ENHANCED NUCLEAR MAGNETISM IN $HoVO_4$ (*)

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ABSTRACT — $HoVO_4$ is a Van Vleck paramagnet with a susceptibility which is large perpendicular to the tetragonal crystal axis, but very small parallel to this axis. The nuclear magnetic resonance spectrum of the single stable isotope ^{165}Ho ($I = 7/2$) shows a corresponding anisotropy in the magnetogyric ratio, which is enhanced by a factor of about 170 in the plane normal to the tetragonal axis. The interactions between the enhanced nuclear moments are predominantly dipolar, with a small anti-ferromagnetic component. On this basis the nuclear spins are predicted to order at about 4 to 5 mK in a novel anti-ferromagnetic arrangement. This is consistent with nuclear orientation measurements at temperatures down to 1 mK obtained by magnetic self-cooling. The anisotropy in the γ-ray emission from ^{166m}Ho ($I = 7$) confirms the existence of a 'spin-flop' phase, and the nuclear magnetic moment of this isomer is determined as $3.60 \pm 0.06\ \mu_N$. The sign of the nuclear electric quadrupole parameter of ^{165}Ho in $HoVO_4$ is shown to be positive, $(P/h) = +25.9 \pm 0.3$ MHz.

1 — INTRODUCTION

In a paramagnetic solid compound, the various levels of the magnetic ion are split by interaction with the 'crystal electric field' set up by the ligand ions around the magnetic ion. Such splittings vary from ten to several hundred cm^{-1}, but do not necessarily raise all the degeneracy. For an ion with an odd number of electrons, a

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two-fold degeneracy ('Kramers degeneracy') must remain, which can only be lifted by the application of a magnetic field. Under such circumstances, the magnetic susceptibility, at low temperatures where only a pair of such levels is occupied, follows Curie's law (with a modified value of the Curie constant), until, below some characteristic temperature determined by the interactions between the magnetic ions, an ordered magnetic state sets in. In contrast, for ions with an even number of electrons ('non-Kramers ions'), all the degeneracy may be removed, or at least the ground state is a singlet. Such a singlet state can have no permanent magnetic moment, and at temperatures so low that only this level is populated, the susceptibility reaches a constant value, independent of temperature. This condition is often known as 'Van Vleck paramagnetism', since the explanation was first given by Van Vleck [1]. If the ground state has large matrix elements of the Zeeman interaction with other low-lying states (say at 10 to 20 K), this temperature independent susceptibility may be quite sizeable. Such a situation is most likely to occur for ions of the 4f group, where a magnetic moment per ion of order 1 Bohr magneton can be induced in the singlet state by the application of a field of one tesla.

In such a magnetization, no entropy is removed, and it follows that no magnetic cooling is possible by adiabatic demagnetization in such a simple electronic system. However, the nucleus of such an ion may possess a spin I and a nuclear magnetic moment, with a a nuclear entropy of $R \ln (2I+1)$. When an electronic moment is induced by the application of an external magnetic field, the magnetic hyperfine interaction produces a field at the nucleus which, for a 4f ion, may approach 10^2 tesla for an electronic moment of $1\ \mu_B$. The nuclear levels are then split through the action of this hyperfine field $\mathbf{B}_e$ by an amount which is much larger thant hat produced by the external field $\mathbf{B}$. For moderate values of $\mathbf{B}$, the induced electronic moment $\mathbf{m}$ is proportional to the applied field $\mathbf{B}$, and since $\mathbf{B}_e$ is proportional to $\mathbf{m}$, the net field $(\mathbf{B}+\mathbf{B}_e)$ acting on the nuclear moment is also proportional to $\mathbf{B}$. The nuclear Zeeman energy is

$$-\mathbf{m}_n \cdot (\mathbf{B}+\mathbf{B}_e) = -\mathbf{m}_n \cdot \mathbf{B}\,(1+K) = -\mathbf{m}_n\,(1+K) \cdot \mathbf{B}$$

This equation shows that the Zeeman energy, and the resultant splitting of the nuclear levels, arises from the field $(\mathbf{B}+\mathbf{B}_e)=\mathbf{B}\,(1+K)$, but it can equally well be regarded as resulting from the interaction of **B** with an abnormally large nuclear magnetic moment $\mathbf{m}_n(1+K)$. The latter is called the enhanced nuclear magnetic moment, and K is often called the 'enhancement factor'. In special cases K may be over 100, and the 'enhanced nuclear magnetic moment' may be some tenths of a Bohr magneton.

