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Phase transition of square-lattice antiferromagnets at finite temperature

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The magnetic properties of the two-dimensional J_1-J_2 model with both exchanges J_1 and J_2 being antiferromagnetic and a single-ion anisotropy at nonzero temperature are investigated. As $J_2/J_1 < 1/2$ ($>1/2$), only the Néel (collinear) state exists. When $J_2/J_1 = 1/2$, both the Néel and collinear states can exist and have the same Néel temperature. The calculated free energies show that there can occur a phase transition between the two states below the Néel point when the single-ion anisotropy is strong enough. It is a first-order transition at nonzero temperature. It is possible that the doping in real materials can modify the ratio of J_2/J_1 to reach $1/2$ so as to implement the phase transition.

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I. INTRODUCTION

A square lattice antiferromagnet can be described by the well-known two-dimensional (2D) J_1-J_2 model. In this model both the nearest neighbor (nn) and next nearest neighbor (nnn) exchanges are antiferromagnetic (AF), so that it was believed to be a frustrated system. This model could be used to describe the structures in real materials. It was first related to the copper oxide monolayers in the Cu-based high-temperature oxide superconductors,[1] and then to magnetic planes in some other materials.[2–6] The most representative structure that could be well described by this model might be the Fe monolayers in the Fe-based superconductors La-O-Fe-As[7–13] and BaFe$_2$As$_2$.[14] Because of its importance, the J_1-J_2 model has been carefully studied by various methods. However, the study has been mainly focused on its properties, especially its possible phase transition at 0 K.[15–17] Investigations concerning nonzero temperature[18–24] have been comparatively much fewer, although the real materials are at finite temperature. Despite the already given physical results of the system by these investigations, there may be some interesting features still hidden at finite temperature.

In this paper, we study the J_1-J_2 model as a representative of such a Fe plane, focusing our attention on the properties at nonzero temperature. The physical quantities of the quantum model at finite temperature are calculated. A remarkable result is that when $J_2/J_1 = 1/2$, there may occur a phase transformation below the Néel point T_N.

II. THE HAMILTONIAN AND METHOD

The AF Hamiltonian of a square lattice is $H = \frac{1}{2}\sum_{i,j} J_{ij}\boldsymbol{S}_i \cdot \boldsymbol{S}_j - D\sum_i (S_i^z)^2$. The first term is Heisenberg exchanges. Only the nn and nnn exchanges J_1 and J_2 are considered, both being positive. The second term presents a single-ion anisotropy. If a 2D AFM system has no any anisotropy, there will be no spontaneous sublattice magnetizations in it.[24,25] It was indeed possible for the single-ion anisotropy to appear in real materials.[26] We term the exchanges J_1 and J_2 and anisotropy D as Hamiltonian parameters. We let Boltzman constant $k_B = 1$ so that all the quantities, including Hamiltonian parameters, temperature T, and sublattice magnetization $\langle S^z\rangle$, become dimensionless. $\langle S^z\rangle$ is the assembly thermostatistical average of spin operator S^z. We fix $J_1 = 1$ and change the J_2 value in computation. D is assumed to be two or three orders of magnitude less than J_1. In the real La-O-Fe-As materials the spin quantum number might be larger than $1/2$.[27] Therefore, the cases of some of the lowest spin quantum numbers are considered.

It was proposed that there might be four possible spin configurations,[28,29] among which the two named as AF1 and AF2[30] had lower energies. They are depicted in Fig. 1, and were called Néel state and collinear state, respectively. In either of the configurations, the lattice is divided into two sublattices. The spins within each sublattice are parallel to each other, and the spins of the two sublattices are antiparallel to each other. The spin averages of the two sublattices are denoted as $\langle S_1^z\rangle$ and $\langle S_2^z\rangle$, respectively. Since there is no external field, $\langle S_1^z\rangle = -\langle S_2^z\rangle = \langle S^z\rangle$. We calculate the stable configurations by the many-body Green's function method under random phase approximation.[31] According to our calculation results, when $J_2/J_1 < 1/2$, the stable state is AF1 configuration where the nn spins are antiparallel to each other, showing that the nn exchange is dominant. While for $J_2/J_1 > 1/2$, the stable state is AF2 where the nnn spins are antiparallel to each other. This conclusion holds at any temperature, for any S and nonzero D values. We also tested other possible ordered states including the two suggested in Refs. 28 and 29, and none of them was stable at nonzero temperature.

