$CaMn_2Sb_2$: a fully frustrated classical magnetic system

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We show by means of density functional calculations that $CaMn_2Sb_2$ is very close to a mean-field critical point known for the classical Heisenberg model on the honeycomb lattice. Three entirely different long range ordered magnetic phases become degenerate at this point: the Neel phase and two different spiral phases. We speculate that the unusual physical properties of this compound, observed in recent experiments, in particular the enigmatic intermediate temperature phase, are due to this proximity.

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Introduction: $CaMn_2Sb_2$ is an interesting implementation of a nearly classical spin system on a honeycomb lattice. Such systems have been attracting the attention of researchers since the seminal paper of Rastelli *et al* from 1979[1]. The basic model involves the nearest neighbor (nn) interaction J_1 and the second neighbor interaction J_2. In the classical limit, the ground state of this $J_1 - J_2$ model, for antiferromagnetic $J_{1,2}$, is the Neel phase where all nearest neighbor bonds are fully antiferromagnetic, if $J_2/J_1 < 1/6$. Interestingly, for $1/6 < J_2/J_1 < 1/2$, there are two degenerate solutions, corresponding to two different spiral phases (in one of them the two spins in one unit cell are always antiparallel, and the spiral propagation vector is perpendicular to a nn bond, in the other the two sublattices are rotated by a particular angle with respect to each other, and the spiral vector is parallel to a bond). At $J_2/J_1 > 1/2$ the ground state is the stripe phase with alternating FM pairs (Fig. 1). Both critical points, $J_2/J_1 = 1/2$ and $J_2/J_1 = 1/6$ are triple points: in case there is an additional parameter, for instance the third neighbor exchange J_3, three phases meet at these points: the Neel phase and the two spiral phases at $J_2/J_1 = 1/6$, and the stripe phase and the two spiral phases at $J_2/J_1 = 1/2$. Whenever a third parameter is added, be it the third neighbor exchange[1] J_3, uniaxial anisotropy[1] or biquadratic coupling[3] K, complex phase diagrams arise, with the four phases described above, and additional phases such as zigzag antiferromagnetism.

The crystal structure of $CaMn_2Sb_2$ is shown in Fig. 2. The Mn sublattice consists of honeycomb layers in which every other atom is shifted perpendicular to the plane. This interesting geometry leads to a rather short Mn-Mn distance, 3.18 Å, with substantial direct overlap between the Mn d orbitals and as a result sizable direct antiferromagnetic exchange. In addition, there are two superexchange paths available. One connects the nearest neghbor Mns, with an Mn-Sb-Mn angle of 70°, and the other connects the second neighbors, with an angle of 108°. Mn in this compound has valency 2+, and therefore in the high spin state it would have a magnetic moment of 5 μ_B, reduced by hybridization and fluctuations. Experimentally at low temperature the J_1-driven Neel phase was found, with a magnetic moment of 2.8-3.4 μ_B. At $T = 85$ K this phase gives rise to another phase of unknown origin, which experimentally resembles weak ferromagnetism, but no long range antiferromagnetic order was detected. Finally, at $T \gtrsim 200$ K the material becomes paramagnetic, exhibiting at $T \gtrsim 300$ K a Curie-Weiss behavior with an effective moment $M_{CW} = 1.4\,\mu_B$. The unusual character of the intermediate temperature phase, as well as the very low Curie-Weiss moment, suggest that frustration characteristic of honeycomb magnetic models may play a role. The low-temperature phase shows an activation transport behavior with an activation gap ~ 40 meV, while the intermediate temperature phase exhibits a strong increase (up to a factor of 100) of the resistivity.[4]

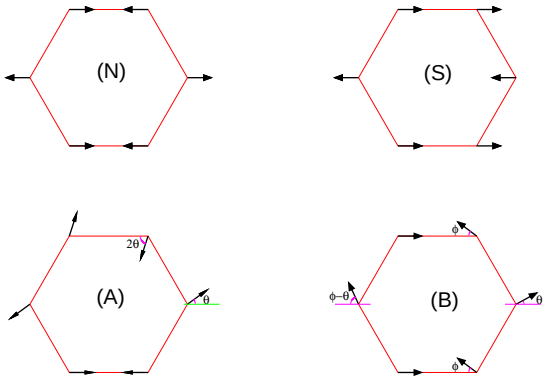

FIG. 1: Four antiferromagnetic patterns discussed in the text. Note that the spiral A coincides with the phase N at $\theta = 0$ and spiral B with the phase N N at $\phi = \pi$ and $\theta = 0$, and with S at $\phi = 0$ and $\theta = \pi$. At the same time the two spirals cannot be continuously transformed into each other except in this limiting cases.

