## NUCLEAR ORIENTATION EXPERIMENTS

IN

## PARAMAGNETIC, ANTIFERROMAGNETIC

## AND

## FERROMAGNETIC SUBSTANCES

by

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L. Katz, K.G. McNeill, M. LeBlanc and F. Brown Canadian Journal of Physics <u>35</u>, 470 (1957)
Nuclear Orientation of Mn<sup>54</sup> in Antiferromagnetic Single Crystals

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Nuclear Orientation of Co<sup>60</sup> in Antiferromagnetic Cobalt Ammonium Sulphate Single Crystal

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## NUCLEAR ORIENTATION EXPERIMENTS IN PARAMAGNETIC, ANTIFERROMAGNETIC AND

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## ABSTRACT

Through the technique of adiabatic demagnetization of paramagnetic salts substances may be cooled to temperatures of the order of  $0.1^{\circ}$ K and  $0.01^{\circ}$ K. At these low temperatures the hyperfine structure interaction can produce an appreciable degree of nuclear orientation. The orientation of an assembly of radio-active nuclei may be detected by measuring the anisotropy in the emission of gamma radiation. By this method we have investigated nuclear orientation in paramagnetic, antiferromagnetic and ferromagnetic substances.

We have studied the nuclear orientation of Pr<sup>142</sup> and Yb<sup>175</sup> introduced as impurities in paramagnetic single crystals of cerium magnesium nitrate. The anisotropy of the 1.57 Mev  $\sigma$ -ray of  $Pr^{142}$  was measured as a function of temperature in the range 0.003°K to 1.0°K both in zero external magnetic field and in a field of 320 gauss parallel to the trigonal crystal axis. Values for the magnetic moment of  $Pr^{142}$  were assigned from our results for two assumed decay schemes; these are 0. 11 nuclear magnetrons for the spin assignments 2 2 - 2 = 0 and 0. 15 nuclear magnetons for the spin assignments  $2 - \frac{1}{2} 2 - \frac{2}{2} 0$ . Similar experiments were carried out on Yb<sup>175</sup>. Measurements were made in a variety of external magnetic fields up to 700 gauss, and at temperatures as low as 0.003°K. No anisotropy was observed for the 396 kev  $\pi$ -ray, nor for the 282 kev  $\pi$ -ray. The most likely explanation for this result is that the lifetime of the  $\pi$ -emitting state is about  $10^{-10}$  seconds. This conclusion has since received independent confirmation.

We have established that nuclear orientation can be produced in antiferromagnetic single crystals. We have explored some of the possibilities and features of nuclear orientation in this class of substances by investigating salts of manganese and cobalt with transition temperatures differing by an order of magnitude. Single crystals of these antiferromagnetic salts were cooled in thermal contact with potassium chrome alum and the anisotropy of the gamma radiation emitted by  $Co^{60}$  and  $Mn^{54}$  introduced in the lattice was observed. These measurements show that the hyperfine structure splittings in the antiferromagnetic state are comparable to those found in the paramagnetic state and give indications that nuclear spin relaxation times may be of the order of minutes and hours in antiferromagnetic materials at temperatures below  $1^{\circ}$ K.

We have attempted to detect nuclear orientation arising from a possible hyperfine structure interaction at the anion in antiferromagnetic  $MnBr_24 H_20$  and  $Mn Ci_24 H_20$ . To detect the nuclear orientation we observed the anisotropy of the gamma radiation emitted by  $Br^{82}$  introduced into  $MnBr_24 H_20$  and  $1^{131}$  in both  $MnCl_{24} H_{20}$  and  $MnBr_{2}4 H_{20}$ . This attempt yielded negative results.

The anisotropy of the gamma radiation of  $\operatorname{Co}^{60}$  in a ferromagnetic single crystal of cobalt metal was measured before and after heat treatment of the crystal. The results before heat treatment show a significant discrepancy with the data reported by other workers and differ from those found for the heat treated crystal. A qualitative explanation of these results in terms of crystalline stacking faults in cobalt metal is presented.

Work was initiated on nuclear orientation in binary ferromagnetic alloys. The nuclear orientation may arise from the hyperfine structure interactions which may exist in one or both components of a ferromagnetic binary alloy. The intermetallic compound chosen for special study was MnBi. Although only preliminary and inconclusive results on the orientation of  $Mn^{54}$  nuclei in this substance were obtained the technique adopted is briefly described.

### ABSTRACT

Through the technique of adiabatic demagnetization of paramagnetic salts substances may be cooled to temperatures of the order of  $0.1^{\circ}$  K and  $0.01^{\circ}$  K. At these low temperatures the hyperfine structure interaction can produce an appreciable degree of nuclear orientation. The orientation of an assembly of radioactive nuclei may be detected by measuring the anisotropy in the emission of gamma radiation. By this method we have investigated nuclear orientation in paramagnetic, antiferromagnetic and ferromagnetic substances.

We have studied the nuclear orientation of  $Pr^{142}$  and Yb<sup>175</sup> introduced as impurities in paramagnetic single crystals of cerium magnesium nitrate. The anisotropy of the 1.57 Mev. % -ray of Pr<sup>142</sup> was measured as a function of temperature in the range of  $0.003^{\circ}$  K to  $1.0^{\circ}$  K both in zero external magnetic field and in a field of 320 gauss parallel to the trigonal crystal axis. Values for the magnetic moment of Pr<sup>142</sup> were assigned from our results for two assumed decay schemes, these are 0.11 nuclear magnetons for the spin assignments  $2 \xrightarrow{0} 2 \xrightarrow{2} 0$  and 0.15 nuclear magnetons for the spin assignments 2  $\xrightarrow{1}$  2  $\xrightarrow{2}$  0. Similar experiments were carried out on Yb<sup>175</sup>. Measurements were made in a variety of external magnetic fields up to 700 gauss, and at temperatures as low as 0.003° K. No anisotropy was observed for the 396 kev 8-ray, nor for the 282 kev 8-ray. The most likely explanation for this result is that the lifetime of the

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We have established that nuclear orientation can be produced in antiferromagnetic single crystals. We have explored some of the possibilities and features of nuclear orientation in this class of substances by investigating salts of manganese and cobalt with transition temperatures differing by an order of magnitude. Single crystals of these antiferromagnetic salts were cooled in thermal contact with potassium chrome alum and the anisotropy of the gamma radiation emitted by  $\mathrm{Co}^{60}$  and  $\mathrm{Mn}^{54}$  introduced in the lattice was observed. These measurements show that the hyperfine structure splittings in the antiferromagnetic state are comparable to those found in the paramagnetic state and give indications that nuclear spin relaxation times may be of the order of minutes and hours in antiferromagnetic materials at temperatures below  $1^{0}$ K.