III. MAGNETIC PROPERTIES

In Fig. 2 we plot the curves of spin average $\langle S^z\rangle$ versus T at various J_2 values. In this and following figures, we always use the solid and dashed lines to represent the results of AF1 and AF2 configurations, respectively. The temperature at which $\langle S^z\rangle$ becomes zero is the Néel point, denoted as T_N. Because we merely research the case of nonzero temperature, when we mention zero temperature, we actually mean the temperature very close to zero, which is denoted by 0^+. To describe the dependence of the curves on the J_2 value, we concentrate our attention to two physical quantities: Néel temperature T_N and the spin average $\langle S^z\rangle$ at 0^+ K, the latter hereafter denoted as $\langle S^z(0^+)\rangle$. As J_2 increases from zero to 0.5, both T_N and $\langle S^z(0^+)\rangle$ decrease. At $J_2 = 0$, it is an ordinary nn AF exchange system, and there is no competition to cause frustration. As J_2

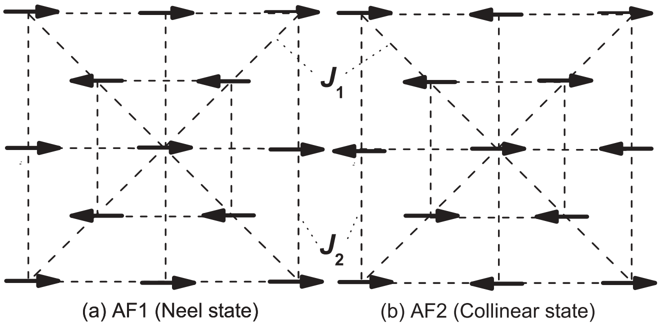

FIG. 1. (a) AF1 and (b) AF2 configurations.

increases from 0, the competition between J_2 and J_1 emerges and becomes stronger. This results in the drop of both T_N and $\langle S^z(0^+)\rangle$.

When $J_2 = 0.5$, the competition between J_1 and J_2 is the strongest. As J_2 rises from 0.5, the role of J_2 becomes more important and the competition becomes comparatively weaker. As a consequence, both T_N and $\langle S^z(0^+)\rangle$ increase.

Figure 3 plots the results of T_N as a function of J_2 at different S and D values. This figure is in fact a phase diagram that contains three phases: AF1, AF2, and paramagnetic (P) phases. A solid line is the border line between phases AF1 and P, and a dashed one is the border between AF2 and P. As J_2/J_1 approaches 1/2 from either side, the competition between J_1 and J_2 becomes stronger and makes T_N lower. At $J_2/J_1 = 1/2$, T_N is the lowest. Calculations show that when $J_2 > 1$, T_N is linearly proportional to J_2.

Figure 4 plots curves of $\langle S^z(0^+)\rangle$ versus the J_2 value. As temperature approaches to 0^+ K, the thermodynamic fluctuation goes to zero but quantum fluctuation still exists in an AF system. A smaller $\langle S^z(0^+)\rangle$ value represents a stronger quantum fluctuation. As J_2/J_1 approaches 1/2 from either side, the competition between J_1 and J_2 lowers the $\langle S^z(0^+)\rangle$ value.

As $J_2 > 1$, the curves of $\langle S^z(0^+)\rangle$ versus the J_2 value are almost flat. This means that when J_2 is sufficiently large, it is predominant compared to the J_1 value, so that the quantum fluctuation at 0^+ K caused by the competition between J_1 and J_2 is almost unchanged with the variation of the J_2 value. Nevertheless, no matter how large the J_2 value is, $\langle S^z\rangle$ of AF2 is always smaller than that of AF1 when $J_2 = 0$. This is because when $J_2 > 0$, there is always a competition between J_1 and J_2. While in the case of $J_2 = 0$, there is no such a competition, and only the nn AF exchange plays a role.