We have performed first principle calculations of the electronic and magnetic properties of $CaMn_2Sb_2$. We found Mn to be in the high spin state and $d(5\uparrow)$ config-

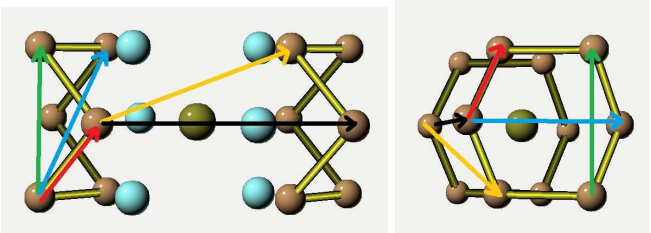

FIG. 2: (color online) Crystal structure of $CaMn_2Sb_2$, showing examples of the nearest neighbors (J_1, red), 2nd neighbors (J_2, green) and 3rd neighbors (J_3), blue, inside a MnSb layer, as well as the nearest (J_{z1}, yellow) and 2nd (J_{z2}, black) interplanar neighbors. Mn atoms are shown by gray spheres, Sb by cyan ones and Ca by green ones.

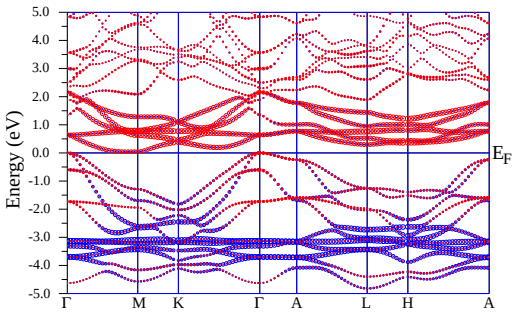

FIG. 3: (color online) Calculated band structure of $CaMn_2Sb_2$ in the antiferromagnetic Neel phase. The symbol size is proportional to the Mn character (spin-up in blue, below the Fermi level, and spin-down in red, above the Fermi level.

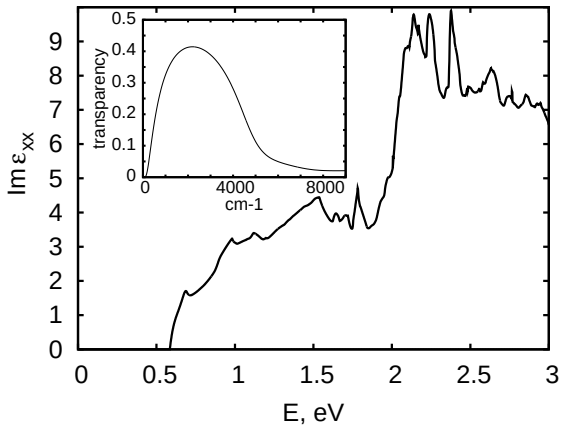

FIG. 4: The calculated dielectric function of $CaMn_2Sb_2$. The inset shows the corresponding transmission coefficient (the thickness of the slab was chosen to roughly match the amplitude of the transmission coefficient in Ref. [4]i, and a uniform week absorption was added to account for the experimentally observed in-gap states).

uration. We also found a small gap consistent with the experiment, and magnetic interactions dominated by the nearest neighbor exchange. Most interestingly, we found that the second neighbor exchange is 4-6 times smaller than the nearest neighbor one, while the third neighbor exchange and the biquadratic exchange are very small, and the magnetic anisotropy is of the easy-plane type. In this regime classical spins on the honeycomb lattice are highly frustrated, with two spiral and two collinear phases nearly degenerate. We speculate that this frustration is the cause of the unusual magnetic phase diagram.

Calculations. The calculations in this paper were performed with the Linear Augmented Plane Wave code WIEN2k[5], using the following crystallography: symmetry group #164, $P\bar{3}m1$, a =4.522 Å, c =7.458 Å, $z_{Ca} = 0$, $z_{Mn} = 0.3784$, $z_{Sb} = 0.7487$, and a Generalized Gradient Approximation for the exchange-correlation potential. In agreement with previous calculations[4] we found that Mn in strongly polarized, and Mn moments are well localized, as demonstrated by the fact that all magnetic configurations converge to about the same magnetic moment, $\sim 4\ \mu_B$, and the calculated exchange energies are much smaller than the magnetization energy. The lowest energy among various collinear states has the Neel state, in which the nn Mn have opposite spins.