We have attempted to detect nuclear orientation arising from a possible hyperfine structure interaction at the anion in antiferromagnetic  $MnBr_2^4$  H<sub>2</sub>O and  $MnCl_2^4$  H<sub>2</sub>O. To detect the nuclear orientation we observed the anisotropy of the gamma radiation emitted by  $Br^{82}$  introduced into  $MnBr_2^4$  H<sub>2</sub>O and I<sup>131</sup> in both  $McCl_2^4$  H<sub>2</sub>O and  $MnBr_2^4$  H<sub>2</sub>O. This attempt yielded negative results.

The anisotropy of the gamma radiation of Co<sup>60</sup> in a ferromagnetic single crystal of cobalt metal was measured before and after heat treatment of the crystal. The results before heat treatment show a significant discrepancy with the

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Work was initiated on nuclear orientation in binary ferromagnetic alloys. The nuclear orientation may arise from the hyperfine structure interactions which may exist in one or both components of a ferromagnetic binary alloy. The intermetallic compound chosen for special study was MnBi. Although only preliminary and inconclusive results on the orientation of  $Mn^{54}$  nuclei in this substance were obtained the technique adopted is briefly described.

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## INTRODUCTION

In this thesis we present the results of experiments in nuclear orientation in paramagnetic, antiferromagnetic and ferromagnetic substances.

Several methods have been proposed to obtain oriented systems of nuclei and extensive experimental results have already been obtained from the application of these ideas. An excellent review of the methods suggested and the experimental work done has been given by Steenland and Tolhoek (1957). The magnetic hyperfine structure method of orienting nuclei in paramagnetic single crystals has been established by Daniels et al (1951) and Gorter et al (1951) and has proved useful in establishing details of nuclear decay schemes, and in evaluating nuclear magnetic moments (e.g. Grace and Halban 1952). As part of a program to exploit the potentialities of such experiments, we have also made use of this method to orient Pr<sup>142</sup> and Yb<sup>175</sup> in cerium magnesium nitrate and investigated the anisotropy in the emission of the gamma radiation from these isotopes.

Since the decay scheme of  $Pr^{142}$  is fairly well known our measurements enabled us to deduce a value for the magnetic moment of  $Pr^{142}$ . This project was undertaken concurrently at Oxford and the results are in good agreement. No anisotropy was observed for the 396 kev %-ray, nor for the 282 kev %-ray which occur in the decay of Yb<sup>175</sup>. The orientation of this isotope was also concurrently studied by the Oxford group in the ethylsulphate lattice and anisotropies were measured for these two gamma rays. Our negative results can be explained and reconciled with the positive results obtained by the Oxford group by assigning a lifetime of the order of  $10^{-10}$  seconds to the **X**-emitting state. This conclusion has recently been confirmed by Vartapétian (1957) who measured a lifetime of 3.4 x  $10^{-9}$  seconds for this state.

It had been suggested that nuclear orientation could occur through the hyperfine structure interaction in antiferromagnetic crystals (Daunt 1951, Gorter 1951). We undertook to test this suggestion using  $McCl_2$   $4H_2O$  which has an antiferromagnetic transition at a temperature relatively high with respect to the temperature range generally required for nuclear orientation.

Single crystals of MnCl<sub>2</sub>4H<sub>2</sub>O containing some Mn<sup>54</sup> were cooled in thermal contact with potassium chrome alum. The intensity of the 835 kev gamma ray from Mn<sup>54</sup> nuclei was observed parallel and perpendicular to the preferred axis of antiferromagnetic alignment. The measurements showed that the manganese nuclei were in fact aligned along the preferred axis. To further confirm this method of orienting nuclei a similar experiment was carried out using antiferromagnetic MnBr<sub>2</sub>4H<sub>2</sub>O also containing some Mn<sup>54</sup>. Although an anisotropy in the emission of the gamma radiation from Mn<sup>54</sup> was observed, the long time required for the anisotropy to reach a maximum

in these experiments, about 100 minutes in the first case and some 8 hours in the second, cast some doubt on the value of this method. The slow increase of the anisotropy, hence of the nuclear orientation may be attributed to long nuclear spin relaxation times and to slow heat conduction from the crystals. Since nuclei of different ions incorporated in the lattices of the same crystal may have different relaxation times this could provide a method of distinguishing between these processes. Some  $\rm Co^{60}$  and  $\rm Mn^{54}$  was introduced in a single crystal of  $\rm MnCl_24H_20$  and the anisotropy of the gamma radiation was observed simultaneously in separate counting equipment. The measurements showed only a negligible anisotropy for the  $\rm Co^{60}$ gamma radiation hence no conclusive information on this point was derived from this experiment.

The theory of Van Kranendonk and Bloom (1956) predicted that the nuclear spin relaxation time in antiferromagnetic substances should be strongly dependent on the transition temperature. In order to investigate this prediction and to obtain further information on the general features of nuclear orientation in antiferromagnetic single crystals we undertook the following series of experiment. We studied the orientation of  $Mn^{54}$  in  $MnSiF_66H_20$  with a low transition temperature of  $0.1^{\circ}K$ ,  $Co^{60}$  in  $CoCl_26H_20$  and  $Co(NH4)_2$  (SO4)<sub>2</sub>  $6H_20$  with transition temperatures at  $3^{\circ}$  K and  $0.084^{\circ}$  K respectively. Significant anisotropies, hence nuclear orientation, was observed in all these crystals, but the experiments did not provide unambiguous evidence of long nuclear relaxation times. The magnitude of the anisotropies was generally comparable to those observed for the same nuclei in paramagnetic single crystals at corresponding temperatures. This indicates that the hyperfine structure interactions are not appreciably altered in the antiferromagnetic state.

