Frustration-Induced Vanishing of Magnetic Moments in $R\mathrm{Mn}_2$ Systems

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The $R\mathrm{Mn}_2$ compounds are characterized by an instability of the Mn moment in a highly frustrated crystallographic structure. Although quite general, this problem has not yet been treated. A model derived from the Hubbard Hamiltonian is proposed. It accounts for the new physics observed: complex ordered phases where magnetic and nonmagnetic sites coexist and unusual dependence on external parameters.

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The very peculiar properties of the $R\mathrm{Mn}_2$ intermetallic compounds, where R is a rare-earth element, are associated with the instability of the itinerant-electron antiferromagnetism in a frustrated lattice.

These compounds crystallize in either the $C14$ hexagonal (R=Pr, Nd, Sm, Ho, Er, Tm, Lu, or Th) or the $C15$ cubic (R=Y, Sm, Gd, Tb, Dy, or Ho) Laves phase structure. The Mn atoms occupy the corners of regular tetrahedra, stacked in a base-to-base and summit-to-summit sequence in the hexagonal structure and in a corner-sharing way in the cubic one.[1] In both cases, due to the topology of the atomic packing the Mn lattice is highly frustrated.

On the other hand, the Mn moments in the $R\mathrm{Mn}_2$ series are very close to the magnetic-nonmagnetic (M-NM) instability. Below a critical Mn-Mn distance Mn remains nonmagnetic, i.e., in compounds with R=Sc or a heavy lanthanide like Ho, Er, Tm, and Lu. Above the critical distance, i.e., with light lanthanides, R=Pr, Nd, Sm, and Gd, large moments with antiferromagnetic (AF) interactions are found.[2] Complex magnetic orderings are then observed due to the lattice frustration. They set in at a first-order transition accompanied by a large volume discontinuity[2] which is accounted for by a substantial jump of the Mn moment at the ordering. In the compounds near the critical Mn-Mn spacing the magnetism becomes extremely sensitive to the external parameters such as temperature, pressure, magnetic field, or alloying. A good illustration is given by TbMn_2. In the paramagnetic phase this compound exhibits strong short-range order. As the temperature is decreased two close magnetic transitions develop. At low temperature, the magnetic structure can be destabilized by an applied field, leading to magnetic isotherms with large field hysteresis.[3] Application of pressure induces a dramatic decrease of the ordering temperature of the Mn ions, at a rate of 36 K/kbar.[4] The substitution of only 3% of Tb by Sc is enough to destroy the Mn moment.[5]

The case of DyMn_2 is particularly interesting, as although all the Mn sites are chemically equivalent, only a fraction of them bears a magnetic moment. This mixed phase has been observed by NMR (Ref. 6) and by powder neutron diffraction.[7]

Here we study a model which we expect contains the essential features of these systems: instability of the magnetic moment and frustration. The interplay between these two effects leads to the unusual phases and properties observed.

In the $R\mathrm{Mn}_2$ compounds in which a Mn ordering takes place the Néel temperature is roughly independent of the rare earth R ($T_N \sim 100$ K).[1,2] This shows that the R-R and R-Mn exchange interactions are 1 order of magnitude smaller than the Mn-Mn interactions: We then neglect them. We use for the Mn lattice a Hamiltonian derived from the Hubbard model close to the M-NM instability.

Using the functional-integral technique, the partition function of the Hubbard Hamiltonian can be written as an integral over N auxiliary variables μ_i (in the static approximation):[8]

$$Z=\int d\mu_i \exp[-\beta F(\mu_i)]\,, \tag{1}$$

where

$$F(\mu_i)=F_0-\frac{1}{\beta}\mathrm{Tr}\ln(1-VG_0)+\sum_i \frac{U\mu_i^2}{4}\,. \tag{2}$$

In this expression F_0 and the Green's function G_0 are related to the noninteracting part of the Hamiltonian,

$$\mathcal{H}_0=\sum_{k\sigma}\varepsilon_k c_{k\sigma}^{\dagger}c_{k\sigma} \tag{3}$$

and V is a nonuniform potential,

$$V=-\tfrac{1}{2}U\sum_i \mu_i(n_{i\uparrow}-n_{i\downarrow})\,. \tag{4}$$

At zero temperature, the integral over μ_i in Eq. (1) is usually replaced by a saddle-point approximation. The auxiliary variables μ_i are determined by minimizing $F(\mu_i)$ and this is equivalent to a local Hartree-Fock approximation: $\mu_i=\langle n_{i\uparrow}-n_{i\downarrow}\rangle$.

