NMR-ON STUDIES OF EUROPIUM VANADATE AND HCP COBALT

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Abstract

The quadrupole interaction on Eu^{3+} in $EuVO_4$ was investigated using low temperature nuclear orientation. The interaction strength, P, on the ¹⁵²Eu nuclei was measured as 1±4 MHz, with a total cooling time of 24 hours. This low value is attributed to either the high symmetry of the europium lattice postion, or a very long (greater than one day) spin lattice relaxation time.

The NMR frequency of 59 Co was measured at low temperature, using the first observation of thermometric NMR in a conductor. The motive was to measure the frequency pulling in cobalt metal, and the resonance was observed to be 218.4(4) MHz at 70mK, which is 1.5 MHz below the 1 K value. The frequency pulling effect on the nuclear resonance is due to the Suhl-Nakamura interaction between the nuclear spins.

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Chapter 1

Theory

1.1 Introduction

This thesis describes investigations made using low temperature nuclear orientation and nuclear magnetic resonance on ordered nuclei on $EuVO_4$ and hexagonal close packed (hcp) cobalt.

1.1.1 Europium Vanadate

Europium vanadate is a Van Vleck paramagnet, with the zircon crystal structure. The conditions at Eu^{3+} defect sites have recently been investigated in some depth (see Chapter 3.) For reasons of crystal symmetry, the techniques employed in these experiments (which are based on optical hole-burning) are unable to investigate the Eu^{3+} lattice positions. The aim of the investigations into $EuVO_4$ was to measure the strength of the quadrupole interaction on the europium nuclei at the Eu^{3+} lattice sites.

1.1.2 Cobalt

During investigations into the NO characteristics of 89m Y in hcp cobalt, the Munich group observed an anomalous line shape at approximately 217MHz in the yttrium nuclear magnetic resonance[1]. It has been suggested (Turrell[2]) that this was due to the nuclear resonance of the cobalt host being frequency-pulled by nuclear spin-spin interactions down to the yttrium resonance. The line shape then resulted from the heating effect due to

absorption of rf power by the *cobalt* spins in the same manner as is observed in the thermometric technique pioneered by Kotlicki and Turrell[3].

The low-temperature resonance (T < 1 K) of ⁵⁹Co has not been measured before. Also the thermometric technique first used by Kotlicki and Turrell has not been applied to conductors. For these reasons, the measurement of the low temperature NMR line in stable cobalt is an interesting goal to pursue.

This chapter describes the background theory required to understand the experiments and their results. Chapter 2 will explain the experimental setup. The results for europium vanadate are presented in Chapter 3 and those for cobalt in Chapter 4. In this chapter, Section 1.2 introduces the physical principles behind nuclear orientation (NO) and nuclear magnetic resonance on oriented nuclei (NMR-ON), section 1.3 covers the theory of NO in more detail, section 1.4 discusses hyperfine interactions, and Section 1.5 covers NMR. Frequency pulling—the effect investigated in cobalt—is introduced in Section 1.6.

1.2 Introduction to NMR-ON

Nuclei with non-zero spin have a magnetic dipole moment and those with spin greater than one half have an electric quadrupole moment. (The nuclear magnetic moments and quadrupole moments of ⁵⁹Co, ⁶⁰Co, ¹⁵²Eu and ¹⁵⁴Eū are shown in Table 1.1.) Interactions between the magnetic moment and a magnetic field, and/or the electric quadrupole moment and an electric field gradient (EFG), will lead to a discrete set of energy sublevels of the nucleus, the different orientations of the spin relative to the magnetic field / EFG having different energies. A nucleus with magnetic dipole moment $\vec{\mu}$ and quadrupole moment Q_{ij} in a magnetic field \vec{B} and electric potential V has a classical energy

$$E = \vec{\mu} \cdot \vec{B} + \sum_{i} Q_{ii} \frac{\partial^2 V}{\partial x_i^2}.$$
(1.1)

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·	Isotope	Spin	Dipole Moment	Quadrupole Moment
			μ_N	bn
	⁵⁹ 27Co	7/2	+4.627(9)	+0.41(3)
`	$_{27}^{60}$ Co	5	+3.799(8)	+0.44(5)
	¹⁵² ₆₃ Eu	3	-1.95	+2.71
	¹⁵⁴ ₆₃ Eu	3	+1.5	+2.3, 3.9

Table 1.1: Nuclear electric quadrupole and magnetic dipole moments for the Co and Eu nuclei studied [4].

If the \vec{B} and $\nabla^2 V$ are directed along the z-axis, i.e. there is axial symmetry, then the nuclei can be described by the orthonormal states $|II_z\rangle$, and the Hamiltonian for the nuclei is:

$$\mathcal{H} = I_z \Delta_\epsilon + P[I_z^2 - \frac{1}{3}I(I+1)]$$
(1.2)

with

$$\Delta_{\epsilon} = \frac{\mu B}{I} \tag{1.3}$$

$$P = \frac{3}{4}eQ\frac{\partial^2 V}{\partial x^2}\frac{1}{I(2I-1)}$$
(1.4)

Usually one deals with a situation where the interaction is dominated by either the dipole or quadrupole interaction. The nuclear sub levels in these cases are shown in Figure 1.1 for ⁶⁰Co (I = 5) in a magnetic field and ¹⁵²Eu (I = 3) in an EFG.

Gamma ray emission from an individual nucleus is, in general, anisotropic—the probability distribution for the γ -ray will be a function of the angle between the detector and the nuclear spin axis. If, therefore, one can create an ensemble of nuclei with net orientation (for example, an alignment of the nuclear spins in a given direction,) one would expect to observe an anisotropy in the emission of γ -rays. If an ensemble of nuclei is held in a field at a low enough temperature (of the order of the nuclear level splitting) then the lower energy states will be more populated than the higher states, leading to a



Figure 1.1: Nuclear sublevels for: a) 60 Co in a magnetic field and b) 152 Eu in an EFG, both along the z-axis.

net orientation of the nuclei. This is the method of *low temperature nuclear orientation* (LT-NO.)

Figure 1.2 shows the angular distribution of the normalised γ -ray intensity from hcp ⁶⁰Co<u>Co</u> at three temperatures. Note how, as the temperature approaches zero, the radiation intensity in the direction of the c-axis (along which the magnetisation lies, and about which the system possesses axial symmetry) tends to zero, while the intensity of the radiation perpendicular to the c-axis reaches a value of approximately 1.25 times the warm intensity.

In nuclear magnetic resonance nuclei are excited between their magnetic sublevels by radiofrequency (rf) radiation, tuned to the energy difference between these levels. This excitation causes a change in the level populations, and will therefore cause a change in the observed anisotropy of the γ radiation from the sample. In NMR-ON the nuclear resonance frequency is measured by observing this change in anisotropy.



Figure 1.2: Calculated polar plot of normalised γ -ray intensity, $W(\theta)$, for hcp ${}^{60}\text{Co}\underline{\text{Co}}$ at T=5, 15, and 100 mK. The vertical axis is parallel to the c-axis, and the magnetic field at the nucleus.

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Figure 1.3: Simplified ⁶⁰Co Decay Scheme. Numbers on right indicate the spin and parity of the nuclear state. Both γ rays are pure quadrupole. The β particle has a maximum energy of 330 keV.

The theory of nuclear orientation is well established, and for a more complete derivation of the results discussed below the reader is referred to *Low Temperature Nuclear Orientation*[5], and in particular Chapter 2 by Krane[6]. The NO notation used here was first formally set up by Blin-Stoyle and Grace[7].

1.3 Probability Distribution from Oriented Nuclei

1.3.1 Physical Background

The emission of a γ -ray from a nucleus will typically be preceded by a β or α particle decay, or electron capture. This will lead to one or more intermediate nuclear states, from one of which the observed γ -ray is emitted. A typical simplified decay scheme (in this case ⁶⁰Co) is shown in Figure 1.3. We shall first look at the γ decay of a parent nucleus, of known initial conditions, and later introduce the effects of intermediate radiations between the known state and the state from which the γ -ray is emitted.

Consider a nucleus of spin I_i in a magnetic field along the z-axis, which decays via a γ

decay of pure multipole order 2^{L} to a nucleus of spin I_{f} . (We shall not consider here the effect of a mixed-order decay.) The nucleus has $2I_{i} + 1$ possible values of its z-component of spin, m_{i} , with occupation probabilities $a_{m_{i}}$.

Ignoring polarisation effects, the directional (by which we mean angular) probability distribution of the gamma ray from a known state, m_i , is given by summing the directional distribution of each of the possible decays, weighted by their relative probabilities, as given by angular momentum coupling theory. For a γ -ray of known z-component of spin, M, the directional distribution is the modulus-square of the spherical harmonic $Y_L^M(\theta, \phi)$. The angles θ and ϕ are the usual spherical coordinates, between the detector and the z-axis. The distribution from the state m_i is therefore:

$$W_{m_i}(\theta) = \sum_{m_i \to m_f} w(m_i \to m_f) |Y_L^M(\theta, \phi)|^2, \qquad (1.5)$$

with $m_i = m_f + M$.