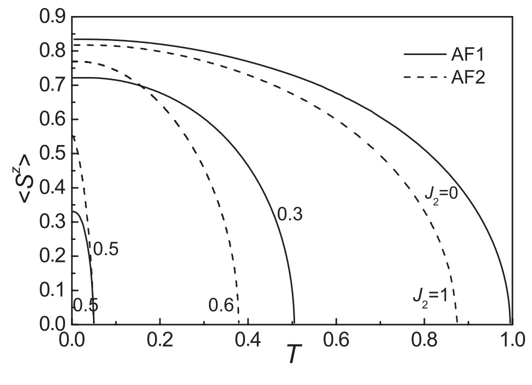

FIG. 2. $\langle S^z\rangle$ vs T curves for $S = 1$ and $D = 0.01$. The numbers labeling the curves are the J_2 values. When $J_2 < 0.5(>0.5)$, the state is AF1 (AF2). When $J_2 = 0.5$, both states exist.

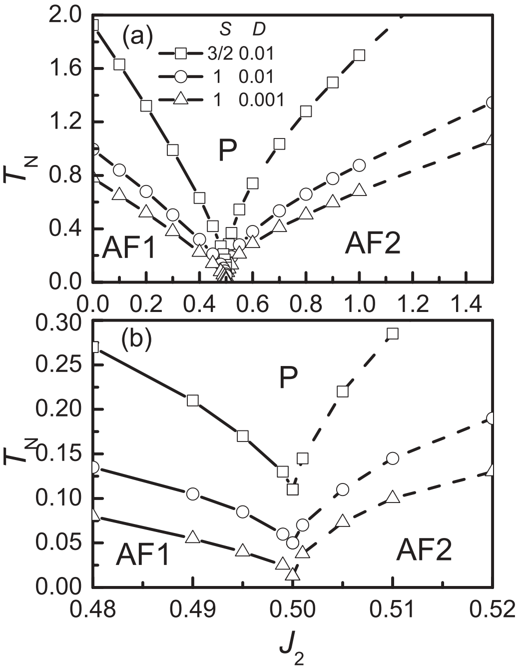

FIG. 3. (a) Néel temperature vs J_2 value. (b) Enlargement of the region around $J_2 = 0.5$. The lines are guides to the eyes.

The effect of the anisotropy D value and spin quantum number S is embodied in Figs. 3 and 4. As the D or S value is smaller, the $\langle S^z\rangle$ value at any temperature is smaller, and the Néel point T_N is as well.

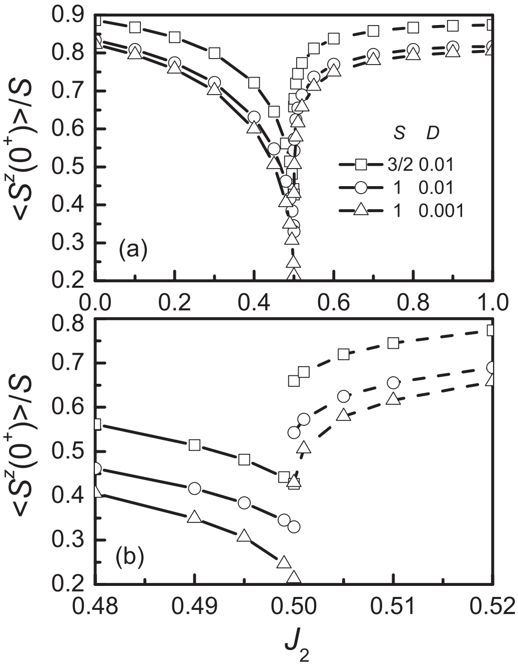

FIG. 4. (a) $\langle S^z(0^+)\rangle$ vs J_2 value. (b) Enlargement of the region around $J_2 = 0.5$. The lines are guides to the eyes.

IV. POSSIBLE PHASE TRANSITION

Now let us discuss the case of $J_2/J_1 = 1/2$. At first thought, in this case the competition between J_1 and J_2 is strongest so that the AF configurations may be totally frustrated and either AF configuration is difficult to hold. However, our calculation shows that for any nonzero D value, both AF1 and AF2 states can exist as displayed by Figs. 2 to 4. In Fig. 2, the solid and dashed lines marked by "0.5" show that both the states can exist and have the same T_N point under the parameter $J_2/J_1 = 1/2$. In Fig. 3 it is shown that both AF1 and AF2 reach the same Néel temperature when J_2/J_1 reaches 1/2 for various S and D values. Figure 4(b) reveals that both AF1 and AF2 have nonzero $\langle S^z(0^+)\rangle$ as J_2/J_1 reaches $1/2$.

