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Nuclear Orientation and Its Application in Solid State Physics*

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Abstract

The techniques of nuclear orientation and nuclear magnetic resonance of oriented nuclei are introduced and some of their applications to various problems in solid state magnetism are described. In particular, the magnetic properties of materials can be studied by investigating quadrupole interactions, hyperfine field distributions, Knight shifts, spin–lattice relaxation and magnetic structure.

1. Introduction

A system of radioactive nuclei oriented at temperature T by an interaction of energy E_N will exhibit directional anisotropy in the intensity of its nuclear emissions if $E_N \gtrsim k_B T$. For γ rays, the radiation that is most easily and most commonly observed, the nuclear spin system must be cooled to $T \sim 0{\cdot}01$ K, a temperature readily obtainable in a demagnetization cryostat or dilution refrigerator. In the nuclear orientation (NO) experiment the angular distribution of the emitted radiation is measured to obtain information of interest both to the solid state physicist and the nuclear physicist. In this paper, we will consider only those applications of NO to solid state physics. It should be noted that there are other (dynamic) ways of producing oriented nuclei, e.g. optical, microwave and double-resonance methods (Ambler 1952; Jeffries 1952) but, since these are restricted to special systems and are rarely used to study radiation patterns, they will not be discussed here. A refinement of the NO technique first suggested by Bloembergen and Temmer (1953) and first demonstrated by Matthias and Holliday (1966) is the detection of nuclear magnetic resonance of oriented nuclei (NMRON) by monitoring the change in the angular distribution of the radiation when a resonant radio frequency (RF) field is applied.

For an ensemble of nuclei with spin I and magnetic moment μ oriented with rotational symmetry about some axis, the degree of order is completely specified (Blin-Stoyle and Grace 1957) by the $2I+1$ 'orientation parameters'

$$B_\nu = \sum_{M=-I}^{I} (2\nu+1)\, C(I\nu I; M\,0)\, a(M)\,. \tag{1}$$

Here $\nu \leqslant 2I$, M is the magnetic quantum number, the $C(I\nu I; M\,0)$ are Clebsch–Gordan coefficients and $a(M)$ is the normalized population of the Mth substate. Note that the population distribution amongst the substates can be expressed in terms of

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the B_ν, which themselves are proportional to the magnetic multipole moments, that is, $B_1 \propto \langle M \rangle$, $B_2 \propto \langle 3M^2 - I(I+1) \rangle$ etc. If the ensemble is in internal thermodynamic equilibrium, it can be described by a temperature T and $a(M) \propto \exp\{-E_N(M)/k_B T\}$.

The population distribution being known through equation (1), electromagnetic theory can be applied to derive the γ-ray emission pattern from the oriented ensemble. In general the observed γ ray is preceded by one or more unobserved transitions,

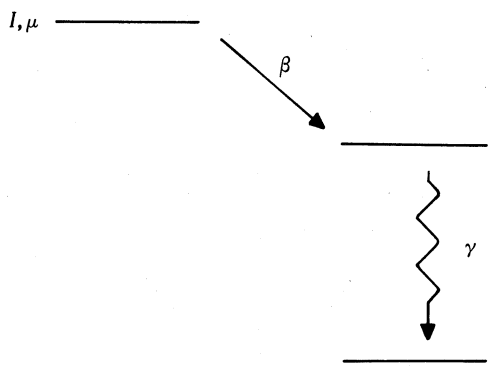

Fig. 1. Typical decay scheme: the observed γ ray is preceded (in this case) by a β decay from the oriented parent state.

e.g. a β decay as in Fig. 1, and the normalized intensity measured at angle θ to the quantization axis is given by (Blin-Stoyle and Grace 1957; de Groot *et al.* 1965)

$$W(\theta) = \sum_{\nu=0}^{\lambda} B_\nu U_\nu F_\nu \mathrm{P}_\nu(\cos\theta). \tag{2}$$

Here the coefficients U_ν and F_ν depend only on the radioactive decay; the U_ν are angular momentum coefficients giving the attenuation of the orientation during the preceding decays while the F_ν are angular momentum coefficients for the observed transition and depend, in particular, on the multipole character L of the radiation. The P_ν are Legendre polynomials and the summation is carried out over even ν, with λ being $2I$ or $2L$, whichever is the smaller.

Obviously the emission patterns for α and β radiation can be obtained in a similar manner using angular momentum theory and nuclear theory. Of particular note, for β decays involving the weak interaction, parity is not conserved and the leading anisotropic term in the expression for the β-ray intensity involves B_1; recall that the first demonstration of parity nonconservation in weak interactions was the NO experiment of Wu *et al.* (1957).

2. Methods of achieving Nuclear Orientation

In order to attain enough order in the nuclear spin system to produce a significant γ-ray anisotropy, it is necessary that the leading anisotropic term in equation (2), i.e. the $\nu = 2$ term, differs appreciably from zero. This can be achieved by utilizing the hyperfine interaction in magnetic materials. Prior to 1960, most NO experiments were performed using paramagnetic salts and the solid state information that was obtained related to the elucidation of the spin Hamiltonian (Abragam and Pryce

1951) describing the electronic and nuclear spins (for a discussion of these effects see e.g. de Groot *et al.* 1965 and Freeman and Watson 1965). One experiment was performed on ^{60}Co oriented in ferromagnetic cobalt metal (Grace *et al.* 1955), and ^{54}Mn and ^{60}Co had been oriented in antiferromagnetic hosts (Daniels and Leblanc 1958; Daniels *et al.* 1961; Miedema and Huiskamp 1961). In 1960 a very important experiment by Samoilov *et al.* (1960) demonstrated that nuclei of diamagnetic atoms could be polarized by dissolving them in a ferromagnetic host. It is important to know the temperature accurately in NO experiments and this can be measured by monitoring the γ-ray anisotropy of an isotope, whose decay scheme is well known, dissolved in a host for which the hyperfine interaction is also known; for example, ^{60}Co–**Fe** (Stone and Turrell 1962).