The initial state of the nucleus, $|I_i, M_i\rangle$, can be written as a superposition of the product states $|L, M\rangle|I_f, m_f\rangle$ of the γ -ray and the final nuclear state. Using the Wigner-3j notation:

$$|I_i, m_i\rangle = \sum_M |I_f, m_f\rangle |L, M\rangle (-1)^{I_i + m_i} (2I_i + 1)^{1/2} \begin{pmatrix} I_i & I_f & L \\ m_i & -m_f & -M \end{pmatrix},$$
(1.6)

with $m_i - m_f - M = 0$. Therefore, if we start in the known state $|I_i, m_i\rangle$ the $w(m_i \to m_f)$ are simply the squares of the coefficients of the $|I_f, m_f\rangle|L, M\rangle$:

$$w(m_i \to m_f) = (2I_i + 1) \begin{pmatrix} I_i & I_f & L \\ m_i & -m_f & -M \end{pmatrix}^2.$$
 (1.7)

(For those who are unfamiliar with the Wigner 3-j notation, they are related to the Clebsch-Gordan coefficients by:

$$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} = \frac{(-1)^{j_1 - j_2 - m}}{\sqrt{2j + 1}} C(j_1 m_1, j_2 m_2; j - m)$$
(1.8)

with $|j_1 - j_2| \le j \le j_1 + j_2$, and $m_1 + m_2 + m = 0$.)

Returning to the case of the parent nucleus in an orienting field, the distribution is found by summing the weighted contribution from each parent state:

$$W(\theta) = \sum_{m_i} a_{m_i} W_{m_i}(\theta).$$
(1.9)

If the parent spins are in thermal equilibrium with the lattice, the a_{m_i} are simply described by the Boltzman distribution

$$a_{m_i} = \frac{e^{-\beta\epsilon_i}}{\sum_{m_i} e^{-\beta\epsilon_i}},\tag{1.10}$$

$$\beta = 1/k_B T. \tag{1.11}$$

Whilst this formulation of the directional distribution gives a simple physical insight into the process of NO, it is very unwieldy to calculate, and gives no simple comparison between the anisotropy of one γ decay and another. (It *is* useful, however, where one is selectively exciting a particular nuclear sub-level, as, for instance, in a quadrupole interaction, or a magnetic interaction perturbed by a quadrupole interaction. In this case, writing the anisotropy in terms of the occupation probabilities is the most straightforward analysis.) Further, if the decay is preceded (as is almost always the case) by one or more (usually unobserved) nuclear decays, the calculation of the a_{m_i} would be a very laborious process, since the population distributions within the daughter nucleus would have to be calculated from the distributions of the parent, a_{m_0} , using angular momentum coupling, which gives:

$$a_{m_i} = \sum_{m_0} a_{m_0} (2I_0 + 1) \begin{pmatrix} I_i & I_f & L \\ m_i & -m_f & -M \end{pmatrix}^2.$$
(1.12)

1.3.2 Nuclear Orientation Parameters

The oriented nuclear state may alternatively be described in terms of the statistical tensors[6]:

$$\rho_q^k(I_i) = \hat{k} \sum_m (-1)^{(I_i+m')} \begin{pmatrix} I_i & I_i & k \\ -m' & -m & q \end{pmatrix} \langle I_i m | \rho | I_i m' \rangle$$
(1.13)

$$\hat{x} = (2x+1)^{1/2},$$
 (1.14)

which describe the initial (mixed) state of the nuclei in an ensemble. Here ρ is the density matrix describing the initial state of the nuclei,

$$\rho = \sum_{m_1, m_2} |I_i m_1\rangle \langle I_i m_2|. \tag{1.15}$$

The directional distribution of the radiation is now written as

$$W(\theta,\phi) = \sqrt{4\pi} \hat{I}_i \sum_{kq} \rho_q^k(I_i) F_k \hat{k}^{-1} Y_k^q(\theta,\phi), \qquad (1.16)$$

where the F_k are the directional distribution parameters, which will be described later.

If the system possesses axial symmetry about an axis (typically a crystal axis, or the applied field) and we choose the z-axis in this direction, then $\langle I, m | I, m' \rangle = \delta_{m,m'}$ and the density matrix ρ will be diagonal, i.e.

$$\langle I_i m | \rho | I_i m' \rangle = a_m \delta_{m,m'}. \tag{1.17}$$

(Note that the off-diagonal terms of the density matrix are usually negligible in comparison to the diagonal terms. If the system possessed exact axial symmetry the nuclear lattice would never relax to the temperature of the crystal, but would remain forever in its initial state.)

Since -m' + m + q = 0 (from equation (1.13)) only terms with q = 0 will now appear in the sum, and therefore

$$W(\theta) = \sum_{k} B_k F_k P_k(\cos \theta).$$
(1.18)

This is the usual expression used to calculate the directional distribution of γ -rays in NO, with

$$B_{k} = \hat{I}_{i}\rho_{0}^{k}(I_{i}) = \hat{k}\hat{I}_{i}\sum_{m}(-1)^{I_{i}+m} \begin{pmatrix} I_{i} & I_{i} & k \\ -m_{i} & -m_{i} & 0 \end{pmatrix} a_{m_{i}}.$$
 (1.19)

These parameters are plotted versus temperature for ${}^{60}\text{Co}\underline{\text{Co}}$, and versus the quadrupole interaction strength for ${}^{152}\text{Eu}/{}^{154}\text{Eu}$ at 13 mK, in Figure 1.4.

Conservation of parity means that the γ -ray distribution is invariant under spacereversal, and therefore the sum in (1.18) is only over k = even terms (including k = 0.)

1.3.3 Directional Distribution Coefficients

The directional distribution coefficients are given by Krane as:

$$F_k(LI_fI_i) = (-1)^{I_f + I_i + 1} \hat{k} \hat{L}^2 \hat{I}_i \begin{pmatrix} L & L & k \\ 1 & -1 & 0 \end{pmatrix} \begin{cases} L & L & k \\ I_i & I_i & I_f \end{cases}.$$
 (1.20)

where $\begin{cases} j_1 & j_2 & j_{13} \\ j_3 & j & j_{23} \end{cases}$ is a Wigner 6-j symbol, coupling the three angular momentum states, j_1, j_2 and j_3 .

The F_k have been tabulated (see, for example, Appendix 5 of Low Temperature Nuclear Orientation.)

1.3.4 Deorientation Coefficients

The orientation of the state from which the observed γ -ray is emitted is described by the orientation parameters $B_k(I_i)$. In general this transition of the nucleus is preceded by one or more decays, and it is the orientation of the parent nucleus $B_k(I_0)$, which is known, or which we are trying to measure. The reorientation of the nucleus due to these intermediate decays can be described by writing the $B_k(I_i)$ as

$$B_k(I_i) = U_k(I_0I_iL)B_k(I_0).$$
(1.21)



Figure 1.4: Calculated orientation parameters, B_k , for a)⁶⁰Co<u>Co</u> (hcp), versus temperature; b) ¹⁵²Eu/¹⁵⁴Eu versus quadrupole interaction, P, at 13 mK

The U_k factors are the deorientation coefficients and are calculated from angular momentum coupling theory. The deorientation due to a decay between two states I_1 and I_2 which carries angular momentum L is:

$$U_k(I_1, I_2L) = (-1)^{I_1 + I_2 + L + k} \hat{I}_1 \hat{I}_2 \begin{cases} I_1 & I_2 & k \\ I_2 & I_2 & L \end{cases}.$$
 (1.22)

Where the observed decay is preceded by more than one decay, the total deorientation is simply the product of all previous decays:

$$U_k(I_0I_i) = U_k(I_0I_1L_1)U_k(I_1I_2L_2)\dots U_k(I_nI_iL_n)$$
(1.23)

These coefficients have been calculated for a large number of decays and are tabulated in Appendix 5b of *Low Temperature Nuclear Orientation*.

1.3.5 Final Considerations

We should also consider here the reorientation of the nuclear spins whilst in the excited state of the daughter nucleus, and the solid angle correction of the detectors.

In most decay schemes used in NO and NMR-ON experiments, the lifetime of the state I_i is much shorter than any reorientation times and so this effect can be ignored.

The effect of the solid angle subtended by the detectors can be described by a parameter, $Q_k(\theta)$. In most experiments, the solid angle is small and the $Q_k(\theta)$ can be treated as constant and close to unity.

Now we have as a final expression for the directional distribution of the radiation:

$$W(\theta) = \sum_{k \text{ even}} B_k U_k F_k Q_k P_k(\cos \theta), \qquad (1.24)$$

with $k \leq 2L, 2I$.