Since as J_2/J_1 goes to 1/2 from either side, T_N reaches the same value [see Fig. 3(b)], it is understood that the Néel point is uniquely determined by the Hamiltonian parameters, although there may be more than one state.

Figure 4(b) shows that when $J_2/J_1 = 1/2$, $\langle S^z(0^+)\rangle$ values of the two states are not the same, and that of AF2 is higher. This can be explained from the pictures in Fig. 1. In the AF2 configuration, every spin is parallel to a half of its nn spins and antiparallel to another half, respectively, while in AF1, every spin is antiparallel to all of its nn spins. Thus the quantum fluctuation of AF1 at 0^+ K is stronger than AF2. The nnn spins may also play a role in causing frustration, but, intuitively, should not be so important as the nn ones.

Since both configurations can exist, one may ask which one is stabler. At fixed temperature and volume, the state with lower free energy is stabler. The free energy can be evaluated numerically by means of the internal energy via $F(T) = E(0^+) - T\int_{0^+}^{T}\frac{E(T')-E(0^+)}{T'^2}\,dT'$. Before calculating the free energy, one has to compute the internal energy, which is defined as the thermostatistical average of Hamiltonian, $E = \langle H\rangle/N$, where N is the site number in the 2D plane. The correlation functions $\frac{1}{2}\sum_{i,j} J_{ij} S_i^+ S_j^-$ involved in the energy are carefully calculated by use of the spectral theorem.[32] Figure 5 plots $E(T)$ for $S = 3/2$ and $D = 0.01$ and 0.05. $E(T)$ increases with temperature monotonically as it should be. In Fig. 5, $E_2(T) > E_1(T)$, but the internal energy cannot be used to determine which state is stabler, since the entropies of the two states are different. The corresponding free energies are plotted in Fig. 5. $F(T)$ decreases monotonically with temperature. It is seen that $F_1(0^+) < F_2(0^+)$, which means that near zero temperature the AF1 configuration is stabler. However, $F_2(T)$ drops faster than $F_1(T)$, and the two curves cross at a temperature, which means that above this temperature AF2 is stabler. Thus it is concluded that below T_N an AF1-AF2 phase transformation may occur. By comparison of Figs. 5(a) and 5(b), it is seen that as the anisotropy D is raised from 0.01 to 0.05, both $F_1(0^+)$ and $F_2(0^+)$ drop, the former decreasing more, and thus the AF1-AF2 phase transformation temperature rises.

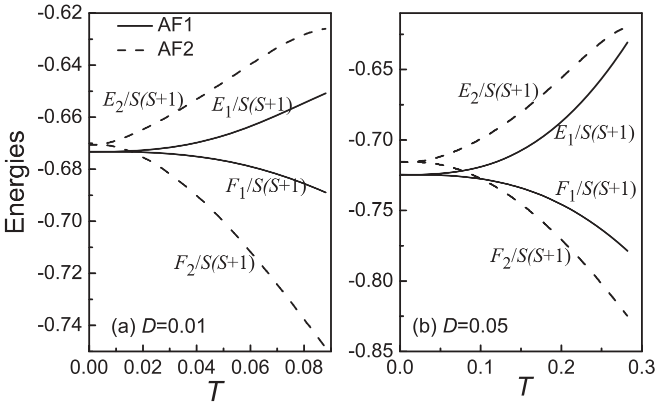

FIG. 5. The internal energies $E(T)$ (ascending curves) and free energies $F(T)$ (descending curves) at $J_2 = 0.5$ and $S = 3/2$. (a) $D = 0.01$ and (b) $D = 0.05$.

In Fig. 6 we plot the free energy curves for $S = 1,2,5/2$, each with two D values. The common features in this figure and Fig. 5 are that $F_2(T)$ always decreases faster than $F_1(T)$, and as D rises, both $F_1(0^+)$ and $F_2(0^+)$ drop, the former dropping more. In Fig. 6(a), where $S = 1$, for either D value, $F_1(0^+)$ is much lower than $F_2(0^+)$, and up to T_N, the two curves do not cross. Therefore, in this case, there is no phase transformation below the Néel point. As for $S = 3/2$, the AF1-AF2 transformation may occur, as having been revealed by Fig. 5. In Fig. 6(b), as $D = 0.01$, $F_1(0^+)$ is higher than $F_2(0^+)$, and up to T_N, the two curves do not cross, indicating AF2 being always stabler and lack of the phase transformation. While when D is raised to 0.05, $F_1(0^+)$ drops to such a position that $F_1(0^+) < F_2(0^+)$, and the two curves $F_1(T)$ and $F_2(T)$ cross below T_N. Therefore, a phase transformation may occur. The analysis of Fig. 6(c) is similar to that of Fig. 6(b).