In many cases, the hyperfine interaction in an ordered magnet can be represented by an effective magnetic field $\boldsymbol{H}_N$ (Marshall 1958) which can be quite large. Thus cobalt and gold nuclei in iron experience fields of 29 and 130 T respectively (Koster and Shirley 1971). The field can be parallel or antiparallel to the electronic magnetization. In the case of a multidomain ferromagnet, an external field $\boldsymbol{H}_0$ must be applied to magnetically saturate the sample and produce an orientation axis unique to the whole specimen. Then $\boldsymbol{H}_N$ may be in the same direction as $\boldsymbol{H}_0$ (positive) or in the opposite direction (negative).

In atoms with an atomic moment, there are a number of contributions to the hyperfine interaction between the unpaired electrons and the nuclei (Marshall 1958; Watson and Freeman 1961). For 3d transition ions with quenched orbital angular momentum, the dominant contribution comes from the unpairing of the inner core s electrons which interact with the nuclei via the Fermi contact interaction, while in rare earth ions the most important contribution is due to the unquenched orbital moment. For diamagnetic atoms dissolved in ferromagnetic hosts, polarized conduction electrons produce the dominant contribution to $\boldsymbol{H}_N$, again through Fermi contact interaction.

Of course, nuclei can be oriented directly by a laboratory field if it is large enough; this is the 'brute force' method (Gorter 1934; Kurti and Simon 1935). With the fields available from modern superconducting magnets the technique is quite feasible (Brewer 1977). Also nuclei may be aligned by quadrupole interaction (see e.g. Brewer and Kaindl 1978; Ernst *et al.* 1978).

If the nuclei are oriented by a magnetic field, real or effective, the interaction energy is $E_N(M) = -M\mu H_N/I$ and the population difference between adjacent Zeeman levels is $\exp(\mu H_N/Ik_B T)$. For appreciable nuclear orientation $\mu H_N/Ik_B T \approx 1$, and for $\mu = 1$ n.m., $I = 1$ and $H_N = 50$ T this condition is attained for $T \approx 0{\cdot}02$ K.

3. Nuclear Magnetic Resonance of Oriented Nuclei (NMRON)

Consider an ensemble of radioactive nuclei oriented by a hyperfine field and in thermal equilibrium with the lattice at some low temperature T_L. The populations of the nuclear magnetic substates will be described by a Boltzman distribution at T_L, as shown in Fig. 2*a*. Application of an RF field H_1, of sufficient amplitude and with a frequency f satisfying the resonant condition

$$hf = \mu H_N/I, \tag{3}$$

will cause transitions amongst the equally spaced Zeeman levels so that the population

distribution is altered (Fig. 2*b*). Then the γ-ray intensity measured in a given direction (usually $\theta = 0$) will be altered and the resonance so detected (Fig. 2*c*). Note that this method of detection is *extremely* sensitive; the number of ^{60}Co atoms needed is $\sim 10^{13}$ and for shorter-lived isotopes the number can be much smaller.

In the continuous wave (CW) method the frequency of the frequency-modulated (FM) RF field is swept until resonance is detected just as in a conventional CW NMR experiment. The destruction of anisotropy (signal) achieved depends on the FM amplitude (it should be around a linewidth) and its frequency (Barclay 1969). In ferromagnetic metals the linewidth measured is typically ~ 1 MHz, but this has a large inhomogeneous contribution from demagnetizing effects (Kieser *et al.* 1974)

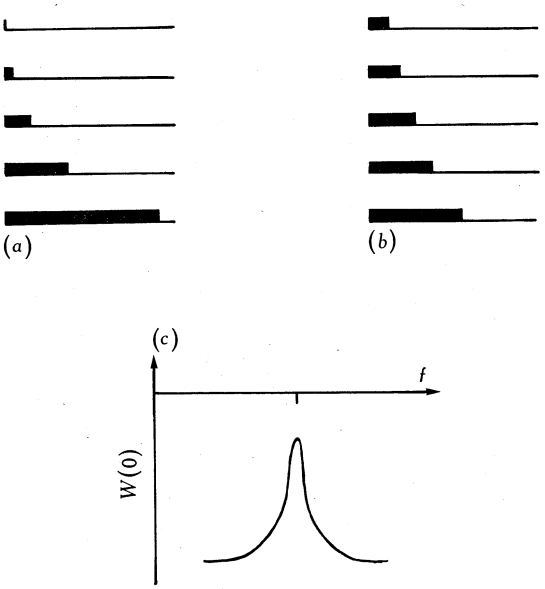

Fig. 2. Showing schematically: (*a*) an equilibrium situation with the magnetic substate populations described by a lattice temperature $T_L = \mu H_N/Ik_B$; (*b*) the altered population distribution after application of an RF field with frequency $f = \mu H_N/Ih$; (*c*) a plot of the γ-ray intensity $W(0)$ versus f showing the resonance.

and can be reduced by careful polishing of the sample (Streater 1976). The amplitude of the RF field is fortunately enhanced via the hyperfine interaction and considerable destruction of anisotropy ($\sim 65\%$) can be achieved without heating the specimen with eddy currents. That a greater signal is not obtained is presumably due to quadrupole effects (Callaghan *et al.* 1974) which produce unequal spacing of the sublevels.