2 — ENHANCED NUCLEAR MAGNETIC RESONANCE

Magnetic resonance offers the most precise method of measuring a nuclear magnetic moment, and it can obviously be applied to find the size of the enhanced moment. In this section the nature of the resonance spectrum is considered. The discussion is restricted to ions of the 4f group, for which the Hamiltonian may be written as

$$\mathscr{H} = \mathscr{H}_{c.f.} + \mu_B \mathbf{B}.(g_J \mathbf{J} - g_I \mathbf{I}) + A_J (\mathbf{I}.\mathbf{J}) + \mathscr{H}_Q \qquad (1)$$

provided that only terms within the ground manifold J are included. The terms in (1) represent respectively the crystal field interaction, the Zeeman interaction (both electronic and nuclear), together with the magnetic dipole and electric quadrupole hyperfine interactions.

Within a singlet state, the expectation values of the operators J_x, J_y, J_z are all zero. This is no longer true when matrix elements to higher levels are included. In second order, perturbations from the matrix elements of J_x in the Zeeman and magnetic hyperfine terms produce an effective Hamiltonian for the ground singlet of the form

$$\mathscr{H}_x = -a_x \left(1/2 \; g_J^2 \mu_B^2 B_x^2 + g_J \mu_B A_J B_x I_x + 1/2 \; A_J^2 I_x^2\right) \qquad (2a)$$

$$- g_I \mu_B B_x I_x + \mathscr{H}_Q \qquad (2b)$$

together with similar terms in y, z. The parameter a_x in $(2a)$ consists of a sum of terms, each containing the square of a matrix element $<e \mid J_x \mid g>$ between the ground state $\mid g>$ and an excited state $\mid e>$, divided by the difference in energy $(W_e - W_g)$:

$$a_x = 2 \ \Sigma \ <e \mid J_x \mid g>^2 \ / \ (W_e - W_g).$$

The three terms in (2*a*) are respectively the induced electronic Zeeman energy, the enhanced nuclear Zeeman interaction, and a term in I_x^2 which behaves like a quadrupole interaction but is a second order effect of the magnetic hyperfine term $A_J\,(J_x I_x)$. By differentiation with respect to B_x, one finds that the induced electronic moment along the x-axis is

$$m_x = a_X\, g_J^2\, \mu_B^2\, B_x, \tag{3}$$

and the effective nuclear magnetic moment operator, enhanced through the hyperfine interaction, is

$$(a_x\, g_J\, A_J + g_I)\, \mu_B\, I_x = \gamma_x\, \hbar\, I_x. \tag{4}$$

The nuclear terms in (2) can now be expressed by the Hamiltonian

$$\mathscr{H}_n = \Sigma_{x,y,z}\,(-\gamma_x\, \hbar\, B_x\, I_x + P_x\, I_x^2) + \mathscr{H}_Q. \tag{5}$$

The quantity $(\gamma_x / 2\pi)$ gives the enhanced nuclear resonance frequency for $B_x = 1$, when $P_x = 0$. In the absence of any enhancement the frequency would be $(\gamma_I / 2\pi)$, where $\gamma_I\, \hbar = g_I\, \mu_B$, so that

$$(\gamma_x - \gamma_I)\, \hbar = a_x\, g_J\, A_J\, \mu_B \tag{6}$$

is the contribution from the electronic moment through the hyperfine interaction.

In (2a) the terms all contain the one parameter a_x, so that they can be expressed in terms of one measured quantity γ_x. From eq. (3), (6) we have

$$m_x / (\mu_B\, B_x) = (g_J / A_J)\, \hbar\, (\gamma_x - \gamma_I) \tag{7}$$

and this gives the electronic moment in Bohr magnetons induced by unit flux density. Similarly,

$$P_x = -1/2\, a_x\, A_J^2 = -\,1/2\,(A_J/g_J\,\mu_B)\,\hbar\,(\gamma_x - \gamma_I)\,. \tag{8}$$

In general the values of $\gamma_x, \gamma_y, \gamma_z$ will be all different, depending on the local symmetry at the magnetic ion. If this symmetry is axial, the complete nuclear Hamiltonian may be written in the form

$$\mathscr{H}_n = -\gamma_{\parallel}\,\hbar\,B_z\,I_z - \gamma_{\perp}\,\hbar\,(B_x\,I_x + B_y\,I_y) + P\,[I_z^2 - 1/3\,I\,(I+1)], \tag{9}$$

where $P = P_1 + P_2 + P_3$ is the sum of three contributions. The second of these arises from the second order effect of the magnetic hfs; from eq. (8) we have

$$P_2 = P_z - 1/2\,(P_x + P_y) = 1/2\,(A_J/g_J\,\mu_B)\,\hbar\,(\gamma_{\perp} - \gamma_{\parallel})\,. \tag{10}$$

