Magnetism of competing high-spin/low-spin states in $Ba_2NiO_2(AgSe)_2$ and related two-orbital two-electron systems

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We discuss the thermodynamic and magnetic properties of a competing high-spin/low-spin two-orbital two-electron model on a square-lattice possibly relevant to the material $Ba_2NiO_2(AgSe)_2$ (BNOAS). We focus on parameter regimes where a high-spin ($S = 1$) and a low-spin ($S = 0$) state are energetically close to each other and discuss various exchange processes in such a system. The model we study is a variant of, but different from the Kondo-necklace model proposed for the system by Jin et al [1]. Although there are similarities between the two models in terms of the ground-state phases and their symmetries, the detailed properties of the different phases and the phase transitions are entirely different and should be easy to distinguish from an experimental point of view.

I. INTRODUCTION

Following the discovery of high-temperature superconductivity in the cuprates, many new families of materials have been synthesized with competing magnetic and superconducting phases. In particular, several iron based families of superconductors are known to have competing magnetic and superconducting phases and, at stoichiometry, are often modelled as multi-orbital nearly itinerant - nearly localized, spin-one systems [2].

The discovery of superconductivity in the nickelates has brought renewed interest to these systems as well [3]. Although much recent excitement comes from doping the $Nd_{n+1}Ni_nO_{2n+2}$ family of materials where nickel ions have a Ni^{1+} ionic state with d^9 electron configuration providing an excellent analog of the cuprates, there are other nickelate families with the more usual Ni^{2+} ionic state and d^8 electron configuration [4, 5]. Our work is focused on competing high-spin and low-spin states in these latter systems.

Jin et al [1, 6] have recently studied the material $Ba_2NiO_2(AgSe)_2$ (BNOAS) by Density Functional Theory (DFT) and found a rather striking result. Ni atoms have d^8 electronic configuration, with competing spin-zero and spin-one states, where the lowest energy state has spin-zero. Depending on the value of the Hubbard repulsion U, this lowest energy singlet state can be made of two electrons occupying two different orbitals ($d_{x^2-y^2}$ and d_{z^2}). A lower energy of this singlet compared with the triplet amounts to an *antiferromagnetic* intra-atomic exchange, which goes against the Hund's rules. Jin et al have proposed an effective Kondo-necklace model, where the two electrons on an atom are exchange coupled by an antiferromagnetic intra-atomic exchange. In addition, one of the electrons (in the $d_{x^2-y^2}$ orbital) has an exchange interaction with electrons on neighboring atoms in the plane, whereas the electron in the other state (in the d_z^2 orbital) provides an analog of the local spin in the Kondo models. It may be very weakly coupled to spins in neighboring planes, however, to leading order, its only coupling is to the other spin in the same atom. This leads to a Kondo-necklace model with two spin-half operators $\vec{S}_{1i}$ and $\vec{S}_{2i}$ at each site of the square-lattice and Hamiltonian:

$$H = J \sum_{\langle i,j \rangle} \vec{S}_{1i} \cdot \vec{S}_{1j} + J_l \sum_i \vec{S}_{1i} \cdot \vec{S}_{2i}, \qquad (1)$$

where the first sum runs over nearest-neighbor pairs. At small J/J_l the system is in a non-magnetic singlet phase, where the two spins on each atom combine to form a singlet state. At large J/J_l, the system is in the Neel phase with long-range antiferromagnetic order. The two phases are separated by a quantum critical point in the universality class of the 3-dimensional classical Heisenberg model [9].

Here we will focus on an alternative model for this insulating system with d^8 electron configuration and two d-holes in two orbitals with competing high-spin and low-spin states. In a two-orbital system, two electron (or two-hole) configuration leads to one triplet and 3 singlets. Two of the singlets correspond to the two electrons occupying the same orbital, while a singlet and a triplet corresponds to the electrons occupying different orbitals. We will assume that the intra-atomic Hund's coupling is the normal *ferromagnetic* one so that the triplet state is lower in energy when the two electrons occupy different orbitals. However, Hubbard repulsion U, crystal field splittings and ligand interactions are such that one of the singlets formed from holes occupying the same orbital is lower in energy than the triplet state. Since intra-atomic Hund's exchange is typically of order 1 eV, we will assume that the other two singlet states are significantly higher in energy and not relevant to the low energy properties. A similar competing low-spin/high-spin scenario has been discussed recently for Ni d^8 ions in the material NiO_2 by Jiang et al [7].

