HIGH-FREQUENCY AND -FIELD EPR OF EXCHANGE-COUPLED LANTHANIDE CENTERED [$GdNi_6$] AND [$LnNi_6$] CLUSTERS

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Introduction

Magnetic properties of clusters of transition metals are of great interest since the discovery of the phenomenon of single-molecule magnetism and the experimental manifestation of quantum tunnelling of the magnetization in nano-scale magnets. In this context, systems involving lanthanides are still scarce and little understood. Moreover, molecular species combining interacting *4f* and *3d* open-shell ions are very rare. We have developed the synthesis of a comprehensive family of unique clusters with formula (TMA)[$Ni_6Ln(pro)_{12}$](ClO_4)$_4$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Y; pro = proline), which offer an excellent opportunity to undertake a systematic study on the nature of the magnetic super−exchange between Ni^{II} and lanthanides. Preliminary magnetic studies reveal high−spin ground states in some of the above compounds. The weakness of the magnetic coupling complicates the interpretation of the bulk measurements since it is difficult to separate the effect of this coupling from zero-field splitting effects. This makes these systems particularly suited for a detailed HFEPR study since such an investigation should allow determining the structure of the magnetic states resulting from the exchange between paramagnetic ions, and determine the value and nature of the zero-field splitting parameters. A resulting comprehensive picture on the magnetic properties of the system formulated above could well be a landmark in the field of molecular magnetism, since very few *4f* − *3d* hetero−polynuclear complexes have been described, and none, with the proposed combination of techniques.

Experimental

Polycrystalline samples of [$GdNi_6$] and [$LnNi_6$] cluster complexes were investigated using the mm and sub-mm spectroscopy facility at the NHMFL including the 25 T Keck magnet. Preliminary results were obtained from the EMR facility using the 17 T superconducting magnet.

Results and Discussion

We have found EPR properties of the two clusters investigated as different as they are in the magnetic domain. The [$GdNi_6$] cluster exhibits spectra typical for a Kramers (half-integer spin) system (not shown). These are not particularly informative, pointing to immeasurably small zero-field splitting in the high-spin ground state (S = 13/2). On the other hand, the HFEPR spectra of the [$LnNi_6$] cluster (Figure 1, inset) are characteristic for a non-Kramers (integer-spin) system and can be best described by the single-ion anisotropy of the Ni^{II} ion in the ground S = 1 state. The resonance field vs. transition energy dependence of the HFEPR spectra (Figure 1) allows to extract zero-field splitting of the ground state, which is equal to D = 5.5(1) cm^{-1}, with a rhombic term E = 0.8(3) cm^{-1}. The g-matrix values are: g_x = 2.06(3), g_y = 2.21(4) and g_z = 2.30(3). These values agree well with the magnetic susceptibility data.

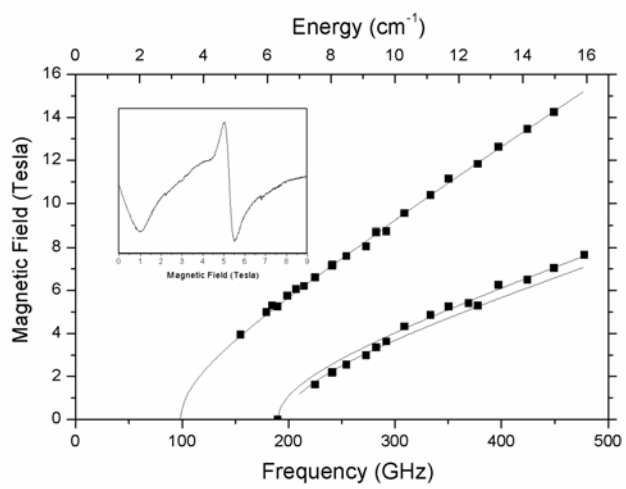

Figure 1. Resonance field vs. transition energy dependence of the HFEPR resonances in the [$LnNi_6$] cluster.