We resumed the attempt to distinguish between the effect of long nuclear relaxation times and gradual cooling in these crystals. In this second attempt we prepared a single crystal of  $MnSiF_6 GH_0$  containing some  $Co^{60}$  as an The measurements in this case showed a relatively impurity. large anisotropy and a comparison with the results of the experiment with Mn<sup>54</sup> in this lattice indicated a more rapid rise of the anisotropy in the case of  $co^{60}$ . Consequently a single crystal of this salt containing both  $Mn^{54}$  and Co was grown. Preliminary measurements with this crystal seem to indicate that the anisotropies increase at the same rate. The difference in rise times observed with each isotope in the crystals separately mounted must then be ascribed to different rates of cooling and the contribution of relaxation processes remains obscure. In a similar experiment both Co and  $Mn^{54}$  were introduced in a single crystal of CoCl\_6H\_0. Measurements showed a large anisotropy for the Mn gamma radiation. However the effect observed for the Co<sup>60</sup> was too small to provide any reliable comparison in the rate of cooling of the different nuclei.

Nuclear magnetic resonance experiments in paramagnetic and antiferromagnetic substances have shown that in some cases a hyperfine structure coupling exists in the cation. This free ion is expected to be diamagnetic and normally would not give rise to a hyperfine structure interaction. However in the solid state the electron configuration may be modified in such a way that the amplitude of the wave function of the unpaired electrons does not vanish at the position of the cation and a hyperfine interaction occurs if the nucleus has non-zero spin.

This phenomenon provides a possibility of greatly extending the number of nuclei that may be oriented by static methods. Experiments were undertaken to attempt to detect nuclear orientation arising from this interaction by measuring the gamma ray distribution of radioactive nuclei at these crystal sites. A single crystal of MnBr<sub>2</sub>4H<sub>2</sub>O containing Br<sup>82</sup> was prepared and cooled and the anisotropy of some of the gamma rays occurring in the decay of this isotope was measured. In similar experiments I<sup>131</sup> was incorporated as an impurity in the lattice of MnBr<sub>2</sub>4H<sub>2</sub>O and MnCl<sub>2</sub>4H<sub>2</sub>O single crystals and the anisotropy of the 396 kev gamma ray from this nucleus was investigated. No anisotropies were observed in any of these experiments. This may be due to long nuclear relaxation times and inadequate cooling. This work is discussed in Chapter IV, Part II.

Measurements on metallic cobalt containing some Co<sup>60</sup> have shown the possibility of nuclear orientation in a ferromagnetic material by the hyperfine structure interaction (Grace et al 1955, Khutsishvili 1955). We undertook to extend this method and determine whether a hyperfine structure coupling occurred in both components of a ferromagnetic binary alloy and could produce nuclear orientation of both types of nuclei. The material selected for this study was the intermetallic compound MnBi. Only the initial phases of this project have been completed and no significant effects have been observed to date with  $Mn^{54}$  in this lattice. Measurements on  $Bi^{207}$  in this lattice have not yet been carried out. The experimental approach is described in Chapter V, Part II.

In preparation for the above experiment the author sought to acquaint himself with various techniques of cooling metallic specimens to temperatures below  $0.05^{\circ}$ K. To test these different techniques the author used a single crystal of cobalt metal containing some  $Co^{60}$ . The anisotropy of the  $Co^{60}$  gamma radiation when referred to the reported data served as a thermometric parameter and a measure of the effectiveness of the method of cooling. In the course of this work a significant discrepancy was observed between the anisotropies measured at various temperatures of the cooling agent and the results reported by the Oxford group. Subsequently the crystal was heat treated for some 10 minutes at about  $1000^{\circ}$ C and the measurements repeated. It was found that the anisotropies corresponding to various temperatures of the coolant

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salt were appreciably reduced and now showed much better agreement with the Oxford results. These experiments and a tentative explanation are presented in Chapter V, Part I.

The general method of orienting nuclei by the magnetic hyperfine structure interaction in paramagnetic, ferromagnetic and antiferromagnetic crystals is reviewed briefly in Chapter I.

The apparatus used in our experiments was set up by previous workers in this laboratory and is also described briefly in this thesis.

## CHAPTER I GENERAL REMARKS ON NUCLEAR ORIENTATION

In nuclear orientation experiments we wish to produce a preferential population of certain directions in space in an assembly of nuclei. An isolated nucleus with spin I can be considered to be in a (2I+1)-fold degenerate state. If a weak magnetic field is applied, say in the z-direction so that the degeneracy is resolved we have (2I+1) independent states and we may regard each different state as corresponding to a different orientation of the nuclear spin with respect to this axis. The different orientations or magnetic substates are such that the z-component of the spin I has a value m called the magnetic quantum number which varies from -I to +I in unit steps.

For an assembly of nuclei with random orientation the probability  $W_m$  of finding a nucleus in a substate m will be  $\frac{1}{2I+1}$  and will be independent of m. To produce an orientation of the nuclei along a direction fixed in the laboratory system, we must alter the relative populations of the magnetic substates of the nuclei from this normal equilibrium value. Then for the assembly of nuclei the probability of the various substates m will vary with m. When in an assembly of nuclei the populations of nuclei the populations of nuclei along a states are no longer equal but equal numbers of nuclear spins are distributed among the +m and -m states, the nuclear spins are oriented in direction

only and not in sense and we speak of an alignment. However when the plus and minus m substates are no longer equally populated, there occurs a preponderance of spins in one direction over those in the opposite direction, the nuclei are oriented in both sense and direction and a net magnetic moment arises due to the nuclear magnets. The situation is then referred to as a nuclear polarization. The word orientation is used when no distinction is made between polarization and alignment.

The methods of producing nuclear orientation may be divided into static (stationary) and dynamic (non-stationary) In the dynamic methods differences in the population methods. of the various m states are effected by causing transitions either between the various levels of the nuclei or of another system which interacts with the nuclear spin system by means of resonance radiation. We are not concerned with this approach to nuclear orientation in this thesis. The general aspects of the subject are reviewed in the paper by Steenland and Tolhoek (1957). In the static methods the temperature is lowered until a considerable difference in the equilibrium populations of the various m states occurs. Except for some very special cases the energy differences between the different m states are so small that temperatures obtainable only by adiabatic demagnetization must be used in order to produce any appreciable nuclear orientation by static methods.

