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SINGLET GROUND STATE MAGNETISM

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Abstract. — We discuss the magnetic behavior of rare earth systems where the crystal-field-only ground state of the rare earth ion is a singlet. As exchange increases in such a system, magnetic ordering at zero temperature occurs through a polarization instability of the singlet ground state. Such a process leads to a threshold value for the ratio of exchange to crystal-field interaction necessary for magnetic ordering even at zero temperature. We discuss the magnetic behavior, with regard to both theory and experiment, as this threshold is approached and exceeded. We use the experimental behavior of the rare earth compounds of NaCl-structure with group V elements to illustrate the crystal-field-only behavior, and the behavior as exchange increases up to and beyond the critical value for magnetic ordering.

I. Introduction. — For rare earth materials, it is possible for the crystal-field effects to be comparable in importance to exchange effects in determining the qualitative nature of magnetic ordering. Indeed under appropriate circumstances the crystal-field can compete with and dominate exchange effects in determining the answer to the basic question of whether the material orders magnetically at all. This is the situation when the crystal-field-only ground state of the rare earth ion is a singlet (This can occur only for a non-Kramers ion with an even number of 4 f electrons and consequently integral J for the ground state multiplet.) Then as exchange increases, magnetic ordering at zero temperature occurs not through the usual process of alignment of permanent moments, but rather through a polarization instability of the crystal-field-only singlet ground state [1-4].

For such materials, there is a threshold value for the ratio of exchange to crystal-field interaction necessary for magnetic ordering even at zero temperature [1-4]. Here we will discuss the magnetic behavior as this threshold is approached and exceeded. After pointing out some of the most striking qualitative features of the experimental magnetization behavior in singlet ground state systems, we will use a simple two-singlet-level model to show how one can understand the existence of magnetic ordering in crystal-field singlet ground state systems. First, we show that one can explain many of the gross features of such induced magnetic behavior with a rather simple molecular field theory. Then we will discuss the onset of magnetic ordering from the viewpoint of collective excitation theory. Besides offering a clear physical picture of the threshold effect for ordering in induced moment systems, this discussion will show the existence of a type of exciton quite different from ordinary spin waves.

After treating the theory, we shall return to a more quantitative discussion of the experimental situation. To do this, we shall discuss the behavior of the most extensively studied singlet ground state systems, the rare earth compounds of NaCl structure with group V elements. We shall first discuss the behavior characteristic of the crystal-field-only limit, using the fact that TmSb acts as a model crystal-field-only material [5] to illustrate that behavior. Then we shall treat experiments on mixed terbium-yttrium antimonide which directly show [6] the transition from Van Vleck paramagnetism to antiferromagnetism at low temperature as the fraction of Tb increases (corresponding to increasing magnitude of antiferromagnetic exchange).

Besides strengthening our understanding of a type of magnetic ordering fundamentally different than that occurring through the usual process of alignment of permanent moments, experiments on the rare earth-group V compounds relate to two quite general questions in rare earth magnetism. First, the results show that in these materials the point charge model gives a good description of the crystal-electric-field (This contrasts with evidence presented by Williams and Hirst [7] that this does not seem to be true for dilute rare earths in noble metal hosts.) Second, high field magnetization experiments in the paramagnetic regime where one induces very large anisotropic moments, serve to measure the size of possible higher degree (than quadratic in magnetization) exchange energies [8, 9], and also measure any anisotropy in such exchange.