It has been shown[8,9] that the main contributions to F come from the one-site $F_1(\mu_i^2)$ and two-site $F_2(\mu_i\mu_j)$ terms. Two situations can occur: (i) F_1 is minimum for $\mu_i = \pm\mu$ ($\mu \neq 0$). In this case all sites are magnetic and the ground state can be ordered due to the magnetic exchange energy [i.e., $F_2(\mu_i\mu_j)$]. This is the case for U larger than a critical value. (ii) F_1 is minimum for $\mu_i = 0$. A magnetic moment can exist only if the two-site interactions are large enough. This occurs close to the M-NM transition.

F_1 and F_2 can be calculated numerically for a given band structure.[9] For small values of μ_i the following expressions for F_1 and F_2 can be derived from Eq. (2):[10]

$$F_1 = \sum_i \tilde{\Delta}\mu_i^2, \quad F_2 = -\tfrac{1}{2}\sum_{i\neq j} \tilde{J}_{ij}\mu_i\mu_j , \tag{5}$$

with

$$\tilde{\Delta} = \frac{U}{4}\left[1 + \frac{U}{N}\sum_{k,q}\frac{f(\varepsilon_k) - f(\varepsilon_{k+q})}{\varepsilon_k - \varepsilon_{k+q}}\right],$$

$$\tilde{J}_{ij} = -\frac{U^2}{4N}\sum_{k,q} e^{iq(R_i - R_j)}\frac{f(\varepsilon_k) - f(\varepsilon_{k+q})}{\varepsilon_k - \varepsilon_{k+q}},$$

$\tilde{\Delta} < 0$ in case (i) and $\tilde{\Delta} > 0$ in case (ii) above. In the following we suppose that $\tilde{\Delta} > 0$: The magnetic moment at a given site, μ_i, which minimizes $F_1 + F_2$ will be different from zero only if the molecular field around it is large enough to overcome the one-site energy $\tilde{\Delta}$. Thus we consider that μ_i can take three values, $\mu_i = 0, \pm\mu$. This is the main difference from the earlier calculations where magnetic moments were supposed to have only two values, $\pm\mu$.[8,9] Of course, for finite values of μ_i other contributions to F_1 and F_2 must be taken into account. However, the saddle-point approximation yields the same type of expression (5)[9] (only the coefficients $\tilde{\Delta}$ and $\tilde{J}_{ij}$ are changed).

Equation (1) is then equivalent to the partition function of the following spin Hamiltonian:

$$H = \sum_i \Delta S_i^2 - \tfrac{1}{2}\sum_{i\neq j} J_{ij}S_iS_j , \tag{6}$$

where $\Delta = \tilde{\Delta}\mu^2$, $J_{ij} = \tilde{J}_{ij}\mu^2$, $S_i = 0, \pm 1$. At low temperatures we expect this mapping to be a good starting point. It can be improved by taking into account longitudinal as well as transverse fluctuations. (Moreover, it can be pointed out that this equivalence is also obtained in the large-U limit when $\Delta < 0$, and J_{ij} is then the superexchange interaction.) This model breaks the rotational invariance of the Mn spins. This is appropriate for $R\mathrm{Mn}_2$ compounds where Mn atoms are indeed located on a site of high uniaxial symmetry leading to a large anisotropy.[11]

For describing the $R\mathrm{Mn}_2$ compounds we use Eq. (6) with $\Delta > 0$. We keep the first- and second-neighbor interactions J_1 and J_2; $J_1 > 0$ (AF interactions), and J_2 will be taken >0 or <0. For transition-metal compounds U is of the order of the bandwidth, which implies that Δ and J_1 are of the same order of magnitude.