Once the resonance condition has been attained, the RF field can be switched off resonance so that the nuclear spin system relaxes back to equilibrium with the lattice. Thus the spin–lattice relaxation time T_1 can be determined (Templeton and Shirley 1967). A difficulty with the analysis of T_1 is the lack of knowledge of the initial condition of the spin system after resonance. It should also be noted that the high temperature approximation, namely $\mu H_N/Ik_B T \ll 1$, usually employed in

conventional NMR theory, is obviously not valid for NO so that, in general, the analysis requires the use of multiple exponents (Gabriel 1969; Bacon *et al.* 1972). If the concentration of radioactive nuclei is large enough, it should be possible to describe the nuclear spin ensemble by a spin temperature T_S rendering the analysis of T_1 easier, but there are still inconsistencies, perhaps due to inhomogeneities and skin depth effects (Kieser and Turrell 1976). At the moment the most reliable method of measuring T_1 is the nonresonant NO experiment in which the lattice temperature is changed, e.g. by fast partial demagnetization (Chaplin *et al.* 1970), and the subsequent relaxation of the nuclear spins is measured by monitoring the γ-ray intensity. This method works well because typically T_1 is ~ 100 s.

Another technique borrowed from conventional NMR and applied successfully to NMRON is the single-passage method introduced by the Monash group (Barclay *et al.* 1970). This method has proved very successful in determining small quadrupole interactions (Callaghan *et al.* 1974).

More recently another important development has been the pulsed NMRON method introduced by the Duntroon group (Foster *et al.* 1977*a*, 1977*b*; Wilson *et al.* 1977). In this technique the oriented nuclear spin system is subjected to pulses of an RF field at the resonance frequency and the subsequent response of the spin system is again obtained by measuring the spatial distribution of γ rays. Of course, it would be very difficult to monitor as a function of time the precessing radioactive spins in a plane transverse to the orienting hyperfine field (z axis). However, the Duntroon group cleverly use a final pulse to rotate the spin pattern and detect along the z axis so that the resulting distribution of z-spin components depends on whether or not there had been coherence in the transverse plane. Thus, to observe a free induction decay, two pulses are used rather than the one in a conventional NMR experiment; to observe a spin echo, three pulses are used. A novelty of the experiment is the greater multiplicity of echoes that are observed over that in conventional NMR because the radiation pattern depends on higher multipoles B_ν. With pulsed NMRON one can measure T_1 and T_2, which is a measure of spin–spin interaction in solids. It should also be possible to measure quadrupole interaction frequencies much smaller than the NMR linewidth by observing the amplitude modulation of the T_2 decay.

Yet a further development (H. R. Foster, personal communication) is FM pulsed NMRON which combines the advantages of the CW and pulsed techniques so that a greater sensitivity is obtained in detecting resonances. The peak RF power that can be put into the spin system without excessive eddy current heating is much greater than with the CW method. Also, spin–lattice relaxation no longer competes as a reorientation process during the much shorter RF irradiation time. Consequently about 75% destruction of anisotropy is achieved.

4. Experimental Procedures

The low temperatures required for NO experiments are usually obtained with a demagnetization cryostat or dilution refrigerator. In the former, a convenient salt for reaching $T \sim 0{\cdot}01$ K is chrome potassium alum while for lower temperatures, at the expense of a reduced heat capacity, cerium magnesium nitrate can be used. Alternatively a demagnetization stage, using cerium magnesium nitrate or an enhanced nuclear coolant, such as $PrNi_5$, can be added to the dilution refrigerator. Actually,

modern versions of the refrigerator now reach temperatures of a few mK. In either apparatus, the specimen is soldered, if it is a metal, or glued to a copper cold finger which has a large area of contact with the salt pill or mixing chamber of the refrigerator. Usually a demagnetization cryostat is designed with auxiliary 'guard pills' and a 'heat shield' to reduce heat flow to the main cooling salt. A typical demagnetization cryostat is shown in Fig. 3. In a well-designed system the specimen can be maintained

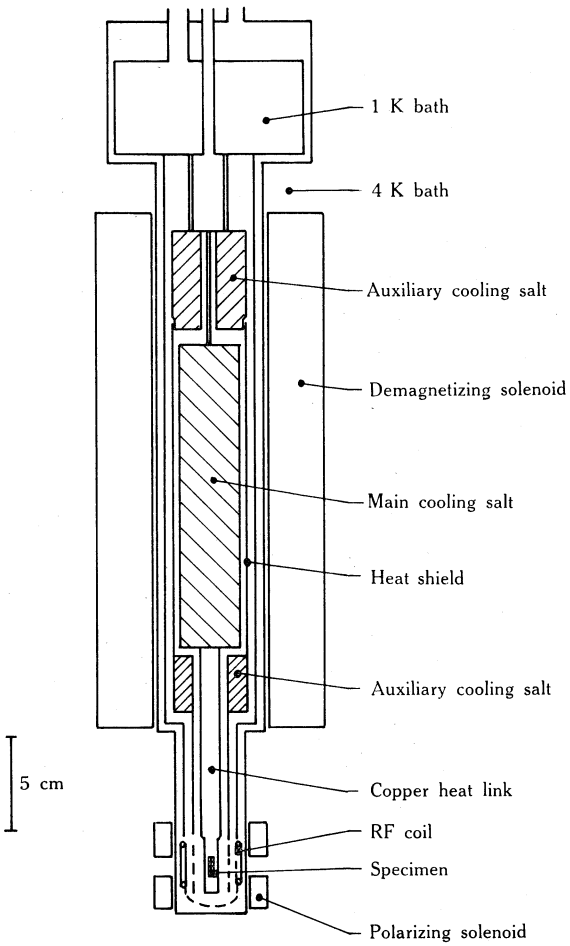

Fig. 3. Diagram of an adiabatic demagnetizing cryostat.

at a very low temperature for many hours. Of course, in the dilution refrigerator the low temperature is maintained continuously. For the NMRON experiments a coil can be wound around the specimen either inside the specimen chamber, perhaps on a heat shield, or outside on a glass tip as in Fig. 3.

The γ rays are detected outside the cryostat with NaI or Ge(Li) detectors, the former having higher efficiency and larger size, the latter having much better resolution. Also the Ge(Li) detector is quite insensitive to changing magnetic field which is sometimes an important consideration. The detection of β and α rays is more

difficult because these radiations do not penetrate the walls of the cryostat. Early β–NO experiments used light-pipes which cause considerable cryogenic problems. In recent years some success has been attained using solid state detectors, the main difficulty being their failure to operate at helium temperatures.