We have described the γ radiation from an oriented ensemble of nuclei with known decay scheme in terms of constant parameters which can be read from tables or simply

•	•	•		· .		•		
Parent	$\gamma~{ m Energy}$	Ref.	γ Type	Proportion	U_2	U_4	F_2	F_4
nucleus	keV			- ·	 		۰.	,
		•	·		·	. · · ·		. *
⁶⁰ Co	1173		E2	100%	0.939	0.798	-0.448	-0.304
	1332	•	E2	100%	0,704	0.227	-0.598	-1.069
				· · ·		·		
$^{152}\mathrm{Eu}$	1408	1	$\mathbf{E1}$	21%	0.828	N/A	-0.418	N/A
	779	2	E1	13%	0.750*	N/A	0.346	N/A
	1085^{+}	3	E2	10%	0.817*	0.382	-0.529	-0.816
	· · · ·		•		· ·			
¹⁵⁴ Eu	1274	1	E1	35%	0.828	N/A	-0.418	N/A

Table 1.2: Nuclear orientation parameters for relevant decays of 60 Co, 152 Eu and 154 Eu [5]. *Ref.* refers to graph number in Figure 3.5; nuclear decay data from [8] and [9] *Angular momentum of beta decay is mixed; I have taken J=1. † includes 15% contribution from 1089 keV decay via Gd.

calculated, and one simple orientation coefficient which depends only on the interaction between the nucleus and its environment, and is independent of other nuclear considerations. In the experimental procedure $W(\theta)$ can be compared at a low temperature to the normalisation value taken at a "high" temperature (1 K).

The nuclear orientation parameters U_k and F_k , relevant to the decays of 60 Co, 152 Eu and 154 Eu used in this thesis, are shown in Table 1.2. Figure 1.5 shows the relative intensities of the γ radiation, $W(\theta)$, versus T, at $\theta = 0$ and $\theta = \pi/2$ for 60 Co<u>Co</u>.

1.4 The Hyperfine Interaction

Nuclear magnetic moments are small—on the order of one thousandth of the magnetic moment of the electron. The magnitude of the interaction energy between the nucleus and an applied field is the product of the magnetic moment and the applied field. Since any system is disordered unless its thermal energy becomes comparable to, or less than, the energy differences which characterise the system, high fields and low temperatures

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Figure 1.5: Calculated $W(\theta)$ versus T for ⁶⁰Co<u>Co</u> at $\theta = 0$ and $\theta = 90^{\circ}$.

are needed to produce a significant nuclear orientation. For example, a ⁶⁰Co nucleus in a field of 20 Tesla has an energy splitting between adjacent sub-levels equivalent to 6 mK. It is possible, but experimentally difficult, to achieve measurable nuclear orientation using the combination of a high laboratory field and very low temperature in this way. This technique is called, appropriately, "brute force NO."

1.4.1 Ferromagnetic Cobalt

In 3-d magnetic materials, the unpaired electrons in the 3-d shell are strongly polarised this is the source of the magnetism of the sample. These electrons partially polarise the electrons in the other atomic orbitals, and of particular importance are the s-orbitals. The wavefunctions of these electrons are non zero at the nucleus, and even a small spin polarisation of their spins can lead to a very strong hyperfine interaction. This interaction, called the *contact term* can be represented by an effective magnetic field B_{hfi} acting on the nuclear moment. These fields can be large (e.g. the hyperfine field in iron is 33 T) and significant nuclear orientation can be achieved by cooling to temperatures

obtainable with a helium dilution refrigerator (12mK in our experiments.)

The wavefunction of an electron in the n^{th} s-shell can be written as the sum of the spin-up and spin-down wavefunctions, $\psi_n^{\uparrow} + \psi_n^{\downarrow}$, and therefore

$$\vec{B}_{c} = \frac{8\pi}{3} g \mu_{B} \sum_{n} [|\psi_{n}^{\dagger}|^{2} - |\psi_{n}^{\downarrow}|^{2}] \vec{S}_{n}$$
(1.25)

where \vec{B}_c is the field at the nucleus, g the Lande-g factor and μ_B is the Bohr magneton. \vec{S}_n is the net spin of the n^{th} s-shell electrons. We assume a point nucleus, and therefore can take the value of the electron wavefunction at the origin in calculating the hyperfine interaction. \vec{S}_n is proportional to the atomic spin, \vec{S} , in a 3-d magnet, and \vec{S} is parallel to the magnetisation, \vec{M} . We therefore write the field at the nucleus as

$$B_c = \frac{AS}{\hbar \gamma_n},\tag{1.26}$$

with

$$A = \frac{\gamma_n}{\hbar} \frac{8\pi}{3} \frac{g\mu_0}{S} \sum_n [|\psi_n^{\dagger}|^2 - |\psi_n^{\downarrow}|^2] S_n.$$
(1.27)

1.4.2 Europium Vanadate

Previous investigations into the HFI on Eu^{3+} (see Chapter 3) indicate that the dominant interaction with the nucleus is between the nuclear quadrupole moment and an electric field gradient (EFG) at the nucleus. Unlike the magnetic interaction, the quadrupole interaction is insensitive to the sign of the z-component of the nuclear spin, and the splitting between levels is not equal (see Figure 1.1.)

The strength of the quadrupole interaction is described by the parameter P (equation (1.4)), which is usually given in MHz.

1.5 NMR on Ordered Nuclei

It is sufficient here to consider the rf coil as simply providing quanta of electromagnetic energy (in packets $\hbar \omega$) to excite the nuclei between their levels. The consequent change in the level populations is observable as a change in gamma ray anisotropy. One can also consider the applied rf field as rotating (tilting) the nuclear moment in a classical sense. In this treatment, resonance occurs when the rf frequency matches the precession frequency of the spins in the magnetic field which causes the sub-level splitting. If the field at the nucleus is B, then

$$\Omega = \gamma_n B, \tag{1.28}$$

where γ_n is the gyromagnetic ratio of the nucleus:

$$\vec{\mu}_n = \gamma_n \hbar \vec{I}. \tag{1.29}$$

For a thorough treatment of nuclear magnetic resonance, the reader is referred to one of the standard texts, e.g. the book by Slichter[10].

Nuclear orientation will occur when the nuclei are cooled to temperatures low enough that the nuclear spins are significantly ordered. It is observed by studying dilute radioactive nuclei in a cold host crystal. The nuclei relax to the temperature of the crystal because of spin-lattice interactions, which determine the spin-lattice relaxation (SLR) time, T_1 . (The existence of a nuclear-spin temperature itself depends on a strong nuclear spin-spin interaction, characterised by a time T_2 , which maintains a Boltzmann distribution of nuclear sub-levels.) Observation of NMR-ON requires a SLR time which is short enough that the nuclear spins relax to the temperature of the host, but long enough that the low power levels that can be applied at low temperatures (limited by rf heating and the cooling power of the cryostat) can significantly change the state of the nuclear system.

In conventional NMR-ON, one observes the resonance of dilute radioactive nuclei. Nuclear spin-spin interactions are very small in this case, and the inherent resonance linewidth is correspondingly narrow (typically 10 kHz in a ferromagnetic host). This homogeneous broadening gives the response of each nuclear spin packet to applied radiation. The resonance is generally broadened much further by variations in the environment at the atomic site. These variations (due to defects, impurities, demagnetising effects etc.) produce an inhomogeneous broadening of the resonance, typically of about 1 MHz. This means mean that there are $\sim 10^5$ independent wavepackets within the sample, or that an rf field at a precise frequency will only be on resonance with 10^{-5} of the nuclei.

The rf radiation can be applied over a range of spin packets by modulating the frequency of the radiation, typically over a range 1/2 to 1/10 of the resonance width. This reduces the magnetic field applied to each nucleus, and would make the observation of NMR-ON difficult without the effect of *magnetic enhancement*, which results in an rf-field at the nucleus much larger than the applied field. The enhancement results from the electronic magnetisation of the sample being aligned along the easy-axis, or an easy-plane, of the crystal. The electronic magnetisation follows an rf field applied perpendicular to the easy axis, resulting in a field on the nucleus which is enhanced by the hyperfine interaction. The enhancement factor is

$$\eta \approx \frac{B_{hfi}}{B_0 + B_A},\tag{1.30}$$

 B_0 being any applied static field, parallel to the easy axis. The field felt by the nucleus is ηB_1 , where B_1 is the rf field applied to the sample. Here we have represented the magnetocrystalline energy which causes the magnetisation to lie along the easy axis by an *anisotropy field*, B_A , acting on the electronic magnetisation.

1.6 Frequency Pulling Effect

The dominant term in the NMR frequency of the host nuclei in a 3-d ferromagnetic material is the hyperfine interaction between the atomic electrons and the nuclear magnetic moment. This is due mainly to core polarisation of the s-wave electrons, interacting with the nucleus through the contact term (the overlap of the electron wavefunctions with the nucleus). The NMR frequency determined by this interaction is perturbed by weaker interactions between the nuclei, which change the sub-level splittings.

1.6.1 Nuclear-Nuclear Interactions

The direct interaction between nuclei is given simply by the energy of two interacting dipoles, and has a maximum value of

$$E_{dipole} \lesssim \frac{\mu_0}{4\pi} \frac{|\vec{\mu_1}| |\vec{\mu_2}|}{r^3}.$$
 (1.31)

For a typical atomic separation $r \sim 1\text{\AA}$, and a nuclear magnetic moment of μ_n this is on the order of 1kHz. This interaction is clearly negligible between non-nearest neighbours.

Rudermann and Kittel[11] showed that there is an indirect interaction between the nuclei through a nuclear-driven polarisation of the conduction electrons. This interaction has an energy on the order of A_C^2/E_F , where E_F is the Fermi energy of the sample, and A_C is the energy of the interaction between the nucleus and the conduction electrons (which will be due to the contact term if the conduction electrons are s-wave.) This is typically equivalent to a frequency shift of a few kHz.