The energy differences between the various m states can result from interaction between the magnetic moment of

nuclei and a magnetic field, and interaction of the electric quadrupole moment of nuclei and an inhomogeneous electric field. Thus nuclear orientation will depend on the magnetic fields and inhomogeneous electric fields present at the nucleus.

In order to use the interaction of the nuclear electric quadrupole moment with an inhomogeneous electric field to orient nuclei, gradients of the order of  $10^{14}$  Volts/cm<sup>2</sup> are required at a temperature of  $0.01^{\circ}$  K. Pound (1949) pointed out that inhomogeneous fields of this magnitude may be set up by the asymmetric electron cloud which occurs in certain chemical bonds as is shown by the electric hyperfine structure splittings observed. This method has been successfully applied (Dabbs et al 1956).

The direct interaction between the nuclear magnetic moment and a strong external magnetic field (when no stronger forces act on the nuclei) can in principle bring about the required energy differences so that at sufficiently low temperatures an appreciable difference in equilibrium populations of the various m states arises and leads to nuclear polarization. This approach to the problem commonly referred to as the Brute Force Method (Gorter 1934), (Kurti and Simon 1933) has been applied with success (Dabbs 1955). It was not used in our work and we will not discuss it further.

It was pointed out that magnetic fields much more powerful than those generally available in the laboratory are already present at the nucleus of certain atomic systems.

These magnetic fields may be of the order of  $10^5$  to  $10^6$  gauss and arise from the magnetic moment of the unpaired electrons surrounding the nucleus. The coupling or interaction of the nuclear magnetic moment with its surrounding electrons gives rise to hyperfine structures in optical and paramagnetic resonance spectra, and is referred to as the magnetic hyperfine structure interaction. It has been suggested that the hyperfine structure interaction may cause the desired differences in the energy levels corresponding to the various m states of the nuclei so that at temperatures of some hundredths of a degree the lowest energy levels will be preferentially populated and an appreciable nuclear orientation may be achieved.

To obtain nuclear orientation however it is first necessary that the magnetic field of the electronic moments be itself oriented with respect to some direction fixed in the laboratory system. The direction of this field will depend on the orientation of the electron spins and orbits. Several mechanisms may determine the orientation of the electronic moments. Among these are the crystalline electric fields, external magnetic fields and exchange interaction (ferromagnetic and antiferromagnetic). We discuss each separately although all these factors may be present in an actual situation.

## A Crystalline fields

The strength and symmetry of the powerful magnetic field at the position of the nucleus will depend on the electronic configuration. In an assembly of isolated atoms (or ions) this magnetic field will have random orientation. In the solid state however the neighbouring atoms set up an electric field called the crystalline field which may alter the electronic configuration and also influence the orientation of the electronic spins and orbits. Due to the regular arrangement of the atoms in crystals this crystalline field may have directional properties. Hence not only will the different relative orientations of the nucleus and atomic moment have different energies but different orientations of the nucleus and electronic system as a whole with respect to some crystalline direction will have different energies.

The behaviour of a paramagnetic ion under the influence of a crystalline inhomogeneous electric field has been treated by several authors and it has been shown that the energy levels of a paramagnetic ion in a crystal possessing axial symmetry about the z-axis may be represented by the following Hamiltonian. (Abragam and Pryce 1951, Bleaney and Stevens 1953).

 $\mathcal{H} = D \left[ S_z^2 - \frac{1}{3} S (S+1) \right] + A S_z I_z + B \left( S_x I_x + S_y I_y \right) \dots (1)$ 

This Hamiltonian is formulated in terms of an effective electron spin S defined by setting the multiplicity of the electronic levels equal to 2S + 1. I is the nuclear spin and the A and B terms represent the hyperfine structure splitting due to the interaction between the nuclear magnetic moment and the magnetic field of the unfilled electron shells. The term in D represents the splitting of the electronic levels by the crystalline electric field. We assume that no external magnetic field is present and we neglect terms due to the nuclear quadrupole in the crystalline electric field gradient.

To illustrate the influence of the crystalline environment in terms of this Hamiltonian we consider two special situations. In the first the crystalline fields lead directly to nuclear orientation by causing a preferred direction of the electronic angular momentum. In the second the crystalline fields lead indirectly to nuclear orientation through an anisotropic hyperfine structure interaction.

i) The manganous ion  $Mn^{++}$  in the free state according to Hund's rule is in a  ${}^{6}S_{5/2}$  state and should show no hyperfine structure. According to Abragam and Pryce (1951) the hyperfine structure may be due to an admixture of the ground state and higher states with unpaired s-electrons. The hyperfine structure is therefore isotropic and A = B in the Hamiltonian given above.

If the electronic angular momentum behaves like a free spin no preferred direction for the nuclear spin will exist. In such a case no nuclear orientation could be expected at any temperature.

Although the hyperfine structure coupling is practically unconnected with orbital electronic motion, and hence independent of the particular crystalline surrounding, it has been found that the crystalline environment may still lead to a preferred direction for the electronic angular momentum and thus to nuclear orientation along this preferred direction. This situation may be visualized in the following way. The asymmetric crystalline field will cause a distortion of the individual electron orbits so that the charge cloud instead of being spherically symmetric may become slightly elongated or contracted along a crystal axis. The dipole-dipole energy of the spins varies with their orientation with respect to the axis of this distortion, and the orientation of the resultant spin of the ion with respect to this crystal axis will have different energies. The 2S + 1 spin states will no longer be equally probable. This is referred to as the fine structure or Stark splitting and is represented by the D term in the Hamiltonian given above. This Stark effect causes a splitting of the 6-fold degenerate electronic ground state of Mn<sup>++</sup> into 3 doublets. It has been found that in three Mn<sup>++</sup> salts investigated by paramagnetic resonance: manganese fluosilicate, manganese ammonium sulphate and manganese bismuth nitrate (Bleaney and Ingram 1951), (Trenam 1953), the overall Stark splitting is of the order of 0.3°K. This means that below about 0.05 K even in the absence of an external magnetic field, only the lowest level will be appreciably populated. This lowest state is  $S_z = \pm 5/2$  for the fluosilicate and the

double nitrate  $(^{D} < 0)$  and predominantly  $S_z = \pm 1/2$  for the Tutton salt (D>0). The isotropic magnetic hyperfine coupling is of the same order as the Stark splitting so that alignment of the electron spins is accompanied by alignment of the nuclear spins.

ii) In the case where S = 1/2 the term in D vanishes. This means that the crystalline field has no direct effect on the spin. There is however another mechanism which can align the electronic moment and lead to nuclear alignment.