P_1 and P_3 arise from $\mathscr{H}_Q$, and represent interactions of the nuclear electric quadrupole moment with the electric field gradients of the 4f elecron cloud and of the lattice respectively. They are given by the standard formulae [2]:

$$P_1 = -\,\frac{3\,e^2\,Q\,<r^{-3}>}{4\,I\,(2\,I-1)}\,<J\,\|\,\alpha\,\|\,J>\,<3J_z^2 - J\,(J+1)>, \tag{11}$$

where $<3\,J_z^2 - J\,(J+1)>$ is the expectation value for the ground singlet state, and

$$P_3 = -\,\frac{3\,Q\,A_2^0}{I\,(2\,I-1)}\,(1-\gamma_{\infty})\,. \tag{12}$$

The advantage of an enhanced n. m. r. experiment is that it can measure the principal values $\gamma_x, \gamma_y, \gamma_z$ for each ion. For axial symmetry these reduce to two, $\gamma_{\parallel} = \gamma_z$, and $\gamma_{\perp} = \gamma_x = \gamma_y$. Then the induced electronic moment per unit field can be calculated by using equation (7), which shows it will have similar anisotropy to γ. Also, the 'pseudo-quadrupole' interaction can be found by using (8), or, with axial symmetry, eq. (9). These calculations require only the values of g_J and A_J, which for lanthanide (4f) ions are known with precisions of order 1%. This means that P_2 is in general known much more accurately than P_1 or P_3.

3 — RESONANCE MEASUREMENTS ON $HoVO_4$.

$HoVO_4$ has the tetragonal zircon structure, in which all the Ho^{3+} ions are magnetically equivalent with tetragonal symmetry about the crystal c–axis, which we take to be the z–axis. The ground state of the Ho^{3+} ion is $4f^{10}$, $^5I_8$; thus $J = 8$, and $g_J = 1.242$. For the single stable isotope ^{165}Ho, $I = 7/2$, and $A_J = +812$ MHz, $(\gamma_I / 2\pi) = 9.0$ MHz T^{-1}. The crystal field acting on the Ho^{3+} ion has tetragonal symmetry, and splits the $(2J + 1) = 17$ states into 9 singlets and 4 doublets. Optical spectroscopy [3] has shown that the ground state is a singlet, which in a good approximation can be characterized as $|J_z = 0>$. The first excited state is a doublet at 21 cm^{-1} = 30 K, which on the same basis can be written as $|J_z = \pm 1>$. For the singlet, matrix elements of J_z (with levels above 200 cm^{-1}) are small; on the other hand there are large matrix elements of J_x, J_y (or J_+, J_-) with the doublet at 21 cm^{-1}. Thus at helium temperatures the electronic susceptibility should be independent of temperature, very small along the c-axis but large in the plane normal to this axis, as found by Swithenby [4].

Enhanced n.m.r. measurements [5] have been made at frequencies up to 500 MHz on single crystal samples of $HoVO_4$, and on diluted crystals containing 2% and 0.1% of Ho in YVO_4. In the latter two samples, the value of $(\gamma_\perp / 2\pi)$ at 2 K is 1526 ± 3 MHz T^{-1}, while $|P/h|$ is 25.3 ± 0.2 MHz; no precise measusement of $(\gamma_\parallel / 2\pi)$ could be obtained, but it is estimated to be about 15 to 20 MHz T^{-1}. From these results the corresponding values of the induced electronic moment are calculated using eq. (7) above to be 2.32 μ_B per tesla perpendicular to c-axis, and ~0.02 μ_B per tesla parallel to this axis. This confirms that the anisotropy is very large, about 100 to 1. The sign of P cannot be determined in such a resonance experiment, but the three contributions to (P/h) are $(P_2/h) = +35.3 \pm 0.1$ MHz, $(P_1/h) = -34 \pm 1$ MHz, and $(P_3/h) = +5$ to $+10$ MHz. The first of these is the most accurate, being calculated using eq. (8) above;

the last contribution, from the lattice, is the most uncertain and should be of the order of 25 MHz to account for the observed value of $|P/h| = 25.9 \pm 0.3$ MHz for $HoVO_4$.

The magnetic resonance spectrum of ^{165}Ho is shown in fig. 1 for 2% Ho in YVO_4 and for concentrated $HoVO_4$. In the latter case the measured values of $(\gamma_\perp/2\pi)$ range from 1625 MHz T^{-1} down to 1260 MHz T^{-1}, depending on the shape of the sample. This shows that the internal field has values up to ±10% of the applied field, The apparent variation of $\gamma_\perp$ with sample shape arises from changes in the demagnetizing field, and the results confirm that these are in excellent agreement with the values calculated from the induced moment of 2.32 μ_B per tesla quoted above. On the other hand the value of $|P/h|$ is independent of shape and the same as in the diluted crystals. In view of the large contribution