II. Qualitative Characteristics of Induced Moment Magnetism. — Figure 1 shows a possible crystal-field level splitting scheme for the ground state multiplet of Pr^{3+} in a site of hexagonal symmetry, and possible
For simplicity we consider a two level model where the crystal-field-only ground state is a singlet, and the excited state is also a singlet at a splitting $\Delta$. Besides simplicity, this two-singlet-state model has the advantage of showing purely induced moment (i.e. crystal-field-only wave function admixture effects). (Physically this model would describe reasonably well the low temperature behavior of $^{100}$Pr$^{3+}$ in a hexagonal environment if the two lowest states were singlets as shown in figure 1, well removed in energy from higher lying crystal-field states.) We consider a Hamiltonian,

$$\mathcal{H} = \sum_i V_i - \sum_{i \neq j} \beta_{ij} J_i \cdot J_j - g\beta H \sum_i J_{ix}$$  \hspace{1cm} (1)$$

with a crystal-field term, an exchange term, and a Zeeman term (The exchange here is isotropic, but can be generalized to include anisotropy effects apt to occur in practice.)

1. Molecular field theory. — By conventional first-order perturbation theory, the susceptibility per ion in the absence of exchange is

$$1/\chi = (\Delta/2 \beta^2 a^2) \left[1/\tanh(\Delta/2T)\right]$$  \hspace{1cm} (2)$$

where

$$\alpha = <0_+ | J_+ | 1_+ >$$  \hspace{1cm} (3)$$

with $|0_+ >$ and $|1_+ >$ denoting the crystal-field-only ground and excited states.

If one includes exchange in the molecular field approximation, the only change in $1/\chi$ is the replacement

$$1/\tanh(\Delta/2T) \rightarrow \left[1/\tanh(\Delta/2T)\right] - A \cdots$$  \hspace{1cm} (4)$$
Thus the effect of exchange on $1/x$ in the molecular field theory [2] as illustrated in figure 2a is to simply rigidly shift the curve of $1/x$ vs $T$ downward (ferromagnetic exchange) or upward (antiferromagnetic exchange). The value of $A$ for which the susceptibility diverges at $T = 0$ gives the threshold value of exchange for ferromagnetic ordering. This is $A = 1$. For $A$ exceeding the threshold value, it is a simple procedure to self-consistently find the magnetization as a function of temperature. This is given by

$$<J_z>/\alpha = \sin 2\theta \tanh \{A/T \left( \frac{1}{2} \cos 2\theta + \frac{1}{2} A(1 - <J_z>/\alpha) \sin 2\theta \right) \}$$

(7a)

with

$$\tan 2\theta = A <J_z>/\alpha.$$  

(7b)

The resulting magnetization for fixed $A$ as $A$ varies is shown in figure 2b. The most notable features, as shown in figure 3, are the reduction of $T_c$ and the reduction of $<J_z>/\alpha$ from its maximum «free ion» value of unity as $A$ decreases.

So we see that this simple molecular field theory explains the overall trend and the most prominent qualitative features of the induced magnetic behavior in the rare earth-group V compounds.

Figure 4 illustrates one interesting characteristic of singlet-ground-state systems, the specific heat behavior. The broad peak is the Schottky anomaly associated with the crystal-field splitting from the ground state to the first excited state. Location of this peak unambiguously identifies the crystal-field splitting. The figure also shows a lower temperature, sharper peak associated with magnetic ordering, shown for the case when the ordering temperature is below the temperature of the Schottky anomaly. This specific heat anomaly is much less prominent than that usual for magnetic ordering. This decrease in the specific heat peak associated with magnetic ordering basically comes about because much of the entropy of the system has already been removed by the ions dropping into the singlet crystal-field ground state before magnetic ordering occurs [2].

The behavior shown in figures 2, 3, and 4 allows a simple understanding of the approach to ferromagnetic ordering in fcc Pr-Th alloys [16] as Pr concentration increases, and the occurrence of ferromagnetism in fcc elemental Pr metal [17]. Increasing Pr concentration in the alloys corresponds to increasing the ratio of ferromagnetic exchange to crystal-field splitting, so that $1/x$ per Pr ion drops similar to the behavior in figure 2a. For elemental fcc Pr, the threshold ratio is exceeded slightly, and ferromagnetism occurs. From susceptibility measurements one recognizes the onset of ferromagnetism at 8.7 K, yet there is no detectable specific heat anomaly. This is understandable considering the behavior shown in figure 4. From the Schottky specific heat behavior [17], the crystal-field splitting to the first excited state is about 69 K, so one expects an even greater decrease in the relative importance of the specific heat anomaly at ordering than that shown in figure 4. Because the exchange is only slightly beyond the threshold, the ordered moment at low temperature is only about 20% of the free ion moment. Use of the experimentally observed $T_c$ and low temperature magnetization in a molecular field theory analysis [17] yields a value of crystal-field splitting about half that obtained from the Schottky specific heat. This probably reflects the severe demands
placed on accurate parameter values in such an analysis treating the steeply rising portion of the curves in figures 3a and 3b.

