction and an antiferromagnetic next-nearest neighbor interaction. The net nearest-neighbor exchange parameter is $J_1 \approx J_{SE} + J_{Mn-Au}^{(1)}$, where $J_{Mn-Au}^{(1)} < 0$ and $|J_{SE}| < |J_{Mn-Au}^{(1)}|$, while $J_2 \approx J_{Mn-Au}^{(2)}$, where $J_{Mn-Au}^{(2)} > 0$. Since $J_{SE} \propto 1/\Delta_{\uparrow\downarrow}$ and $J_{Mn-Au} \propto 1/\Delta_{\uparrow\downarrow}^2$, as $U$ increases both $J_1$ and $J_2$ shall decrease, but $J_1$ will decrease more rapidly as $J_{SE}$ starts to play a more dominant role.

This is precisely what we observe in the calculations. Fitting to Eq. 1 we were able to reliably extract the constants $J_1$ and $J_2$, which remained robust regardless of the number of additional neighbors we included in the fit. The extracted constants are summarized in Table I along with the constants from Ref. [22]. In all cases the $J_1$ parameter is ferromagnetic and $J_2$ is antiferromagnetic. Consistent with the argument above, the nearest-neighbor exchange $J_1$ is very sensitive to correlations, decreasing by a factor of $\sim 3$ for $U = 3.7$ eV and $\sim 6$ for $U = 4.7$ eV. In contrast, the decrease for $J_2$ is moderate for $U = 3.7$ eV and very small when $U$ is increased further to $U = 4.7$ eV. Our LSDA value of $J_2$ is in good agreement with Ref. [22], while we find $J_1$ to be larger by a factor of 2.

The band structure for MnAu$_2$ with $U = 4.7$ eV is shown in Fig. 1(c) and the DOS is in Fig. 2(b). As described, the primary effect of introducing $U$ is to move the Mn $d$ bands away from the Fermi level, which decreases the hybridization of Au with Mn, localizing Mn and decreasing the energy difference between FM and layered AFM configurations. This in turns lowers the polarization of the Au bands, which mediate the transferred interaction, which then weakens the ferromagnetic exchange of $J_1$. We conclude that the spiral instability in MnAu$_2$ is driven by correlation effects which enhance the importance of the superexchange interaction relative to the transferred interaction induced by Au polarization.

Finally, we tried to identify the microscopic reason for the transferred interaction to change sign between $c/2$ and $c$ along the $c$–axis. A natural explanation would be in terms of the Fermi surface nesting at an appropriate $q_z$. We note that $q_z$ does not have to coincide exactly with the spiral wave vector; adding superexchange will shift it towards shorter wavelengths. Unfortunately, one cannot use the nonmagnetic MnAu$_2$ for investigating nesting effects, as the Mn moments are very large and a linear response treatment is not appropriate. The hypothetical (Au$^{1-})_2$ system is more appropriate due to the similarity of the band structures in Figs. 1(a) and 1(b), which become increasingly more alike with increasing $U$. To check for nesting, we calculated the noninteracting one-electron susceptibility for (Au$^{1-})_2$, defined as

$$\chi_0(q) = \sum_{\alpha,\beta,k} \frac{f(\epsilon_{\alpha,k} - q/2) - f(\epsilon_{\beta,k+q} + q/2)}{\epsilon_{\beta,k+q} - \epsilon_{\alpha,k} + i\gamma}.$$  

Note that this expression neglects any matrix elements arising from the fact that Au wave functions deviate from plane waves. We found a weak maximum at $q = \{0, 0, 2\pi/c\}$, which would support antiferromagnetically aligned layers and would induce $J_1 > 0$ and $J_2 < 0$, opposite to what is needed for the experiment and what has been derived in Table I from the calculations. As it stands, further progress in understanding the Au-mediated transferred interaction requires calculations of the full spin susceptibility, which includes matrix elements and Stoner renormalization. At the present moment we do not have the capability to perform these calculations.

IV. CONCLUSION

We have revisited the origin of spirals in MnAu$_2$ using accurate, full potential, noncollinear DFT calculations, and found that contrary to previous findings, DFT alone is not sufficient to sustain a helical spiral state. We find that the spirals in MnAu$_2$ are supported by Hubbard correlations, which localize the Mn $d$ electrons and strongly reduce the ferromagnetic coupling between neighboring Mn layers. This mechanism is in contrast to the common origin of spirals, which are typically due to relativistic effects such as the DM interaction or one-electron effects such as Fermi surface nesting. This uncommon physical origin may be present in other materials where traditional explanations of spirals fail, such as FeAs.

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