Zeitschrift: Helvetica Physica Acta
Band: 41 (1968)
Heft: 6-7

Artikel: Magnetism of induced moment systems
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DOI: https://doi.org/10.5169/seals-113923

Magnetism of Induced Moment Systems

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(18. IV. 68)

Abstract. The magnetic behavior of compounds with crystal-field-only singlet ground states is discussed. We first discuss the magnetization behavior of such systems in the absence of exchange. The case of $TmAl_3$ is used as an example to show the type of information about the crystal-field energy levels one can hope to gain by the use of high field anisotropic magnetization measurements. A brief discussion is given of the way in which self induced magnetic ordering occurs as exchange increases for a magnetic system with a crystal-field-only singlet ground state. Finally, we comment on the value of magnetization measurements as a spectroscopic tool in systems where by alloying one increases the exchange beyond the critical value necessary for magnetic ordering.

For rare earth compounds, such as those of NaCl structure with group V anions [1–8], the crystal electric field can be comparable to, or even dominant over the exchange field between rare earth ions. Thus, the crystal-field is expected to play a very important role in the nature of the macroscopic magnetic properties and of the collective excitations for such materials. Indeed, for rare earth compounds with singlet crystal-field ground state for the rare earth ion, the exchange interaction must exceed a certain critical value relative to the crystal-field to have magnetic ordering even at zero temperature [2, 9–11].

In this paper we first discuss the magnetization behavior of singlet crystal-field ground state systems in the absence of exchange. In particular, the anisotropic magnetization predicted [6, 7], and in the case of TmSb found experimentally [8], represents one of the few cases where the origin of a macroscopic magnetic anisotropy is quantitatively understood in a straightforward and fundamental way. We will point out the way in which susceptibility and magnetization experiments can essentially be used as a spectroscopic tool in such systems to investigate the crystal-field energy levels. The case of $TmAl_3$, a system with Van Vleck susceptibility [12], will be used as an example to show the type of information about the crystal-field energy levels one can hope to gain by the use of high field anisotropic magnetization measurements.

A brief discussion will be given of the way in which self induced magnetic ordering occurs as exchange increases for a singlet crystal-field ground state system. In particular, we will point out the existence of a collective excitation instability criterion [10, 11] for such ordering at zero temperature. Finally, we will discuss the value of magnetization measurements as a spectroscopic tool in systems where by alloying one increases the exchange beyond the critical value necessary for magnetic ordering.

For rare earth ions with integral J (total angular momentum) in the free ion ground state manifold, the crystal-field-only ground state may be a singlet level.

In particular this occurs for the rare earth compounds of NaCl structure with group V anions. If the exchange interaction is not sufficiently strong to overcome the moment quenching tendency of the crystal field, such compounds do not order magnetically. This is the case for Tm and Pr compounds of this type. However, for the Tm compounds it is possible to induce a large moment with applied field at low temperature through polarization of the Γ_1, ground state wave function. In the low field regime (magnetization linear with applied field), this Van Vleck susceptibility (which exists because of admixture of the first excited level, a Γ_4 triplet, to the Γ_1 ground state) is isotropic for a cubic material. For high fields (approaching and exceeding one hundred kilo-Oersteds) one expects a large nonlinear magnetization with values approaching that of the free ion moment. Theory [6, 7] predicts the development of a large anisotropy in the magnetization in the nonlinear region. The difference at zero temperature between the magnetization with field in the ⟨111⟩, easy, direction and the ⟨100⟩, hard, direction occurs because for fields up to several hundred kilo-Oersteds the only significant admixture into the Γ_1 state for H along a ⟨100⟩ direction is from the Γ_4 first excited state; while for H along ⟨111⟩, in the nonlinear regime there is significant admixture from the second excited state, of Γ_5 symmetry.

Experimental [8] results for the anisotropic magnetization in TmSb at 1.5 °K are shown in Figure 1. Theoretical curves are also shown in the figure. These are for fourth order anisotropy only. (Paramagnetic resonance [13] indicates that this is essentially the case for TmN, and in any case the magnetization behavior is quite insensitive to the parameter x giving the ratio of fourth to sixth order anisotropy [14]). Then the theory depends only on one parameter, W, giving the absolute energy scaling of the crystal field levels. W was obtained by matching the experimental susceptibility at $T = 0$. (The sign of W in this case corresponds to negative charge on the Sb sites.) The agreement between theory and experiment at 1.5 °K is excellent.

