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Enhanced nuclear magnetic resonance in holmium nicotinate

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Abstract. The optical absorption spectrum of holmium nicotinate dihydrate $[\text{Ho}(\text{C}_5\text{H}_4\text{NCO}_2)_3(\text{H}_2\text{O})_2]_2$ shows that for the holmium ion the lowest level of the ground manifold $^5\text{I}_8$, split by the ligand field, is a singlet, with two other singlets at $8.1(1)$ and $15(1) \text{ cm}^{-1}$. At 4.2 K and below, nuclear resonance from ^{165}Ho , $I = \frac{7}{2}$ is observed at 500 MHz , enhanced from 9 MHz T^{-1} to over 3.3 GHz T^{-1} . The nicotinate structure contains dimeric molecules of holmium ions, for which an extension of the theory of the enhanced nuclear resonance is given.

1. Introduction

Following investigations of other members of the lanthanide nicotinate series, this paper reports similar measurements on the holmium compound $[\text{Ho}(\text{C}_5\text{H}_4\text{NCO}_2)_3(\text{H}_2\text{O})_2]_2$. The crystals are monoclinic, space group symmetry $\text{P}2_1/c$, with dimensions $0.9567(6) \text{ nm}$, $1.1596(2) \text{ nm}$ and $1.7811(4) \text{ nm}$ for the lattice constants a , b , c ; the angle $\beta = 91.4$ degrees (Prout *et al* 1985). The ground state of the trivalent holmium ion is $4f^{10}$, $^5\text{I}_8$, and the ground manifold $J = 8$ should be split into singlets by the ligand field. This is confirmed by optical absorption spectroscopy, that includes measurements of the Zeeman effect in fields up to 9 T . For the single stable isotope ^{165}Ho , $I = \frac{7}{2}$, the natural NMR frequency is $9.0(1) \text{ MHz}$ in a field of 1 T . In the singlet electronic ground state of this nicotinate compound, an enhanced NMR spectrum is observed, with frequency increased to over 3 GHz in a field of 1 T . The 'enhancement' arises through the induced electronic moment, that gives a greatly increased magnetic field at the nucleus through the hyperfine interaction. The details reported in this paper include an analysis of the effect on the spectrum of the presence of dimeric pairs of ions.

This work continues a series of optical and magnetic studies of trivalent lanthanide ions in single crystals of lanthanide nicotinate dihydrates that has been carried out in recent years (Baker *et al* 1986a,b, 1987). These crystals are composed of dimeric molecules with formula $[\text{Ln}(\text{C}_5\text{H}_4\text{NCO}_2)_3(\text{H}_2\text{O})_2]_2$, denoted here and below by LnND, in which Ln denotes a lanthanide ion. Much earlier studies, including x-ray diffraction and electron paramagnetic resonance (EPR), on neodymium and gadolinium nicotinate, each diluted in lanthanum nicotinate, are cited in the references above. The monoclinic crystals contain two dimeric molecules per unit cell, related by a reflection in the ac

plane. The ions occur in relatively isolated, centro-symmetric pairs, the separation between the two ions being ≈ 0.43 nm. There is no point symmetry at the site of the lanthanide ion. Studies by x-ray diffraction (Moore *et al* 1972, Prout *et al* 1985) have shown that the crystals are iso-structural throughout the lanthanide series, the variations in the parameters being only 0.03 nm in a , 0.06 in b , 0.08 in c , and 1.5° in the angle β .

An earlier paper (Baker *et al* 1986b) reports optical and magnetic studies of thulium nicotinate (TmND), where the ground state of the Tm^{3+} ion, $4f^{12}, {}^3\text{H}_6$ is found to be the non-Kramers doublet $|J, \pm M_J\rangle$, with $M_J = J = 6$. In a second paper (Baker *et al* 1988) magnetic resonance transitions between the levels are observed by EPR at 17 GHz. There is also a strong, frequency independent signal at MHz frequencies, that appears at a field of 0.17 T. The width of this line arises from internal dipolar fields, and decreases at lower temperatures. At 0.5 K three hyperfine lines are resolved, as expected for a pair of ${}^{169}\text{Tm}$ ions, each with nuclear spin $I = \frac{1}{2}$. The mechanism by which such transitions are allowed is not clear.