1.6.2 Suhl-Nakamura Interaction

As discussed in Section 1.4, the hyperfine interaction on the nucleus of a 3-d ferromagnet can generally be described by an isotropic interaction with a Hamiltonian:

$$\mathcal{H}_{hfi} = -A\vec{S} \cdot \vec{I}. \tag{1.32}$$

This Hamiltonian is correct only to first order in A, since it neglects all possible couplings between \vec{I} and \vec{S} .

In the case of dilute nuclei in a ferromagnet, the correction to (1.32) due to interactions between \vec{I} and \vec{S} acting on neighbouring nuclei is negligible, since the coupling A is much smaller than the exchange interaction between the electrons, J. (Since the electrons are very strongly coupled, any perturbation due to a nuclear spin has a negligible effect on the interaction energy with neighbouring nuclei.) For instance, if one tilts the spin, $\vec{I_j}$, of the nucleus at lattice site j, by an angle θ , then the relative perturbation of the electronic states will be of order $(A/J)I_j^z\theta$

There is a perturbation to this Hamiltonian due to the mixing of atomic states with different values of S coupled by the nuclear spin. This interaction causes a quadrupole-like change in the energies of the sub-levels, but is negligible in cobalt.

Where the nuclei are dense, however, (as is the case for the ⁵⁹Co in ⁶⁰Co<u>Co</u>), the interaction between nuclei through the coupling of \vec{I} and \vec{S} can be significant because a perturbation to the electron states is carried across the order of $J/\hbar\omega_e$ atomic neighbours by the exchange interaction. The interaction between dense nuclei and the electron spins is now of order $(A/J)I_z(J/\hbar\omega_e) = AI_z/\hbar\omega_e$, where $I_z = \langle I_j^z \rangle$ is the mean value of I_j^z over the ensemble of nuclei. This interaction leads to a *frequency pulling*—a change of the NMR frequency at temperatures where the nuclear magnetisation (I_z) becomes appreciable.

The frequency pulling effect can be derived from the macroscopic equations for the

coupled nuclear and electron magnetisation or by considering the interaction between the nuclei due to the Suhl-Nakamura interaction (see, for instance, de Gennes *et al* [12]). Here we take the second approach, which shows that the frequency pulling is due to the Suhl-Nakamura interaction.

This interaction was first derived by Suhl[13] for a ferromagnet and Nakamura[14] for an anti-ferromagnet, and is due to the presence of electron spin wave states within a magnetically ordered lattice of electron spins. Spin waves (also called magnons) are the elementary collective excitation of the magnetised electronic spin system in ferroand antiferromagnetic materials, and are the source of the observed reduction of the magnetism of ferromagnets with increasing T. The excitation energy of these magnons is much greater than the sub-level splitting of the nuclei, and so the nuclei cannot directly excite an electron spin wave state, but they can interact via the absorption and emission of *virtual* magnons. The Suhl-Nakamura interaction is much weaker than the hyperfine interaction, but is long range (typically about thirty atomic spacings), and its effect becomes appreciable at low temperatures. Here, where the nuclear magnetisation becomes significant (the expectation value of the z-component of the spin greater than 1%), the correlation of nuclear spins caused by the interaction leads to the nuclear excitations taking the form of nuclear spin waves. The clearly defined dispersion relation for nuclear spin waves changes the NMR frequency by an amount proportional to the nuclear magnetisation.

1.6.3 Nuclear Spin Wave Dispersion Relation

The Hamiltonian for an electron spin wave with wave vector \vec{k} is written in terms of the magnon creation and annihilation operators, $a_{\vec{k}}^+$ and $a_{\vec{k}}$ respectively:

$$\mathcal{H}_{magnon}(\vec{k}) = \hbar \omega_{\vec{k}} a_{\vec{k}}^+ a_{\vec{k}}.$$
(1.33)

We wish to consider the Hamiltonian of the combined nuclear-spin/electron-spin-wave system, which can be written as a sum of two terms:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'. \tag{1.34}$$

The dominant term is simply the independent energies of the nucleus and the electron spin waves:

$$\mathcal{H}_0 = -(AS + \gamma_n \hbar B) \sum_j I_j^z + \sum_{\vec{k}} \hbar \omega_{\vec{k}} a_{\vec{k}}^+ a_{\vec{k}}, \qquad (1.35)$$

and \mathcal{H}' contains the interaction between the nuclei and the spin waves, which will be treated as a perturbation to \mathcal{H}_0 . We have included the hyperfine interaction by treating the nucleus as being in an effective field $B + (AS/\gamma_n\hbar)$; *j* is summed over the positions of the *N* nuclei in the lattice, \vec{k} over the wave vectors of the spin waves.

Consider an eigenstate of \mathcal{H}_0 in which the nuclear state, $|I_1^z, I_2^z \dots I_N^z\rangle$, is arbitrary, and the electrons are in their ground state $|0\rangle$, i.e. there are no spin waves. This is clearly a physical state at low temperatures since the nuclear level splitting is much less than the electron spin wave energy. (The $\vec{k} = 0$ magnon has energy $\hbar\omega_e$; $\hbar\omega_e = \mu_B B_A \gg AS$ —see below)

Turov and Petrov[15] show that there is no first order correction to the eigenvalues of \mathcal{H}_0 due to \mathcal{H}' , but that there is a second order correction to the energy, and this can be represented by the Hamiltonian

$$\mathcal{H}_{eff} = \frac{1}{2} \sum_{j,j'} U_{jj'} I_j^+ I_{j'}^-, \qquad (1.36)$$

with

$$U_{jj'} = -\frac{SA^2}{N} \sum_{\vec{k}} e^{i\vec{k}.(\vec{R}_j - \vec{R}_{j'})} \hbar \omega_{\vec{k}}.$$
 (1.37)

The I_j^+ and I_j^- are usual ladder operators, acting on the nucleus at site j:

$$I_{i}^{+} = I_{i}^{x} + iI_{i}^{y}, (1.38)$$

$$I_j^- = I_j^x - iI_j^y. (1.39)$$

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Equation (1.36) is the Suhl-Nakamura interaction, derived by Suhl by summing over all possible virtual spin-wave exchanges in a cubic ferromagnet.

The interaction term only operates on the nuclear states, and so we can split the Hamiltonian (to second order in \mathcal{H}') into independent terms for the nuclear and electronic states:

$$\mathcal{H} = \mathcal{H}_n + \mathcal{H}_e, \tag{1.40}$$

with

$$\mathcal{H}_e = \sum_{\vec{k}} \hbar \omega_{\vec{k}} a_{\vec{k}}^{\pm} a_{\vec{k}} \tag{1.41}$$

and

$$\mathcal{H}_n = -(AS + \gamma_n \hbar B) \sum_j I_j^z + \frac{1}{2} \sum_{j,j'} U_{jj'} I_j^+ I_{j'}^-.$$
(1.42)

The ladder operators, I_j^+ and I_j^- , raise and lower the z-component of the spin of the nucleus j. According to Turov and Petrov, the N nuclei in the ensemble under consideration are identical particles, and therefore the state vector of the ensemble is given by the Slater determinant constructed from the individual nuclear states $|I_j^z\rangle$. An operator acting on one nucleus therefore acts on the whole ensemble—it can be said to belong to the whole crystal. There is, therefore, an equivalent representation of the operators, given by their Fourier transforms into the \vec{k} -space of the nuclear Bravais lattice:

$$I_{\vec{k}}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{j} e^{i\vec{k}.\vec{R}_{j}} I_{j}^{\dagger}, \qquad (1.43)$$

$$I_{\vec{k}} = \frac{1}{\sqrt{N}} \sum_{j} e^{-i\vec{k}.\vec{R}_{j}} I_{j}^{-}.$$
 (1.44)

These operators represent the elementary excitations of the nuclear spin system. In other words: they are the nuclear spin wave creation and annihilation operators. The eigenfrequency spectrum of these operators will therefore give the frequency spectrum of possible excitations of the nuclear lattice. The NMR frequency will be given by the

eigenfrequency of the $\vec{k} = 0$ wave, since this is the wave representing coherent excitations of the nuclear spins. We shall therefore solve for the eigenfrequency spectrum.