2. COLLECTIVE EXCITATION THEORY. — Understanding the behavior of the collective excitations of singlet-ground-state systems is of interest for several reasons. First, one obtains what is probably the best physical picture of the threshold behavior for magnetic ordering in terms of the instability of one of the collective modes. This «soft» mode instability is analogous to the phonon instability in some ferroelectrics. Second, the dispersion behavior for the energy of the elementary excitations is of interest since understanding it provides the basis for calculating the various thermodynamic properties. Third, and of great potential importance, is that one can hope to observe directly the excitation spectrum by neutron scattering, and thereby directly determine the form of the exchange interaction. The final reason for studying the collective excitations is that these are a type of exciton that exists both in the paramagnetic and magnetically ordered regimes, and that are quite different from ordinary spin waves. Indeed, we shall see that there are no spin waves for a two-singlet-level system.

The most appropriate technique for treating the collective excitation theory is the pseudospin formalism [4, 18]. Using this formalism one develops a theory where the difference in occupation number of crystal-field-only states in the paramagnetic regime, or of molecular field states in the ordered regime plays a role analogous to that of magnetic moment, or of the expectation value of the spin component along the direction of magnetization, for ordinary ferromagnetic systems.

The pseudospin formalism for the two singlet level problem is a variation of the well-known effective spin Hamiltonian technique, and is based on the fact that the Hamiltonian for any two level system can be written in terms of four spin ½ operators which correspond to $2 \times 2$ matrices with unity as one element and zero as the other elements. This allows us to exactly transform the Hamiltonian of eq. (1) to the following form [4] in terms of pseudospin ½ operators.

$$\mathcal{H} = \sum_i \varepsilon_i S_i - \sum_{i \neq j} J_{ij} \left\{ x_{01} S_i^- + x_{10} S_i^+ + x_{00} S_i^- S_i^+ + x_{11} S_i^+ S_i^- \right\} \left\{ x_{01} S_j^- + x_{10} S_j^+ + x_{00} S_j^- S_j^+ + x_{11} S_j^+ S_j^- \right\}. \quad (8)$$

Here $\varepsilon_i$ is the energy difference between the molecular field single ground and excited states, and the $x_{am}$ are given by the various matrix elements of $J_{ij} = ^i J_\| - ^i J_\perp \varepsilon_a$ (the unit vector along the z-axis in pseudospin space is denoted $\varepsilon_z$) between the molecular field single ion states.

Once the Hamiltonian is in the form of eq. (8) (which in the paramagnetic regime formally reduces to the Hamiltonian for an Ising system in a transverse magnetic field [4]) one can treat the problem with the powerful techniques developed for treating conventional spin Hamiltonians; however, the calculations are still quite involved, especially since they must be done self-consistently, and the true ground state is not known.

One can find the collective excitation dispersion behavior at zero temperature by considering the equations of motion of the pseudospin operators. One can make a series of increasingly involved approximations, at each step treating the motion of the pseudospin operators more exactly. The simplest treatment is the Random Phase Approximation, where, after taking commutators, one replaces $S_\pm$ in the equations of motion by its self-consistently determined expectation value.