The band structure and density of states in this configuration are shown in Fig. 3. One can clearly see that all five d orbitals of Mn are fully polarized, while the reduction of the moment from 5 to 4 μ_B is due to hybridization. There is also an indirect excitation gap (of the spin-flip nature), about 50 meV, consistent with the experimentally measured one. The calculated optical gap (minimal direct transition energy) is about 0.7 meV, but the absorption at this energy starts relatively slow (Fig. 4), owing to the fact that the top of the valence band and the bottom of the conductivity band are formed in the different spin channels (in a ferromagnetic case, these transtions would have been optically forbidden; in an antiferromagnetic one, they are allowed but weak). The main absorption edge is located at 2 eV. Compared to experiment[4], the calculated transmission drops at a lower frequency. However, the optical experiments reported in Ref. [4] should be considered as preliminary. One has to wait for more state-of-the-art optical data, preferably for the conductivity, for a full comparison.

In order to understand better magnetic interactions in $CaMn_2Sb_2$, we have calculated the total energies of 10 different magnetic configurations, and mapped the results onto the model Heisenberg that includes 1st, 2nd and 3rd nearest neighbors inside the MnSb layers (J_1, J_2, and J_3), and 1st and 2nd neighbors between the lay-

TABLE I: Calculated exchange parameters and the corresponding Mn-Mn bond lengths. See Fig.2 for graphical examples.

	J_1	J_2	J_3	J_{z1}	J_{z2}
d (Å)	3.179	4.522	5.528	6.219	7.458
J (meV)	91	22	5	11	3

ers (J_{z1} and J_{z2}). The corresponding distances and values are listed in the Table. Note that the definition of J in this paper is such that the pair interaction is $J\sigma_i\sigma_j$, where $\sigma = \pm 1$.

Since the number of energy differences (9) is larger than the number of fitted exchange constants, one can estimate the accuracy of the fitting from the standard fit error. This is on the order of 7–8 meV. Note that on the mean field level J_zs simply renormalize the planar interactions, in other words, assuming perfect interplanar ordering, one can map the 3D problem onto 2D with $J_{1eff} = J_1 + J_{z1} = 102$ meV.

We have also looked for other possible deviations from the Heisenberg model: the biquadratic interaction, which plays an extraordinary important role in Fe-based superconductors, and single-site anisotropy. The former appears to be zero within computational accuracy, in other words, for all possible angles between the Mn spins in the same unit cell the energy is perfectly cosinusoidal, $E = const + 0.5 J_1 \cos\alpha$. The latter (magnetic anisotropy) is zero in plane (although formally hexagonal symmetry allows for magnetic anisotropy when the field is rotated by 30^o, for all practical purposes this effect is negligible), and about 2–3 meV/Fe otherwise, with the direction perpendicular to the plane being the hard axis.

Discussion. The fact that essentially any magnetic pattern can be stabilized in the calculations, and that the energy cost of suppressing magnetism entirely (0.8 eV/Fe) is much larger than the exchange constants indicates that $CaMn_2Sb_2$ should be considered a local moment system, and overall one expects Mn to be subject to considerable Hubbard correlations. The fact that the nearest-neighbor exchange follows the Heisenberg formula nearly exactly also speaks in favor of classical superexchange and the Hubbard model. Yet DFT calculations reproduce the excitation gap well, in fact, better than dynamic mean field calculations[6]. The reasons for such an unexpected success of the DFT are unclear st the moment. Given the sharp increase of the resistivity in the other, intermediate temperature phase, one may think that the Neel phase is affected by some cancellation of errors, not operative in the other phases, which leads to an effective increase of the excitation gap in the intermediate phase.

In the classical phase diagram of an antiferromagnetic

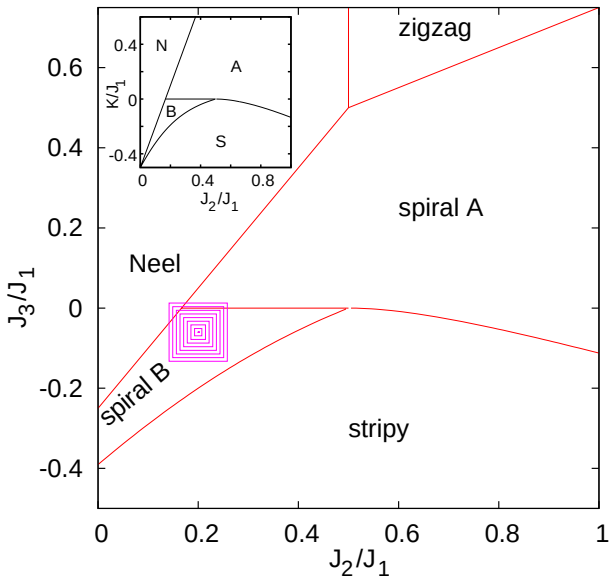

FIG. 5: Phase diagram of the classical $J_1 - -J_2 - -J_3$ Heisenberg model. The phase boundaries are given by the lines $y = (x - \sqrt{x^2 + 2(x-1/2)^2})/2$, $y = (1/2 + 3x - \sqrt{51/12 - 5x + 9x^2})/4$, $y = (6x-1)/4$, $y = (2x+1)/4$, $y = 0$, $x = 1/2$[1]. The square shows the region in the phase diagram where, within computational accuracy, the actual system is located. The insert shows the phase diagram for the $J_1 - J_2 - K$ model, where K is the biquadratic coupling. The phase boundaries are: $y = (3x - \sqrt{1 - 2x + 9x^2})/2$, $y = \sqrt{x - 1/4} - x$, $y = (6x-1)/2$, $y = 0$[3].

