Low-Spin–High-Spin Transitions in Transition-Metal-Ion Compounds*

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Models for low-spin–high-spin transitions in transition-metal-ion compounds are presented. Within a molecular-field scheme, the transition between, and coexistence of, high-spin (Hund's-rule) and low-spin (crystal field) states are described. One- and two-sublattice-spin structures and the influence of magnetic interactions are considered. It is pointed out that the one-sublattice model, which was considered by Chestnut for the singlet-triplet system, applies to the transitions observed in certain organic complexes. We have found that the inclusion of magnetic interactions between ions can yield a magnetically ordered state above a certain transition temperature. This "heat magnetization" is not due to the coupling between levels but rather to a self-consistently determined crystal field splitting. The two-sublattice-spin-structure case exhibits a rich variety of behaviors. These include a low-spin to two-sublattice spin to high-spin transition with the order of the transitions varying with the parameters of the model. Applications to certain Fe^{2+} and Co^{3+} compounds are noted.

I. INTRODUCTION

Because the octahedral-crystal-field energy and the Hund's-rule exchange energy are comparable in the d^4, d^5, d^6, and d^7 systems of transition-metal ions in certain compounds, the transition between, and coexistence of, high-spin and low-spin states has been expected and indeed observed in several situations. In the case of Co^{3+} (d^6), $LaCoO_3$[1] and[2] $GdCoO_3$ exhibit a thermal transition from low spin ($S=0$) to high spin ($S=2$) and[3] Co_2O_3 exhibits a low-spin to high-spin transition with decreasing pressure. In the case of Fe^{2+} (d^6), thermally driven transitions (including first order) have been observed in various ferrous complexes.[4] Examples of Co^{2+} (d^7) with $S=\frac{1}{2},\frac{3}{2}$ have been found as well.[5]

Although the existence of these transitions has been known for several years, a satisfactory understanding and description (particularly in the case of a rapid variation in magnetic moment with temperature or first-order transition) were not present in this literature. Recently, Wajnflasz and Pick[6] have studied a model in which interactions between ions were represented by an Ising model treated in the molecular-field approximation. Although the authors found a first-order phase transition, they incorrectly analyzed the model in this approximation and predicted that the transition temperature was independent of the interaction strength.

Some years ago, in an attempt to understand the magnetic excitation spectrum of tetracyanoquinodimethan-ion-radical salts, Chestnut[7] proposed a simple model of a singlet-triplet system which could qualitatively describe the observed behavior. We wish to point out that, with appropriate interpretation, the model of Chestnut applies and can qualitatively account for the transitions observed in several ferrous complexes. Consequently, the belief of some authors that such an account was not present in the literature is dispelled.

Chestnut's model is shown to be a cooperative model of the low-spin–high-spin transition, based on a two-level [8] single-ion picture. The model is a molecular-field model of a two-body interaction between the ions or the result of a classical treatment of a lattice distortion which couples to the high-spin–low-spin energy-level separation.

It is found that, depending on the parameters, (i) a continuous low-spin to high-spin transition or (ii) a first-order low-spin to high-spin transition or (iii) a thermal depletion of a high-spin ground state can occur with increasing temperature. These are essentially the results of Chestnut. The first-order transition temperature is suppressed by an external magnetic field and disappears at a certain critical value of the field.

Going beyond the work of Chestnut, we have considered magnetic interactions between neighboring high-spin ions and studied them in a molecular-field treatment of the appropriate Ising model. It is found that in addition to the first two possibilities in the absence of magnetic interaction, (a) a high-spin ground state will exhibit long-range magnetic order at finite temperature and a second-order magnetic phase transition and (b) a low-spin ground state can be followed, with increasing temperature, by a high-spin transition with the simultaneous appearance of a magnetization, the latter disappearing at a yet higher second-order transition temperature.