The frustration of the lattice will be described in a triangular lattice instead of the real $R\mathrm{Mn}_2$ structure: In such lattices it is not possible to satisfy all the AF nearest-neighbor interactions. Consider the triangle in Fig. 1. If the energy Δ necessary to create a moment is positive, configuration (b) has lower energy than configuration (a). Thus on a triangular lattice the magnetic moments on some sites can vanish due to frustration.

We have used two different methods for studying this Hamiltonian: (i) Monte Carlo simulations using Metropolis sampling on a 12×12 lattice with periodic boundary conditions (free boundary conditions have also been used to check that no other periodic structure is stabilized). (ii) Approximate calculation of the partition function including exact treatment of three-site correlations. Details will be given elsewhere. Both methods give the same phase diagram at low temperatures, shown in Fig. 2. Four phases are obtained, which can be related to different $R\mathrm{Mn}_2$ compounds as follows.

(I) Nonmagnetic phase (ScMn_2, ErMn_2): For large Δ, $S_i = 0$ at each Mn site.

(II) Mixed magnetic phase (ThMn_2, DyMn_2): This phase is completely new and can be obtained only in a small range of parameters. Because of the frustration of the lattice, on some sites but not all, the molecular field is too small to compensate the energy Δ necessary to stabilize the moment.

(III) and (IV) Magnetic phases (YMn_2, NdMn_2): When $|S_i| = 1$ on each site, two different magnetic orderings can be obtained, depending on the sign of J_2. The evolution of each of these phases with Δ (i.e., with increasing pressure) is different. Starting from phase III one gets phase I in which the magnetism is canceled homogeneously, whereas starting from phase IV yields to the mixed phase II where only partial vanishing occurs.

Since all these phases are observed with either magnetic (Er, Nd, Dy) or nonmagnetic (Sc, Y, Th) rare earths, they are characteristics solely of the Mn lattice.

Now we concentrate on the effect of an external magnetic field h on these ordered phases. The results of a

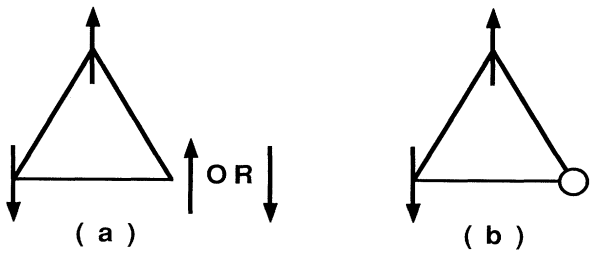

FIG. 1. Competing three-site configurations: (a) three magnetic sites with total energy $E_T = 3\Delta - J_1$. (b) Two magnetic sites with $E_T = 2\Delta - J_1$ (○ indicates nonmagnetic site).

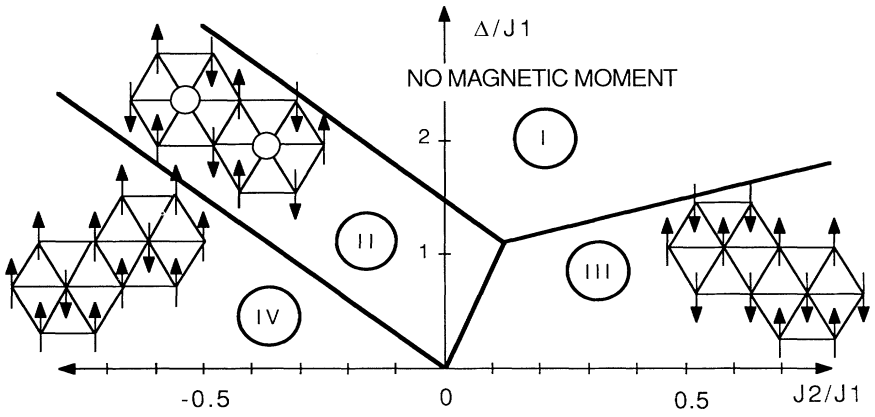

FIG. 2. Phase diagram of the model Hamiltonian [Eq. (6)], at $T=0$ (○ indicates nonmagnetic sites). The borderlines between the different phases are determined by the following: phases I and III, $J_2=\Delta-J_1$; phases I and II, $J_2=J_1/2-\Delta/3$; phases II and III, $J_2=\Delta/9$; phases II and IV, $J_2=-\Delta/3$.