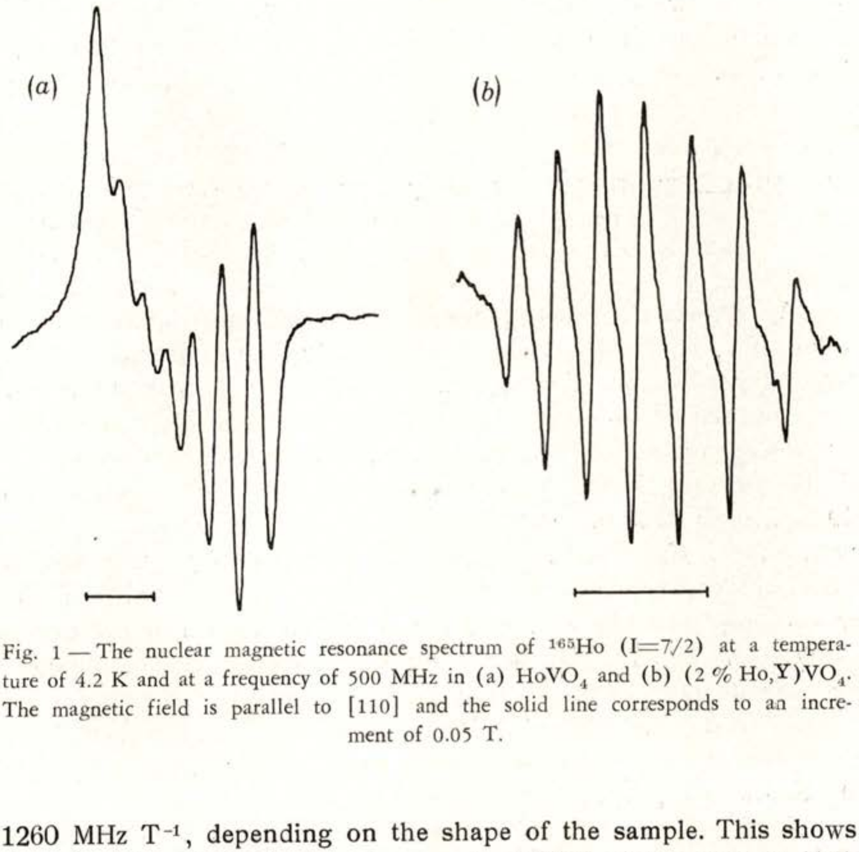

Fig. 1 — The nuclear magnetic resonance spectrum of ^{165}Ho $(I=7/2)$ at a temperature of 4.2 K and at a frequency of 500 MHz in (a) $HoVO_4$ and (b) $(2\%\ Ho,Y)VO_4$. The magnetic field is parallel to [110] and the solid line corresponds to an increment of 0.05 T.

to P from P_2, which is directly proportional to $\gamma_\perp$ (see eq. (10)), it is reasonable to assume that $\gamma_\perp$ is really the same in the concentrated as in the dilute crystals. This is an important deduction, because there is no other way in which the true value of $\gamma_\perp$ (i.e., the value it would have if the internal field were zero) can be ascertained without making some assumption about the nature of the interactions between the ions. These interactions are mainly dipolar, but by taking the actual value of $\gamma_\perp$ to be the same as in the dilute crystals, it can be shown from the measured values of $\gamma_\perp$ that there is a small contribution to the internal field from anti-ferromagnetic exchange interaction.

4 — THE NUCLEAR MAGNETIC MOMENT OF ^{166m}Ho.

An immediate consequence of the large enhancement of the value of $\gamma_\perp$ is that it becomes comparatively easy to produce a large nuclear polarization. For $(\gamma_\perp / 2\pi) = 1.5$ GHz T^{-1}, a field of 2 T perpendicular to the c-axis of the crystal results in a splitting between successive nuclear levels of 3 GHz, which in temperature units is equivalent to 144 mK. In thermal equilibrium at a temperature of 40 mK, over 95% of the ^{165}Ho nuclei will occupy the extreme state with $|I_z| = I$. Under such conditions the emission of γ-rays following the decay of a radioactive holmium nucleus such as ^{166m}Ho $(I = 7)$ will be highly anisotropic. A study of the rate at which the anisotropy grows as a function of the size of the applied field should give an accurate ratio of the nuclear magnetic moment of the radioactive isotope relative to that of ^{165}Ho. Measurements of this type have been carried out in Oxford by the nuclear orientation group of Dr. N. J. Stone [6].