J_1, J_2 2D honeycomb layer there are five planar phases: The Neel (N) phase, where all nearest neighbors order antiferromagnetically, the "stripy" (S) phase where all bond along one direction are ferromagnetic, and forming double stripes order antiferromagnetically, and two spiral phases (A and B) described in the introduction. For $J_2/J_1 < 1/6$ the ground state is N, for $1/6 < J_2/J_1 < 1$ the ground state is degenerate between phases A and B, and for the larger J_2 the ground state is S. Adding J_3 creates a complicated phase diagram, with a new "zigzag" phase emerging at large J_3, which is shown in Fig. 5, where we also for completeness show the phase diagram J_1, J_2, K with a biquadratic interaction, not published before. In this phase diagram, the calculated interactions correspond to the point $J_2/J_{1eff} \sim 0.21$, $J_3/J_{1eff} \sim 0.05$, but the error in these numbers is close to ± 0.08. In other words, according to the calculations the material is extremely close to a highly frustrated critical point where three different phases are degenerate, the Neel phase and two qualitatively different spiral phases, $J_2/J_1 = 1/6$, $J_3 = 0$.

The thermodynamics of the classical Heisenberg model on the honeycomb lattice has not, to our knowledge, been systematically studied and this subject is beyond the scope of the current paper. It is however likely

that the phase boundaries between the zero-temperature phase shift as the entropy is included, so it is tempting to ascribe the transformation at 85 K to a phase transition between the Neel and one of the two spiral phases (more likely the spiral A). Very weak net ferromagnetism is then due to relativistic effects, which can be estimated by the ratio between the magnetic anisotropy energy (2-3 meV) and magnetization energy (800 meV), which is $\sim 3 \times 10^{-3}$, to be compared with the experimental ferromagnetic moment of $7 \times 10^{-3}\ \mu_B \approx 3 \times 10^{-3}\ M_{Mn}$.

No long range order has been observed between 85 and 210 K in neutron scattering; this suggests that the spirals break after relatively short distance and the emerging spiral chunks are randomly distributed over the three equivalent crystallographic directions. Such a state would be very similar to the "magnetic liquid" state in MnSi[7], also called a "cholesteric" phase, or a "blue" phase in the original paper. This state is observed in MnSi near the phase transition into a long-range ordered spiral phase, on the high-temperature (high-pressure) side of the phase transition. Neutron scattering in this phase reveals no long range order, but well-defined spirals of considerable length (several hundred Å), propagating in all crystallographically equivalent directions with equal weight. It is still not clear whether the spirals in the "blue phase" of MnSi form domains (possibly dynamic) or are meandering around, periodically switching directions. Both options are open as well in the intermediate temperature phase of $CaMn_2Sb_2$.

Another corollary of proximity to the critical point at $J_2/J_1 = 1/6$ is that unusual low energy magnetic excitations should be present in the low-temperature Neel phase. More detailed experimental spectroscopic studies are highly desirable.

To summarize, we have shown that $CaMn_2Sb_2$ is extremely close (within computational accuracy) to a critical point where three entirely different magnetic phases are degenerate on the mean field level. We suggest that unusual properties of this compound, obtained in recent experiments, are related to this unique proximity.

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[1] E. Rastelli, A. Tassi, and L. Reatto, Physica B **97**, 1 (1979).
[2] J.B. Fouet, P. Sindzingre, and C. Lhuillier, Eur. Phys. J. B **20**, 241 (2001).
[3] I.I. Mazin, unpublished.
[4] J. W. Simonson, G. J. Smith, K. Post, M. Pezzoli, J. J. Kistner-Morris, D. E. McNally, J. E. Hassinger, C. S. Nelson, G. Kotliar, D. N. Basov, and M. C. Aronson, Phys. Rev. **B 86**, 184430 (2012).
[5] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka and J. Luitz, *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (K. Schwarz, Techn. Universität Wien, Austria, 2001), ISBN 3-9501031-1-2.
[6] K. Haule, unpublished
[7] C. Pfleiderer, D. Reznik, L. Pintschovius, H. v. Löhneysen1, M. Garst and A. Rosch, Nature **427**, 227 (2004).