Monte Carlo simulation are shown in Fig. 3. The parameters ($\Delta=J_1$ and $J_2=0$) correspond to the mixed phase II at $h=0$. At low temperature, three transitions are obtained with increasing applied field. The critical fields are easily calculated by comparing the energies of the different ordered phases: $h_1=\Delta$, $h_2=6J_1-\Delta$, $h_3=6J_1+\Delta$. One unexpected feature can be emphasized: At the second critical field h_2, the number of magnetic sites decreases, whereas at h_1 and h_3 this number increases. Similar results are obtained if the field is applied on a magnetic structure (phase III or IV), with only two transitions in this case. Such transitions where the number of magnetic sites changes imply large magnetovolume effects. This must be taken into account in a more quantitative calculation.

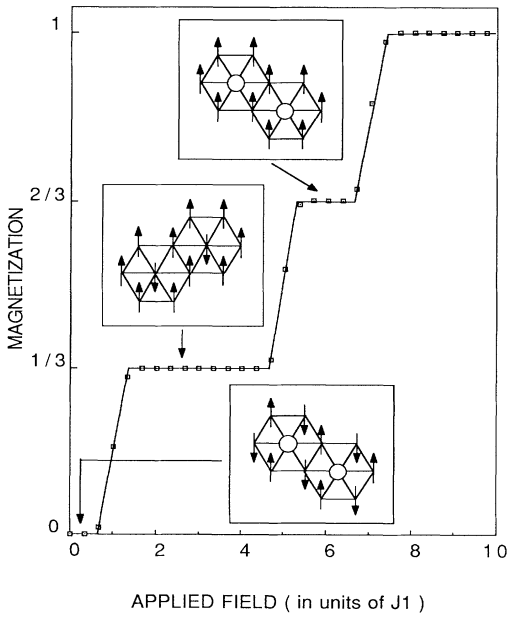

FIG. 3. Effect of an applied field on the mixed phase II.

A first-order transition has been observed in $TbMn_2$, at a field of the order of 6 T.[12] Above this critical field, the magnetization does not saturate; this could indicate the existence of a second critical field, which has not been observed due to the limitation of the available field.

Close to the M-NM transition large amplitude fluctuations of the Mn moment are expected, as shown by neutron polarization analysis in YMn_2 and $(Y,Sc)Mn_2$.[13] These fluctuations can be included in our model by going beyond the Hartree-Fock approximation. Renormalization of the γ coefficient of the specific heat will result, associated with paramagnon-like excitations close to the AF instability,[14] as observed in $(Y,Sc)Mn_2$.[15] These amplitude fluctuations also lead to anomalous dependence of the thermal-expansion coefficient.[2]

To summarize, the unusual properties of RMn_2 systems have been interpreted as the result of frustration in a system which is close to the M-NM instability. We have derived a model from the Hubbard Hamiltonian which contains these two ingredients. Thus we have been able to reproduce the different kinds of magnetic order observed in RMn_2 compounds, including the mixed phase where magnetic and nonmagnetic sites coexist. The effect of an applied magnetic field has also been discussed: Several field-induced transitions have been pointed out.

The model can be improved in different ways: More realistic structures and interactions, as well as magnetovolume effects must certainly be included for a more quantitative analysis. The more complex diagram including longer-range interactions and its evolution with temperature will be soon published.

In fact, this phenomenon must be more general: Frustration is also present in other very common crystallographic structures, such as the fcc one; other systems like

Kondo lattice compounds are also close to an (AF) magnetic instability and may show some similarities with the RMn_2 compounds.

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