Neutron irradiation of a single crystal of $HoVO_4$ produces ^{166}Ho $(I = 0)$, which has a half-life of 27 hours and decays relatively quickly, together with the isomeric state ^{166m}Ho, with a half-life of 1200 years. This isomer decays to ^{166}Er by emitting a β^- particle, followed by a rather complex cascade of γ-rays. The anisotropy of six of these γ-rays, with energies ranging from 184 to 752 keV, have been studied using a single crystal attached to the cold finger of a dilution refrigerator. Measurements of the anisotropy for two of the γ-rays, together with the theoretical fits, are shown in fig. 2. A complete analysis of the data for all six γ-rays gives the magnetic moment of ^{166m}Ho as (+) $3.60 \pm 0.06\ \mu_N$, assuming that of ^{165}Ho to be $+4.125 \pm 0.044\ \mu_N$, as determined by an atomic beam experiment [7].

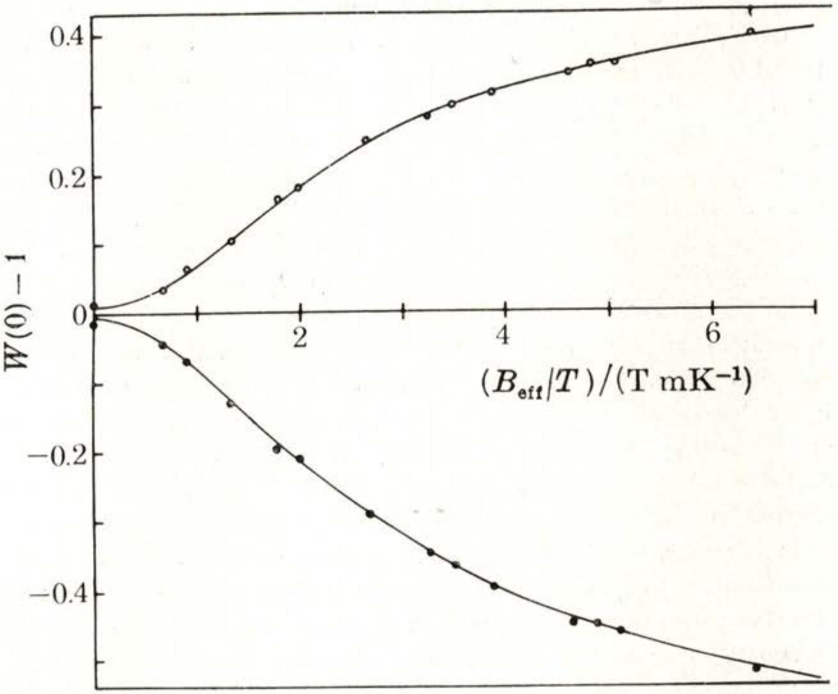

Fig. 2 — Anisotropy in the emission of the 280.5 keV (below) and the 711.7 keV (above) γ-rays from ^{166m}Ho in $HoVO_4$ as a function of B_{eff}/T. B_{eff} is the total magnetic field (applied + hyperfine) acting on the nuclear moment, in tesla, and the temperature is in units of milliKelvin.

5 — NUCLEAR MAGNETIC ORDERING

The conditions of B = 2 tesla and T = 40 mK under which the nuclei are almost completely polarized are of course just those under which the nuclear entropy, which in zero field is R ln $(2I+1) =$

$= R \ln 8$ for ^{165}Ho, has been reduced almost to zero. It follows that an adiabatic demagnetization from such starting conditions must cool the ^{165}Ho nuclei to such a low temperature that they enter a magnetically ordered state. The nature of the ordering depends on the interactions between the Ho nuclear spins. Fortunately, the size of these interactions can in large measure be deduced from the n.m.r. experiments at 2 to 4 K, as can be seen from the following discussion.

In $HoVO_4$ the observed n.m.r. frequency is shifted by the internal field set up by the induced electron moments on the surrounding Ho^{3+} ions, discussed in § 3. In § 2 it has been shown that there is a simple direct relation (eq. (7)) between the induced electronic moment per unit field, and the enhancement of the nuclear moment. By the use of this relation it can be shown [8] that the interactions between the enhanced nuclear moments are mainly dipolar, together with a small anti-ferromagnetic contribution. Since the shift in the nuclear resonance frequency depends only on the *sum* of the local fields, a similar limitation must be present in the information which can be derived about the inter-nuclear interactions. The dipolar interactions can be calculated for every pair of nuclei, but the exchange interactions cannot. It is therefore necessary to introduce an assumption in the latter case. Each Ho ion has four equidistant nearest neighbours, to each of which the bond is similar, involving a path containing only one oxygen ion. It is therefore assumed that the exchange interaction is the same with each of these four neighbours, and zero with all other neighbours, which are considerably further away. On this basis it turns out that the interactions with the four nearest neighbours are still mainly dipolar in origin, and no serious error is introduced by the assumption that interactions with more distant neighbours are completely dipolar.