The NO specimens can be prepared in various ways. For metallic specimens, the radioactive isotope can sometimes be deposited on the surface of the host and diffused into it, or the isotope and host may be melted and re-solidified. Nonmetallic specimens may be prepared from the melt or, if the specimen is a hydrated salt, from a saturated solution. Also, neutron irradiation of a sample can be used if a suitable isotope is thereby produced. Additionally, radioactive atoms can be directly implanted into hosts, this last method sometimes producing quite exotic systems, e.g. Xe–**Fe** (de Waard and Drentje 1969).

5. Experimental Results

For many years NO and NMRON have been used to determine the sign and magnitude of hyperfine fields for different elements through the periodic table in various hosts, mostly iron, cobalt and nickel. These measurements together with those made using NMR, Mössbauer, perturbed angular correlation and other methods have yielded much information (Koster and Shirley 1971; Rao 1975) which can be used to check various models for the dilute ferromagnetic alloy system (see e.g. Shirley and Westenbarger 1965; Campbell 1969). In recent years these techniques have been applied to investigate a wider variety of problems in solid state physics, some of which we shall now discuss.

(*a*) *Quadrupole Interaction in 'Cubic' Systems*

Even though a crystal lattice may be cubic, application of a magnetic field can break this symmetry. Also, for a cubic system which orders magnetically, the symmetry will be broken through interactions between the magnetization and lattice (magnetostriction). Thus we might expect a quadrupole interaction from this effect. Lattice defects can produce quadrupole interaction with the nucleus. Also there can be interaction between the nuclear quadrupole moment and any unquenched orbital angular momentum, i.e. an intra-atomic effect. For axial symmetry, often a good approximation, the strength of the quadrupole interaction can be described in terms of the parameter

$$P = e^2qQ/4I(2I-1), \tag{4}$$

where eq is the electric field gradient at the nucleus and Q is the nuclear quadrupole moment (see e.g. Slichter 1963).

For $P \gtrsim w$, the NMRON linewidth, structure can be seen in the resonance spectrum, while for $\mu H_1/hI < P < w$ sweep asymmetries are observable in single-passage NMRON measurements, and these yield estimates of the quadrupole interaction. Thus for ^{60}Co nuclei in polycrystalline iron a sweep asymmetry is observed and in the single crystal the effect is much larger, with $P = -6{\cdot}5$ kHz (Callaghan *et al.* 1974, 1976). These results suggest that the electric field gradient is defined by the crystal axes, i.e. the effect comes from the lattice. On the other hand, NMRON studies of ^{198}Au–**Fe** (Callaghan *et al.* 1975) indicate a much larger value of $P = 210$ kHz. In this case the interaction is probably due, at least in part, to orbital

angular momentum in the gold atom, since a study of the hyperfine anomaly in gold isotopes in iron (Fox and Stone 1969) suggests strongly that a local orbital moment is induced on the gold atom in the iron host.

(*b*) *Hyperfine Field Distribution in Dilute Alloys*

Measurement of the distribution of hyperfine fields in a dilute ferromagnetic alloy can be compared with the magnetic moment distribution determined by neutron scattering experiments in order to obtain information concerning the variation of conduction electron polarization about an impurity atom. Most experiments of this nature have been performed using NMR or Mössbauer methods. In the former

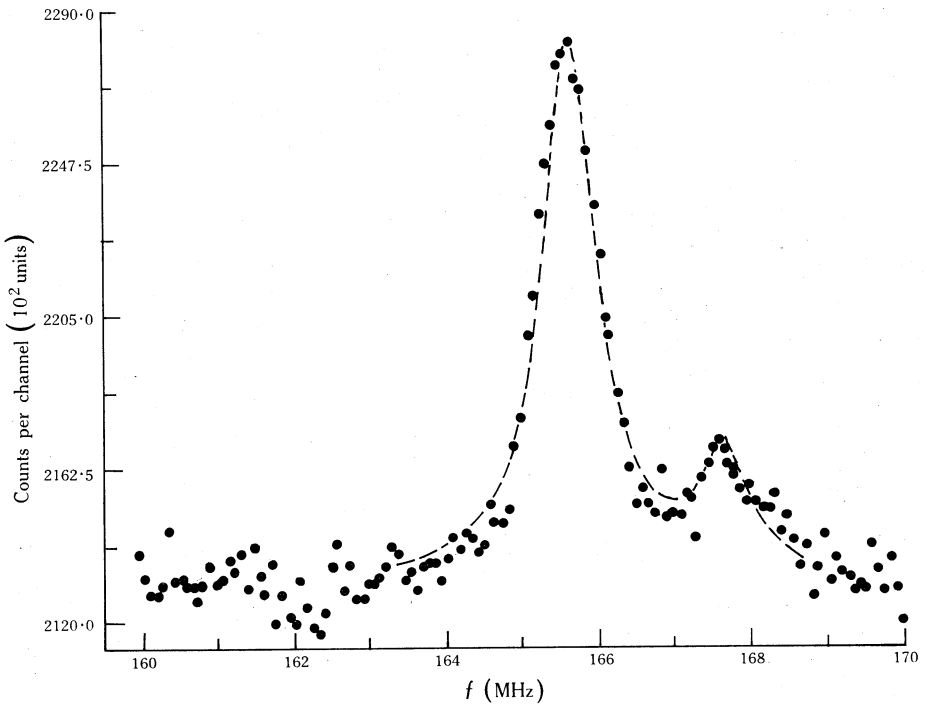

Fig. 4. NMRON spectrum of ^{60}Co in 1% Co–**Fe**. The counting time per channel was 60 s and the modulation width and rate were 0·5 MHz and 100 Hz respectively; the polarizing field was 0·1 T and the specimen temperature was 12 mK. The fitted curves are Lorentzian.

technique the spectra may be difficult to interpret if domain wall nuclei are observed because of varying enhancement factors, anisotropic interactions and different excitation conditions. These difficulties can be obviated by applying a magnetic field large enough to produce magnetic saturation, but then the spectral lines are broadened to $\sim$1 MHz and also sensitivity is lost. In the latter technique all (Mössbauer) nuclei are observed with equal probability but the instrumental resolution is $\sim$2 MHz; also the number of nuclei that can be studied is rather limited.