A study of TmND, diluted to 0.01 mole fraction in LaND, has been carried out by Baker *et al* (1986b). This has shown that the isolated Tm^{3+} ions (that is, ions in Tm–La pairs) have singlet electronic ground states and no EPR spectrum attributable to isolated Tm^{3+} ions is observed. However, EPR spectra of thulium ions, each with a doublet ground state and a member of a dimeric pair, appear in these dilute crystals, and are very similar to those found in TmND.

Extensive optical and magnetic studies of $\text{Tb}^{3+}, 4f^8, {}^7\text{F}_6$ (Baker *et al* 1987) in undiluted TbND show that the electronic ground state of Tb^{3+} in Tb–Tb dimeric pairs is a singlet. An EPR spectrum of low intensity is present from dimeric pairs at defect sites of low abundance. In a diluted compound, 0.01 mole fraction TbND in LaND, the EPR spectra show that the Tb^{3+} ion in Tb–La dimeric pairs has a nearly degenerate non-Kramers doublet ground state $|J, \pm M_J\rangle$, with $M_J = J = 6$. Although Tb–Tb pairs should be present in sufficient concentration to give an EPR spectrum, none is observed.

The presence of doublet ground states for both thulium and terbium ions is a surprising discovery, as there is no point symmetry at the Ln ion sites, so that the ligand field would be expected to split all the manifolds J into singlet states. The differences in the crystal structure are small; 0.01 nm in a , b , c , 0.1° in β , and only 0.001 nm in the separation between the two ions of a pair. It is thus remarkable that in Tm–Tm dimeric pairs the Tm ground state is a doublet, and in Tm–La pairs a singlet, while the reverse is true for the terbium compounds, where Tb^{3+} has a singlet ground state in Tb–Tb pairs, but a doublet in Tb–La pairs.

2. The optical absorption spectrum of HoND

Optical transitions from the lowest levels of the manifold ${}^5\text{I}_8$ to the multiplets ${}^5\text{S}_2$ and ${}^5\text{F}_3$, with wave numbers 18 430 to 18 464 and 20 570 to 20 700 cm^{-1} respectively, have been measured as a function of magnetic field. The various levels are shown in figure 1. All the possible transitions to these multiplets were observed; this is important for the following reason. For an isolated multiplet, the centre of gravity is independent of applied field, and displacement of the centre of the transitions arises only from the Zeeman effect for the ground singlet. These two excited multiplets for holmium are not however completely isolated; the multiplet ${}^5\text{S}_2$ lies ~ 100 cm^{-1} below ${}^5\text{F}_4$, and ${}^5\text{F}_3$ lies some 700 cm^{-1} below ${}^5\text{F}_2$. States of different J belonging to the same manifold (L, S) are admixed by a magnetic field, causing their centres of gravity to move slightly

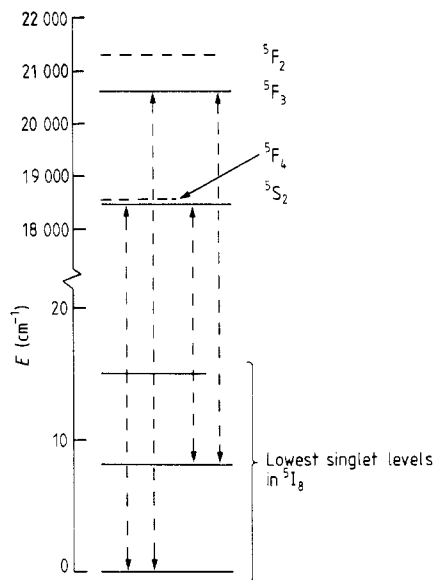


Figure 1. Energy levels in holmium nicotinate dihydrate. The three lowest levels belong to the ground term 5I_8 ; above (not on the same scale) are the four excited multiplets mentioned in the text, with the observed optical transitions.