The large anisotropy in γ means that interactions involving the z-components of the enhanced nuclear moments, which are proportional to $\gamma_{\parallel}^2$, are negligible compared with those involving $\gamma_{\perp}^2$. The nuclei must therefore order, in the plane perpendicular to the c-axis. The four nearest neighbours (nn) lie at equal distances along the x- and y-axes, two above and two below the xy-plane; for the purposes of discussion it is a convenient simplification to treat them as if actually in this plane. Two equivalent ordered spin systems, based on predominantly dipole interactions, are shown in fig. 3. The 'end-on' positions are occupied by dipoles parallel to the central dipole; and the 'broadside-on' positions by anti-parallel dipoles; thus the fields of all four nn add at the centre. Interactions with dipoles outside the diamond shown in the figure are small compared with those inside, and the arrangement gives the largest field at the centre, parallel to the central dipole, and hence the lowest energy.

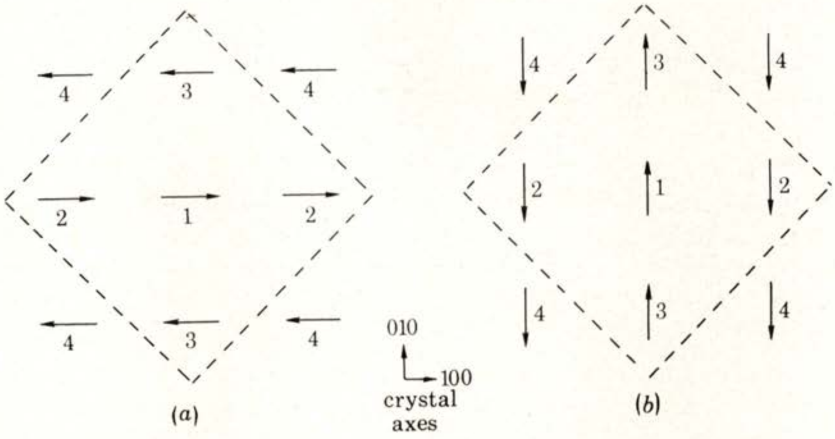

Fig. 3 — Two equivalent anti-ferromagnetic arrangements of the nuclear moments in $HoVO_4$ which give the minimum energy when the interactions between the moments are predominantly dipolar. The largest interactions are those between an ion and its four nearest neighbours lying within the diamond indicated by the broken lines.

Any dipole in the lattice has the same arrangement of neighbours, so that the correct translational symmetry is preserved. The system corresponds to a simple two sub-lattice anti-ferromagnet. If a moment of 1 μ_B exists on each site, the 'molecular field' at each site in this arrangement is $B_{a.f.} = 0.0734$ tesla. An interesting feature of the arrangement is that $B_{a.f.}$ is independent of the size of the anti-ferromagnetic exchange, since two nn are parallel and two anti-parallel, so that their exchange fields cancel. Of course, this occurs only because the dipole forces predominate. If the anti-ferromagnetic exchange were larger by a factor of about four, the stable ordered arrangement would become one in which all four nn are anti-parallel.

A more delailed investigation [8] reveals that there exists a whole range of four sub-lattice 'puckered' arrangements of the type shown in fig. 4. Here the dipoles still all lie in the (001) plane, and each is equally inclined to the four-fold crystal axes. Calculation shows that the energy is independent of the angle β, and is the same as for the arrangements of fig. 3, which correspond to the special cases where $\beta = 0$ and $90°$. However, as soon as an external field is applied along one the four-fold axes, these 'puckered' arrangements become unstable, and the system changes to a simple two sub-lattice anti-ferromagnetic arrangement in which the dipoles are perpendicular to the applied field ('spin-flop'). As the applied field B is increased the dipoles turn towards it, becoming parallel to it when B exceeds a certain critical value. For purely dipolar interactions, the value of this critical field is 0.0146 tesla per μ_B, but when the anti-ferromagnetic exchange interaction is included, it becomes 0.035(8) tesla per μ_B.

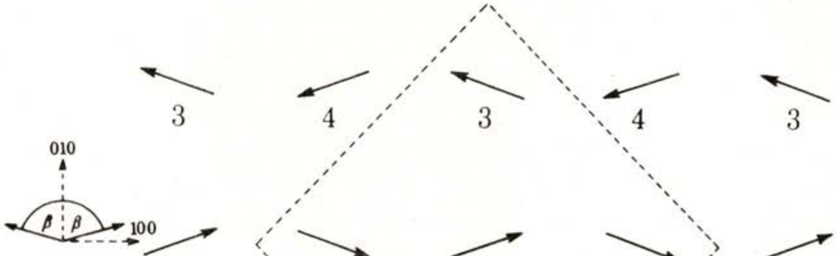

Fig 4 — A 'puckered' arrangement of the nuclear moments. Ions 1,2,3,4 lie on four different sub-lattices. The energy is independent of the angle β, and is the same as for the two sub-lattice configurations of fig. 3, which are special cases corresponding to $\beta = 0°$ and $90°$.

