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First-principles evidence of Mn moment canting in hole-doped $Ba_{1-2x}K_{2x}Mn_2As_2$

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The compound $BaFe_2As_2$ is the proptotypical example of the 122 family of high-T_c Fe-based superconductors that crystallize in the $ThCr_2Si_2$ structure. Isostructural compounds can be formed by replacing Fe with another transition metal; using Mn produces the material $BaMn_2As_2$, which unlike its Fe-based cousin has an insulating ground state with a large magnetic moment of 3.9 μ_B and G-type antiferromagnetic order. Despite its lack of superconductivity, the material is interesting in its own right. Recent experimental studies have shown that hole doping the compound by substituting K for Ba leads to metallic behavior and a spontaneous, weak, in-plane magnetization, which was attributed to the holes fully polarizing independent of the Mn moments, producing half-metallic behavior. However, the observed in-plane magnetization can also be understood as a small canting of the Mn moments. Using density functional theory, we demonstrate that a Mn moment canting occurs upon hole doping the compound. We argue that this is due to the competition between the super- and double-exchange interactions, which we support using a simple tight-binding model of the superexchange–double-exchange interaction and the Andersen force theorem. Our calculations also rule out an in-plane polarization of As holes as an explanation for the in-plane magnetization.

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Introduction. The discovery of the high-T_c Fe-based superconductors in 2008 induced a flurry of interest as researchers worked to understand the role of magnetism in the pairing mechanism and superconducting state [1–7]. Much like the cuprates, the parent compounds of the Fe-based superconductors are magnetically ordered in the ground state, although the similarity diverges from there: The ground state of the parent compounds of the Fe-based superconductors is metallic with long-range magnetic correlations while in the cuprates the ground state is insulating with strong, local electronic correlations [3]. The Fe-based superconductors can be divided into different structural classes, including the 122 class, which crystallizes into the $ThCr_2Si_2$ structure (space group $I4/mmm$). A protypical example of the 122 class is $BaFe_2As_2$ [8,9]. There has been much interest in studying other materials isostructural to $BaFe_2As_2$, such as replacing As with P or Se, or Fe with another transition metal, such as Co, Ni, Ru, or Mn.

$BaMn_2As_2$ is not the parent compound of any known superconductor, but it is interesting in its own right. Unlike its cousin $BaFe_2As_2$, which has a metallic ground state with stripe antiferromagnetic (AF) order and Fe moments of $\sim$0.9 μ_B [8], the ground state of $BaMn_2As_2$ is insulating with G-type antiferromagnetic (G-AF) order. The Mn atoms have moments of $\sim$3.9 μ_B [10–12], aligned along the crystallographic c axis. Metallic behavior can be induced through the application of pressure [13] or through doping, and successful hole doping was achieved by substituting Ba with K [14–16]. An ionic count suggests that Mn is divalent and in the high-spin state, such that its mean field moment would be 5 μ_B, which is reduced by hybridization and fluctuations to 3.9 μ_B. The material is a small band gap semiconductor with an intrinsic activation energy of 0.03 eV, as inferred from electrical resistivity measurements [10].

In heavily hole-doped samples a weak ferromagnetic (FM) magnetization develops along an in-plane direction in $Ba_{1-2x}K_{2x}Mn_2As_2$ [14,16]. When $x = 0.2$, the measured FM magnetization was 0.45 μ_B/f.u., close to the number of introduced holes, so a novel magnetic state was speculated in which the localized Mn moments remained G-AF ordered along the c axis while the mobile holes are polarized in the ab plane [16]. The authors of Ref. [16] argued the hole polarization was half-metallic, implying that if the density of states (DOS) is projected onto the in-plane magnetization direction it will be metallic in one spin direction and approximately insulating in the other.

The proposal of a novel state of two separate magnetic systems with localized Mn moments and mobile holes in the perpendicular direction is somewhat counterintuitive, as such a state is not well defined microscopically. Indeed, the introduced holes in the Mn-As planes can either be Mn holes or As holes (or a combination of the two). In the former case the same electrons that form the local moments will also form Mn bands that host the mobile holes, but these electrons are subject to a strong Hund's rule coupling and cannot form mutually orthogonal magnetic moments. Since in this case one cannot distinguish between the electrons forming local moments and mobile carriers when hole doping, the only way to implement the idea of mobile carriers promoting FM order is by introducing canting, as in the case of the classical double exchange [17,18].