We have also considered a two-sublattice model for which it can be energetically favorable to have one sublattice in the low-spin state and the other in the high-spin state. This requires the presence of two competing molecular fields at each ionic site and the resulting phase diagram exhibits several possibilities. In addition to the possibilities found in the one-sublattice case, the phase diagram includes the following transitions (with increasing

temperature): (i) low spin → two-sublattice spin structure → high-spin; (ii) two-sublattice spin structure → high spin. Most of these transitions are first order and the exceptions, as noted below, are second order. In all cases, the highest-temperature phase is high-spin in the sense that, if the multiplicity of the high-spin state is ν, then $\nu/(1+\nu)$ ions will be high spin due to thermal mixing at high temperatures.

We have not attempted to make a quantitative comparison with experiment; this could require an accounting of spin-orbit effects on the energy-level scheme, more detailed treatment of the lattice dynamics, or perhaps knowledge of residual magnetic effects due to preparation of a given sample.

II. THEORY

A. One-Sublattice Model (Chestnut's Theory)

In this section we present a brief review of Chestnut's model. We do this in order to make its application to the low-spin–high-spin transitions in Fe^{2+} and Co^{3+} complexes clear and establish the notation for our further studies.

We consider an array of N ions in which the high-spin state is at an energy $\Delta - VQ$ relative to the low-spin state on a single-ion picture. Δ and V are taken to be positive and Q is a measure of the distance from the ion to the nearby ions that produce its octahedral environment. At $Q=0$, the ground state is low-spin and the existing crystal field effects dominate the exchange effects to give a t_{2g}^6 ($^1A_1, S=0$) configuration. At $Q=\Delta/V$, the ground state crosses over to high spin and has the high-spin configuration $t_{2g}^4 e_g^2$ ($^5T_2, S=2$). Let n_i denote the occupation number for the ith ion such that if $n_i=0$ the ion is in the low-spin state and if $n_i=1$, the ion is in the high-spin state. If, in addition to the variation of level separation with Q, we include an elastic energy required to distort each octahedral complex, then the Hamiltonian for the system can be written in the simplest approximation as

$$H = N\xi Q^2 + \sum_i (\Delta - VQ) n_i ; \tag{1}$$

here ξ is a positive elastic constant. According to Eq. (1), the second term favors a large Q and consequently high-spin ground state (as in the case of a Hund's-rule free ion) and the first term favors a $Q=0$ low-spin ground state. The competition between these terms determines the actual ground state for given values of the parameters.

The free energy (per ion) is given by

$$f = Kx^2 - kT \ln(1 + \nu e^{-\beta(\Delta - 2Kx)}) , \tag{2}$$

where $x \equiv 2\xi Q/V$, $K \equiv \frac{1}{4} V^2/\xi$, and ν is the multiplicity of the high-spin state. Minimizing with respect to x gives the condition

$$x = \nu/(\nu + e^{\beta(\Delta - 2Kx)}) . \tag{3}$$

The high-spin population is given by $\bar{n} = [\partial/\partial(\beta\Delta)](\beta f)$ which implies, using Eq. (3), that $\bar{n} = x$. Thus Eq. (3) represents a self-consistent equation for $\bar{n}$ in which the thermal population of the high-spin state is related to a gap which is itself linearly related to $\bar{n}$. This result is what would be obtained in a molecular-field treatment of an appropriate two-body interaction model for this system. The lattice model of Eq. (1) and the molecular-field treatment of an interacting system are exactly equivalent as can be seen by the displaced oscillator transformation $Q = \bar{Q} + (V/2\xi N)\sum_i$ in Eq. (1),

$$H = N\xi(\bar{Q})^2 + \sum_i \Delta n_i - \frac{V^2}{4\xi N} \sum_{i,j} n_i n_j . \tag{4}$$

The Hamiltonian represents an infinite-range attractive interaction between the ions (and an independent oscillator term). It is well known that the molecular-field approach is exact[9] for a Hamiltonian with infinite-range interactions and the condition $\bar{Q}=0$ reproduces the result $\bar{n}=x$, following Eq. (3). Consequently, the treatment given here [Eqs. (1)–(3)] apply equally well to an interacting two-level model.[10]

For $S=2$, $\nu=15$ (including orbital degeneracy); the minimum free-energy solutions of Eq. (3) have been studied as a function of K/Δ and temperature. The possible thermal variations of $\bar{n}$ are represented in Fig. 1. If $0.43 < K/\Delta < 1$, a first-order transition occurs from a low-spin to a high-spin state with increasing temperature. For $K/\Delta > 0.55$, $\Delta_{eff} = \Delta - 2K\bar{n}$ becomes negative and the levels cross. Consequently, there is a thermal population of the low-spin state with increasing temperature above the transition, which accounts for the negative slope of $\bar{n}$ vs T. (This has been called a "supertransition" by Chestnut.)

