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A FREQUENCY DEPENDENT "LEVEL CROSSING" RESONANCE IN THULIUM NICOTINATE DIHYDRATE

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Abstract. In TmND a strong resonance of width 170 mT occurs at a field \( B = 0.17 \) T which is found to be independent of frequency between 2 and 600 MHz. Experiments at 15 MHz on a spherical sample of TmND at 0.5 K, to produce narrower lines, show three equally spaced lines whose origin is explained.

Introduction

The lanthanide nicotinate dihydrates (LnND), with the formula \( \left[ \text{Ln} \left( \text{CsH}_4\text{NCO}_2 \right)_3 \left( \text{H}_2\text{O} \right)_2 \right]_2 \), for a homologous series whose monoclinic crystals, space group \( P/2_1/a \), contain two symmetry related dimers per unit cell. Each dimer contains a pair of \( \text{Ln}^{3+} \) ions with separation about 0.43 nm: the two ions in a pair are related by inversion symmetry, but at each \( \text{Ln}^{3+} \) site there is no point symmetry.

In spite of this low symmetry, the ground state of each \( \text{Ln}^{3+} \) ion, \( ^{4}f^{12} \text{H}_6 \), in a pair of \( \text{Ln}^{3+} \) ions in a dimer, is a non Kramers doublet with measured g-value close to the maximum possible theoretical value of 12 \( g_s \) corresponding to \( |M_1| = \pm 6 \) [1]. The energy levels of the pairs of \( \text{Tm}^{3+} \) ions in both LnND containing 0.01 mole fraction of Tm, and undiluted TmND, may be described by the spin hamiltonian with \( S_1 = S_2 = 1/2 \), \( I_1 = I_2 = 1/2 \):

\[
\mathcal{H} = g_s \mu_B B z (S_{1z} + S_{2z}) - 2J S_{1z} S_{2z} + A (S_{1z} I_{1z} + S_{2z} I_{2z}) + \delta (S_{1z} + S_{2z}).
\]

The figure shows the energy level diagram for such a spin hamiltonian with levels labelled with quantum numbers \( M_1 = M_{1z} + M_{2z} \) and \( M_{21} M_{22} \). EPR transitions observed at 17 GHz in dilute material are indicated by vertical bars. As \( g_s \) is the only non-zero component of the electronic g-matrix, only \( \Delta M_s = 0 \) transitions can be excited, requiring an oscillating magnetic field in the \( z \) direction. For \( \delta = 0 \), the eigenstates would be pure \( M_{21} M_{22} \), between which no \( \Delta M_s = 0 \) transitions could occur. Hence the observed transitions are permitted only because of the admixture produced by the terms in \( \delta \). In undiluted TmND at 4.2 K no structure due to \( A \) and \( \delta \) is observed in the two EPR lines of width 54 mT; but as the value of \( g_s \) and \( J \) are nearly the same as for the dilute material, one expects the value of \( A \) to be nearly the same, and the intensities of the EPR lines suggest a similar value for \( \delta \). Hence the energy level diagram for the undiluted TmND is expected to be similar to the figure, precise details depending upon the value of \( \delta \).

In undiluted TmND a resonance line is also observed near 170 mT at low frequencies, independent of frequency between 2 and 600 MHz. The only places on the figure where levels are close enough for such transitions is the three crossings of levels with different \( M_1 \) marked with heavy dots, whose separation depends upon the value of \( \delta \), and it was supposed in [1] that the observed line is an unresolved superposition of the transitions near these level crossings.

Experiments

New measurements have been made on a single crystal sphere of TmND at temperature sufficiently low to depopulate the upper levels, in order to reduce both macroscopic and microscopic variations in the internal field which contribute to the line width. The crystal aligns itself in the applied magnetic field by rolling until \( B \) is parallel to the \( K_1 \)-axis of the maximum susceptibility. At 1.3 K, EPR at 33 GHz in the higher...
field line, shows a linewidth of 15 mT, giving a good resolution of the two line hyperfine structure: the line separation of 30 mT gives nearly the same value of \( \Delta \) as for the dilute material. At 0.5 K, the resonance near to 170 mT at 15 MHz is reduced in width to 6.7 mT revealing three equally spaced lines with overall separation of 30 mT.

The observation of three resolved lines appears to confirm the level crossing model of figure 1, for which the observed line separation corresponds to \( \delta/\hbar = 5.3 \) GHz. This also confirms the deduction in [1] that \( \delta/\hbar \) for TmND should have a similar, though somewhat smaller, value than that for undiluted material, \( \delta/\hbar = 9.5 \) GHz.

More experimental work needs to be done to account for the mechanism and intensities of the lines at low frequencies. Although \( \Delta M_I = \pm 1 \) NMR transitions could be excited at the level crossings, the observed lines are too strong for NMR. However, if some additional term in the spin hamiltonian produced small matrix elements coupling the crossing levels, electronic \( \Delta M_s = 0 \) transitions at low frequencies would be allowed near the “crossings” of similar intensity to EPR in the GHz range. Such terms might arise through an enhanced nuclear Zeeman interaction or an enhanced transferred hyperfine interaction between members of the pair. These matrix elements would prevent the levels from actually crossing, they would have a minimum separation depending upon the magnitude of the matrix element. Such a model produces large transition probability when \( h\nu \) is equal to the energy separation, \( \Delta \), produced by the mixing matrix element at the exact “crossing point”, but the transition probability decreases as \( (h\nu/\Delta)^2 \) for higher frequencies, and should be zero for \( h\nu < \Delta \). Unfortunately, absolute intensities at different frequencies are difficult to compare because of unknown frequency dependence of the sensitivity of the apparatus. A full understanding therefore requires very careful measurement of the frequency dependence of intensities and a comparison with the prediction of specific models, involving more experimental and computational work.