Superstructures at low spin–high spin transitions

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(Received 25 November 2003; published 6 May 2004)

In many transition-metal compounds, in particular those containing Fe^{2+} and Co^{3+}, there occur spin-state transitions between low-spin and high-spin (or intermediate-spin) states. We show that typical interactions between similar spin-state ions are short-range repulsion and long-range interaction which can have different signs depending on the elastic anisotropy of the lattice and on the direction between respective ions. Due to such character of effective interactions at the spin-state transitions there may occur different superstructures—ordered arrangement of different spin states, which in particular may have the form of stripes. The properties of the system $TlSr_2CoO_5$ for which such a superstructure was recently observed experimentally are discussed from this point of view.

DOI: 10.1103/PhysRevB.69.184401 PACS number(s): 71.70.Ch, 61.72.Yx, 64.60.Cn

There exist many transition-metal compounds in which, due to a competition between crystal-field splitting and intra-atomic Hund's rule exchange, different spin states lie close in energy. Such is often the situation for Fe^{2+} and Co^{3+}. For these ions the low-spin (LS) state (occupation of d levels $t_{2g}^6 e_g^0$, $S=0$), intermediate-spin (IS) state ($t_{2g}^5 e_g^1$, $S=1$), and high-spin (HS) state ($t_{2g}^4 e_g^2$, $S=2$) can be stabilized at different conditions. In some cases there occur spin-state transitions caused, e.g., by change of pressure, temperature, or composition. There are many examples of such transitions among Fe^{2+} compounds,[1,2] in particular with organic ligands. Among systems with Co^{3+}, the best known (and still controversial) is the case of $LaCoO_3$. For a long time it was assumed that there occurs in it the LS-HS transition with increasing temperature,[3] but more recent calculations[4] and experiments[5] point rather to the LS-IS transition.

Usually spin-state transitions occur between homogeneous states having predominantly one particular spin state; often they are of first order. However as we shall show below, a quite different and interesting situation may occur: the interaction between ions with different spin state may be such that at the spin-state transitions an intermediate state may be stabilized, in which there appears a *spin-state superstructure*—an ordered arrangement of different spin states of the same ionic species, e.g., an alternation of HS and LS states. Recently the first example of such superstructure was observed in a layered cobaltite $TlSr_2CoO_5$ (Ref. 6) and its presence was suggested for $NdBaCo_2O_{5.5}$.[7]

In the present paper we consider the form of interactions determining the character of spin-state transitions, suggest a general mechanism which can lead to spin-state superstructures, and qualitatively explain the superstructure observed in $TlSr_2CoO_5$.

Conventional description of spin-state transitions[8,9] relies on interactions induced by lattice distortions. Ions with different spin states have different ionic radii, e.g., Co^{3+} in the LS state in VI-fold coordination has the ionic radius 0.545 Å, and in the HS state 0.61 Å. Consequently, if we change the spin state of an ion, e.g., by transforming one of the LS Co's into a HS state, it amounts to introducing an''impurity'' with larger size into a matrix (the so-called ''sphere in the hole'' model[8]). This introduces strain in a crystal, and coupling to this strain provides the mechanism of interaction between impurities. In a model of isotropic elastic continuum generally used in treating LS-HS transitions,[8,9] the only interaction remaining is that through the ''image forces'' due to a stress-free surface of the sample,[10] which is attractive. With such an attractive interaction one indeed obtains homogeneous structures, transitions between which may be of first order.