For other values of K/Δ, there is no phase transition; there is only thermal population of a magnetic ($-\infty < K/\Delta < 0.43$) or nonmagnetic ($K/\Delta > 1.0$) state.

The phase diagram is shown in Fig. 2. We find a liquid-vaporlike critical point C. Also shown are the phase boundaries for $\nu=2$ and $\nu=3$. The latter case may apply to the high-spin state in the presence of spin-orbit coupling, with a $J=1$ multiplet lying lowest.

It is interesting to note that the case $\nu=1$ does not exhibit a phase transition except at $K/\Delta=1$, and in that case it is a second-order transition.[11] Although this case is not relevant from the point of view of high-spin–low-spin transitions, it is an interesting limiting case of this study. For $\nu > 1$, the multiplicity of the high-spin state plays an essential role in attaining the first-order transition. A low-temperature expansion of the free energy yields a $-kT\ln\nu$ term which represents a gain of entropy associated with the high-spin multiplicity.

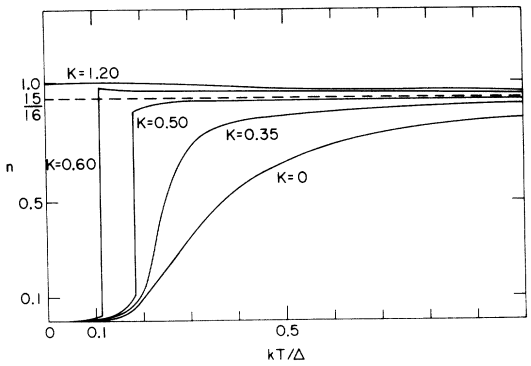

FIG. 1. Thermal variation of the order parameter n for different values of (K/Δ), $[\nu/(\nu+1)=\frac{15}{16}]$.

This term is, of course, absent in the $\nu=1$ case for which no first-order transition is found. These results agree with the general considerations of Landau: for $\nu>1$ there is no symmetry change involved in the problem so that either we find a first-order transition or no transition at all; for $\nu=1$, the problem is symmetric under the interchange of the two spin levels (for $\Delta=K$ only) and it is indeed this symmetry that is broken at the second-order phase transition.

As shown in Fig. 3, we have checked that an applied magnetic field favors the high-spin state: The transition temperature is lowered with increasing field and goes to $T=0$ °K at a critical field given by $\mu H_c=\frac{1}{2}(\Delta-K)$; here μ is the effective moment of the high-spin state.

B. Influence of Magnetic Interactions

In this section, we study the effects of magnetic interactions between high-spin ions in the model considered in Sec. II A. The magnetic term that is added to the Hamiltonian is written

$$-\sum_{i,j} J_{ij} n_i n_j S_i S_j$$

and represents an Ising interaction between spin S_i and S_j ($J_{ij}>0$). A single-ion Hamiltonian is defined as

$$H_0^i=\Delta n_i-\sigma n_i-HS_i n_i \tag{5}$$

and the corresponding partition function (per ion) is

$$Z_0=1+3e^{-\beta(\Delta-\sigma)}(1+2\cosh\beta H+2\cosh 2\beta H). \tag{6}$$

S_i takes on the value -2, -1, 0, 1, 2, and the factor of 3 corresponds to the orbital degeneracy associated with the $t_{2g}^4 e_g^2$ configuration. From the variational principle of statistical mechanics we write

$$\phi=-kT\ln Z_0+\mathrm{Tr}\rho_0(H-H_0),\quad \rho_0\equiv e^{-\beta H_0}/Z_0,$$