In the Heisenberg representation, we can write the equation of motion for $I_{\vec{k}}^{\dagger}$ as

$$\frac{lI_{\vec{k}}^{\dagger}}{dt} = \frac{i}{\hbar} [\mathcal{H}_n, I_{\vec{k}}^{\dagger}]$$
(1.45)

$$= i[(AS + \gamma_n \hbar B)I_j^+ + \sum_{j'} U_{j'j}I_{j'}^+ I_j^z]$$
(1.46)

If we substitute for $U_{j'j}$, the second term contains the Fourier transform (FT) of $I_{j'}^+$, and simplifies to:

$$\frac{SA^2}{\sqrt{N}}e^{-i\vec{k}.\vec{R}_j}\sum_{\vec{k}}\frac{1}{\hbar}\omega_{\vec{k}}I^{\dagger}_{\vec{k}}I^z_j.$$
(1.47)

Substituting the inverse FT of (1.43) for I_j^+ in the first term of (1.46), and using the fact that the $I_{\vec{k}}^{\dagger}$ are independent we can remove the summation over \vec{k} . If we also linearise the equation by replacing I_j^z by its thermodynamic mean value, $I_z = \langle I_j^z \rangle$, then

$$\frac{dI_{\vec{k}}^{\dagger}}{dt} = i \left[AS + \gamma_n \hbar B + \frac{SA^2 I_z}{\hbar \omega_{\vec{k}}} \right] I_{\vec{k}}^{\dagger}.$$
(1.48)

By inspection this leads to an eigenfrequency spectrum for the $I_{\vec{k}}^{\dagger}$ of

$$\Omega_{\vec{k}} = \frac{AS}{\hbar} \left[1 + \frac{AI_z}{\hbar\omega_{\vec{k}}} \right] + \gamma_n B.$$
(1.49)

The replacement of the operator I_j^z with its thermodynamic mean value is easy to justify in the very low temperature case, where $\langle I_j^z \rangle \approx I_j^z$. At higher temperatures this is not true, and this linearization requires justification. De Gennes *et al.*[12] show that even at moderately low T (with ~ 1% nuclear alignment), there are still well defined nuclear spin waves (characterised by a clear position in \vec{k} -space) and therefore an eigenfrequency spectrum, and thus this substitution is still valid.

Thus, through the interactions between the nuclear spins, via the weak but long range Suhl Nakamura interaction, there exists within a cold, concentrated nuclear lattice



Figure 1.6: Magnitude of the nuclear spin wave frequency verses wave number, calculated from Equation (1.49) The straight line is the NMR frequency without the Suhl-Nakamura interaction, Ω_0^0 .

the possibility of nuclear excitations in the form of nuclear spin waves. The dispersion relation for these waves is shown schematically in Figure 1.6. In this graph Ω_0 is the value of $\Omega_{\vec{k}}$ at $\vec{k} = 0$, and Ω_0^0 is the NMR frequency without the Suhl-Nakamura interaction.

Chapter 2

Experimental

2.1 Experimental Setup

2.1.1 The Cryostat

To obtain the low temperatures ($T \lesssim 50$ mK) necessary to observe nuclear orientation, a helium dilution refrigerator (made by S.H.E.) was used for all experiments. At 100 mK the refrigerator had a cooling power of about 60 pW, which varied roughly as T^2 below this temperature. The base temperature of the fridge, for a sample with no radioactive self heating, was about 12 mK. The dilution fridge is a standard tool for low temperature physics, and therefore will not be described here. The interested reader is referred to *Experimental Principles and Methods Below 1 K* by Lounasmaa[16].

The cryostat required 35 litres of helium to cool and fill, and boiled-off about fifteen litres of helium per day. Once cooled, experiments were run for durations varying between two days and two weeks.

Samples were mounted on the end of the copper cold finger, in the centre of a superconducting solenoid. This was mounted outside the vacuum can, and could provide a vertical field of up to 2 Tesla. The EuVO₄ crystal was wrapped in copper foil and clamped to the cold finger with two small copper strips. The cobalt samples were soldered directly to an extension on the cold finger. The arrangement of the cobalt foil and the rf coils used is shown in Figure 2.1.

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Figure 2.1: Arrangement of Co foil and rf coils on cold finger

2.1.2 Supplying RF Power

RF power was supplied to the sample from a tuned L-C tank circuit mounted on the 1 K shield. Care was required in setting up to avoid a thermal touch between the coil and the cold finger/sample. Because of the large cooling power of the 1 K cooling plate, commercial teflon coated copper coaxial cable could be used to transfer the rf power through the cryostat.

The width of the ⁶⁰Co<u>Co</u> resonance is dominated by inhomogeneous broadening, and it is necessary to frequency modulate the rf signal to observe the resonance. The signal generator used had an internal control that produced a frequency modulation of depth 100kHz; broader modulation could be obtained by external programming. Removing the frequency modulation from the signal gives a very straightforward method for distinguishing between genuine NMR-ON peaks, and false peaks which can result from rf heating of the sample due to resonances in the coil/tank circuit/transmission line system.

We also wished to observe the resonance of the ⁵⁹Co nuclei (using the thermometric technique, which will be discussed in Chapter 4.) In the case of concentrated nuclear

spins, the broadening of the resonance peak is dominated by nuclear spin-spin interactions and the nuclei respond to a wide range of frequencies. With this homogeneous broadening it is not necessary to modulate the rf frequency. However, it is important that there be no resonances in the tank circuit close to the NMR frequency. For this reason the coil was tuned with a two capacitor circuit (mounted at the coil) to give a known resonance frequency and to match the 50Ω impedance of the coaxial cable connected to it. The coil was tuned with the resonance midway between the ⁵⁹Co and ⁶⁰Co NMR frequencies. The tank circuit was built for each experiment, and is described in Appendix A.

A pick-up coil was included in the circuit, matched to the coaxial cable using a 50Ω metal oxide resistor, but was not required during the experiments.

Two coil configurations were utilised: one was a Helmholtz pair on either side of the thin sample; the other consisted of a two turn ellipsoidal solenoid arranged with the sample along the axis. The latter gave the best resonance height/non resonant heating ratio, but the former was often necessary due to the geometric arrangement of the sample. The axis of the rf coil was horizontal.

2.1.3 Gamma Ray Detection.

For the experiments on cobalt, the gamma rays were counted using a pair of NaI(Tl) scintillation counters, each of which had a diameter of 4 inches and a length 4 inches. These were placed perpendicular to each other outside the cryostat, with one on a vertical axis through the sample. To reduce the effect of the applied magnetic field on the counters, the photomultiplier tubes (PMTs) were seperated from the crystals by a 60 cm plexiglass light pipe. The PMTs were stabilised against temperature drifts, and the effect of an applied field, by using a temperature stabilised diode to provide a reference pulse height[17]. The signal was passed through a stabilising amplifier, gated for the γ -ray photoelectric peak, and then converted to a square pulse. The pulses were counted

on a PC running commercial acquisition software, which also controlled the rf frequency and collected data on the temperature of the cold finger.

The ¹⁵²Eu and ¹⁵⁴Eu decays involve many γ -rays closely spaced in energy (see Figure 3.3,) and in order to make quantitative measurements it was necessary to resolve these transitions. To achieve this resolution a 52 mm diameter x 45 mm single crystal germanium detector was used. Stabilisation was not necessary, but counting efficiency was very low. The raw spectrum was accumulated on a multichannel analyser program, and count rates determined from the areas of several γ -peaks.

2.1.4 Miscellaneous

During the course of experiments, the temperature of the cold finger was monitored using a carbon resistance thermometer. The resistance was measured by a four wire resistance bridge, connected to the computer by optical cables, to prevent electrical noise affecting the bridge. For magnetic field sweeps, the coil current could be monitored with a digital voltmeter.

The rf power was provided by a Marconi signal generator. Fractional frequency error was less than 10^{-6} . A frequency modulation of 100kHz depth was used, with a scan frequency of 1 kHz. Power was transferred to the top of the cryostat by 50 Ω coaxial cable, where it could be amplified by a 30dB rf amplifier if needed, before being passed into the cryostat. For the experiments on EuVO₄, a ⁶⁰Co<u>Co</u> thermometer was used. This was a single crystal of hcp Co, approximately 10mm x 1mm², with an activity of 1 μ Ci. By measuring the anisotropy of the γ -rays from this crystal we could calculate the temperature of the cold finger.

2.1.5 Analysis.

All collected data were stored on a PC. The γ -ray counts were taken while sweeping the frequency up and down, and filed separately. The results were manipulated and graphed on a spreadsheet. Where needed, curve fits were performed on a separate program.

In general, it was best to view the counts for each detector individually, looking for a change in count rate. This should be of opposite sign for the two counters, as can been seen from Equation (1.24), in which $P_k(0) = 1$ and $P_k(\pi/2) = -1/2$.

2.2 Sample Preparation

2.2.1 EuVO₄

This was a single crystal of Eu(Sm)VO₄ with 1.5% Sm and 98.5% Eu. It was donated to us by Prof. B. Bleaney, at the Clarendon Laboratory, Oxford, England. The sample was irradiated in the thermal neutron facility at TRIUMF (B.C., Canada) for approximately two hours in a neutron flux density of $10^{10} \rightarrow 10^{11}$ neutrons cm⁻² s⁻¹.

The activity of the ¹⁵²Eu was 5μ Ci. Table 2.1 shows the natural abundances, thermal neutron cross sections, and lifetimes for the europium isotopes considered here. From these data we find that the activity of the ¹⁵⁴Eu nuclei is approximately 4% of the activity of the ¹⁵²Eu.

2.2.2 Cobalt

Three samples of cobalt were tested. The first was a 1cm x 1mm² single crystal of hcp cobalt, donated to us by the Munich group, for the purposes of investigating the frequency pulling effect. This was irradiated at TRIUMF to give an activity of 1μ Ci, and was not annealed before use. This crystal was mounted to the cryostat in two configurations, first clamped directly to the cold finger, and secondly attatched to the cold finger by a 2cm

			· .	• .
Isotope number	Natural abundance	Half life	Neutron cross section	Products
n ¹ -				
151	48%	stable	5900bn	¹⁵² Eu
•			2800bn	$^{152m}\mathrm{Eu}$
153	52%	stable	320bn	¹⁵⁴ Eu
	·			
152		12y		78% ¹⁵² Sm; 28% ¹⁵² Gd
152_{m}	· ·	9.3h	•	23% ¹⁵² Sm; 77% ¹⁵² Gd
154	•	16y		$100\% \ ^{154}{ m Gd}$

Table 2.1: Abundance, half life, thermal neutron capture cross section and neutron capture/decay products for the isotopes of europium studied [18][19].

piece of 22 gauge copper wire. In the latter configuration, the sample was attached to a wooden support with G.E. varnish to provide mechanical stability.