In real crystals, however, the elastic interactions are more complicated. Thus, e.g., in weakly anisotropic cubic crystals there appears an interaction between impurities which decays rather slowly, as $1/R^3$, and, most important, which has a different sign in different directions:[10,11]

$$V(\vec{r},\vec{r}\,') = -Cd\,Q_1 Q_2 \frac{\Gamma(\vec{n})}{|\vec{r}-\vec{r}\,'|^3}, \tag{1}$$

where C is a constant of the order of unity, $\vec{r}-\vec{r}\,' = |\vec{r}-\vec{r}\,'|\cdot\vec{n}$, Q_1 and Q_2 are the ''strengths'' of impurities [$Q_i \sim (v_i - v_0)$ where v_i is the volume of the impurity and v_0 is the corresponding volume of the matrix], and the angular dependence of the interaction (1) is determined by a function of the direction cosines of the vector $\vec{r}=\vec{r}_1-\vec{r}_2$:

$$\Gamma(\vec{n}) = n_x^4 + n_y^4 + n_z^4 - \tfrac{3}{5}. \tag{2}$$

Here the elastic anisotropy is characterized by the parameter $d = c_{11} - c_{12} - 2c_{44}$, where c_{ij} are the corresponding elastic moduli. We see that, e.g., for $d<0$ the interaction (1) is positive (repulsive) along the [100], [010], and [001] directions and attractive along face and body diagonals [110] and [111], and vice versa for $d>0$. Thus we see that, in contrast

to usual assumptions, the interaction between similar states (e.g., between HS ions in a LS matrix) may be repulsive, at least in certain directions.

One can also show that the nearest-neighbor (nn) interaction via short wavelengths or optical phonons is typically also repulsive. Thus, e.g., in a perovskite lattice, when one puts a large HS ion at a certain site, it pushes apart the surrounding oxygens, so that it is more favorable to have small LS ions at the nn sites. Consequently, the effective interaction between similar ions at the nn sites is repulsive (or equivalently, it is attractive between LS and HS states). As is clear from these arguments, one can expect in this case that not only homogeneous states (LS or HS), but also certain states with ordered LS and HS ions can appear at certain conditions.

A convenient way to describe spin-state transitions and eventual superstructures is to map this situation to an effective lattice gas, or Ising model. Let us consider the situation in which each ion can be in two states, e.g., LS and HS [it may be also LS and IS (Refs. 4 and 5) or, in the case of $TlSr_2CoO_5$, IS and HS states;[6] for simplicity we speak below about LS and HS]. We introduce pseudospin operators $\sigma_i = \pm 1$, so that $\sigma_i = -1$ corresponds to a LS state, and $\sigma_i = 1$ to a HS state at site i. According to our general discussion we can model the situation by the effective Ising-type interaction $\Sigma J_{ij}\sigma_i\sigma_j$, containing in general short-range repulsion, and a long-range part which decays as $1/R^3$ and which may have different signs in different directions; this longer-range interactions depend on the details of the crystal structure, elastic anisotropy, etc., see Eq. (1). The relative energies of different spin states, e.g., HS vs LS, will be described in this language by the effective ''magnetic field''—the term $h\sigma_i$.

It is known that the Ising model with long-range interactions can give rise to a variety of different ordered structures [see the well-known ANNNI model[12] or the treatment of the two-dimensional (2D) Ising model with the ''Coulomb'' interaction in Ref. 13]. In this paper we consider a simplified model, which nevertheless contains the essential physics, keeping only a small number of pair interactions. In contrast to the treatment of Refs. 11 and 13, where one has studied systems with fixed concentration of particles (in our mapping—fixed ''magnetization''), in our present problem the relative number of different spins (LS and HS ions) is not fixed. Consequently we should consider our system not for fixed density (magnetization), but for fixed chemical potential (magnetic field); the role of the temperature can be also mapped onto a magnetic field.[8]

We consider a 2D square lattice, modeling the situation in $TlSr_2CoO_5$, which is the layered compound with perovskite-like CoO_2 plane similar to CuO_2 plane in high-T_c cuprates. The Hamiltonian of our model is

$$H = J_1 \sum_{\langle ij\rangle = \mathrm{nn}} \sigma_i\sigma_j + J_2 \sum_{\langle ij\rangle = \mathrm{nnn}} \sigma_i\sigma_j - h\sum_i \sigma_i . \qquad (3)$$

Here the first term describes the nearest-neighbor interaction, which, as we argued above, is repulsive, $J_1 > 0$; the second term is the next-nearest-neighbor interaction along x and y directions ([100] and [010]) which we also take to be repulsive. The last term in Eq. (3) describes the difference of the on-site energies of LS and HS states, which can be changed, e.g., by pressure, etc. (For Co^{3+} the effective field h will be equal to $h = 6J_H - 2\Delta$, where J_H is the Hund's rule exchange and Δ is the crystal-field splitting between t_{2g} and e_g levels.)