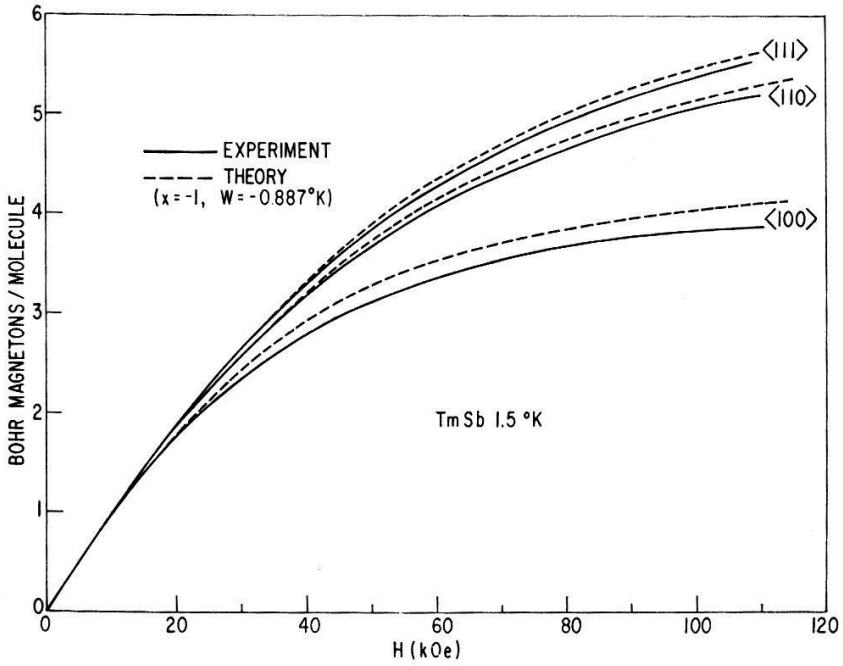

Figure 1

Magnetization of TmSb at 1.5 °K. Theory is for $x = -1$, $W = -0.887$ °K. (After O. Vogt and B. R. Cooper, J. appl. Phys. *39*, 1202 (1968).)

Buschow and Fast have found Van Vleck susceptibility behavior in $TmAl_3$ which has Cu_3Au structure. If the crystal-field acting on the Tm^{3+} ion corresponds to effective charges centered on the twelve nearest neighbor Al sites, one can calculate the value of x from a point charge model, and this value is independent of the sign of charge on the Al sites. One can then, just as for the TmSb, find W by matching the experimental susceptibility [12] at very low temperature. This then permits calculation of both the behavior of $1/\chi$ versus T and of the magnetization as a function of field at any specified temperature. There are, however, two radically different possibilities depending on the sign of the effective charge on the Al sites giving the crystal-field. If this charge is positive, W is negative, and the ordering of the crystal-field levels is as in TmSb with a Γ_1 ground state. If the charge is negative, W is positive, and the crystal field levels are reversed in order. Then the ground state is a Γ_3 nonmagnetic doublet.

Theoretical curves for both signs of W in $TmAl_3$ are shown in Figure 2, where in both cases W has been chosen to match the $T = 0$ limit of the experimental susceptibility [12]. There is one great qualitative difference between the two sets of theoretical curves. The easy and hard directions reverse on changing the sign of W. Thus anisotropic magnetization experiments would distinguish the sign of W. Susceptibility measurements are not sufficient for this purpose, since in the linear regime where the magnetization is isotropic, there is only a small difference between the $1/\chi$ versus T curves for the two W values (both chosen to match χ at $T = 0$).

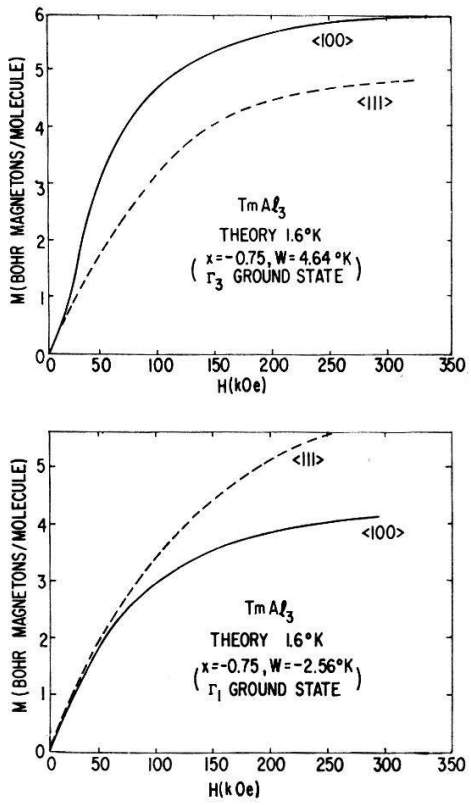

Figure 2

Theoretical curves for magnetization of $TmAl_3$, at 1.6°K. The magnetization is shown for two values of W, one positive and one negative. In both cases the value of W has been chosen to match the zero temperature limit of the experimental susceptibility.