The second sample was a 5μ m thick single crystal (hcp) donated to us by Dr. D. Chapman of the Australian Defense Force Academy, University of New South Wales, Australia. This sample had been spark cut from a single crystal rod, mechanically polished, irradiated and finally cut and electropolished, and was sent to us soldered to a copper finger. The c-axis of the crystal was in the plane of the foil. Its activity was approximately 100 μ Ci.

Given time constraints, it was not possible to prepare a third single crystal of hcp cobalt. As it is not necessary to use a single crystal to investigate the frequency pulling effect, a 4μ m foil of 99.9% cobalt foil was purchased from Goodfellows. This was cut to a suitable size (1/2 cm by 1cm), and irradiated at TRIUMF for a day. The foil was annealed for eighteen hours at 650°C in a hydrogen atmosphere. Cobalt undergoes a slow phase transformation from hcp to fcc between 350 and 400°C, and so the crystal was cooled rapidly (within a few minutes) to prevent regions of hcp structure growing.

The foil was soldered at both ends to a suitably shaped piece of OFHC (oxygen free, high conductivity) copper foil (0.25mm thick), which was then clamped to the cold finger. A galium alloy was used as a solder—its low melting point (30°C) ensuring that the foil was not heated during soldering, which could cause the growth of hcp regions. The activity of the sample was approximately 3μ Ci.

Chapter 3

Europium Vanadate

The first $({}^{7}F_{1})$ excited state of Eu³⁺ is just 500 K above the ground $({}^{7}F_{0})$ state. Elliott[20] examined the hyperfine interaction in these ions, and predicted that mixing between these two low lying states should lead to a reduction in the nuclear Zeeman splittings. This reduction should be relatively insensitive to the host material. Shelby and Macfarlane[21], and Erickson and Sharma[22] have measured the effective nuclear magnetic moment of the Eu nuclei using optical hole burning on Eu³⁺ dilute in YAlO₃. They report a nuclear magnetic moment shielded by about 80%.

The rare earth vanadates have been studied by the Oxford group of Bleaney, Leask and co-workers. One material studied, europium vanadate, has a tetragonal crystalline structure of the zircon type with space group D_{4h}^{19} (14₁/amd) (Stubican[23]), and is a Van Vleck paramagnet. Optical hole burning and optically detected nuclear quadrupole resonance experiments on EuVO₄[24][25] have concentrated on measuring the quadrupole interaction at defect sites and explaining the apparently high (approximately thirty) number of defect lines. These optical hole burning techniques use the ${}^7F_0 \rightarrow {}^5D_0$ excitation, which is forbidden at lattice sites in zero applied magnetic field by symmetry considerations. NMR-ON is not restricted by this consideration, and measuring the resonance frequency would give the quadrupole interaction on the 152 Eu and 154 Eu nuclei at the lattice positions, and hence the intrinsic electric field gradients in the crystal could be calculated.

Judd, Lovejoy and Shirley[26] made the first NO measurements on europium, using

Chapter 3. Europium Vanadate



Figure 3.1: Simplified nuclear decay scheme of 152 Eu, showing decays relevant to this experiment, and nuclear level spin/parity assignments. All energy levels are in keV[9].

neodymium ethylsulphate as a host.

The crystal studied here was $Sm(1.5\%)Eu(98.5\%)VO_4$, supplied to us by the Oxford group. The ionic sizes of the Sm and Eu ions are very similar, so the former should not perturb the Eu nuclear parameters. However, the magnetic Sm ions could reduce the Eu spin-lattice relaxation time, T_1 , significantly.

3.1 Results

Figures 3.1 and 3.2 show the parts of the europium decay schemes relevant to this discussion. The nuclear orientation parameters for these decays of ¹⁵²Eu and ¹⁵⁴Eu are listed in Table 1.2. The γ -ray spectrum measured for the sample and the cobalt thermometer is shown in Figure 3.3. This is one of the spectra used to calculate peak areas. It can be seen that the γ peaks are well distinguished by the detector.

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Figure 3.2: Simplified decay scheme of 154 Eu[8], details as for Figure 3.1.



Figure 3.3: Gamma ray spectrum from $EuVO_4$ crystal and cobalt thermometer as measured by 4000s count on germanium detector



Figure 3.4: Measured γ -ray intensity, W(0), for cobalt γ -rays and 1086 and 1408 keV γ -rays from EuVO₄, during cooling of EuVO₄ crystal

The crystal was cooled for about 24 hrs. Figure 3.4 shows the counts (versus time) for the 60 Co thermometer and two Eu peaks (both from 152 Eu.) Each point shows the counts in a live time of 4000s on the detector. The graphs were compiled from the peak-search results of the multi-channel analyser program being used.

The temperature of the sample can be found from the value of W(0) for the cobalt thermometer. From Table 3.1, the value of W(0) is $74.1\pm.8\%$. This corresponds to a temperature of $13.15\pm.3$ mK.

The HFI at the Eu nucleus is predominantly quadrupolar, and has a Hamiltonian ([25])

$$\mathcal{H} = P[I_z^2 - \frac{1}{3}I(I+1) + \frac{1}{3}\eta(I_x^2 - I_y^2)].$$
(3.1)

Chapter 3. Europium Vanadate



Figure 3.5: Calculated W(0), for ¹⁵²Eu and ¹⁵⁴Eu, versus the quadrupole interaction, P, at 13mK. See Table 1.2 and Figure 3.1 for curve identity,

 η is a function of the axial asymmetry at the ion position, and is zero for the intrinsic sites; P is the parameter (with dimensions of frequency) describing the interaction, given by Equation (1.4). Figure 1.4 shows the values of B_2 and B_4 versus P for ¹⁵²Eu and ¹⁵⁴Eu at a temperature of 13.2 mK; Figure 3.5 shows the expected anisotropy along the c-axis, at 13.2 mK, versus the quadrupole interaction strength, P. From this graph it is possible to convert a measured anisotropy, W, into a quadrupole interaction, P.

Table 3.1 lists, for the europium γ -rays with good counting statistics and known orientation parameters, values of W(0) - 1 in two counting periods after the fridge had cooled down. These results were compiled from the data in Figure 3.4 by summing eight points, starting at t = 0, 40,000 and 90,000 seconds. The first value gives the warm (> 1 K) normalisation count for each peaks. The quadrupole interaction strength is derived from Figure 3.4. The errors on the values of W(0) - 1 are one standard deviation (i.e. \sqrt{N}) on the statistical error. The error on the weighted mean was calculated from the standard deviation of the set of values, and is much greater than the error implied by the

Isotope	peak	Peak	Warm	Cold va	lues, 1	Cold V	alues 2
	keV	Ref.	Counts, 10^3	W(0)-1	$P(\mathrm{MHz})$	W(0) - 1	P(MHz)
60	•						
⁶⁰ Co	1173		55	-0.249(13)		-0.257(13)	
	1333		50	-0.267(9)	•	-0.262(9)	
· .	total	,	105	-0.258(8)		-0.259(8)	
152 0	*. 0.4.4		100	. 0. 01 0 (0)			
¹⁰² Eu	344	. 4	162	+0.013(9)	+2.6(1.8)	+0.021(9)	+4.2(1.8)
1	780	2	49	-0.055(20)	+17(6)	-0.020(20)	+6(6)
	1086	3	36	-0.089(44)	-16(8)	-0.075(44)	-13(8)
	1408	1	54	-0.001(8)	-0.2(1.8)	-0.006(8)	-1.4(1.8)
¹⁵⁴ Eu	1275	1	15	-0.046(27)	-11(6)	-0.029(27)	-7(6)
Weighte	d Mean				2(14)	s	1(8)

Table 3.1: Gamma-ray counts at different times during europium vanadate cool down. "Peak Ref." refers to curve in Figure 3.5

counting statistics. The results for the ¹⁵⁴Eu peak are not included in the mean because of the uncertainty in the value of the nuclear quadrupole moment (see Table 1.1), which makes normalisation between the two nuclei difficult.

Approximately 50% of the decays in the 344 keV peak are preceded by the 780 keV γ decays shown in Figure 3.2. Another 25% are preceded only by an L = 1 mixed beta decay. If we ignore the effect of the remaining 25% of the decays and assume that the beta decay is dominated by the J = 1 decay, then we can calculate a value $U_2F_2 \sim -0.4$. This is the value which has been used to calculate the value of P.