It is straightforward to see that for only nn repulsion ($J_1 > 0$, $J_2 = 0$) three states can be realized at $T = 0$ for different values of h: the state with all $\sigma_i = -1$ (LS states) and with the energy (per site) $E_{\mathrm{LS}} = J_1 z/2 + h$ where z is the number of nearest neighbors (in our case $z = 4$); the state with alternating spins $+1, -1, +1, \ldots$, forming a two-sublattice ''antiferromagnetic'' structure in a bipartite lattice (we consider below only such a case), $E_{\mathrm{LS/HS}} = -J_1 z/2$, and the homogeneous HS state with all $\sigma_i = 1$ and $E_{\mathrm{HS}} = J_1 z/2 - h$. Consequently, we would have jumplike phase transitions between these states with increasing h, from the LS state at $h < -J_1 z$ to an ordered array LS/HS/LS/HS $\cdots$ for $-J_1 z < h < J_1 z$, and to a HS state for $h > J_1 z$. Thus we see that this model quite naturally leads to the formation of a state with a superstructure of LS and HS states, similar to the one observed in Ref. 6.

One important difference of this simple case and the experimental situation observed in Ref. 6 is that the ratio of LS to HS states (IS to HS in the real case of $TlSr_2CoO_5$) is not 1:1 as above, but 1:2, IS states forming diagonal stripes in the 2D square lattice. But just such a state appears when one takes into account the second term in the Hamiltonian, Eq. (3).

In order to determine the ground-state phase diagram of the model (3) we employed a Metropolis Monte Carlo algorithm combined with a single spin-flip dynamics to cool the states to zero temperature.[13] We further compared the energies of all possible periodic states with unit cells up to size 5×5. In this way we found four regions with different ordered ground states: a ferromagnetic and an antiferromagnetic phase, a 2×2 checkerboard structure which is degenerate with (2,2) stripes, and a (2,1)-stripe phase. The resulting phase diagram for $h > 0$ is shown in Fig. 1 [as is clear from the form of the Hamiltonian (3), the phase diagram for $h < 0$ can be obtained by changing σ to $-\sigma$, i.e., by reflecting the phase diagram in Fig. 1 relative to the x axis and changing $+ \leftrightarrow -$].

Since all the ground states are simple diagonal stripes [except for the checkerboard phase which is however degenerate with the (2,2) stripe phase] we mapped the model onto a one-dimensional effective model, which is simpler to analyze and which served us for a detailed analysis (see the appendix). This study confirms the conclusions presented above and reproduces the phase diagram of Fig. 1.

To summarize, away from the boundaries all systematic checks revealed no phases but the ones shown in Fig. 1. Note, however, that on the boundary lines interesting degeneracies occur. Thus, e.g., on the line $h = 4J_1 + 4J_2$ separating the ferromagnetic and the (2,1) phase all diagonal stripes $(n,1)$ consisting of n spins $\sigma = +1$ and one spin $\sigma = -1$ are degenerate. We stress, however, that these degeneracies are of no phenomenological relevance for the superstructures