In the latter case the mobile carriers are different (As holes) and can be polarized in a different direction. This would require the DOS near the top of the valence band to be mostly As. In this situation the problem is mathematically similar to the well-known case of Co-doped FeS_2, where an analytical treatment predicts that the system may be half-metallic or non magnetic depending on the effective mass and Stoner parameter I [19].

Despite this possibility, we show below that As polarization can be ruled out both numerically and analytically.

The main argument in Ref. [16] against Mn moments canting was based on the lattice symmetry. These authors correctly point out that the Dzyaloshinskii-Moriya interaction [20,21], a common source of such canting, is excluded here because the local Mn environment is symmetric with respect to inversion about the Mn site. However, the Dzyaloshinskii-Moriya interaction is not the only known source for such noncollinearity. As mentioned above, the double-exchange mechanism [17,18] is also well known for generating canting in metallic AF systems due to the competition between the superexchange, which favors AF alignment, and the tendency for mobile carriers to maximally delocalize, which favors FM alignment.

The authors of Ref. [16] also analyze their NMR spectra in comparison with x-ray and magnetic neutron diffraction and conclude that a canting of Mn moments is unlikely. However, the authors appreciate that this is an indirect and involved argument and considered it as secondary to their symmetry argument which, as explained above, is not valid.

Correspondingly, we consider it an open question as to whether or not canting is present in hole-doped $Ba_{1-2x}K_{2x}Mn_2As_2$, and in the following we address it using first-principles calculations. We conclude that the system is canted and the mechanism for that is the double exchange between the mobile holes and the localized spins. We find that the DOS is not half-metallic when projected onto the magnetization, contrary to the expectations of Ref. [16]. Analytical considerations using parameters derived from our first principles calculations give further support for our conclusions.

Qualitative considerations. Let us first consider a hypothesis of spin-polarized As holes. Inducing FM behavior upon doping would be the result of a competition between the kinetic energy and the Stoner (Hund) interaction $-Im^2/4$ [19], with the Stoner parameter $I_{As} = 1$ eV for As. For $x = 0.2$ holes/As the system is heavily doped and can be approximately thought of as a metal, in which case the Stoner criterion $I_{\mathrm{As}}N(0) > 1$ is appropriate. We calculated the DOS for collinear, undoped $BaMn_2As_2$, attributing the full DOS to the As atoms, and shifted the Fermi energy to simulate a doping level of 0.2 holes/As, finding $N(0) = 0.54$ spin^{-1} eV^{-1} As^{-1} (see the next section for methods). The Stoner criterion is therefore not satisfied and in-plane FM polarization would not be supported. Later in this Rapid Communication we use the full DOS to compare $-Im^2/4$ against the changes in the one-electron energies to confirm that the FM polarization of As holes is not supported.

Now let us consider the double-exchange scenario in which the carriers are Mn holes and must, by virtue of the Hund's rule, be parallel to the local moments. The condition for double exchange is $J_H \gg t$ [17,18], where t is the one-electron hopping amplitude. Since the Hund's coupling J_H in $3d$ metals is strong ($0.7 - 0.9$ eV) this condition is easily satisfied in $BaMn_2As_2$. Double exchange requires mobile carriers and thus in $BaMn_2As_2$ would only emerge upon doping. The mobile carriers can delocalize and lower their kinetic energy if they are moving on a uniform FM background, and this preference for ferromagnetic ordering must compete with superexchange, which is responsible for the observed G-AF order. It is known that for strong superexchange this competition results in a canted state of angle θ [22,23], where θ is the angle between the two antiparallel Mn moments (180° is G-AF order), and in a single-orbital tight-binding approximation the explicit form for the canting angle is

$$\cos\left(\frac{\theta}{2}\right) = \frac{tx}{4Jm^2}, \tag{1}$$

where x is the doping per Mn, J is the superexchange parameter, and m is the local Mn moment. Substituting typical values for t and J (later we present accurate calculations of these quantities), $t \sim 200$ meV, $Jm^2 \sim 500$ meV, and the experimental moment $m = 3.9\ \mu_B$, we obtain $\theta \sim 177.7°$, implying that each Mn moment cants by 1.15° and hence $M_{FM} = 2m\sin(1.15°) = 0.16\ \mu_B$/f.u. This is on the right order, although about a factor of three too small compared to the experiment.

Now we present accurate calculations of the above quantities using first-principles density functional theory.