It would appear, then, that NMRON might be a useful complementary technique for these studies, offering the resolution of NMR while allowing all nuclei to be

observed with equal probability. This has been demonstrated by NMRON experiments on dilute Co–**Fe** alloys (Kieser and Turrell 1975; Streater 1976). Fig. 4 shows the spectrum for ^{60}Co in 1% Co–**Fe**. Theoretically it is difficult to explain such spectra quantitatively. One can compare the data with a simple model (Rubinstein 1968; Stauss 1971) in which a given cobalt atom experiences additive and isotropic shifts in a hyperfine field due to the proximity of other cobalt atoms randomly distributed in near neighbour shells. Then a satellite which should appear at a frequency lower than the main line due to a nearest neighbour cobalt atom is missing, while the satellite that is observed at a higher frequency due to a cobalt atom in the next-nearest neighbour shell is enhanced in intensity (see Fig. 4). This could be due to a repulsion effect between nearest neighbour cobalt atoms (Le Dang Khoi *et al.* 1974) and/or broadening of the nearest neighbour line by anisotropic interactions (see e.g. Cranshaw 1972).

(*c*) *Knight Shift in Ferromagnets*

The application of a magnetic field to a ferromagnetic metal may produce a field at the nucleus which differs from that value calculated by simple addition of $\boldsymbol{H}_N$ and $\boldsymbol{H}_0$. The Knight shift K (a term borrowed from the language of conventional NMR describing the shift in nonferromagnetic metals) is defined by the relation

$$\Delta f = (\mu \Delta H_0 / Ih)(1+K). \tag{5}$$

Here Δf is the NMR frequency shift observed in changing the applied field by ΔH_0. The existence of this effect was first indicated by an NO experiment (Hagn and Eska 1974).

In simple metals the dominant contribution to the normal Knight shift is the Fermi contact interaction between the nucleus and the conduction electrons, which become magnetically polarized on application of a field, and it is positive. In paramagnetic transition metals there are also contributions from the localized unpaired electrons including core polarization and orbital (Van Vleck) effects. In ferromagnetic metals a static atomic moment exists and, as we have seen, even in zero field there is a large static hyperfine field coming from polarized conduction and core s electrons and any orbital moment. Application of a field can perturb the electronic wavefunctions thereby modifying these contributions to H_N and producing a Knight shift.

The best measurement to date of a ferromagnetic Knight shift was obtained in a conventional NMR experiment on stable ^{59}Co in single crystal h.c.p. cobalt (Fekete *et al.* 1976). The result was $K = 1{\cdot}94 \pm 0{\cdot}25$ %, and this was used to estimate the high field spin and orbital electronic susceptibilities, allowing the conclusion that h.c.p. cobalt is a weak itinerant-electron ferromagnet.

Previous NMRON experiments on ^{57}Co, ^{58}Co and ^{60}Co in iron (Kopp and Brewer 1977) in fields up to only 0·8 T gave inconsistent results and a re-investigation of ^{192}Ir–**Fe** (Daly *et al.* 1975) indicated a value of K much smaller than previously obtained by Hagn and Eska (1974). It should be mentioned that measurements of K in ferromagnets are quite difficult. In broad-line NMR, care has to be taken to allow for quadrupole effects, which cause additional centroid shifts in the line shape, demagnetization effects at low applied fields, hyperfine anomalies between different