For ions in the iron group the 3d electrons are in the outer shell and consequently they are strongly exposed to the electric field of the neighbouring water dipoles. The influence of the electric field on the orbits of the 3d electrons may be larger than the spin-orbit coupling. The crystal field in a large number of these salts arises from an octahedron of water molecules surrounding the magnetic ion and it will have a symmetry dictated by the crystal structure. The orbits of the electrons may then be more strongly distorted in certain planes than in others. This "locking into" the field of the neighbours of the orbital motion may greatly reduce the orbital moment. It is then said that the orbital angular momentum is "quenched", i.e. the expectation value of the components of the orbital angular momentum  $L_z$ ,  $L_y$ ,  $L_x$  is zero.

However the spin-orbit coupling cannot be completely neglected. When it is taken into account and combined with the influence of the crystalline field on the orbital angular

momentum in perturbation calculations two general consequences usually follow. First the lowest level of the ion may be characterized by an effective spin  $S^1 = 1/2$  and a two-fold. degeneracy remains. Second, the quenching of the orbital angular momentum is partially removed and the expectation values of  $L_z$ ,  $L_y$ ,  $L_x$  are no longer zero. Indeed the expectation value for  ${\rm L}_{\rm Z}$  is generally different from that of  ${\rm L}_{\rm X}$  and  $L_v$ . Further the magnitude of the field which the unpaired electrons produce at the nucleus varies with the orientation of the electron spin  $S_z$ . The electron which produces this field at the nucleus is to be considered as distributed in space according to some wavefunction. It is the nature of this wavefunction, i.e. the shape of the "electron cloud", which is responsible for the variation with orientation of the field at the nucleus, and the shape and orientation of this electron cloud is determined by the crystalline potential. This means that the magnitude of the magnetic field at the position of the nucleus will be stronger in the direction of some crystal axis than in any other direction. The hyperfine structure interaction is then anisotropic, i.e. A  $\neq$  B in the Hamiltonian given above and the direction and magnitude of the anisotropy is linked to the crystal structure. In fact it has been found in a number of salts investigated by paramagnetic resonance that the hyperfine structure is exceedingly anisotropic (Bleaney 1950).

Although we have restricted our discussion to two special cases in some actual instances both a Stark splitting and an anisotropic hyperfine structure may be present. In such cases these two mechanisms will determine the orientation of the electronic moment and hence of the nuclear spin. In principle when the effective electronic spin S, the nuclear spin I, and the values of the constants D, A, and B are known, the energy differences of the various levels may be calculated. Such calculations may be extremely complicated and a detailed discussion has been given by Bleaney (1951b). The method of nuclear alignment through the influence of the crystalline field is known as Bleaney's Method (Bleaney 1951a).

### B External Magnetic Field

At temperatures of a few hundredths of a degree a small magnetic field of a few hundred gauss should completely polarize the electronic magnetic moments since kT is much smaller than the splitting of the electronic spin states in the magnetic field. If a hyperfine structure coupling is present and the temperature is low enough so that the thermal energy kT is of the order of the energy differences corresponding to different orientations of the nuclei in the magnetic field of the electrons, the lower levels will be preferentially occupied and an appreciable nuclear polarization will occur. This method was suggested independently by Gorter and Rose and is known as the magnetic hyperfine structure polarization method (Gorter 1948, Rose 1949).

In the ideal case the electronic moments to be polarized by the external magnetic field should behave like free spins. In practice however a preferred direction for the electronic moments already exists. This as we have pointed out above may be due to a Stark splitting in the crystalline field and may arise from the anisotropy of the interaction of the electronic spin and nucleus system with the crystalline field. The method will then be most effective when the magnetic field can be applied parallel to the axis of preferred direction already present in the crystal.

The Hamiltonian for the energy levels of the ions now has the form:  $\mathcal{P}$ 

 $\mathcal{F} = g_{\parallel} \mathcal{B}_{\underline{x}} S_{\underline{x}} + g_{\underline{x}} \mathcal{B}(H_{\underline{x}} S_{\underline{x}} + H_{\underline{y}} S_{\underline{y}}) + D \left[ S^2 - \frac{S}{3} (S+1) \right] + AS_{\underline{x}} I_{\underline{x}} + B(S_{\underline{x}} I_{\underline{x}} + S_{\underline{y}} I_{\underline{y}})$   $\dots (2)$ 

where  $g_{\parallel}$  and  $g_{\perp}$  are the values of g, the spectroscopic splitting factor parallel and perpendicular to the z-axis, (3 is the Bohr magneton,  $H_{z}H_{y}H_{x}$  are the components of the external magnetic field in the z,y,x directions respectively. The terms in D, A and B have the same meaning as in equation (I). We again assume that contributions from the interaction of the electric quadrupole moment with the electric field gradient are negligible.

To illustrate various aspects of this method we discuss briefly the polarization of Co<sup>60</sup> nuclei in cerium magnesium nitrate (Ambler et al 1953, Wheatley et al 1955).

Trenam (1953) investigated the paramagnetic resonance of  $Co^{++}$  in the isomorphous crystals of bismuth magnesium nitrate.

For the Co<sup>++</sup> ion in this lattice the effective spin is  $S' = \frac{1}{2}$  hence the D term vanishes in the Hamiltonian given in equation (2). There are two Co<sup>++</sup> ions in the unit cell. Assuming that the nuclear magnetic moment of Co<sup>60</sup> is 3.5 nuclear magnetons and I=5 Wheatley et al (1955) have calculated the constants in the Hamiltonian from Trenam's data for Co<sup>59</sup> (Trenam 1953).