Computational methods. To perform our calculations, we used noncollinear density functional theory (DFT) with the Perdew-Burke-Ernzerhof generalized gradient approximation [24] to solve the electronic structure of $Ba_{1-2x}K_{2x}Mn_2As_2$ using the full potential linear augmented planewave code ELK [25] and PAW potentials as implemented in VASP [26–29]. As mentioned, $BaMn_2As_2$ belongs to the space group $I4/mmm$, and we used lattice parameters $a = 4.16570$ Å and $c = 13.52110$ Å and the optimized internal parameter for As $z_{\mathrm{As}} = 0.358$. Good convergence was achieved with a $12 \times 12 \times 11$ k-point mesh and including 30 empty eigenstates per atom per spin in the calculation. In ELK, hole doping was accounted for in the virtual crystal approximation (VCA) in the standard way by replacing the Ba atoms with fictitious atoms of fractional nuclear charge between that of Ba and Cs. The DOS around the Fermi energy of $BaMn_2As_2$ is dominated by Mn and As states and hybridization with Ba is minimal, and so VCA is quite accurate. In VASP, hole doping was achieved via direct atomic substitution of K for Ba in a cell with two Ba atoms, four Mn atoms, and four As atoms; both Ba atoms are related by symmetry and thus replacing one or the other with K is equivalent. In either case the calculations were performed without using any rotational symmetry to allow for arbitrary canting.

Results. All reported results were calculated using ELK unless otherwise noted. We confirmed that the ground state of $BaMn_2As_2$ is G-AF. The calculated Mn moments are 3.64 μ_B within a muffin-tin radius of 1.259 Å, in reasonable agreement with experiment and previous calculations [12]. We found an indirect band gap of 0.2 eV, also in agreement with previous calculations [12].

To study if canting can be stabilized, we used the fixed-spin moment method to rotate the Mn moments in the xz plane and calculated the energy for several different values of θ. In this procedure the moment direction was constrained and the moment amplitudes were allowed to relax. For our calculations we chose a VCA doping level of $x = 0.2$, corresponding to the hole doping level reported in Ref. [16]. The results of these calculations are depicted in Fig. 1(a).