Figure 5 shows the dispersion curve for the collective excitations at $T = 0$ in the RPA. This is for a simple cubic lattice with nearest neighbor ferromagnetic exchange. In the paramagnetic regime, the energy gap at $k = 0$ decreases as the exchange increases, and vanishes when $A$ attains a critical value of 1.04. At this value of $A$, the $k = 0$ soft mode becomes unstable, and there is a second order phase transition to ferromagnetic ordering. This critical value of $A$ is about 4% larger than in the molecular field theory because the true ground state is not the molecular field ground state. For $A$ exceeding the critical value for ferromagnetic ordering, the energy gap at $k = 0$ increases with increasing $A$.

One can extend the treatment to finite $T$ by using the technique of studying the equations of motion for the retarded time Green's Functions. The dispersion behavior [4] is shown in figure 6 for exchange slightly larger than the critical value. As $T/A$ increases from zero, the $k = 0$ mode energy drops toward zero, at first slowly, then precipitously when $T$ is close to $T_c$. For $T > T_c$, the $k = 0$ mode frequency increases again. For high temperatures, the $E_k$ approach $\Delta$, and the dispersion tends to disappear.

From the self-consistent determination of the excita-
Fig. 6. — Upper panel: Change of dispersion curve as temperature is raised through $T_c$ for $A = 1.05$, $T_c/A = 0.1$. Lower panel: Corresponding magnetization versus temperature.

section behavior, one also finds the temperature dependence of the magnetization. The most striking feature is the sharp drop in magnetization close to $T_c$.

As $T_c/A$ increases, the RPA magnetization is discontinuous at $T_c$ for values of $T_c/A > 0.1$. This is in distinction to the behavior in molecular field theory where the transition is always second order. The discontinuity in magnetization for the RPA collective excitation theory is most significant for values of $T_c/A$ near unity, where it is quite substantial. Also, the excitation spectrum is considerably narrower than for lower $T_c$. As $T_c/A$ increases still further in the RPA, while the discontinuity in magnetization persists, the size of discontinuity decreases, and the magnetization approaches the molecular field behavior.

The approach to molecular field behavior in the RPA for large exchange is easily understood. First, we point out that there are no spin waves in our induced moment system even if we allow $A \to \infty$. This is because the two states of a single ion go to $| \pm m \rangle$ with $m > \frac{1}{2}$ in our model as $A \to \infty$ (Here $m$ denotes the $J_s$ quantum number. For example, for Pr$^{3+}$ in a hexagonal crystal-field, the two lowest singlet states are

$$1/\sqrt{2}(| + 3 \rangle - | - 3 \rangle)$$

and

$$1/\sqrt{2}(| + 3 \rangle + | - 3 \rangle).$$

As exchange increases from zero, these states mix; and in the limit of large exchange, the states become $| \pm 3 \rangle$ and $| - 3 \rangle.$ The spin waves involve transitions to $| m \pm 1 \rangle$, and these are higher-lying states not taken into account for our model system. Second, as $A \to \infty$, there are also no excitations of the type we have considered, since the coupling vanishes between the two single ion states (i.e. $< m | J_s | - m > = 0$).

Basically, the first order transition occurs because the long wavelength, «soft», modes dropping in energy offer a catastrophically effective channel of depopulation of the ground state.

Actually, one can do calculations including correlation effects between the motion of the pseudospin at neighboring sites. Such calculations indicate the presence of a first order magnetic transition even at zero temperature.

A question that arises is whether this first order transition would occur in an exact treatment of the two singlet level problem. While the answer is not known, there are some complimentary studies currently being carried out [19, 20] that may help in answering this question at least at zero temperature. These studies develop series expansions for the energy in the ratio of exchange to crystal-field interaction in a way similar to the expansion in exchange over temperature used to treat critical phenomena in conventional magnetic systems.

Of course, in a real physical system there are spin waves. In Pr$^{3+}$ in a hexagonal crystal-field these would involve transitions to higher lying crystal-field levels. Then in a real physical singlet ground state system, with increasing exchange one would expect to go from a regime where the excited states are basically the sort of excitons we have been discussing to a regime where the excited states are spin waves.