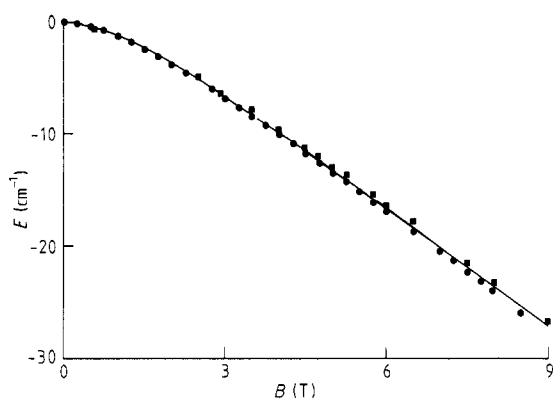


Figure 2. Depression of the energy of the ground singlet in holmium nicotinate, measured by optical absorption spectroscopy with field B along the a axis of the crystal. ■, points from the transition to the excited state 5F_3 . ●, points from the transition to the excited state 5S_2 .

with increasing field. The effects of such movements can be estimated by making measurements involving both multiplets, and the displacement of the ground state by the Zeeman energy can be deduced from the optical measurements.

In the absorption spectrum observed at 4.2 K, transitions from two thermally excited states are also visible. On reducing the temperature they disappear, confirming that they arise from low-lying excited states in the ground multiplet. In zero applied field, the measurements show that above the singlet ground state there is a second singlet with an energy of $8.1(1) \text{ cm}^{-1}$, and a third singlet at $15(1) \text{ cm}^{-1}$. The displacement of the ground singlet by the Zeeman effect, in fields up to 9 T along the a axis of the crystal, is shown in figure 2. In small fields the effect is quadratic, as expected for a singlet, but it becomes linear above a field of 3.5 T, the gradient then being $3.53(3) \text{ cm}^{-1} \text{ T}^{-1}$.

The number of experimental points that can be taken in the optical spectrum at low fields is too small to allow a precise measurement of the quadratic Zeeman effect. However, the range of data up to 9 T can be analysed as a combination of quadratic and linear Zeeman effects by assuming that the ground state has a matrix element only to one excited state. For such a two-level system, the matrix element of J_z between the two

states is found to be 6.09(6), with a separation in zero magnetic field of 10.1 cm^{-1} . A correction is needed to account for the local magnetic fields of other holmium ions in the crystal. This does not alter the matrix element of J_z , but increases the separation to $10.7(1) \text{ cm}^{-1}$. The difference between this and the observed values for the excited singlets is small, and within the limitations of the model.

3. Enhanced nuclear magnetic resonance

3.1. Theory

For a free ion with nuclear spin I , the magnetic Hamiltonian including hyperfine structure is

$$g_J \mu_B (\mathbf{J} \cdot \mathbf{B}) + A_J (\mathbf{J} \cdot \mathbf{I}) - \gamma \hbar (\mathbf{B} \cdot \mathbf{I}). \quad (1)$$

When the $(2J + 1)$ electronic levels are split into singlets by the crystal field, for small values of applied magnetic field the Zeeman effect is quadratic, with energy

$$-\sum_e \langle e | g_J \mu_B B J_z | 0 \rangle^2 / W_e = -(a/2)(g_J \mu_B B)^2$$

for the ground singlet of each ion. Here e is an excited state of energy W_e . In the nicotates, the existence of relatively isolated pairs of ions suggests that each pair should be treated as a unit; where necessary, subscripts 1, 2 are used to identify each ion.

The presence of the second ion may be expected to have an important effect on the enhanced nuclear resonance spectrum. When a magnetic field is applied, the electronic moment induced on the second ion produces an additional field acting on the first ion of the pair, and vice versa. For a pair this can be regarded as a 'bootstrap' effect, and evaluated as follows, the smaller fields of more distant ions being neglected. For small values of field B , applied along a principal axis of the magnetic anisotropy tensor, the electronic energy may be written as

$$W = -(a/2)[g_J \mu_B (B + bm_2) + A_J I_1]^2 - (a/2)[g_J \mu_B (B + bm_1) + A_J I_2]^2. \quad (2)$$

Here, bm_2 is the field at the first ion arising from the electronic moment m_2 on the second ion, and bm_1 the corresponding field at the second ion. The hyperfine energy for the two nuclei is also included in (2) through the terms in A_J . For simplicity, directional subscript x , y or z is omitted, and m , I are shorthand for components along the appropriate axis. In practice the fields $bm \ll B$, so that, of the field of a neighbour, only the component parallel to \mathbf{B} is important.