3.2 Discussion

Taking the weighted mean of all the results for 152 Eu gives a quadrupole interaction of 1.4 ± 4 Mhz. The error is calculated from the distribution of the results. There are two possible explanations for such a small interaction:

Chapter 3. Europium Vanadate

- 1. The electric field gradient at the nucleus is indeed small. This could be a result of the tetragonal symmetry of the Eu^{3+} lattice position in $EuVO_4$. This symmetry is relatively higher than for the defect sites studied in the hole burning experiments, which reported values for $P \sim 40$ MHz.
- 2. There is a sizeable quadrupole interaction at the nucleus, but the spin-lattice relaxation time, T_1 , is too long for NO to be observed in the time for which the experiment was run. This would mean that $T_1 \gtrsim 1$ day, which is certainly possible. If this conjecture is correct, it means that the 1.5% Sm content was not effective in reducing T_1 appreciably. In this case the experiment might be repeated with a crystal containing a greater amount of samarium (which could be provided by the Oxford group.)

Chapter 4

Cobalt

4.1 Frequency Pulling

Section 1.6 introduced the idea that there exists within a cold ferromagnetic conductor elementary excitations of the nuclei in the form of nuclear spin waves. These spin waves are localised in \vec{k} -space and have a defined dispersion relation, due to the Suhl-Nakamura interaction between the nuclear spins. The Suhl-Nakamura interaction results from the exchange of virtual magnons between nuclear spins. The frequency spectrum of the nuclear spin waves is given by:

$$\Omega_{\vec{k}} = \frac{AS}{\hbar} \left[1 + \frac{AI_z}{\hbar \omega_{\vec{k}}} \right] + \gamma_n B, \qquad (4.1)$$

and this spectrum is plotted in Figure 1.6.

Nuclear magnetic resonance is the excitation of nuclei between their magnetic substates. Classically the phenomenon occurs when the frequency of the applied rf radiation matches the Larmour precession frequency of the nuclei in the magnetic field producing their level splitting. The latter case corresponds to a coherent rotation of the nuclei about an axis in a frame of reference rotating about the z-axis at the frequency of the applied radiation. In the case that there are clearly defined nuclear spin waves, the nuclear resonance resonance is the excitation of the $\vec{k} = 0$ mode. In this case we can calculate the frequency of the "wave" from equation 4.1 with $\vec{k} = 0$. This gives us a nuclear frequency of magnitude:

$$\Omega = \left| \frac{AS}{\hbar} \left[1 + \frac{AI_z}{\hbar\omega_0} \right] + \gamma_n B \right|.$$
(4.2)

The value of ω_0 is given by:

$$\omega_{\vec{k}} \xrightarrow{\vec{k} \to 0} \gamma_e B_A = \omega_e, \tag{4.3}$$

where B_A is the magnetocrystalline anisotropy field. The nuclear frequency can be writ-

teņ

$$\Omega = \Omega_0 + \Delta \Omega \tag{4.4}$$

where Ω_0 is the unpulled nuclear resonance frequency:

$$\Omega_0 = \left| \frac{AS}{\hbar} + \gamma_n B \right|, \tag{4.5}$$

and $\Delta\Omega$ is the frequency pulling:

$$\Delta \Omega = \left| \frac{AS}{\hbar} \right| \frac{AI_z}{\hbar \omega_e}.$$
(4.6)

In the usual case where the nuclear frequency is dominated by the HFI, and the applied field, B, represents a small correction to this, the frequency pulling can be well approximated by

$$\Delta \Omega \approx \frac{AI_z}{\hbar \omega_e} \Omega_0 \tag{4.7}$$

or

$$\left|\frac{\Delta\Omega}{\Omega_0}\right| \approx I_z \frac{\Omega_0}{S\omega_e}.$$
(4.8)

At the low temperatures at which this effect is significant, Ω_0 , ω_e and S are constant, and so I_z contains all the temperature dependence of the frequency pulling.

The magnetocrystalline anisotropy energy in hcp cobalt may be approximated by

$$E = K_0 + K_1 \sin^2(\theta) + K_2 \sin^4(\theta) + \cdots$$
 (4.9)

where θ is the angle between the magnetisation of the crystal and the c-axis (the easy axis). This anisotropy energy can be represented by an effective field (directed along



Figure 4.1: Frequency pulling for 59 Co<u>Co</u>, as predicted from the Suhl-Nakamura interaction.

the easy axis) acting on the electron spins. This anisotropy field, B_A , has a magnitude $2K_1/B_S$, where B_S is the magnetic induction due to the spontaneous magnetisation, M_S , i.e. $B_S = 4\pi\mu_0 M_S$.

In hcp cobalt the spontaneous magnetisation is 1.48 Am^{-1} at low temperatures, which corresponds to an induction of 1.85T, and $K_1=0.75 \text{ MJm}^{-3}[27]$. This gives an anisotropy field of $8.1 \times 10^5 \text{ Am}^{-1}$, or 1.0 T. We therefore have an electron frequency

$$\omega_e = 2\pi 28 \text{GHz} = 1.8 \cdot 10^{11} \text{s}^{-1}. \tag{4.10}$$

The magnetic moment per atom is $1.72\mu_B$, which implies an atomic spin of $0.85\hbar$, and therefore:

$$\left|\frac{\Delta\Omega}{\Omega^0}\right| \approx 9.2 \cdot 10^{-3} I_z \tag{4.11}$$

The frequency pulling, as predicted by these values, is shown in Figure 4.1

4.2 The Thermometric Technique

In nuclear magnetic resonance power is absorbed by the nuclear spins. The energy deposited will be transferred to the host material through spin-lattice interactions. If the rf field is applied at the resonance frequency of the nuclei of the host material, then the power absorbed by the nuclei may be comparable to the rf absorption in the material. In this case the temperature of the sample will be raised, and the NMR of the stable nuclei can be detected by the change in the γ -ray anisotropy of the radioactive dopant.

This thermometric technique of measuring NMR was first used by Kotlicki and Turrell on ${}^{54}\text{Mn}{}^{55}\underline{\text{MnCl}_2.4\text{H}_2O}[3]$. It is dependent on suitable SLR times to transfer power from the abundant host spins to the dilute radioactive spins via the lattice. This technique is considerably more difficult to apply in conductors because there is eddy current heating in the surface of the sample. This thesis reports the first measurement of thermometric NMR in a conductor.

Figure 4.2 shows schematically the important heat flow processes.

4.3 Samples

The samples have been described in Section 2.2.2. Two samples were tested on which no thermometric NMR was observed. They were a 10mm x 1mm² hcp single crystal, and a 4μ m thick polycrystalline fcc foil. The sample which gave positive results was the 5 μ m thick hcp single crystal from Australia.

There is a fundamental restriction on the measurement of the thermometric technique: the ratio of the power absorbed by the nuclei to the rf heating in the skin depth of the sample. This means that one cannot improve on a poor signal by simply increasing the rf power, and that the measurement should be insensitive to sample thickness. The thin samples were used so that the 60 Co resonance could also be observed—allowing

⁶⁰Co spins ⁵⁹Co spins T_1 TCrystal rf power

Cold Finger ţ

Figure 4.2: Schematic representation of the important heat flow processes in NMR-ON

calculation of the unpulled ⁵⁹Co resonance.

It is believed that the resonance was only detected in the one sample for two reasons:

- Rf efficiency: the only configuration in which this crystal did give observable resonances was with a two turn solenoid applying rf parallel to the crystal surface. With rf applied perpendicular to the surface no resonance was found.
- 2. Statistics: the observed peak was small compared to the change in anisotropy due to the non-resonant heating of the sample. This means that the high count rates given by this crystal were essential in observing resonance. (There was typically a change of 0.5% in the γ -ray intensity at resonance, compared with a 6% change due to the non-resonant heating.)

It should be noted that a highly active sample does produce radioactive self heating, due mainly to the absorption of beta particles. A sample of ⁶⁰Co with an activity of 100 μ Ci has a radioactive self heating of 65nW. However, using the formula for dE/dx given by Krane[28], and by integrating over the foil on a spreadsheet, it is estimated that $\stackrel{<}{\sim}$ 10% of the energy of the β particles was deposited in the crystal. This corresponds to a self heating of $\stackrel{<}{\sim}$ 7nW, and a temperature rise of approximately 1mK, assuming that the $Q = T^2$ relationship for the cooling power of the fridge is valid at base temperature, and that the base temperature can be taken as a constant correction.

The base temperature of the dilution fridge was never reached with either of the thin films (and self-heating was certainly not a problem in the fcc foil). The reason for this problem is not understood at this time.

4.4 Results

Figure 4.3 shows the best thermometric NMR spectrum obtained for the 100 μ Ci crystal. It is the sum of five sweeps (in the downward direction), with a dwell time at each







frequency of 100 seconds, and a step size of 100 kHz. The run clearly shows the 59 Co peak at a frequency of 218.91(6) MHz, with a width of 1.0(1) MHz. Figure 4.4 shows the 60 Co resonance, measured on three runs sweeping the frequency down. The dwell times and step sizes are as for Figure 4.3

Table 4.1 shows the measured resonances, both for ⁶⁰Co and ⁵⁹Co, with their respective anisotropies. The frequency was swept up and down; sweeps with the same conditions were taken consecutively, and added to give the results shown. The peaks were fitted assuming a Gaussian peak shape on a straight line background. The results from sweep (a) should be treated with some caution, as it only contains a single sweep, and is subject to a large amount of noise and poor statistics.