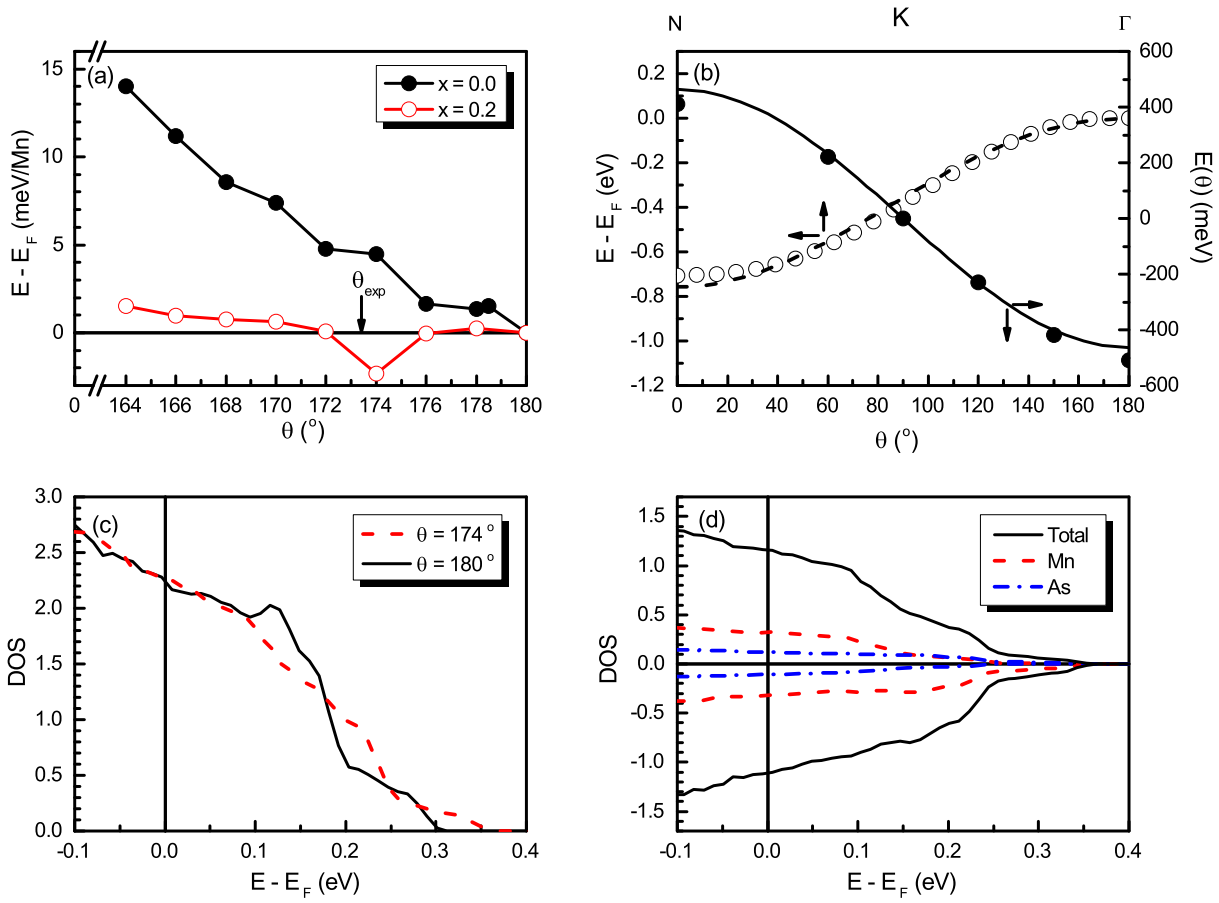

FIG. 1. (Color online) (a) The energy as a function of the angle θ. The black curve is the undoped ($x = 0.0$) case and the red (gray) curve is the doped ($x = 0.2$) case. The black arrow references θ_{exp} [16]. (b) *Left and bottom axes*: The closed black circles are the energy dependence of undoped $BaMn_2As_2$ as a function of the relative angle between the Mn moments. The black line is the fit of $Jm^2 \cos\theta$. *Right and top axes*: The open circles are the top valence band of $BaMn_2As_2$ along the $N - \Gamma$ symmetry line. The dashed line is the nearest neighbor tight binding fit. (c) The total DOS for $x = 0.2$ doping near the Fermi energy for collinear (black line) and canted (dashed red [gray] line) systems. (d) The spin-resolved As (blue [gray] dash-dotted lines) and Mn (red [gray] dashed lines) partial DOS and the spin-resolved total DOS (solid black lines) projected along the direction of the in-plane magnetization.

The results in Fig. 1(a) show that the undoped system does not exhibit canting, as is expected for an insulator without mobile carriers. For $x = 0.2$ the canting angle is predicted to be $\theta \approx 174^\circ$, or 3° per Mn moment, in excellent agreement with the angle defined in Ref. [16] from the ratio of the experimentally measured FM and AF moments, $\theta_{\text{exp}} = 2\cos^{-1}(0.45/7.8) = 173.4^\circ$ [shown as the black arrow in Fig. 1(a)]. One can also see how doping leads to strong cancellation between the super- and double-exchange terms, as even at $\theta = 164^\circ$ the energy difference with the collinear state is 1.5 meV/Mn, in contrast to 14.0 meV/Mn for the undoped case.

The energy scales for canting are on the order of a couple meV, as is seen in Fig. 1(a), which leads to difficulties when trying to calculate the canting angle self-consistently using either VASP and ELK. When using a $Ba_2Mn_4As_4$ unit cell in VASP and replacing 50% of Ba atoms with K to simulate $x = 0.25$, we stabilized canting solutions with $\theta = 174^\circ$ and energy $E(\theta) - E(0) = -0.8$ meV/Mn. However, depending on the canting angle used to initialize the calculation, sometimes VASP relaxed to a larger canting angle. The undoped compound always converged to the collinear solution. We ran into similar problems with ELK. At $x = 0.2$ we were able to converge to two different solutions, one with $\theta \approx 176^\circ$ and energy -0.25 meV/Mn and the other with $\theta \approx 168^\circ$ with energy -0.06 meV/Mn. We note that the energies here are smaller than the fixed-spin moment calculations, because the self-consistent rotation of the moment is not accurate enough to find the minimum energy for canting with sufficient precision. We stress that these calculations are only used to indicate a qualitative tendency towards canting and that the agreement between all-electron and pseudopotential methods allows one to be convinced that in actual experiments the ground state is a canted antiferromagnet. A quantitative determination of the canting angle is only possible using fixed-spin moment calculations, as they are stable and reproducible. Further discussions will make use of fixed-spin moment calculations only.