The combined moment on the two ions is

$$m_1 + m_2 = -dW/dB = a(g_J \mu_B)^2 [(B + bm_2) + (B + bm_1)]. \quad (3)$$

From this the net moment of the dimer is found to be

$$2m = m_1 + m_2 = 2a(g_J \mu_B)^2 B / [1 - a(g_J \mu_B)^2 b] \quad (4)$$

and the electronic energy W can be written in the form

$$W = -(a/2)(g_J \mu_B B' + A_J I_1)^2 - (a/2)(g_J \mu_B B' + A_J I_2)^2. \quad (5)$$

Here $B' = B/[1 - a(g_J \mu_B)^2 b]$ is the effective field acting on one ion, with a similar term for the second ion. Note that in equation (5), the moment m given by $-dW/dB'$ is the same as that obtained by using $-dW/dB$ with equation (2).

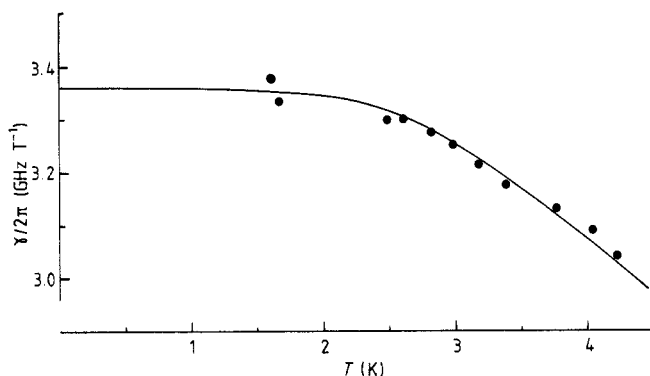


Figure 3. Measured values for the *a* axis of the enhanced nuclear magnetic resonance frequency per tesla, for temperatures from 4.2 down to 1.6 K. The line shows the fit to the relation

$$\gamma/2\pi = A_1 + A_2 \tanh(D/2kT)$$

with $A_1 = 0.6$, $A_2 = 2.76$ (both in GHz T⁻¹), and $D/k = 11.6$.

The Hamiltonian for the quadratic Zeeman effect for a pair of ions, including the nuclear interactions, is then

$$H = -a(g_J\mu_B B')^2 - (I_1 + I_2)B'(\gamma_I\hbar + ag_J\mu_B A_J) - (a/2)A_J^2(I_1^2 + I_2^2). \quad (6)$$

In this expression the enhanced NMR term is

$$(I_1 + I_2)B'(\gamma_I\hbar + ag_J\mu_B A_J) = (I_1 + I_2)B[\gamma_I\hbar + ag_J\mu_B A_J]/[1 - a(g_J\mu_B)^2 b]. \quad (7)$$

This formula shows that the enhancement term for the NMR frequency is proportional to the factor $a/[1 - a(g_J\mu_B)^2 b]$ and not just to a . The induced electronic term is also proportional to $a/[1 - a(g_J\mu_B)^2 b]$ and not to a , so for each ion the usual relation

$$m/\mu_B = (g_J/A_J)\hbar(\gamma - \gamma_I)B \quad (8)$$

is valid. This neglects the small difference between γ_I and $\gamma_I/[1 - a(g_J\mu_B)^2 b]$, which just allows for the additional field at one nucleus generated by the induced electronic moment on the other ion. On the other hand the pseudo-quadrupole terms vary just as a , so they cannot be deduced immediately from the enhancement of the NMR frequency unless the value of b is small (in fact it is less than 0.06).