It is deduced from Figs. 5 and 6 that the condition for the AF1-AF2 phase transformation to occur is that the D value should be large enough so that $F_1(0^+) < F_2(0^+)$. Otherwise, $F_1(0^+) > F_2(0^+)$ and there is no phase transformation, because $F_2(T)$ always decreases with temperature faster than $F_1(T)$. In the case of $S = 1$, when the D value continues to increase, then both the solid and dashed lines are lower, and if D is strong enough, it is expected that the two free energy lines will cross and the phase transition will occur.

It should be noted that both AF1 and AF2 are stable states but with different energies, so that it is a first-order transition. There is certainly an energy barrier between the two states. Unlike a classical system, the energy barrier in the present quantum system is difficult to reckon since it involves nonequilibrium states.

A question arises from the barrier how to actualize the AF1-AF2 phase transformation. For instance, in the case of

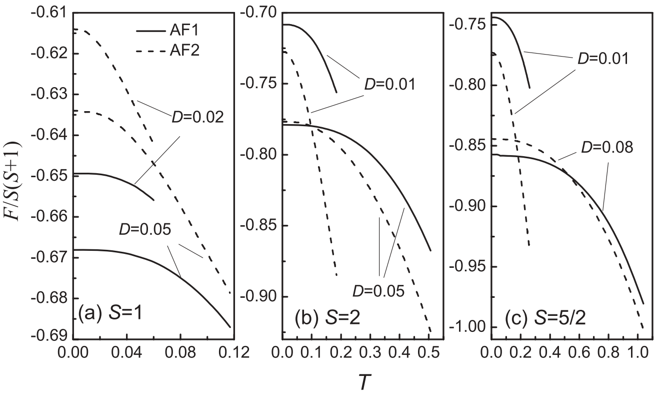

FIG. 6. The free energies at $J_2 = 0.5$ and several S and D values. (a) $S = 1$, (b) $S = 2$ and (c) $S = 5/2$.

Fig. 5(b), suppose that the system is initially under room temperature. When temperature is decreased to below the Néel point, the state becomes AF2. As temperature reaches the AF1-AF2 transformation point, how can the AF2 configuration overcome the barrier to get to AF1 configuration? We suggest that applying a strong impulsive magnetic field along the direction that is perpendicular to the spin direction can make the system reach the stabler state.

Finally, we would like to briefly discuss the possibility of adjusting the ratio J_2/J_1 to become 1/2 in real materials. The results from the band structure calculation of LaFeAsO were that $J_2/J_1 > 1/2$,[27,29,30,33] thus the Fe planes in this crystal were in the AF2 state. In this kind of material both the nn and nnn exchanges between Fe atoms were mediated by As atoms.[27] Because the Fe 2D plane was sandwiched by As atom monolayers, As atoms played a key bridge role in the indirect exchanges. Since in AFeAsO (A = La, Ce, Pr, Nd, Sm)[10,34] and BFe_2As_2 (B = Ca, Sr, Ba)[35] the Fe-As sandwich structures were the same, the Fe planes in all these crystals were in AF2 states, while LaFePO, which had the same crystal structure as LaFeAsO except that As was replaced by P, exhibited paramagnetism in the normal conducting state.[36] This prompted us to see that the ability of the P atoms in the Fe-P sandwich structure to mediate the exchange interaction was rather weak. Based on this fact, we conjecture that the appropriate doping in As monolayers could modify the ratio J_2/J_1 value and possibly to reach 1/2. It therefore deserves efforts to explore the new material to observe the expected phase transition.

In summary, we find that in a 2D AF system described by the J_1-J_2 model, the phase transformation can occur between the collinear and Néel states under the condition that $J_2/J_1 = 1/2$.

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