We now get back to Eq. (1) and determine its parameters from our calculations in ELK. In Fig. 1(b) we calculated the energy of undoped $BaMn_2As_2$ as a function of the relative angle between the two magnetic moments and fitted it to $E = Jm^2 \cos\theta$, finding $Jm^2 = 463$ meV. We also calculated

the band structure and fitted the top valence band to the nearest neighbor tight binding model, also shown in Fig. 1(b). The fit yielded the hopping amplitude $t = 190$ meV. Using Eq. (1) we find that $\theta = 177.7^\circ$ for $x = 0.2$, in agreement with our previous rough estimate. This prediction is off by a factor of 2.6 when compared with the result of Fig. 1(a), which is reasonable given the simplicity of the model.

To address the microscopic origin of the canting observed in our DFT calculations, it is instructive to compare the DOS for $x = 0.2$ in the VCA for both the uncanted case and the canted case of $\theta = 174^\circ$; see Fig. 1(c). The gain in kinetic energy from allowing the electrons to delocalize upon canting can be estimated by using the Andersen force theorem [30,31] and calculating the change in the one-electron energy of the uncanted and canted systems. Strictly speaking, the force theorem requires taking the same charge and spin density for both cases; in the canted case the self-consistent uncanted potential is rotated within each muffin-tin sphere by 3° and the DOS is generated non-self-consistently. This is not possible in ELK, so we used the self-consistent canted DOS as a proxy assuming that the main changes in DOS are due to canting and not by changing the spin density (indeed, the calculated magentic moment is essentially the same 3.5603 μ_B vs 3.5606 μ_B). Applying the force theorem we can then approximate the total energy change as the change in one-electron energy and the magnetic energy. The former can be computed by integrating the DOS as $\int_{\text{occ}} EN(E)dE$ or, equivalently, as $-\int_{\text{unocc}} EN(E)dE$ and normalizing the computed integral by the number of electrons or holes. The change in kinetic energy can be visualized as the broadening of the unoccupied part of the valence band which results in an upshift of the center of gravity. Using the DOS in Fig. 1(c), we find $\Delta E_{\text{kin}} = 6.6$ meV. The corresponding loss of the exchange energy is $Jm^2(1 + \cos\theta)$, and using $\theta = 174.0^\circ$ gives us 2.5 meV. The energy gain in the one-electron energy is about 2.6 times larger than the energy loss from the exchange interaction. This indicates that canting is favored, but as in the case of relaxing the canting angle self-consistently, the energy scales are quite small.

We now determine whether half-metallic behavior is possible in hole-doped $Ba_{1-2x}K_{2x}Mn_2As_2$, as argued in Ref. [16]. First we check whether a spin channel becomes approximately insulating when the Mn moments are canted. The partial DOS for Mn and As along with the total DOS is projected along the direction of the in-plane magnetization for the canted angle of $\theta = 174^\circ$ in Fig. 1(d). There is no evidence for half-metallic behavior at the Fermi energy; the DOS is that of a weak ferromagnet. It should be noted that the partial densities of states of As and Mn at around $E - E_F \approx 0.25$ eV each become nearly half-metallic, although the polarization directions of the two atoms oppose each other. This suggests that the emergence of half-metallic behavior upon canting is possible, though it is not realized in this system.

Finally we return to the scenario of polarized As holes. As before in our qualitative consideration we calculated the DOS for collinear, undoped $BaMn_2As_2$ and shifted the Fermi energy to simulate $x = 0.2$. Assuming that the full DOS can be attributed to the As atoms, we then manually polarize the DOS and calculate $-Im^2/4$ and compare it with the changes in the kinetic energy. We find that the polarization of As holes is never favored. For full polarization, the gain in Stoner energy is 10 meV while the kinetic energy loss of 150 meV is an order of magnitude larger, so half-metallic polarization is very unfavorable. Of course, in the actual hole-doped system the character of the carriers at the Fermi energy is a combination of Mn and As states, with about three times more Mn-like carriers than As-like carriers, as seen in Fig. 1(d), so it is even more unlikely that the As holes could polarize.

Conclusion. We theoretically investigated hole-doped $Ba_{1-2x}K_{2x}Mn_2As_2$, in which weak ferromagnetism was discovered experimentally and attributed to two groups of carriers, local electrons with spins aligned along c axis, and mobile holes fully polarized in the ab plane. Our first-principles calculations quantitatively reproduce the observed weak ferromagnetism, yet the microscopic physics is better described by a canting of Mn moments induced by double exchange. This conclusion is supported by our numerical calculations and analytical analysis.

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