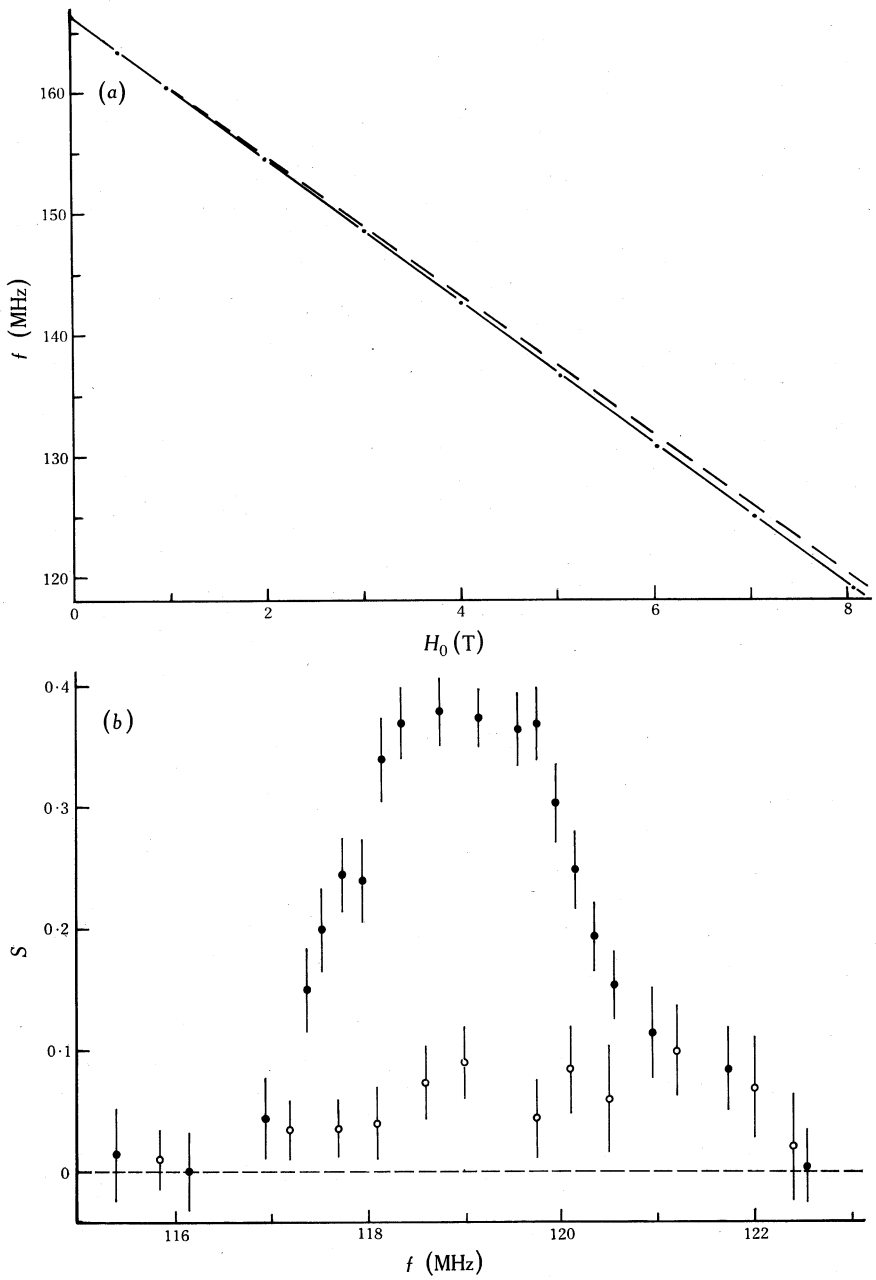

Fig. 5. NMRON determination (H. R. Foster, personal communication) of the ferromagnetic Knight shift K in ^{60}Co–Fe:

(*a*) Measured frequencies in applied fields up to 8 T. The dashed line is the theoretical variation for $K = 0$. The data points include the experimental errors, the main error in the measured value of K being derived from the uncertainty in $\mu(^{60}\text{Co})$.

(*b*) Resonance observed in an applied field $H_0 = 8{\cdot}049$ T using the FM pulsed technique. The signal S is the fractional change in γ-ray anisotropy, $1 - W(0)$, immediately after a pulse of frequency f. The solid and open circles represent data taken with FM on and FM off respectively.

isotopes and additional uncertainties in measured nuclear moment values. Experimentally it is important to make measurements over as wide a range of applied fields as possible.

The most accurate and reliable NMRON determination of the ferromagnetic Knight shift for an impurity nucleus has recently been made by the Duntroon group (H. R. Foster, personal communication), who measure a value of $K = +1{\cdot}4 \pm 0{\cdot}7\%$ for ^{60}Co–**Fe** using the FM pulsed technique in applied fields up to 8 T. Fig. 5*a* shows a plot of K versus H_0 and Fig. 5*b* illustrates the resonance observed in 8 T. The positive value of K for ^{60}Co–**Fe** means experimentally that the downward frequency shift (H_N is negative) is greater in magnitude than estimated from $\mu \Delta H_0/Ih$. Theoretically, it indicates a dominant contribution from orbital (Van Vleck) magnetic moment induced by the applied field, since core polarization effects would be negative and conduction electron polarization would be expected to contribute $\lesssim 0{\cdot}5\%$ based on conventional Knight shift measurements (for copper $K = +0{\cdot}23\%$).

The FM pulsed technique appears to be the best NMRON method of attacking the problem. It is a worthwhile endeavour because measurements of the Knight shift, together with the determination of the anisotropy of H_N in single crystals, provide data with which to test band models in transition metal ferromagnets.

(*d*) *Spin–Lattice Relaxation*

In ferromagnetic metals, NMR, NMRON and nonresonant NO have been used to study spin–lattice relaxation, which is characterized by the time T_1. In unmagnetized multidomain samples, the NMR signal is dominated by the contribution from nuclei in domain walls due to the tremendous enhancement of their response, and the relaxation of these nuclei is understood fairly well (Winter 1961; Weger 1962); the nuclei actually experience a transverse component of hyperfine field produced by thermal motions of the wall. However, it is of interest to measure T_1 in the absence of domains and walls because then the relaxation will be due only to atomic (intrinsic) processes. This can be achieved by applying a field that is sufficiently large to magnetically saturate the sample, and it is in this regime that the inherently more sensitive NO and NMRON techniques are useful because conventional NMR becomes quite difficult (as noted in subsection (*b*) above). This intrinsic relaxation rate in 3d ferromagnetic metals has contributions from conduction electrons, from core electrons and dominantly from the fluctuating orbital current of the d electrons which have a high density of states at the Fermi surface (Moriya 1964). A contribution to the relaxation due to conduction electrons which interact with the nucleus via spin waves has also been proposed (Weger 1962). This term is interesting because it is dependent on applied field which would damp the spin waves.

It is also of interest to study nuclei in domains in unmagnetized and partially magnetized samples because, after all, most of the volume is occupied by domains. This domain relaxation rate has been investigated by NMR and NMRON (see Kieser *et al.* 1974), the latter technique lending itself to the study because all nuclei are sampled equally (see subsection (*b*)). It is found that the domain value for $1/T_1$ exceeds the intrinsic $1/T_1$ value by a factor ranging up to 5 in some cases and that the domain $1/T_1$ is very dependent on field. Measurements have also been made using samples of ^{54}Mn–**Fe** and ^{54}Mn–**Ni** (Kieser 1975). This spin–lattice relaxation in domains is still not understood. The field-dependent conduction electron–spin wave mechanism, transverse hyperfine field components produced by thermal rotations

of domains, and spin diffusion from rapidly relaxing wall spins are all insufficient to account for the observed relaxation rate.