It is possible to extend the pseudospin type treatment to the case where the excited state is a triplet by considering the space spanned by the direct product of two pseudospin $\frac{1}{2}$ systems [18]. However, the generating operators for excited states are much more complicated than the simple pseudospin raising operator that pertained to the two singlet level case. This singlet-triplet problem is more complicated than the singlet-singlet problem, and no detailed calculations have appeared as yet.

IV. Induced Moment Behavior in Rare Earth Group V Compounds of NaCl-structure. — 1. CRYSTAL-FIELD-ONLY BEHAVIOR. — First, we discuss several experiments useful to characterize the magnetic behavior of singlet ground state systems in the absence of exchange. TmSb serves as a model material in illustrating such behavior.

As shown in figure 7 (upper panel) the low field susceptibility [5] of TmSb is of a Van Vleck type. At low $T_c$ as shown in the lower panel, the high field magnetization becomes nonlinear and highly anisotropic [5].

Now the crystal-field Hamiltonian for a cubic material is completely specified by a fourth-order and a sixth-order parameter.

$$\mathcal{K}_{cr} = B_4(0^4_o + 5 \times 0^2_o) + B_6(0^6_o - 21 \times 0^2_o).$$

(9)

Where $0^m_o$ are operators, specified for a given $J$. It is often more convenient to treat two other parameters [21] $x$ and $W$. The ratio of fourth-to-sixth order anisotropy is given by $x$; while $W$ gives the absolute scaling of the crystal-field energy level scheme

$$\frac{B_4}{B_6} = \frac{x}{1 - |x| F(4)} F(6)$$

(10)

with $F(4)$ and $F(6)$ specified constants for a given $J$. 

The high field anisotropic magnetization is especially valuable in determining the relative importance of fourth and sixth order anisotropy. As shown in figure 7, for \( x \approx -1 \) (predominantly fourth-order anisotropy) one matches the experimental behavior very well for all three directions. One could match the susceptibility behavior, indeed even the high field nonlinear magnetization in one direction, with a much larger sixth order contribution; but failure to match the experimental behavior in all directions excludes a substantial sixth order anisotropy [5].

For \( x \approx -1 \), the crystal-field level scheme for Tm\(^{3+} \) depends on only one absolute scaling factor \( W \) determined by matching the low temperature susceptibility. This value, giving a \( \Gamma_1 \) to \( \Gamma_4 \) splitting of 26.6\( ^* \), gives excellent overall agreement with the \( 1/\gamma \) vs. \( T \) and high field \( M \) vs. \( H \) behavior (When the Tm is diluted by about 50% Y, the magnetization per Tm remains unchanged [5], reinforcing the evidence for crystal-field-only behavior in TmSb.) This value of splitting is also consistent with specific heat Schottky anomaly measurements [22].

We note that the observed \( x \) and \( W \) behavior is in basically good agreement with the prediction of the point charge model. This is particularly true of the predominance of the fourth-order effects. For a crystal-field due to effective charges at the nearest neighbor Sb sites, \( x \) depends only on the lattice parameter, and \( x = -0.955 \). The value of the point charge at each Sb site to give the experimental \( W \) is \( 3.85 [e] \).

Neutron scattering experiments [23] have yielded the crystal-field parameters in PrBi. There also, the signs and relative magnitudes of the fourth and sixth order terms are as predicted by the point charge model.

As an interesting side effect to the induced magnetization, we note that as one induces the electronic magnetization with an applied field, one also induces an effective magnetic field at the nuclei via the hyperfine interaction; and this induced hyperfine field amplifies the applied field effect on the nucleus by as much as two orders of magnitude. This gives rise to the giant Knight shifts found by Jones [24] for Pr and Tm in PrP and TmP, respectively. This giant induced hyperfine field effect has recently been used by Andres and Bucher [25] in nuclear cooling experiments in PrPt\(_5\) and PrTl\(_3\) to below 5 mdeg K.