which is an upper bound to the free energy associated with H. Consequently,

$$\phi=-kT\ln Z_0-Kn^2-JM^2+\sigma n+HM\ , \tag{7}$$

where $J\equiv\sum_i J_{ij}$, $n\equiv\mathrm{Tr}\rho_0 n_i$, and $M\equiv\mathrm{Tr}\rho_0 n_i S_i$. The molecular fields σ and H are determined by minimizing Eq. (7), which gives

$$\sigma=2Kn$$

and

$$H=2JM\ .$$

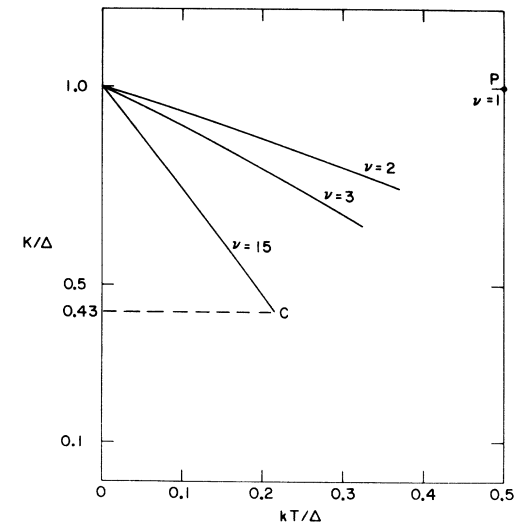

FIG. 2. Phase diagram in the $(T,\ K/\Delta)$ plane for various values of ν: for $\nu=1$, P is an isolated transition point.

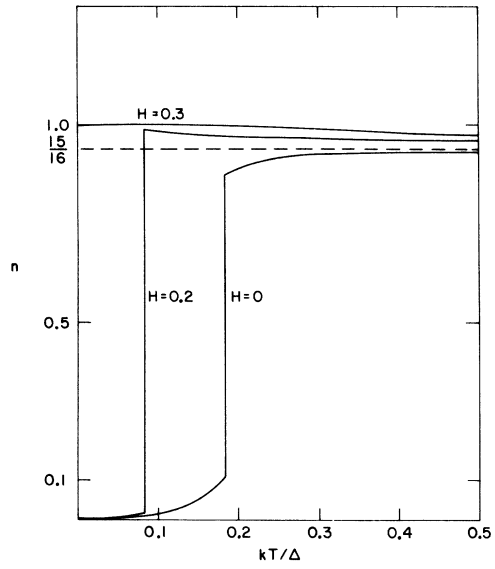

FIG. 3. Influence of a magnetic field on the first-order low-spin—high-spin transition for $K/\Delta=0.5$.

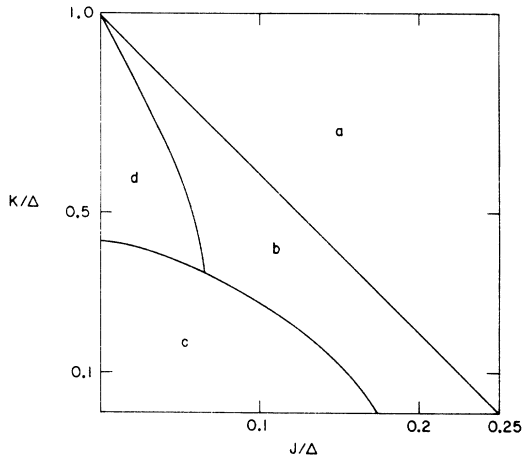

FIG. 4. Phase diagram in the $(J/\Delta, K/\Delta)$ plane for the one-sublattice model with magnetic interactions.

Thus n and M are given by the equations

$$n = 3C/(E+3C) \ , \tag{8a}$$

$$M = 3D/(E+3C) \ , \tag{8b}$$

where

$$E \equiv e^{\beta(\Delta - 2K\sigma)} \ ,$$

$$C \equiv 1 + 2\cosh 2\beta JM + 2\cosh 4\beta JM \ ,$$

$$D \equiv 2\sinh 2\beta JM + 4\sinh 4\beta JM \ .$$

Note that when $\Delta \to -\infty$, $n \to 1$ and the equation for M reduces to the familiar Brillouin function for $S=2$ in molecular-field theory.