## For 3/8 of the ions

 $g_{\parallel} = 7.29, g_{\perp} = 2.34$  A/k = 0.0216°K, B/k = 0.00008°K while for 5/8 of the ions the constants are  $g_{\parallel} = 4.11, g_{\perp} = 4.38, A/k = 0.0065°K,$  B/k = 0.00786°K The ratio 3:5 for the two types of ions was found to fit the nuclear orientation data better than the ratio of 1:2 given by Trenam (1953).

We note that for 3/8 of the ions the hyperfine structure is extremely anisotropic, hence some nuclear alignment would be expected in the absence of an external field as in Bleaney's Method. This was observed by Ambler et al (1953). For these ions the hyperfine interaction is anisotropic with its maximum in the z-direction. Due to this factor and the related large value of g along this axis, when a small external field is applied in this direction we should expect a considerable degree of nuclear polarization in this set of ions at low temperatures.

However for 5/8 of the ions the hyperfine structure is almost isotropic and in zero field no nuclear alignment

would then occur in these ions at any temperature. More accurately, since B is slightly greater than A, the hyperfine interaction is somewhat anisotropic with the maximum in the x-y plane. This means that in zero field these nuclei will show a small degree of alignment in this plane; hence will align perpendicularly to the other set of nuclei. The overall situation consequently does not commend itself for an application of Bleaney's Method. But the large g , value for this set of ions make them very suitable for polarization by a relatively small magnetic field. With a small field, say 100 gauss, in the z-direction the presence of the B term in the hyperfine interaction will tend to mix the nuclear magnetic substates and reduce the nuclear polarization. This effect will become negligible as larger fields are applied. Nevertheless the hyperfine structure interaction of this set of ions will not as readily lead to nuclear polarization as the other group since the A term (and hence the magnetic field at the nucleus) is appreciably smaller. The energy levels for the two types of Co<sup>++</sup> ions in cerium magnesium nitrate with a polarizing field of 280 gauss in the z-direction have been calculated by Wheatley et al and are depicted in their paper (Wheatley et al 1955). This group observed a maximum anisotropy of the emitted gamma radiation of 0.45 at the lowest temperatures using a polarizing field of 200 gauss.

Incorporating the Co<sup>++</sup> ions in magnesium sites in the lattice of cerium magnesium nitrate insures that very

intimate thermal contact with a cold reservoir is established. Crystals of this salt are particularly suitable as a refrigerator for the Co<sup>++</sup> ions for two reasons. First, since the nuclear moment of stable cerium is zero no hyperfine structure interaction is present and dipole-dipole interactions are very weak due to the large distances between the cerium ions in this very diluted salt. Thus very low temperatures can be attained by adiabatic demagnetization from moderate values of H/T. Indeed these crystals have been cooled to temperature of 0.00308°K (Daniels and Robinson 1953). Secondly, the g-values of the Co<sup>+++</sup> ion are highly anisotropic. The g-value in the direction of the crystalline trigonal axis is  $g_{\mu}$ = 0.25 and the g-value in the plane perpendicular to the trigonal axis is isotropic and equal to  $g_{\perp} = 1.84$  (Cooke et al 1953). This means that with a polarizing field applied along g no appreciable temperature rise will result. This direction also corresponds to that most effective for polarizing the Co<sup>++</sup> ions and nuclei.

C) Exchange Interactions:

It is well known that exchange interactions may lead to parallel and antiparallel alignment of the electronic magnetic moments. When the exchange interaction is positive it results in a parallel orientation of spins and we speak of ferromagnetism, in the case of an antiparallel alignment the interaction is negative and we speak of antiferromagnetism. These exchange forces may be anisotropic in which case the preferred direction of the electronic moments will not be determined solely by the crystalline electric field.

i) Antiferromagnetism:

In a number of crystals there is a certain critical temperature called the Néel temperature below which the atomic magnetic moments are arranged alternately parallel and antiparallel due to a negative exchange interaction between nearest neighbours. It is thus possible to divide the magnetic ions into two equivalent interlocking sub-lattices (or more) in such a way that ions of one sublattice all point in a given direction and are immediately surrounded by ions of the other sublattice which point in the opposite direction. For each such sublattice the magnetization approaches saturation as  $T \rightarrow 0$ , but since the sublattices are magnetized in opposite directions the resultant magnetization of the system Thus below the Néel temperature a certain degree of vanishes. alignment of electronic moments will exist which may lead to a nuclear alignment through magnetic hyperfine coupling when the substance is sufficiently cooled, as suggested independently by Gorter (1951) and Daunt (1951). In the ideal case only two sub-lattices with a preferred direction of alignment is desired, however it has been found that in certain substances several sets of sublattices are present with their preferred axis of alignment in different directions. Excellent review articles on antiferromagnetism have been presented recently (Lidiard 1954, Nagamiya et al 1955).

Above the Néel temperature the moments may be disordered but more generally anisotropy forces in the crystals
will constrain the moments to point along certain crystallographic directions. These directions may coincide with the preferred axis or axes of antiferromagnetic alignment as in cobalt ammonium sulphate and manganese fluosilicate. This is particularly evident in the alignment of Mn<sup>54</sup> in manganese fluosilicate reported in this thesis.

ii) Ferromagnetism:

In a ferromagnetic substance if the unpaired electrons can be considered as sufficiently localized so that an appreciable hyperfine structure splitting can be expected then the situation is again analogous to the paramagnetic and antiferromagnetic cases. In a ferromagnetic substance below a critical temperature called the Curie temperature the positive exchange interaction will cause a parallel orientation of the electronic moments in a domain. If a preferred orientation of the domains exists an alignment of the nuclei with respect to this axis can be expected at temperatures of the order of  $0.1^{\circ}$  K and  $0.01^{\circ}$  K. In an external magnetic field which is high enough to cause saturation, the domains will point in the same direction and a polarization of the nuclei may occur at suitable temperatures.

In the absence of an external magnetic field the anisotropy energy of the domains in a single crystal may be of such a nature that several preferred directions for the orientation of the domains exist along different axes in the crystal. Such substances are not very suitable for nuclear

orientation. Nevertheless recently nuclear orientation experiments have been successfully performed in such materials using an external magnetic field to saturate the ferromagnetic moments (Scurlock 1958).