The unpulled ⁵⁹Co resonance can be obtained by scaling the measured ⁶⁰Co resonance



Figure 4.4: The 60 Co NMR-ON resonance, showing counts versus frequency. This is a sum of three runs under the same conditions.

Ref.	field	rf	counts	W(0)	sweep	Resonance	(MHz)		
	\mathbf{T} .	dBm	10 ⁶	· ·	direction	position	width		
						· ·			
⁶⁰ Co NMR-ON resonance:									
	0.3	9	1.5	0.968	up	126.38(3)	0.24(4)		
			· .		down	126.36(3)	.38(5)		
	0.15	7	4.2	0.969	up	126.49(5)	0.26(7)		
	•	· ·	• .		down	126.52(4)	.16(6)		
	0.3	12	1.5	0.971	up	126.36(3)	0.17(5)		
⁵⁹ Co	thermo	ometric	resonand	ce:					
a	0.3	(9	0.4	0.979	up -	217.98(8)	0.7		
	2		• •		down	218.37(14)	1.2		
··b	0.3	9	0.8	0.975	up	218.23(4)	0.46(5)		
					down	217.97(10)			
С	0.15	, 9	2.3	0.984	up	218.77(3)	0.67(4)		
					down	218.91(6)	1.0(1)		
. d	0.3	12	1.1	0.982	up	218.73(5)	0.80(7)		

Table 4.1: Peak positions of nuclear resonances as measured in single crystal hcp ${}^{60}Co\underline{Co}$. 'Ref.' gives entry in Table 4.2. See the text for a full description



Figure 4.5: Detail of Figure 1.5 used to calculate temperature of cobalt crystal during rf as sweeps, corrected for solid angle subtended by detector.

by the ratio of the nuclear g-factors (1.740(5), see Table 1.1.) The measured ⁶⁰Co resonance frequency was 126.42(2) MHz. This can be compared with the value of 126.8(1) MHz observed by Hagn and Zech[29]. The small difference is probably due to different sample geometry. The unpulled frequency is then calculated to be 220.0(6) MHz. The NMR frequency of hcp cobalt has been measured by Kawakami *et. al.*[30], and they report a value of 219.9MHz at a domain wall edge, which agrees with our result. The external field, which is applied perpendicular to the c-axis of the crystal, has an effect $\sim 0.01\%$ on the frequency, and has been neglected.

Figure 4.5 shows the anisotropy, W(0), for ⁶⁰Co<u>Co</u>, for the range of values of interest here. From this we can read off the temperature of the crystal as measured by the anisotropy, and calculate the expected frequency pulling. The calculated values are shown in Table 4.2, and it should be noted that the appropriate temperature was given by the anisotropy at the top of the resonance. At these temperatures the variation in W(0) with temperature is small—an uncertainty of $\pm .001$ in W(0) gives an error of ± 2.5

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Ref.	Sweep	Temperature	Frequency Pulling (MHz)		
	Direction	mK	Measured	Calculated	
	,				
\mathbf{a}	up	71	2.0	1.6	
	down	64	1.5	1.7	
b	up	64	1.7	1.6	
	down	62	2.0	1.8	
с	up	71	.1.1	1.6	
	down	77	1.0	1.4	
d	up	74	1.2	1.5	

Table 4.2: Frequency pulling, measured and calculated, for hcp Co. 'Ref.' gives entry in Table 4.1.

mK. This error in the temperature gives an uncertainty of approximately ± 0.2 MHz in the calculated frequency pulling. The measured values of the frequency pulling are also shown in Table 4.2, and can be compared with the calculated values.

4.5 Discussion

The ⁵⁹Co resonance has been measured at approximately 70 mK using thermometric NMR-ON. The resonance position varied between 217.97(10) and 218.91(6) MHz, with a mean value of 218.4 MHz, across a measured temperature range of $62 \rightarrow 77$ mK (mean: 69 mK). This frequency is 1.6 MHz lower than the unpulled value of 220.0(6)MHz. This difference, which agrees with the calculated value, is attributed to frequency pulling via the Suhl-Nakamura interaction.

This is also the first measurement of thermometric NMR on a conductor. This technique has the potential to investigate any material where a suitable nuclear orientation dopant can be implanted (provided the ratio of nuclear absorption to rf heating is large enough). It is particularly useful when the objective is to compare NMR frequencies and

lineshapes of abundant and dilute nuclear spins.

This experiment on cobalt could be improved in two ways. First, it would be advantageous to obtain lower temperatures where higher anisotropies could be measured. Failure to reach lower temperatures may have been partly due to radioactive self heating, but there appeared to be other cryogenic difficulties. The rf arrangement may have produced extra heating, and/or the dilution refrigerator, which is twenty years old, may have deteriorated. Secondly, a different radioactive nucleus which experiences a larger hyperfine field in cobalt could be used, either to replace the ⁶⁰Co or in conjunction with it. This would allow a more accurate determination of the frequency pulling and its variation with temperature.

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Appendix A

Radio-Frequency Tank Circuit

Reliable formulae and guidelines for building impedance matched tank circuits are hard to find. This information will hopefully be usefull.

Figure A.1 shows the resonant circuit used in these experiments. The resistance, r, is the internal resistance of the inductor. The inductor was a coil wound from two to four turns of copper wire. The capacitors were surface-mount rf/microwave ceramic capacitors from ATC (American Technical Ceramics). These are known to work in helium temperatures. It is likely that any surface-mount ceramic capacitor will work.

Energy losses in this circuit are dominated by radiated energy, and so the Q-value is measured rather than calculated. From a known Q-value, and inductance, L, the resonant frequency of the coil will be given by:

$$\omega_0^2 = \frac{1}{L(C+C')}.$$
 (A.1)



Figure A.1: The tank circuit used in these experiments

Appendix A. Radio-Frequency Tank Circuit

The impedance near resonance is:

$$z = \frac{Q\omega L}{(1+C'/C)^2} \tag{A.2}$$

Using these formulae and a few simple measurements it is comparatively easy to match the impedance of the coaxial cable accurately enough to avoid transmission line resonances. The experiments described here typically used a coil of two of four turns, of diameter 4 mm to 10 mm. The capacitors used were in the range $2 \rightarrow 30$ pF.

To estimate the number of turns required for a given inductance, if a solenoid (with gaps between the turns equal to the diameter of the wire) has n turns, length a and diameter b cm, then

$$L \approx \frac{n^2 a^2}{35a + 40b}$$

L is in μ H.

(A.3)

Appendix B

Mathematica Programs

The calculated graphs in this thesis were produced using simple routines on mathematica. The main functions, and an example of their use, are shown below.

Enter physical constants Units: mK, eV, T, MHz.

 $boltzmann=8.62*10^{-8}$

nuclearMagneton=3.15*10^-8

plank=4.136*10^-9

<<Graphics'Graphics'

Define the functions needed. bCoefficient[k, I, m, a] is the orientation coefficient of order k, operating on m and a —lists of m values and their occupation probabilities. aMagnetic[delta, T, m] and aQuadrupolar[P, T, m] return occupation probabilities for m values in list m, for magnetic and quadrupole field respectively. I is the nuclear spin.

Clear[bCoefficient,aMagnetic,aQuadrupolar]

Module[{k,i,mlist,alist},

bCoefficient[k_,i_,mlist_,alist_]:=

Apply[Plus,

Appendix B. Mathematica Programs

```
* (ThreeJSymbol[{i,-#},{i,#},{k,0}]& /@ mlist)
 * alist
]
]
Module[{delta,t,mlist},
aMagnetic[delta_,t_,mlist_]:=
Exp[# * delta/(boltzmann * t)]& /@ mlist
/ Apply[Plus, Exp[# * delta/(boltzmann * t)]& /@ mlist]
]
Module[{p,t,mlist},
aQuadrupolar[p_,t_,mlist_]:=
Exp[-#^2 * p *plank/(boltzmann * t)]& /@ mlist
/ Apply[Plus, Exp[-#^2 * p*plank/(boltzmann * t)]& /@ mlist]
```

This routine plots the graph of W versus t in Figure 1.5. The orientation parameters are supplied in lists, $\{\{U_2^a, U_4^a\}, \{U_2^b, U_4^b\}\}$ etc., (a) and (b) being the two gamma decays.

spin=5

magMoment=3.799

]

field=21.9

levelSplitting=magMoment*nuclearMagneton*field/spin

u={{.9394,.7977},{.9394*.7491,.7977*.2847}}

f={{-.4477,-.3044},{-.5976,-1.069}}

mValues=Table[m,{m,-spin,spin}]

LogLinearPlot[

Appendix B. Mathematica Programs

Evaluate[

Table[

1+

Apply[Plus,

(ufMean

*Table[bCoefficient[

k, spin, mValues, aMagnetic [levelSplitting, t, mValues]

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*LegendreP[k,Cos[theta]],{k,2,4,2}

]).,

],{theta,0,Pi/2,Pi/2}

٦

]

],{t,2,50},

PlotRange->{Automatic, {0,1.3}},

AxesOrigin->{1,1},

DisplayFunction->Identity

.

Show[{%,Graphics[lineLabels]},

Frame->True,

FrameLabel->{"T, mK", "W"},

DisplayFunction->\$DisplayFunction