We solve Eqs. (8a) and (8b) at various points in the J, K plane (see the resulting phase diagram in Fig. 4) and find several possibilities: (a) The ground state is magnetically ordered and the magnetization vanishes at a second-order transition temperature [Fig. 5(a)]. (b) The ground state is a low-spin nonmagnetic state; a first-order transition leads to an ordered high-spin state, and the magnetization vanishes at yet a higher second-order transition temperature [Fig. 5(b)]. (c) There is a thermal population of the magnetic level with no magnetic ordering. (d) There is a first-order transition (low spin to high spin) with no magnetic ordering. Cases (c) and (d) are similar to that found in the $J=0$ case (Fig. 1) for $K/\Delta < 1$ and are expected in the region $J/K \ll 1$. Case (b) exhibits two Curie temperatures for the appearance and vanishing of the magnetization. As far as we know, this situation has not been observed in magnets. It is interesting to compare this case with "heat magnetization" as predicted by Kitano and Trammell.[12] These authors consider a singlet-triplet system in which a crystal field Δ splits the $S_z=0$ triplet state from the singlet. The $S_z=\pm 1$ levels are split from the $S_z=0$ triplet by a molecular field, proportional to the average spin. They further allow that the effective spin operator has a nonvanishing matrix element λ between the $S_z=0$ triplet level and the singlet level. This leads to an effective single-ion Hamiltonian with levels given by

$$\epsilon_1 = \tfrac{1}{2}\Delta - [(\tfrac{1}{2}\Delta)^2 + J^2M^2\lambda^2]^{1/2} \ , \tag{9a}$$

$$\epsilon_2 = \tfrac{1}{2}\Delta + [(\tfrac{1}{2}\Delta)^2 + J^2M^2\lambda^2]^{1/2} \ , \tag{9b}$$

$$\epsilon_3 = \Delta - JMS_i \ , \tag{9c}$$

$$\epsilon_4 = \Delta + JMS_i \ . \tag{9d}$$

For $\lambda = 0$, these equations reduce to the case considered by Blume,[13] with ϵ_1 reducing to the singlet energy level. These equations are similar to Eq. (5); in Eqs. (9a)–(9d) the thermal variation of the levels comes from their dependence on the molecular field M; in Eq. (5) in addition to a dependence on M, the levels have a thermal dependence through the molecular field σ which arose from interactions with the lattice vibrations (or residual ion-ion interactions). Kitano and Trammell found a second-order transition for the appearance of heat magnetization, whereas we found a first-order transition accompanied by a first-order low-spin to high-spin transition.

In the limit $K=0$, case (b) is still possible even though the molecular field σ is absent. The molecular field M must now carry the transition and we attribute the persistence of this phase at $K=0$ (see Fig. 4) to the orbital degeneracy (=3) associated with each spin level. If the spin levels were not orbitally degenerate we expect to obtain the spin-2 counterparts of the spin-1 results by Blume[13] and would thereby find that the region of the J-axis that describes case (b) in Fig. 4 would be zero.

C. Two-Sublattice Model

In this section we study a two-sublattice model

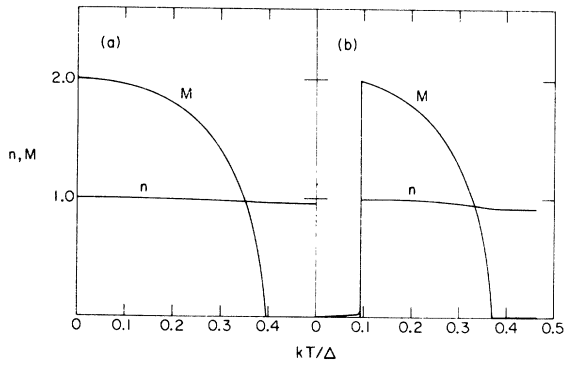

FIG. 5. Thermal variation of the order parameters n and M in the one-sublattice model with magnetic ordering: (a) magnetically ordered ground state; (b) nonmagnetic ground state.

of a low-spin–high-spin transition. We consider the possibility of a transition to a two-sublattice spin structure in which one sublattice is predominantly high spin and the other low spin. This situation is believed to occur in $LaCoO_3$ (see Raccah and Goodenough, Ref. 1) and a two-sublattice model for such a transition has been studied by one of us.[14] This model incorporates the structural change found in $LaCoO_3$ with the resulting modifications of the local crystal fields to obtain a first-order change in translational symmetry (to lower symmetry *above* the transition) with a concomitant low spin to two-sublattice spin structure.