In cases where the exchange interaction is large (e.g. when an antiferromagnetic of ferromagnetic ordering occurs) the nuclear orientation can no longer be discussed solely in terms of the energy levels of an isolated atom or ion as represented by the spin Hamiltonian given above. We must then introduce terms of the form J S<sup>1</sup> S<sup>J</sup>, where J is a parameter proportional to the magnitude of the interactions, and S<sup>1</sup> and S<sup>J</sup> are the spin vectors of the i th and j th ion. When J  $\rangle$  A, the electron spin performs many transitions between different m states in a time  $\frac{1}{4}$  A and the effective magnetic field at the nucleus may be significantly modified. Since in this thesis we only present some experimental data on nuclear orientation in such environments we will not attempt to discuss this difficult topic in greater detail.

In the above discussion we have considered separately three factors which may align the electronic moments and through the hyperfine structure interaction or through an effective magnetic field at the nucleus bring about a nuclear orientation. In an actual instance some combination of these mechanisms may be operative. An example mentioned was the experiment with  $\operatorname{Co}^{60}$  in cerium magnesium nitrate where nuclear orientation occurred in zero field by Bleaney's Method. The

orientation was enhanced and nuclear polarization produced by the application of an external magnetic field. This is also the case in the orientation of  $Pr^{142}$  reported in this thesis.

We have also referred to our experiment with manganese fluosilicate where the nuclear alignment by Bleaney's method merges into nuclear alignment by antiferromagnetic ordering as proposed by Daunt and Gorter.

### General Remarks on the Angular Distribution of Gamma Radiation:

The orientation of an assembly of nuclei may be detected in several ways: for example, by measuring the anisotropy of emission of  $\prec$ ,  $\beta$  and  $\checkmark$  rays or by measuring the differential absorption cross section of polarized neutrons. By far the easiest technique and the one we have used in our research is the detection of the gamma rays emitted by some radioactive isotopes. We restrict our remarks to this method.

Since gamma radiation carries integral units of angular momentum the wave function of the radiation will not be spherically symmetric with respect to the nucleus. When a nucleus makes a radiative transition in which the angular momentum I and its component m along an axis of alignment change by  $\Delta I$  and  $\Delta m$  respectively, the polar diagram of the radiation will depend on the values of I, m,  $\Delta I$  and  $\Delta m$ . For an assembly of nuclei with random orientation the radiation will be isotropic. If, however, some orientations are preferentially populated the resulting radiation may no longer be isotropic and the polar diagram will depend on the relative populations of the various m states and the multipole order of the transition.

The radiation emitted by excited nuclei can be classified according to the angular momentum carried away by the photon, and the parity changes involved in the transition. If the angular momentum carried away from the nucleus is  $\lambda$  then the radiation is said to be of multipole order 2<sup> $\lambda$ </sup>. The polarization of the electromagnetic wave depends on the

nature of the radiation which can be either electric or magnetic. The nature of the radiation depends on both the multipolarity and the parity change involved in the transition. Since no attempt was made in this research to study the polarization of the radiation, we will not discuss this topic further. The angular distribution of the radiation depends only on the multipole order and not on the parity. The necessary formulae may be developed starting from the wave function for the photon and using the rules of addition of angular moments (Daniels 1957).

The relative populations of the various m-states of the gamma emitting state will be determined by the initial relative population of the m-states of the parent nucleus and all the transitions by which the parent nucleus transforms to the gamma emitting state. To illustrate the approach we consider one of the simplest cases where there is emission of a beta ray to an excited state of the daughter nucleus followed by a gamma ray de-excitation to the ground state as shown schematically in the diagram.



We assume that the spin of the various levels and the angular momentum carried away in the beta and gamma transitions are all known and proceed as follows: Firstly, we determine the polar diagram for the limiting case where all radioactive parent nuclei are effectively aligned; i.e., are in a definite nuclear substate M. We can write at once:

$$\Psi_{J}^{M} = \sum_{m \neq m, \neq M} C_{M m m}^{J j j} \beta_{j} \theta_{j}^{m} \cdots (1)$$

where  $|J - j_1| \leq j \leq |J + j_1|$ . The  $C_{Mm_1m_2}^{JJ_1J_2}$  are the Wigner or Clebsch-Jordan coefficients that can be evaluated from the tables given in Condon and Shortley (1953). Now we can evaluate for all  $m_1$  that appear in this summation.

where the  $\chi_{j}^{m_{a}}$  are the components of the normalized wave functions for the photons of multipole order  $2^{j2}$ . Should the transition involve a mixture of radiations, all their wave functions are considered and the relative importance of the radiations of different orders is taken into account by introducing weighing factors  $\prec$ ,  $\beta$  and  $\checkmark$  where  $\prec^{2} + \beta^{2} + \checkmark^{2} + \ldots = 1$ .

Returning now to the case of a pure multipole transition the probability of emission along the angle  $\theta$  between the crystal axis and the direction of emission is obtained by forming the product  $\Psi_{J}^{M}\Psi_{J}^{M}\Psi_{J}^{M}$  and integrating this latter expression over all space but not over the angle  $\theta$ . Thus we find:

$$I_{M}(\Theta) = \int \left| \frac{\Psi_{J}}{J} \frac{\Psi_{J}}{J} \frac{\Psi_{J}}{J} \right| d\tau'$$

$$= \int \left| \sum_{\substack{m_{i}+m_{a} \\ = M}} \sum_{\substack{m_{e}+m_{a} \\ = M_{e}}} C^{J} j j_{i}} C^{J} j_{a} \frac{J_{e}}{J_{e}} \frac{M_{e}}{J} \frac{M_{e}$$

The eigenfunctions (3) and (0) form othonormal sets orthogonal to each other so that finally:

$$I_{M}(\theta) = \sum_{\substack{m_{1}+m_{2} \\ = M}} \sum_{\substack{m_{0}+m_{2} \\ = m_{1}}} \left( \begin{pmatrix} J & J & J \\ M & m_{1} \\ M & m_{1} \\ m_{1} & m_{2} \\ m_{2} & m_{2} \\ m_{1} & m_{2} \\ m_{2} & m_{2} \\ m_{1} & m_{2} \\ m_{1} & m_{2} \\ m_{2} & m_{2} \\ m_{2} & m_{2} \\ m_{1} & m_{2} \\ m_{2} & m_{2} \\ m_{1} & m_{2} \\ m_{2} & m_{2} \\ m_{1} & m_{2} \\ m_{2} & m_{2} \\ m_$$

This is an expression of the form:

$$I_{M}(\theta) = 1 + a_{M}\cos^{2}\theta + b_{M}\cos^{4}\theta + \dots + \lambda_{M}\cos^{2}\theta \dots (5)$$
  
where 2 is the multipole order involved.