2. Induced Antiferromagnetism in TbxY\(_{1-x}\)Sb. — The induced moment ordering process has been directly studied [6] by substituting Y for Tm in TBSb\(_s\) (\( T_N \approx 15.1 \)°K for TBSb). Yttrium is essentially identical to the heavy rare earths in its valence electron behavior, but has an empty 4\( f \) shell. Thus substituting Y for Tm essentially does not change the crystal-field but does reduce the effective exchange field acting on a given Tm ion. In this way one can reduce the exchange below the critical value necessary for magnetic ordering.

As shown in figure 8, mixed crystals have been made across the whole composition range [6]. The lattice constant has only a small variation indicating a correspondingly small change in the crystal-field splitting (This has been confirmed by specific heat measurements [26].)

Susceptibility measurements have been done [6] for all compositions. The results of some of these are shown in figure 8 to give an idea of the behavior found. The measurements were done on all samples for \( T \) up to 300 \( ^\circ \)K, but only the lower temperature results are shown. The susceptibilities in figure 8 are per mole Tm.

At high Tm concentrations, one has the peak in susceptibility characteristic of antiferromagnetic materials. This shifts to lower temperature as the Tm concentration decreases, and at the same time the peak value of susceptibility per Tm shifts upward. However, in distinction to magnetic ordering in permanent
moment systems, the peak in normalized susceptibility does not grow indefinitely as \( T_B \) goes to zero. Instead, at a concentration of about 40 \% Tb, \( T_B \) goes to zero; and for Tb concentration below that one has a Van Vleck susceptibility which approaches the finite crystal-field-only limit at \( T = 0 \) as Tb concentration decreases further.

As shown in figure 9, one can analyze [6] the inverse susceptibility behavior as Tb concentration varies on the basis of molecular field theory. The theoretical curves shown then depend on only two parameters: \( W \) specifying the crystal-field and \( \lambda \), proportional to Tb concentration, giving the exchange. The overall agreement of theory and experiment is quite good, considering the large amount of data to be fit (It should be pointed out that since the data is normalized per Tb ion, the experimental points at low concentration are quite sensitive to the correct determination of the Tb concentration.) The \( W \) found corresponds to a \( \Gamma_1 \) to \( \Gamma_4 \) splitting of 11.9 \( \text{K} \). This is less than half the value for [5] TmSb.

As shown in figure 10, one can also calculate the variation of \( T_N \) with Tb concentration on the same theoretical basis, and again the agreement is good [6]. Thus one has good agreement for the threshold behavior for the magnetic ordering and for the behavior below the exchange threshold at low fields where only a small magnetization is developed.

One can also use high field nonlinear magnetization measurements [6] to study the magnetic behavior with decreasing Tb concentration. For concentrations below 40 \% Tb, that is below that necessary for antiferromagnetism at \( T = 0 \), one obtains anisotropic magnetization behavior similar in character to the crystal-field-only behavior shown in figure 7 for TmSb. However, the high field anisotropic magnetization is not matched quantitatively by the linear molecular field theory using the values of crystal-field and exchange parameters that describe the susceptibility and Néel temperature behavior. This is not surprising since one expects that higher degree exchange effects [8, 9] (i.e., exchange field cubic or higher degree in the magnetization) should be significant for systems with large orbital contributions to the magnetic moment. Such effects then show up most strongly in the large magnetization regime. High field anisotropic magnetization experiments can then be used to unambiguously identify and measure these higher degree exchange effects. As reported elsewhere [27] at this Conference, such measurements and analysis have recently been performed for \( \text{Tb}_x\text{Y}_{1-x}\text{Sb} \), measuring the cubic exchange field coefficients and indicating the presence of yet higher degree contributions.

In conclusion then, we have tried to show that crystal-field singlet ground state systems have many properties of striking interest in themselves, and that study of such systems should also help our understanding of orbital contributions to magnetization and magnetic ordering in rare earth systems.

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