6 — CALCULATION OF THE NÉEL TEMPERATURE

On a molecular field model, the condition for an ordered state to set in can be derived as follows. In each sub-lattice, the magnetic moment is given by

$$m = \chi\,(B + B_{a.f.}\,m) \qquad (13)$$

where m, χ are the magnetic moment and susceptibility and $B_{a.f.}$ is the molecular field per unit moment calculated for the ordered state. (To avoid problems about units, we work always in μ_B per ion; thus the unit of χ is μ_B per tesla). Eq. (13) may be written in the form

$$m\ (1 - \chi B_{a.f.}) = \chi B, \qquad (14)$$

from which it appears that when $\chi\ B_{a.f.} = 1$, a finite value of m (spontaneous magnetization) can exist when $B = 0$. Thus an ordered state sets in at temperatures below the point at which χ exceeds $(B_{a.f.})^{-1}$, and no assumption is made about the way in which χ varies with temperature.

In this relation χ is the sum of the enhanced nuclear susceptibility χ_n, calculated for zero interaction between the spins, and the temperature-independent contributions from the induced electron moments. The latter is 2.32 μ_B per tesla, while the former can be calculated from the values of $\gamma_\perp$ and P. If P were zero, χ_n would follow Curie's law; however, the overall quadrupole splitting is $12\ (P/h) = 310$ MHz, which is equivalent to about 14 mK, so that departures from Curie's law become significant in the mK region. The n.m.r. results provide the values of $\gamma_\perp$ and of $|P|$, but do not determine the sign of P, though it is probably positive. The nuclear susceptibility can readily be calculated for either sign of P, and the results are shown in fig. 5, where the contribution from the induced electron moment has also been included. If P is negative, the lowest nuclear levels are $I_z = \pm 7/2$, which have no moment perpendicular to the c-axis; χ_n therefore reaches a value almost independent of temperature below about 10 mK. If P is positive the lowest levels are $\pm 1/2$, which have large perpendicular moments; χ_n therefore rises above the Curie's law value, as shown in fig. 5. The Néel temperature occurs when χ attains the value $(B_{a.f.})^{-1} = (0.0734)^{-1}$, giving $T_N = 4.8$ mK if P is positive. This prediction has been confirmed

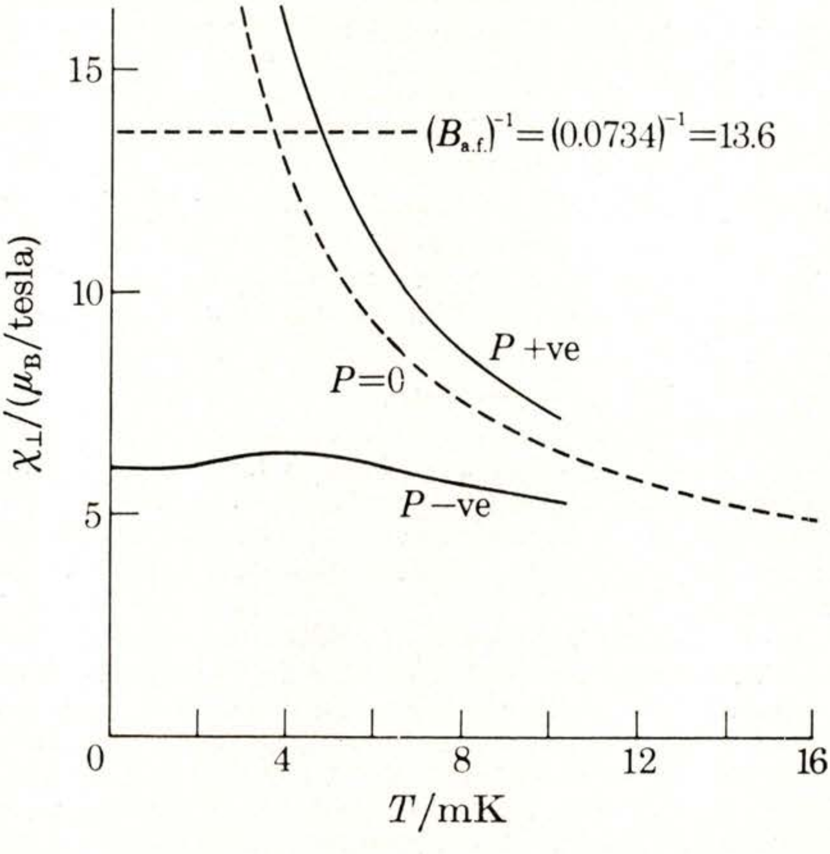

Fig. 5 — The perpendicular susceptibility of $HoVO_4$ in the mK region. $\chi(T) = 2.32 + F(T)$, where 2.32 μ_B per tesla is the induced electron moment and F(T) is calculated from the spin Hamiltonian (eq. 9) for $P/h = +25.9$ MHz and for $P/h = -25.9$ MHz. For $P = 0$, $F(T) = 41.9$ μ_B per tesla. The Néel temperature is given by the intersection of the broken horizontal line with the calculated susceptibility curve.

experimentally by measurements of the radio-frequency susceptibility after adiabatic demagnetization [9], which show a maximum in the region 4 to 5 mK. This confirms that P is positive, since fig. 5 shows that there is no anti-ferromagnetic solution when P is negative.