II. EXCHANGE PROCESSES AND THE MODEL HAMILTONIAN

The overlap between orbitals on neighboring atoms leads to inter-atomic exchange processes. A general two-band Hubbard model for the nickelates was studied by Hu and Wu [10], who used perturbation theory to argue for a Kugel-Khomskii type spin-orbital model [8] with many possible terms.

Here we take as our starting point for deriving the effective low energy Hamiltonian two key assumptions motivated by the work of Jin et al: (i) One spin-zero and one spin-one state forms the low energy subspace of our system and all others states are at significantly higher energy. Thus, all inter-atomic exchanges must be projected on to these low energy states of each atom. (ii) Hopping in the planes is much larger for spins in one of the orbitals (e.g. $d_{x^2-y^2}$) than the other (e.g. d_{z^2}). These considerations lead to the following inter-atomic exchanges in decreasing magnitude:

1. Spin-one Heisenberg exchange J: The largest inter-atomic exchange is a Heisenberg exchange coupling J between neighboring atoms when both are occupied by spin-one states. For this exchange, overlap between $d_{x^2-y^2}$ orbitals is sufficient. The difference from the Kondo necklace model of Jin et al is that the projection to the low energy subspace means that the Heisenberg coupling is between spin-one states on neighboring atoms. It is not a coupling for spin-half or just one of the two spins. That is forbidden by the large intra-site Hund's coupling.

2. Triplet hopping process K: When there is a spin-zero on one site and a spin-one on a neighboring site, the two sites can exchange their spin states. This is a much weaker process than the Heisenberg exchange as it requires overlap of both (e.g. $d_{x^2-y^2}$ and d_{z^2}) orbitals on neighboring atoms and thus may require either a lattice distortion or a higher-order process. In our model we will ignore this term in the numerical study. Qualitatively, it is important in the non-magnetic phase where even a very small value is relevant to the dispersion of spin excitations.

3. Triplet-pair creation/destruction process W: A pair of triplets with total spin-zero can turn into a pair of spin-zero states on neighboring sites and vice versa. This process will require cross overlap between neighboring $d_{x^2-y^2}$ and d_{z^2} orbitals. We will assume this process is the weakest and will not discuss it any further. It may be important in how the system comes to thermal equilibrium but not in describing the equilibrium phases themselves.

Thus, our low energy states on an atom are characterized by $n_i = 0$ or 1, with $n_i = 0$ corresponding to spin-zero and $n_i = 1$ to the spin-one state. In addition, when $n_i = 1$, there are three spin states corresponding to $S_i^z = 0, \pm 1$. Thus, there are 4-states per atom. The effective Hamiltonian can be expressed in terms of n_i and the quantum spin-one operators $\vec{S}_i$ as:

$$H = \Delta \sum_i n_i + J \sum_{\langle i,j \rangle} n_i n_j \vec{S}_i \cdot \vec{S}_j, . \tag{2}$$

We will assume that the parameter Δ is greater than zero so that the lowest energy state on each atom has spin-zero.

III. GROUND STATE PHASES OF THE MODEL

Ground state phases and properties of the Kondo-necklace models have been studied previously. The ground state properties of the present model can be obtained using prior results in the literature [11–13]. Like the Kondo-necklace model, this model has two phases. For small J/Δ the model is in a non-magnetic singlet phase, where each atom is occupied by electrons in a spin-zero state. For large J/Δ the model is in a *spin-one* Neel state with long-range antiferromagnetic order. However, there are key differences in the properties of the two phases and the phase-transition between the two models.

Neel phase: The Neel phase is characterized by long-range antiferromagnetic order and magnon excitations. The key difference between the models lies in the behavior of the uniform susceptibility. In the present model, deep in the Neel phase, the susceptibility has the temperature dependence of an antiferromagnet, that starts to go down below a temperature of order $2J$, where short-range antiferromagnetism develops. At low temperatures, as the spins are locked antiferromagnetically they have only a weak transverse susceptibility [11–13]. In contrast, in the Kondo-necklace model, as one gets away from the critical point, the low temperature uniform susceptibility becomes large. This is because the local spins become nearly free and thus develops almost Curie-like susceptibility, which can become large at low temperatures [9].