Briefly, in the notation of Eq. (1), the model considered was

$$H = N\xi Q^2 + \sum_{i\in A} (\Delta - VQ)n_i + \sum_{i\in B} (\Delta + VQ)n_i \quad , \qquad (10)$$

where the summations are restricted to either sublattice A or sublattice B. The translation

$$Q = \bar{Q} + \frac{V}{2\xi N}\left(\sum_{i\in A} n_i - \sum_{i\in B} n_i\right)$$

leads to an interacting model with interactions of the form

$$\frac{-V^2}{4\xi N}\left(\sum_{\substack{i\in A\\ i\in B}} n_i n_j + \sum_{\substack{i\in B\\ j\in B}} n_i n_j - 2\sum_{\substack{i\in A\\ i\in B}} n_i n_j\right) ,$$

i.e., the intrasublattice interaction is attractive and the intersublattice interaction is repulsive (with twice the strength of the attractive interaction). We have generalized this model by allowing the attractive and repulsive interactions to be independent parameters. This could correspond to, for example, a situation in which there is simultaneously lattice interactions and genuine two-body forces, so that the ratio of the interaction strengths would not be exactly 2.

We define the molecular fields on sublattice A and sublattice B, respectively, as

$$\sigma_A = 2Kn_A - Ln_B , \quad \sigma_B = 2Kn_B - Ln_A ,$$

where K and L are constants ($2K = L$ corresponds to the lattice model of Ref. 14) and n_A and n_B are the thermal high-spin occupations of sublattice A and sublattice B, respectively. n_A and n_B are the solutions of the two equations

$$n_A = 15/(15 + e^{\beta(\Delta - 2Kn_A + Ln_B)})$$

and

$$n_B = 15/(15 + e^{\beta(\Delta - 2Kn_B + Ln_A)}) ,$$

which minimize the free energy

$$\phi = -kT\ln(1 + 15e^{-\beta(\Delta - 2Kn_A + Ln_B)}) - kT\ln(1 + 15e^{-\beta(\Delta - 2Kn_B + Ln_A)}) + K(n_A^2 + n_B^2) - Ln_An_B \quad .$$

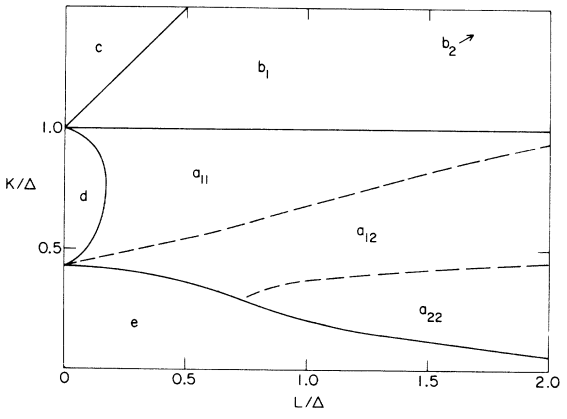

FIG. 6. Phase diagram in the $(K/\Delta, L/\Delta)$ plane for the two-sublattice model.