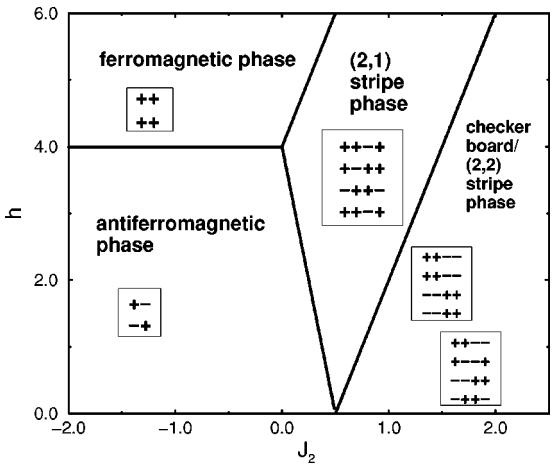

FIG. 1. Phase diagram of the model (3). The type of pseudospin ordering is shown for each possible phase. (The sign + corresponds, e.g., to a high-spin state, and the sign − to a low-spin or intermediate-spin state.) Note that we fixed the energy scale by putting $J_1=1$.

studied here, since they are strictly confined to the ''one-dimensional'' phase boundaries.

The phase diagram obtained above resembles that of the well-known ANNNI model, cf. Fig. 1 in Ref. 14, with the difference that because of the ferromagnetic coupling between nn spins in one direction in the ANNNI model, (2,1) stripes in the latter are vertical and not diagonal, as in our case (see the Appendix for details). Also, our result agrees with Ref. 15 where the model Eq. (3), is discussed for $h=0$.

From the results presented above we see that in a large part of the phase diagram we obtain the phase with (2,1) diagonal stripes; this phase exactly corresponds to the spin-state superstructure observed experimentally in $TlSr_2CoO_5$.[6]

We also considered the generalized model, including the interaction between the sites along diagonals in the plaquette, which according to Eqs. (1) and (2) should be attractive (ferromagnetic): the corresponding model in the spin language is

$$H=J_1\sum_{\langle ij\rangle=\mathrm{nn}}\sigma_i\sigma_j+J_2\sum_{\langle ij\rangle=\mathrm{nnn}}\sigma_i\sigma_j+J_d\sum_{\langle ij\rangle=\mathrm{diag}}\sigma_i\sigma_j$$

$$-h\sum_i\sigma_i, \qquad (4)$$

where $J_1, J_2>0$, $J_d<0$.

We found no new ground-state phases emerging for this case, but the effect of the diagonal coupling J_d is merely to shift the phase boundaries in Fig. 1 by $J_d/2$ to the right (see the Appendix).

For a longer-range interaction, e.g., the one of the type (1), certain other states may appear, depending on the ratio of the constants of the Hamiltonian. The description of these states is a formidable problem even in 1D case, especially at finite temperatures[12] (see also the results of numerical calculations in Ref. 13). We will not discuss all the details of this problem here; our main aim is just to demonstrate the possibility of the appearance of states with spin-state superstructures at corresponding transitions. We see that such superstructures indeed occur quite naturally if we take into account realistic interactions of HS and LS states via lattice deformation, including elastic anisotropy and interaction with optical phonons. In particular, the superstructure observed experimentally in $TlSr_2CoO_5$ is stable for a certain range of parameters if we include nn and nnn interactions along [100] and [010] directions.

Concerning the details of the properties of $TlSr_2CoO_5$ and of the theoretical description thereof, a few extra points should be mentioned. We discussed above only the origin and type of ordering in the ground state, assuming localized electrons. In reality $TlSr_2CoO_5$ undergoes the first-order insulator-metal transition with increasing temperature at about 300 K. We do not discuss this transition in this paper, but one can argue that the energy gap in the low-temperature phase may be connected with the occurrence of the spin-state superstructure. From this point of view one probably may consider this state as a result of the formation of the spin-state density wave, starting from the high-temperature metallic phase. (The treatment presented above would correspond to a strong-coupling limit of this picture.)

Another point worth mentioning is the suggestion[16] that an orbital degeneracy may play a role in the properties of $TlSr_2CoO_5$. In general, indeed, there may exist e_g degeneracy in the IS state and t_{2g} degeneracy in both the IS and HS states of Co^{3+}. However from the experimental data[6] it follows that this orbital degeneracy is predominantly lifted due to a rather strong tetragonal elongation of the CoO_6 octahedra which exists already in the high-temperature phase and which most probably is connected with the layered structure of this compound. Indeed, the IS state for this distortion is nondegenerate, and only in the HS state there remains a double degeneracy in the t_{2g} sublevels. But the latter in Co compounds is usually lifted by the spin-orbit coupling, which presumably would be the case here as well (Jahn-Teller effect by itself would stabilize for the HS state not an elongation, but a compression of CoO_6 octahedra). This question, however, deserves further study.