NO measurements (Kieser and Turrell 1976; Klein 1977) suggest that even in the fully magnetized state there still remains a field-dependent contribution of $1/T_1$, implying that spin waves are contributing in some way to the relaxation. Fig. 6 shows the results of the Vancouver group (Kieser *et al.* 1974; Kieser and Turrell 1976) and new high field data obtained by the Duntroon group (D. H. Chaplin, unpublished data) using the FM pulsed NMRON method.

In other ordered systems there have been far fewer studies using NO techniques. In antiferromagnetic $MnCl_2 . 4H_2O$ an NO experiment (Gorling *et al.* 1977) indicates $T_1 < 3000$ s at 0·1 K, an estimate based on the time to cool a crystal of the material to low temperatures. In antiferromagnets, to the author's knowledge, no NMRON has been observed (not for the want of trying!) so that accurate determinations of T_1 are lacking for systems that order at low temperatures.

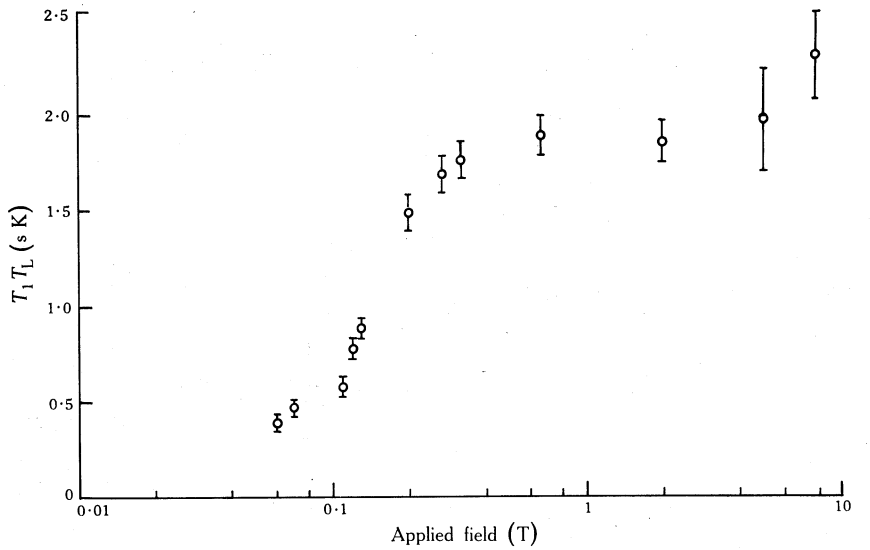

Fig. 6. Values of $T_1 T_L$ for ^{60}Co–Fe in different applied fields. The data for fields up to 0·67 T are from Kieser and Turrell (1976) and those from 0·67 to 8 T are from D. H. Chaplin (unpublished data).

(*e*) *Magnetic Structure Studies*

Until quite recently the great majority of NO experiments have been performed on ferromagnetic metals. The first NO experiment investigating the spin-flop transition in an antiferromagnet was performed on $CoCl_2 . 6H_2O$ using ^{54}Mn (Turrell *et al.* 1972). Gorling *et al.* (1974, 1977) have carried out an extensive study of the antiferromagnet $MnCl_2 . 4H_2O$ which has a Néel temperature $T_N = 1 \cdot 6$ K. In these experiments, the atomic magnetization is deduced from measurements of the spatial distribution of ^{54}Mn γ rays since the atomic moments define the orientation axes through the hyperfine interaction. The antiferromagnetic, spin-flop and paramagnetic phases were all investigated, the easy axis of magnetization was determined and molecular fields, including a sizeable second-order anisotropy contribution, were deduced. Furthermore, the spin-flop transition region was found

to be adequately described by a domain structure, and the temperature dependence of the transition field was observed to decrease with decreasing temperature, contrary to previous reports. Figs 7*a* and 7*b* show respectively a typical sweep from 0 to 3 T, with H_0 and the detector along the easy axis, and, in closer detail, a sweep through the spin-flop transition.

More recently, there have been NO investigations of various ordered rare earth materials. Holmium has been studied (Marshak and Turrell 1979) and the canting angle for the helical spin structure has been determined very accurately. Further, the authors demonstrate how NO can be used to obtain the complete structure of a multiaxial ordered system. Thus NO can complement neutron diffraction and, in certain circumstances, e.g. for systems that order at low temperatures or alloys with atomic moments of similar magnitude, it could be more powerful in determining magnetic structure. Terbium and erbium have been studied using ^{54}Mn (Grimm *et al.* 1979). Also, the enhanced nuclear magnet holmium vanadate, $HoVO_4$, has been investigated (Suzuki *et al.* 1978). The latter experiment demonstrates the existence of antiferromagnetic order in the nuclear spin system with a Néel temperature $T_N = 4{\cdot}5$ mK.

(*f*) *Other Systems*

NO is also a useful technique for studying the 'other end' of the alloy system, i.e. transition elements in nonferromagnetic hosts (see e.g. Stone 1971), because, as pointed out in Section 3, only $\lesssim 10^{13}$ radioactive atoms are required so that one really has a dilute alloy. These systems fall into three classes: free paramagnetic ions (e.g. ^{54}Mn–**Au**); Kondo systems with low T_K (e.g. ^{54}Mn–**Ag**); and transition metal alloys (e.g. the giant moment system Co–**Pd**).

Another class of system of topical interest amenable to study by NO is the amorphous alloy ferromagnet. For example, $Co_{80}P_{20}$ has been studied (Dollard *et al.* 1978) using ^{60}Co to determine the sign and magnitude of the cobalt hyperfine field. This experiment was carried out to complement an NMR study by Raj *et al.* (1976) of this alloy system.