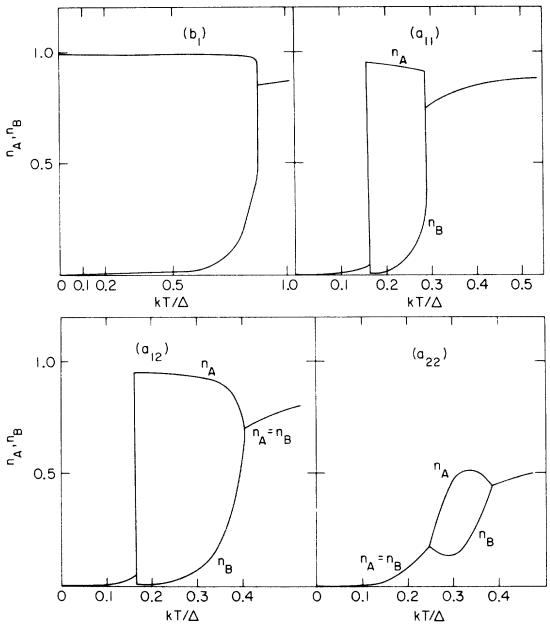

FIG. 7. Thermal variation of the order parameters n_A and n_B in the various regions of the phase plane of Fig. 6.

In Fig. 6, we indicate the various regions of phase diagram in the K, L plane. In the regions denoted a_{11}, a_{12}, and a_{22}, the ground state is low spin and a transition leads to a two-sublattice structure followed by a transition to a high-spin state [Fig. 7(a)]. When the lower transition is first order, the higher can be either first order (a_{11}) or second order (a_{12}). When the lower transition is second order, the higher is always second order (a_{22}). The regions b_1 and b_2 correspond to a ground state that is a two-sublattice spin structure. The transition to the high-spin state is either first order

(b_1) or second order (b_2). The arrow denotes that the b_2 boundary is outside the region of the phase diagram as shown in Fig. 6. Region c denotes thermal population of the low-spin state. In region d, a first-order low-spin to high-spin transition occurs. Region e denotes thermal population of the high-spin state. The behaviors in the regions c–e have already been encountered in the one-sublattice model and the results are qualitatively the same in the region $L/\Delta \ll 1$. Likewise, in the limit $L = \infty$, the one-sublattice solutions are obtained on the $A(B)$ sublattice with $n_B(n_A) = 0$ for all T.

III. SUMMARY

We have presented a description of low-spin to high-spin transitions in a variety of circumstances. We have shown how a self-consistent treatment of crystal field and/or residual-ion–ion interactions can account for a first-order low-spin to high-spin transition. The transitions described in Sec. II A give a good qualitative description of the first-order transitions found in certain ferrous complexes.[4,5] The progressive increase of high-spin population and decreasing level separation with increasing temperature applies well to[2] $GdCoO_3$ and $TbCoO_3$.[15] The two-sublattice model of Sec. II C has application to $LaCoO_3$ as noted earlier.[14]

We have studied the effects of magnetic interactions in the high-spin state and have found the possibility of heat magnetization for certain values of the parameters. We have also found that a first-order low-spin to high-spin transition can be induced by the magnetic interactions alone, provided that orbital degeneracy is present.

There are several ways of refining or generalizing the treatment given here. These include a more detailed treatment of the lattice dynamics, going beyond the molecular-field approximation, inclusion of spin-orbit coupling, inclusion of charge-transfer states, and addition of other spin states.

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[8]The authors of Ref. 6 have considered a four-level model which generalizes that considered here in that they allow the ion to exist at two radii (parametrized by a fictitious spin) for either high or low spin. The two additional levels then represent a given spin state having the "wrong" radius. If these additional states are removed to infinite energy, the models become equivalent. The need for introducing these additional levels is not clear from their presentation and, furthermore, since their thermodynamic order parameter is the ion radius (rather than relative high-spin—low-spin population) the relation to the thermal variation of the magnetic moment is obscure.

[9]See, for example, R. Brout, *Phase Transitions* (Benjamin, New York, 1965).

[10]As it is written, Eq. (4) contains interactions between high-spin ions only. It is easy to see that if the constants Δ and $\frac{1}{4}V^2/\xi$ are redefined, the Hamiltonian can include high-spin—low-spin interactions of the form $n_i(1-n_j)$ and low-spin—low-spin interactions of the form $(1-n_i)(1-n_j)$.

[11]The occurrence of this isolated transition can easily be understood by relating the problem to a spin-$\frac{1}{2}$ Ising model. The transformation $n_i = \frac{1}{2}(\sigma_i + 1)$ transforms Eq. (4) into an Ising model in an external field, the latter being proportional to $\Delta - K$.

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