Fig. 5 shows also that the main part of the susceptibility below 20 mK arises from the enhanced nuclear moments, since the electronic term is constant at 2.32 μ_B per tesla. As T tends to zero, the limiting value of the enhanced nuclear moment reaches $(7/2)\ \gamma_\perp \hbar$, which is equal to 0.38 μ_B. To this the induced electronic moment adds an amount $2.32\ B_{a.f.} = 0.08\ \mu_B$, giving a total moment of 0.46 μ_B. The true' nuclear moment is only 0.0022 μ_B, confirming that the main part of the enhanced nuclear moment is electronic in origin. From the value of the total moment, the size of the applied field as $T \rightarrow 0$ needed to produce orientation of all the dipoles parallel to it (as in a ferromagnet or saturated paramagnet) is $0.46 \times 0.035 = 0.016$ tesla, where 0.035 tesla per μ_B is the critical field per unit moment given at the end of § 5.

7 — NUCLEAR ORIENTATION MEASUREMENTS IN THE ANTI-FERROMAGNETIC PHASE.

In conclusion, we discuss investigations [6] of the anti-ferromagnetic phase of HoVO$_4$ using nuclear orientation techniques. These consist of measurements of the anisotropy in the emission of γ-rays from ^{166m}Ho $(I = 7)$ in the temperature region reached by magnetic self-cooling of the ^{165}Ho nuclear system. A single crystal of HoVO$_4$ is attached to the cold finger of a dilution refrigerator, and magnetized in a field of 1.8 tesla at a temperature of 35 mK. This removes nearly all the nuclear entropy, and on demagnetization final temperatures of 1 mK are reached (estimated from entropy calculations). In the residual field (0.002 T) of the superconductive magnet, a large anisotropy in the γ-ray emission is observed, with axial symmetry about the c-axis of the crystal. This is precisely what would be expected from a pure quadrupole splitting of the nuclear levels, if the crystal remained in a paramagnetic state. However, just the same result would be obtained in the anti-ferromagnetic phase, either with equal numbers of domains oriented in the two directions shown in fig. 3, or with the puckered arrangements of fig. 4., provided that all values of the angle β are equally probable. These observations do not therefore necessarily imply the existence of magnetic order. The latter is, however, confirmed by the following experiments.

A number of measurements were made in which the nuclear demagnetization ended at final fields of up to 0.042 T, applied along an a-axis of the crystal. With $B = 0.042$ T, a large anisotropy in the emission of γ-rays appears in the plane normal to the crystal c-axis. This shows that ferromagnetic alignment of the spins, parallel to the applied field, has been achieved, and confirms that the temperature is still about 1 mK. In experiments at smaller final fields, such as 0.012 T, the spins orient themselves at right angles to the applied field. This confirms the existence of a 'spin flop' phase, which is consistent only with anti-ferromagnetism in the nuclear spin system.

8 — CONCLUSION.

This paper gives a short review of the experimental information which has been obtained on enhanced nuclear magnetism in single crystals of $HoVO_4$. The starting point is an investigation at liquid helium temperatures using nuclear magnetic resonance [5]. This gives, for the stable isotope ^{165}Ho ($I = 7/2$), the size and anisotropy of the enhancement of the nuclear magnetic moment, together with the nuclear electric quadrupole interaction. The experiments show also that the interactions between the nuclear spins and the induced electron moments of the Ho^{3+} ions are close to those calculated for purely dipolar forces, together with a small contribution from anti-ferromagnetic exchange interaction. Independent measurements of the nuclear susceptibility at temperatures down to 100 mK have been shown to be in excellent agreement with the n.m.r. results, in a paper [10] not discussed above.

From the n.m.r. experiments, predictions can be made [8] about the nature of the ordered phase in the nuclear spin system, and the ordering temperature T_N. The interactions between the enhanced nuclear moments are shown to be mainly dipolar, and novel types of spin arrangements are expected, with a variety of anti-ferromagnetic configurations. These predictions are consistent with the results obtained in nuclear orientation experiments [6] using the γ-ray emission from ^{166m}Ho ($I = 7$), and the value of the nuclear magnetic moment of this isomer is obtained with an accuracy of about 2 %.

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