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MAGNETIC PROPERTIES OF LINEAR CHAIN COMPOUNDS FORMED BY LANTHANIDE(III) IONS AND NITRONYL-NITROXIDE RADICALS

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Abstract. – The magnetic properties of novel linear chain compounds containing lanthanide(III) ions (gadolinium, europium) coupled to stable nitronyl-nitroxide radicals are reported. The metal ions and the radicals are regularly alternating along the chain. The magnetic behaviors appears to be dominated by antiferromagnetic interactions between the radicals.

1. Introduction

Low dimensional magnetic materials containing lanthanide ions are practically non-existent [1], but they are in principle quite interesting, because the large unquenched orbital momenta associated to the metal ions may yield novel magnetic behaviors which deserve investigation.

With this in mind we attempted an extension of the procedures which we used [2] to synthesize linear chain compounds with transition metal ions and stable organic radicals such as the nitroxides to obtain analogous derivatives with the lanthanides. Indeed we succeeded to synthesize the first linear chain compounds containing lanthanides and organic radicals and we wish to report here preliminary information on the magnetic properties of gadolinium(III) and europium(III) compounds.

2. Results and discussion

Gadolinium(III) hexafluoroacetylacetonate, $Gd(hfac)_3$, forms with the nitronyl-nitroxide depicted below and which we abbreviate NITet:

linear chains [3] as shown in figure 1. The europium(III) derivative was found to be isomorphous. The metal ion is coordinated to two oxygen atoms of two NITet molecules, and each radical is bound to two different metal ions through its two oxygen atoms. The chains grow along the *b* direction of the monoclinic unit cell.

The magnetic susceptibility of $Gd(hfac)_3$ NITet increases on decreasing temperature down to 4.2 K, but the χT product, figure 2, decreases, passing from the room temperature value of 8.20 emu mol⁻¹ K to

Fig. 1. – Schematic view of the chains in $Gd(hfac)_3$ NITet. Fluorine atoms are omitted for the sake of simplicity as well as the carbon skeleton of the acetylacetonate moieties.

Fig. 2. – Temperature dependence of the observed χT product of $Gd(hfac)_3$ NITet in the 5-300 K range (*); the curves are the fitting to the experimental data with the three models described in the text: the Seiden model (—); the alternating-spin alternating-chain (---); the interpenetrating lattice model (-.-.-).

2.55 emu mol⁻¹ K at 6 K. The magnetic susceptibility of $Eu(hfac)_3$ NITet passes through a maximum at ca. 12 K and then decreases.

The results of the europium derivative are easily

interpreted considering that the ground state of the metal ions is $^7F_0$ and the excited magnetic states are depopulated below 50 K. Therefore the low temperature susceptibility is determined by the interactions between the radicals and the maximum at 12 K indicates a coupling constant of ca. 12 cm^{-1} (we use the spin Hamiltonian in the form $H = JS_1.S_2$). This result is intriguing, because it shows how relatively strong antiferromagnetic interactions can be developed between radicals which are more than 400 pm apart. However it is in agreement with previous findings in mononuclear europium-radical derivatives [4].

The results of $\text{Gd}(\text{hfac})_3\text{NITet}$ are more puzzling, because for a chain where the metal ions and the radicals are not coupled we must expect a Curie behavior, while for a regular chain with either ferro- or antiferromagnetic coupling we must expect the behavior of ferro- or ferrimagnetic chains, with divergence of χ at low temperature [5]. Since the observed behavior is that of χT decreasing with decreasing temperature we may conclude that either the chains are not regular or they are not isolated. According to the former hypothesis we assume that the exchange coupling constants of the gadolinium with the two radicals to which it is bound are different, one ferro- and the other antiferromagnetic. A quantitative calculation of the susceptibility in this hypothesis can be performed using the formulae reported [6] for alternating chains which consider the gadolinium spin as a classical spin and the radical spin as a quantum spin. The agreement with the experimental data is rather satisfactory, as shown in figure 2 but the values of the two coupling constants, $J_1 = -11.45 \text{ cm}^{-1}$, $J_2 = 33.69 \text{ cm}^{-1}$, are much larger than expected for a lanthanide and a radical.

Interchain interactions can be considered within a molecular field model, but also in this hypothesis the values of the parameters which are needed for a good fit of the experimental data are much larger than one anticipates on the basis of the long distance of the chains from each other.

Finally another possibility is that the non-nearest

neighbor interactions between the radicals can determine the observed behavior. In fact the data of the europium derivative indicate that the radicals are indeed antiferromagnetically coupled. We are not aware of any quantitative treatment suitable for a system like this therefore we cannot confirm our suggestion with a calculation. However some support to this hypothesis may come from a rough treatment which reduces the chain to the sum of two independent lattices, one formed by the radicals and the other by the gadolinium ions. Exchange is assumed to be present only within a lattice. The experimental data in this case can be fitted with an antiferromagnetic coupling between the radicals $J_1 = 10.2 \text{ cm}^{-1}$ and the gadoliniums $J_2 = 0.28 \text{ cm}^{-1}$. It is rewarding that the exchange coupling constant between the radicals is very similar to that observed in the europium derivative. More effort is therefore needed in order to confirm our suggestion, but these systems may prove excellent testing grounds for theories of one-dimensional materials with dominant non-nearest neighbor interactions.

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