(*g*) *Thermometry*

As noted in Section 2, one can use NO to determine the temperature of a sample. The γ-ray anisotropy thermometer is obviously useful in NO experiments, but also is suitable in other favourable experimental situations. Note that the sensor (γ-ray detector) is placed outside the cryostat; the NO specimen is put in thermal contact with the system under study and there are no leads to worry about. Useful thermometric isotopes are ^{60}Co and ^{54}Mn which may be put into various hosts, usually iron, cobalt or nickel. In particular ^{60}Co in single-crystal h.c.p. cobalt has the advantage of a long half-life, and no magnetic field is necessary to produce a common axis of nuclear orientation. For temperatures below 10 mK the Kondo system ^{54}Mn–**Cu** is a good thermometer, while for higher temperatures (even up to 1 K) rare earth thermometers, e.g. ^{166m}Ho in single-crystal holmium (Marshak 1978) can be used because the hyperfine interaction in these materials can be very large.

In the last few years there has been critical examination of γ-ray anisotropy thermometry to establish its use as an absolute thermometer. In particular the reader is referred to the excellent review article by Hudson *et al.* (1975) which discusses thermometry below 0·3 K and compares all thermometers used in this regime.

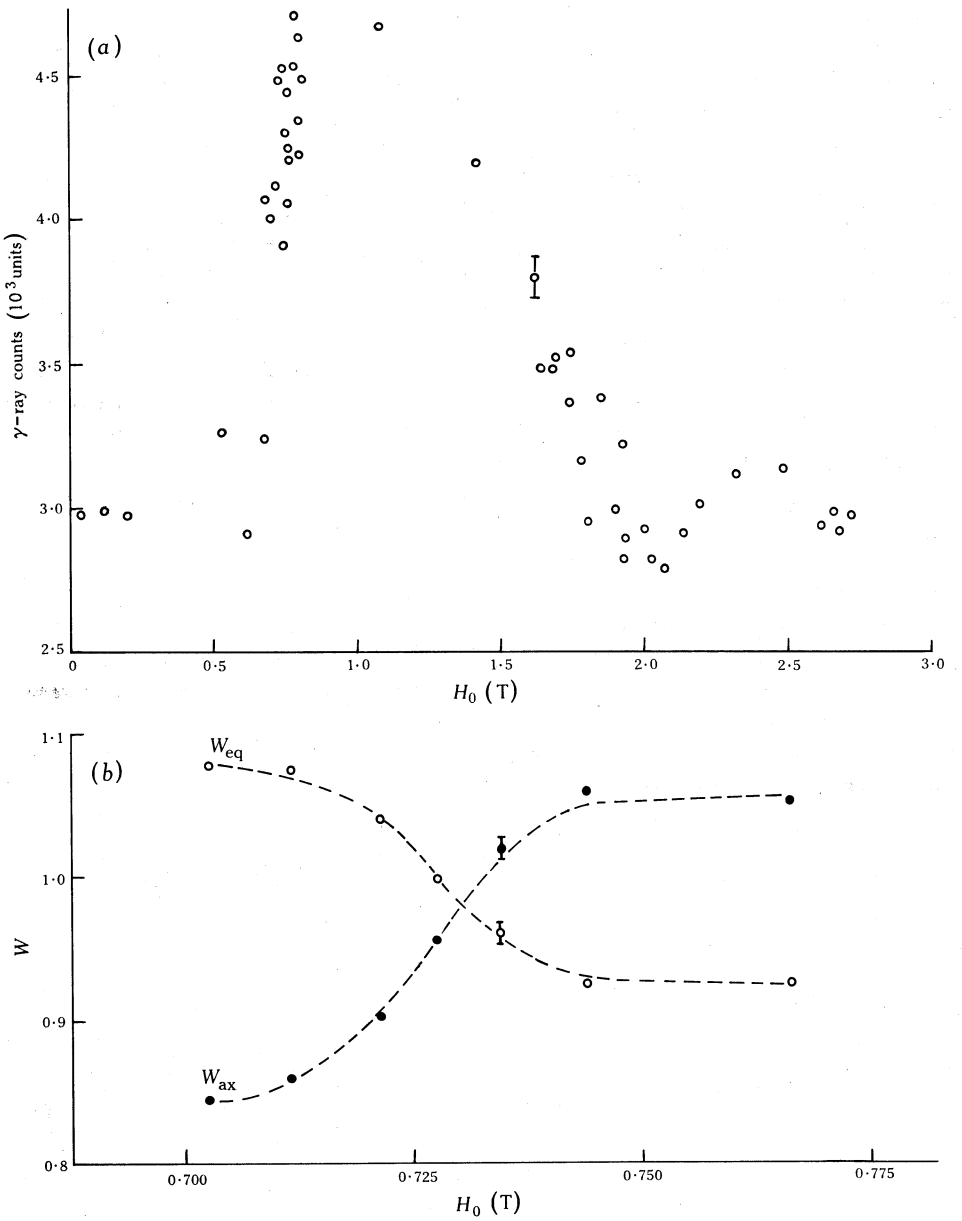

Fig. 7. Results of NO measurements for ^{54}Mn–$MnCl_2 . 4H_2O$:

(*a*) Raw data collected in one field sweep from 0 to 3 T. The detector was placed on the easy axis along which the field H_0 was also applied.

(*b*) Normalized γ-ray intensities W emitted in an 'axial' direction (W_{ax} along the c axis) close to the easy axis and an 'equatorial' direction (W_{eq} in the a^*–b plane) for field sweeps through the spin-flop transition.

Hudson *et al.* conclude that the γ-ray anisotropy thermometer will be useful for comparison measurements with other primary thermometers and for calibrating both fixed points and secondary thermometers.

6. Conclusions

From this outline of the NO and NMRON techniques and their use in a variety of solid state problems, it is hoped that the novelty and wide applicability of these methods has been demonstrated. In particular their very high sensitivity should be noted. Obviously NMRON and conventional NMR often can be brought to bear on the same problem: sometimes one is better in certain situations, sometimes the other, and often the two techniques are complementary. Also, quite recently NO has been used with success in magnetic structure studies.

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