3.2. Experimental results

Measurements of the enhanced nuclear resonance spectrum have been made at frequencies of 400 to 500 MHz at temperatures from 4.2 K down to 1.6 K. The magnetic field was applied in the plane of reflection symmetry, for which the spectra from the two dimers in unit cell coincide. The spectrum is very anisotropic; at 4.2 K the value of $(\gamma/2\pi)$ varies from 3.27 GHz T⁻¹ along the *a* axis, down to 0.69(2) GHz T⁻¹, along the *b* axis. The average line width (*B* along the *a* axis) is 0.013 T (peak to peak in the line derivative). On reducing the temperature, the line width falls to 0.010 T, and the value of $(\gamma/2\pi)$ along the *a* axis rises to 3.38(4) GHz T⁻¹ at 1.67 K, with a quadrupole splitting corresponding to $|P/h| = 67(1)$ MHz. The variation with temperature is shown in figure 3, together with a fit using the relation

$$(\gamma/2\pi) = A_1 + A_2 \tanh(D/2kT). \quad (9)$$

The second term assumes that contributions arise mainly from the ground singlet and first excited singlet at energy D . These are treated as a split (non-Kramers) doublet with equal and opposite induced moments in the two levels, electronic spin-lattice relaxation being sufficiently fast to give a thermal average for the enhanced NMR. Figure 3 shows

that over the limited temperature range of the experiments, equation (9) is a good approximation, with the values $A_2 = 0.60$, $A_2 = 2.76$ (both in GHz T^{-1}), and $D/k = 11.6$, equivalent to a splitting of 8.1 cm^{-1} . The small constant term A_1 is much larger than the unenhanced nuclear resonance value of 9 MHz T^{-1} , and represents contributions from matrix elements to higher levels. At the resonance frequency of 500 MHz , the applied field of $\approx 0.16 \text{ T}$ increases the separation of the lowest singlets by not more than 0.1 cm^{-1} above the value of D in zero field.

Although the spectrum has not been explored at all possible angles, it is found that $(\gamma/2\pi)$ is lower (2.54 GHz T^{-1}) for directions near the dimer axis, and 1.92 GHz T^{-1} perpendicular to this axis. This shows clearly that the direction of maximum electronic moment induced in the ground singlet is not along the dimer axis. In this respect HoND differs from TmND (Baker *et al* 1986a). Our measurements suggest that the direction of maximum moment in HoND is close to the a axis, so that the magnetic field produced on one Ho ion by the other Ho ion in the dimer is smaller than it would be if the moment were along the dimer axis. (If it were, the field of the neighbour would be about 6% of the applied field.)

4. Conclusion

In low fields, the induced moment on each ion may be estimated from the resonance measurements using equation (8), with the values of the parameters $g_J = 1.242$, $A_J/h = 0.812 \text{ GHz}$. Along the a axis the moment increases to $5.17 \mu_B \text{ T}^{-1}$ at the lowest temperatures. Because of the large enhancement of the nuclear resonance frequency, it would be expected that the most important contribution to the observed nuclear electric quadrupole interaction would arise from the second order effect of the magnetic hyperfine interaction. From the last terms in equation (6), the contribution to P/h is $(A_J/2g_J)[(\gamma_{\perp} - \gamma_{\parallel})/2\pi]$. From the values $\gamma_{\perp}/2\pi = 0.69$, $\gamma_{\parallel}/2\pi = 3.38$ (both in GHz T^{-1}), a quadrupole term of $(-)\text{63 MHz}$ is obtained. This is close to the observed value of $67(1) \text{ MHz}$, and indicates that true quadrupole contributions from the 4f electrons and from the field gradient of neighbouring ions are relatively small.

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References

- Baker J M, Bleaney B, Cook M I, Hutchison C A Jr, Martineau P M and Wells M R 1988 *J. Physique Coll.* **49** C8 1515–6
- Baker J M, Bleaney B, Davoust C E, Hutchison C A Jr, Leask M J M, Martineau P M, Robinson M G, Weber R T and Wells M R 1986a *Proc. R. Soc. A* **403** 199–220
- Baker J M, Hutchison C A Jr, Leask M J M, Martineau P M, Robinson M G and Wells M R 1987 *Proc. R. Soc. A* **413** 515–28
- Baker J M, Hutchison C A Jr and Martineau P M 1986b *Proc. R. Soc. A* **403** 221–33
- Moore J W, Glick M D and Baker W A Jr 1972 *J. Am. Chem. Soc.* **94** 1858–65
- Prout K, Marin J M and Hutchison C A Jr 1985 *Acta Crystallogr. C* **41** 201–4