Non-magnetic singlet phase: In the Kondo necklace model, the singlet phase has a dispersive triplet excitation, where the dispersion band-width is set by the inter-atomic exchange energy J. As the phase transition is approached, the excitation gap will go to zero at the antiferromagnetic wave-vector and at $k = 0$, with neutron-scattering spectral weight strongly concentrated near the anti-ferromagnetic wave-vector. In contrast, for the present model, the triplet will be static and completely localized in the absence of the triplet-hopping process discussed earlier. It is the weaker triplet hopping process K that will lead to a dispersion for the excitations. Thus, one would expect the dispersion to be relatively weak and being unrelated to the exchange J it should have a minimum at $k = 0$. In addition, there will be a clustering of the spinful states as when the spin-one

states are clustered together their energy will be significantly lowered than when they are separated.

Ground state Phase Transition: In the Kondo necklace model there is a quantum critical point separating the non-magnetic phase from the antiferromagnet. In contrast, in the present model, there will be a first order phase transition. Well before the gap to spin-one excitations is closed, the exchange energy will lower the collective energy of the Neel state below that of singlets. Thus the system will undergo a phase separation and a first order ground-state phase-transition between the two phases. Since the ground state energy of the spin-one model is known accurately [11] to be approximately $-2.327J$ per site, the phase transition will happen at $J = \Delta/2.327$.

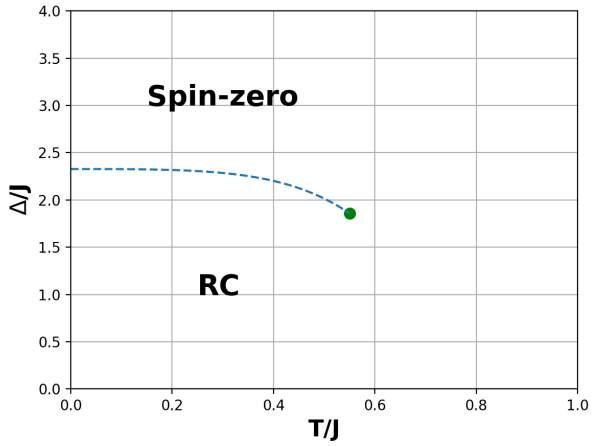

FIG. 1: Sketch of the phase diagram for the model. A line of first order phase transitions, shown by dashed lines, separates the Renormalized Classical phase (RC) from the non-magnetic spin-zero phase. The line of phase transitions terminates at a liquid-gas critical point.

Finite temperature phase transition: In the present model there will be a liquid-gas first order phase transition at finite temperatures ending at a critical point. Even though the spin degrees of freedom cannot order at finite temperatures, the Ising variable n_i can have atrue phase transition. Since the transition will happen at temperatures below the mean-field Neel transition temperature of $8J/3$, by that temperature the short-range order will be well developed. Hence, we can study the behavior to a good approximation by replacing the Heisenberg coupling in the Hamiltonian by its low temperature expectation value which will be only weakly temperature dependent. Thus our model becomes:

$$H = \Delta \sum_i n_i - \tilde{J} \sum_{\langle i,j \rangle} n_i n_j, \tag{3}$$

where $\tilde{J}$ is minus the expectation value of $< \vec{S}_i \cdot \vec{S}_j >$ on a nearest neighbor bond. It is weakly temperature dependent at low temperatures [11]

$$\tilde{J}(T) = \frac{2.327}{2} J - aT^3. \tag{4}$$

The T^3 term comes from the reduction in energy due to the magnons.

By the standard mapping

$$n_i = (s_i + 1)/2, \tag{5}$$

this can be expressed in terms of the Ising variables $s_i = \pm 1$ as:

$$H = -J_I \sum_{\langle i,j \rangle} s_i s_j + h \sum_i s_i + C, . \tag{6}$$

where

$$J_I = \frac{1}{4} \tilde{J},$$

and,

$$h = \frac{\Delta - 2\tilde{J}}{2}.$$

For the Ising model in Eq. 6, the phase transition line is given by $h = 0$, that is $\Delta = 2\tilde{J}$. At $T = 0$ the transition is at $\Delta = 2.327J$. The line of first order transitions will terminate at a critical point, which can be obtained from the solution of the 2D Ising model to be at $T = \frac{2\tilde{J}}{\ln 1+\sqrt{2}}$. In the Δ/J and T plane the phase boundary gradually bends down due to the temperature dependence of $\tilde{J}$ and the critical point is roughly at $\Delta/J = 2$, $T_c/J = 0.55$. The phase diagram is sketched in Fig 1.