There is one particularly striking feature of the positive W curve (corresponding to a Γ_3, nonmagnetic doublet, ground state). This is the sharp rise and inflection in the $\langle 100 \rangle$, easy, magnetization curve for fields of a few tens of kOe. This occurs because, while the nonmagnetic Γ_3 state is not split to first order in H, it does split in higher order. Thus for low temperature, the magnetization suddenly jumps as the nonlinear effects give a splitting between the two Γ_3 states which is comparable to the temperature; and the occupation of the lower of the two Γ_3 states becomes predominant.

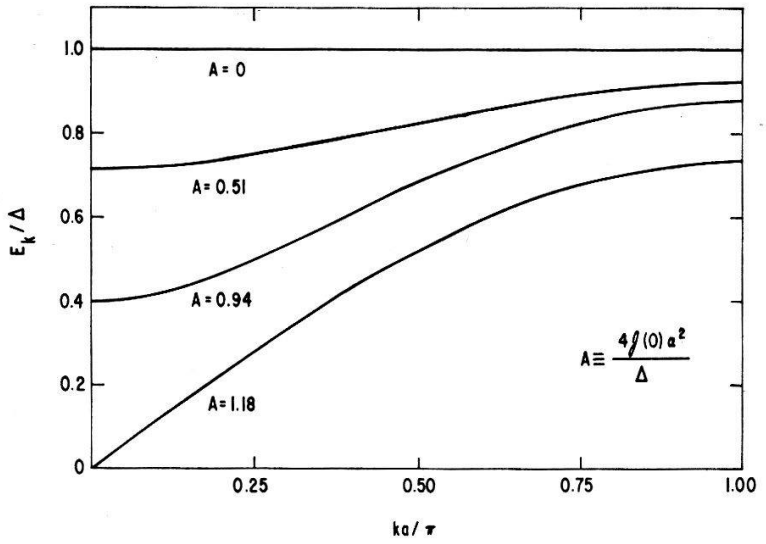

Figure 3

Dispersion curves at zero temperature, for several values of ferromagnetic exchange, of elementary excitations for system of magnetic ions having crystal-field-only singlet ground state and crystal-field-only singlet excited state, with energy splitting Δ between them. The lattice is taken as simple cubic, and the exchange as nearest neighbor only. (After Y. L. WANG and B. R. COOPER, to be published (1968).)

Finally, we briefly consider how the magnetic ordering occurs in singlet crystal-field ground state systems, and how magnetization measurements of the sort discussed here are useful in understanding this behavior. Probably the physically clearest way to picture the ordering process, as exchange approaches the critical value necessary for magnetic ordering with infinitesimal moment at $T = 0$, is to consider the excited state behavior [10, 11, 15, 16]. As shown [11] in Figure 3 for a two singlet level system, for vanishing exchange the excited state is the sharp crystal-field-only level. However, for increasing exchange this excitation takes on the nature of a magnetic polarization wave. (In Fig. 3, α is the matrix element of J_z between the two crystal-field-only wave functions, and $J(0)$ is the zero wave vector Fourier component of the exchange energy. Thus in Figure 3, A is basically the ratio of exchange interaction to crystal-field splitting of the two singlet states, and the exchange is ferromagnetic. Figure 3 is taken from Ref. [11]). The energy gap for the zero wave vector excitation decreases until it vanishes at a critical value of exchange. At this critical value of exchange there is an instability for the growth of such a polarization wave, and long range induced magnetic ordering at $T = 0$ occurs [11].

The present author [10] suggested substituting Y for Tb in the magnetically ordered Tb compounds of NaCl structure with group V elements, in order to reduce

the exchange below the critical value necessary for magnetic ordering. This has now been done [17] for TbSb, and the critical concentration of Y necessary to go from antiferromagnetism to Van Vleck paramagnetism at low temperature is slightly above 50%. Then by analyzing the susceptibility and magnetization for samples with Y concentration well above the critical value (i.e. in the Van Vleck paramagnetism regime), in the same way as has been done for TmSb, one should obtain the crystal field parameters in TbSb. Further by analyzing the shift in susceptibility per Tb ion on going toward the critical concentration, using the existing theoretical framework [2, 6–11], one can obtain information about the exchange (at least the zero wave vector Fourier component of the exchange energy). Finally, analysis of anisotropic magnetization measurements allows the question of anisotropy in the exchange to be analyzed. Thus such measurements should yield much valuable information. Such a study would be most valuable in conjunction with neutron inelastic scattering studies of the excitation spectra. Then one could obtain a complete description of the crystal-field and exchange interactions in an induced moment magnetically ordered compound such as TbSb.

In conclusion, my associates at the General Electric Research and Development Center and I wish to extend our very best wishes to Professor GEORGE BUSCH on the occasion of his sixtieth birthday, and join our colleagues around the world in saluting Professor BUSCH for his great contributions to solid state physics.

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