In conclusion, we considered in this paper the properties of systems undergoing spin-state transitions, such as the ones often observed in materials containing Fe^{2+} and Co^{3+}. We argued that the effective interaction governing the behavior of such systems—the interaction via lattice distortions—is more complicated than the usually assumed attraction between similar spin-state ions: typically the nearest-neighbor interaction is repulsive, and more distant interactions may be of either sign, depending on the elastic anisotropy of the crystal and on the direction between respective ions. As a result of such form of interaction, different superstructures, consisting of ordered distributions of different spin states, can naturally occur in this case. We discussed from this point of view the spin-state superstructure observed in the low-temperature phase of $TlSr_2CoO_5$,[6] and have shown that this superstructure can be explained by our model for a certain range of parameters. It would be interesting to look for similar superstructures in other systems with comparable energies of different spin-states and with spin state transitions.

We are grateful to J. P. Doumerc, D. Förster, and R. Hayn for useful discussions. This work was supported by the Sonderforschungsbereich 608 of the Deutsche Forschungsgemeinschaft, by the Netherlands Foundation for Fundamental Study of Matter (FOM), and by the Netherlands Science Organization (NWO).

APPENDIX

To gain further insight and to corroborate the picture obtained by Monte Carlo calculations and by explicitly comparing the energies of different states, we took advantage of the in principle one-dimensional structure of the relevant configurations (i.e., diagonal stripes, see Fig. 1) and mapped the original Hamiltonian (4) onto a one-dimensional Ising model in a magnetic field with the Hamiltonian:

$$H_{1\mathrm{dim}}=\sum_i \{2J_1 s_i s_{i+1}+(2J_2+J_d)s_i s_{i+2}-hs_i+J_d\}. \tag{A1}$$

Here $s_i=\pm 1$ represents the normalized sums of the spins on the diagonals and the one-dimensional interaction is orthogonal to the stripes. Note that this Hamiltonian contains all possible diagonal stripe configurations. Using this one-dimensional model we checked systematically for possible diagonal stripe configurations up to unit cell of 18.

From Eq. (A1) one sees that—once diagonal stripes are confirmed as ground states—the role of J_d is a mere modification of the next-nearest-neighbor coupling (plus an irrelevant constant) and hence a shift of the phase boundaries by $J_d/2$.

Equation (A1) is also useful to display the similarities to the two-dimensional ANNNI model,

$$H_{\mathrm{ANNNI}}=-\sum_{x,y} (\tilde{J}_1 S_{x,y}S_{x+1,y}+\tilde{J}_2 S_{x,y}S_{x+2,y}+\tilde{J}_0 S_{x,y}S_{x,y+1} + HS_{x,y}) \tag{A2}$$

with $\tilde{J}_1,\tilde{J}_2<0$ and $\tilde{J}_0>0$ as discussed in Ref. 14. Due to the ferromagnetic interaction $\tilde{J}_0$ in y direction, the stripes are vertically oriented in the case of Eq. (A2) and the corresponding one-dimensional Hamiltonian is

$$\tilde{H}_{1\mathrm{dim}}=-\sum_i \{\tilde{J}_1 s_i s_{i+1}+\tilde{J}_2 s_i s_{i+2}+Hs_i+\tilde{J}_0\}. \tag{A3}$$

The Hamiltonian $\tilde{H}_{1\mathrm{dim}}$, Eq. (A3), differs from $H_{1\mathrm{dim}}$, Eq. (A1), for $J_d=0$ by a factor 2 in the couplings and by a constant. The phase diagrams of the models can thus be mapped onto one another by a simple rescaling of the axis.

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