IV. FINITE TEMPERATURE PROPERTIES: NUMERICAL LINKED CLUSTER EXPANSIONS

In this section we study properties of the model more quantitatively at high temperatures using Numerical Linked Cluster Expansions (NLC) [14]. In these expansions, extensive properties on a lattice $\mathcal{L}$ with N sites, in the limit $N \to \infty$, are calculated as a sum over all linked clusters c as

$$P(\mathcal{L})/N = \sum_c L(c) \times W(c) \tag{7}$$

Here $L(c)$, called the lattice constant, is the number of times the cluster arises in the lattice, per lattice site. The quantity $W(c)$ is the weight of the cluster. It is defined recursively through the property on the finite cluster c as

$$W(c) = P(c) - \sum_s W(s), \tag{8}$$

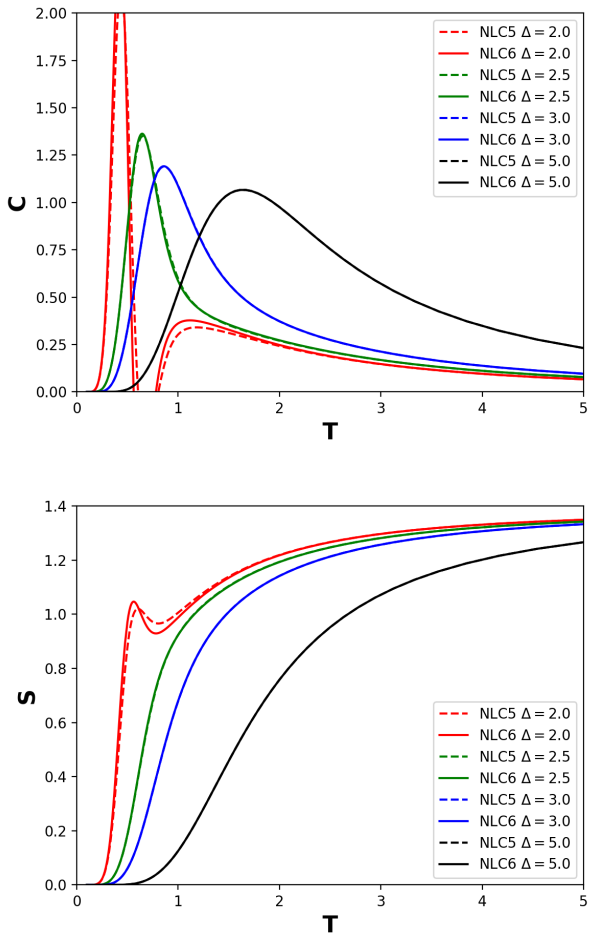

FIG. 2: Specific heat and entropy as a function of temperature for different values of Δ.

where the sum runs over all proper sub-clusters s of the cluster c.

We use the numerical linked cluster method to calculate the heat capacity per site C, the entropy per site S, the uniform susceptibility per site χ and the antiferromagnetic structure factor $S_{\pi,\pi}$. Calculations are done to 6th order, that is weights of all linked clusters with 6 or less bonds are included in our study.

In Fig. 2 we show the heat capacity and entropy as a function of temperature, while in Fig. 3 we show the uniform susceptibility and antiferromagnetic structure factors. Results are shown for 5th and 6th orders of NLC. The NLC results converge rapidly in a phase with short correlation length but will breakdown as one approaches a critical point or a system with long-range order.

We focus on the spin-gapped phase and the transition region as at smaller Δ the model maps at low temperatures to the spin-one antiferromagnet. The NLC will breakdown in the Renormalized Classical phase [15], which is a well-understood phase in itself, and not of primary interest in this paper.

We can see that for $\Delta = 2.5J$ or higher NLC converges well and the system goes into a non-magnetic state with a spin-gap and activated thermodynamic properties at low temperatures. In the transition region near $\Delta = 2J$, while NLC breaks down at the lowest temperatures shown, it shows strong evidence for a nearby first order transition. The system first goes into a singlet state as the internal energy of the antiferromagnet remains higher than that of the singlet. But, at a lower temperatures the NLC is trying to capture a jump in entropy, a sharp peak in the heat capacity mimicking a latent heat, enhanced uniform susceptibility and antiferromagnetic structure factors. Describing these transitions more quantitatively is beyond the scope of the NLC.

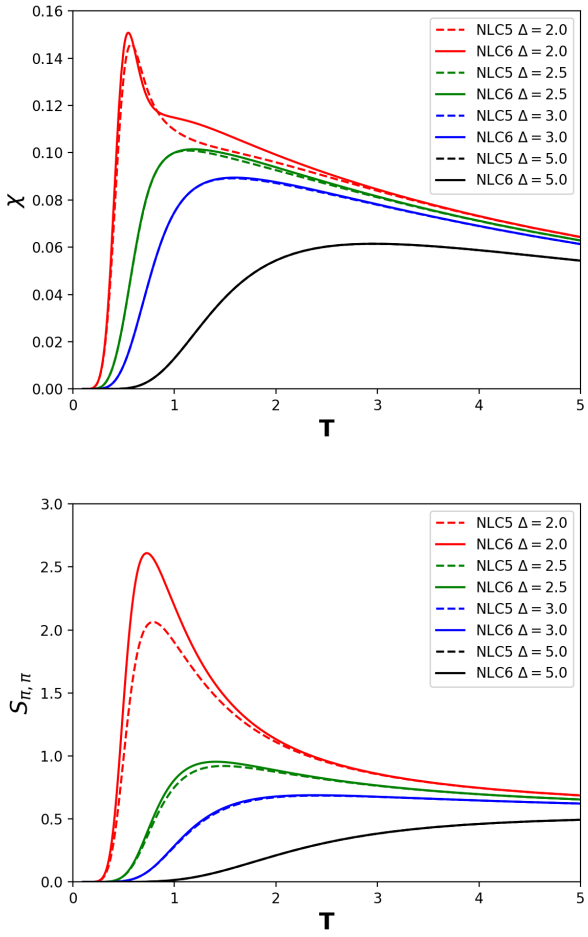

FIG. 3: Susceptibility and Antiferromagnetic structure factor as a function of temperature for various values of Δ.

Such a non-uniform magnetic behavior and a first order phase transition are hallmarks of the current model. In contrast, in the Kondo-necklace model, one has a zero temperature quantum critical point separating the two phases and no phase transition is expected at any finite

temperatures [9].

V. SUMMARY AND CONCLUSIONS

In this paper we have studied the magnetic and thermodynamic properties of a two-electron two-orbital model system with competing high spin (S=1) and low spin (S=0) states, possibly relevant to the nickelates with a d^8 electronic configuration. The model has some similarities to the Kondo-necklace model proposed earlier by Jin et al [1]. However, detailed experimental properties are quite different and should be easy to distinguish experimentally. It is the purpose of the paper to bring out these differences.

Being a two-dimensional model, there cannot be a Neel phase at finite temperatures. Instead, there is a Renormalized Classical phase for the spin-one antiferromagnet, which will develop Neel order at $T = 0$ or at finite temperatures in presence of anisotropy or 3-dimensional coupling. This phase is separated by a first order phase transition from a non-magnetic spin-zero phase. The line of first order transitions terminates at a liquid-gas critical point.

The magnetic behavior in the vicinity of the transition is quite unusual as the uniform magnetic susceptibility can be non-monotonic as a function of temperature. There can be hysteresis and a meta-stability of the low-spin and high-spin phases. At the phase transition there should be a jump in entropy and a latent heat.

We have discussed various inter-atomic exchanges that can arise in such a system. Jiang et al [7] have discussed the importance of charge transfer energy and the tuning (and crossing) of singlet-triplet gap as a function of the charge transfer energy. Thus, it is possible that different materials may be in different parts of the phase diagram. Some maybe magnetic, some non-magnetic and maybe some will have parameters close to the critical values.

This manuscript was focused on the parent insulating materials. But, it is interesting to speculate about doping and superconductivity. From that point of view also this model may provide a sharp difference from the proposal of Jin et al. Upon doping in the singlet phase, the Kondo-necklace model should lead to the usual t-J model, whereas this model should lead to a spin-one or type II t-J model recently proposed by Zhang and Vishwanath [16], with the possibility of triplet superconductivity.

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