When the radiation is not a pure multipole, this expression contains the parameters  $\prec$ ,  $\beta$ ,  $\chi$ , ... mentioned earlier. It should be remarked that when the probability is formed from  $|\Psi_J^M \overset{*}{} \Psi_J^M|$  there are non-zero cross terms with factors  $\prec \beta$ ,  $\prec \chi$ , ... which appear. It turns out that they modify considerably the angular dependence.

If there is a cascade of two or more gamma rays to the ground state, then the formulae become somewhat more involved since repeated use of the rules for summation of angular momentum has to be practiced.

Steenberg (1953) has obtained formulae for the angular distribution of the radiation as a function of temperature for different methods of nuclear alignment and polarization. Using his notation we have for any temperature:

$$I (\Theta) = \sum_{M} W_{M} I_{M} (\Theta)$$

.... (6)

where the  $W_{M}$  are the temperature dependent relative populations of the substates M. The complete analytical expressions for  $W_{M}$  are rather complicated. Steenberg gives for each method of nuclear orientation a perturbation calculation carried to the second order.

A useful measure of the polar diagram and therefore of the nuclear orientation is the anisotropy factor  $\boldsymbol{\mathcal{E}}$  which may be defined with respect to an axis of alignment as follows:

$$\mathcal{E} = \frac{I_{\text{Plane}} - I_{\text{Axis}}}{I_{\text{Plane}}} \qquad \dots (7)$$

which in terms of the intensity distribution I ( $\theta$ ) discussed above can be written:

$$\mathcal{E} = \frac{I(\pi/2) - I(0)}{I(\pi/2)} \dots (8)$$

where the I are the normalized intensities of the radiation with respect to an axis of alignment.

To measure this parameter it is sufficient to use simultaneously two counters, one along the axis of alignment and the other perpendicular to it. The variation of the anisotropy as a function of temperature is readily obtained as the sample cools and warms up with time. In general the correct decay schemes can be deduced from the measurement of this anisotropy factor, or alternatively if the decay scheme is known, a value can be assigned to the nuclear magnetic moment of the parent nucleus.

### CHAPTER II DESCRIPTION OF THE APPARATUS

### A The apparatus for adiabatic demagnetization

The cryostat and susceptibility bridge used in our experiments were constructed by previous workers in this laboratory and have been described in detail elsewhere (Lamarche 1956). Some additions were made to the equipment. For the sake of completeness we describe briefly the apparatus, as we have used it, in this chapter.

The paramagnetic specimen to be cooled by adiabatic demagnetization is suspended inside a glass container or "sample tube" which is connected to a high vacuum system. The "sample tube" fits snugly inside a mutual inductance coil which is part of a ballistic galvanometer circuit used in reading the susceptibility of the sample and hence in determining its temperature. The sample tube and the coil are immersed in a liquid helium bath contained in the usual set of dewars. The pressure on this helium bath may be reduced by pumping with a large capacity Kinney mechanical pump.

### The High Vacuum System

A schematic diagram of the high vacuum system, whose main function is to insulate the salt thermally before demagnetization, is given in Figure 1.

The pumping equipment consists of a mercury diffusion pump preceded by a rotary pump and followed by a liquid air



FIGURE I VACUUM SYSTEM

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trap. It produces a vacuum of the order of  $10^{-6}$  mm. of mercury. A 5 litre reservoir with its own mercury manometer can be evacuated from the high vacuum side and serves as a back vacuum for the diffusion pump should it be required to stop the rotary pump temporarily.

The sample tube can be evacuated through two paths, a narrow and a broad one. Provisions are made to evacuate the syphon used in the transfer of liquid helium and the high vacuum side of the mercury and of the oil manometers.

The exchange gas can be obtained from the 300  $\text{cm}^3$ reservoir which also has its own mercury manometer, or alternatively by taking fresh helium gas from the helium bath through the pressure line leading to the manometers. To read the pressure and help in detecting leaks in the system, one gauge, two manometers and three discharge tubes have been The Phillips gauge with a range of 25 microns down to attached. 0.001 microns of mercury is used to indicate the pressure in the sample tube as well as other parts of the system when The three discharge tubes are conveniently located to desired. help in leak detection and to show the nature and the approximate pressure of the gas at different points. The high tension for the discharge tubes is obtained from an automobile spark coil.

To pump over the liquid helium bath, a large capacity Kinney mechanical pump has been installed in a room adjacent to the laboratory and is linked to the apparatus by a 5 inch pipe. The pressure over the helium bath is read on a mercury

manometer from atmospheric pressure down to about 40 mm. of mercury. For lower pressures an oil manometer is used. The density of this oil (Apiezon B) is 15.85 times smaller than that of mercury. At maximum pumping speed, a temperature of  $1.3^{\circ}$  K can be obtained; to help in attaining this temperature some liquid air is kept in the cap which seals the liquid helium dewar.

### The Sample Tube

The sample containers used throughout our experiments had essentially the same design. They were made of pyrex glass, with an outer diameter of 18 mm. which gives a good fit with the susceptibility coil, an inner diameter of 15 mm. and an overall length of 25 cm. The specimens used were fixed to a strip of mica, or placed inside a lucite cylinder which was suspended by nylon threads between glass hooks at top and bottom of the sample holder. To allow for some leeway in suspending the specimen and to enable the glass tube to be sealed without burning the thread, the bottom thread is attached to the glass hook by a tungsten coil spring.

### The Magnet

An iron core, water cooled electromagnet with adjustable gap and interchangeable pole pieces was used in these experiments. With a 2 inch gap and pole pieces 4 inches in diameter this magnet produces a maximum field of 22 kilogauss with a power output of 75 kilowatt. Since the water pressure available in the laboratory is below that required for maximum



FIGURE 2

# MUTUAL INDUCTANCE BRIDGE

• • •

power dissipation the magnet was generally operated at 160 volts and 200 amperes, i.e., 21 kilogauss.

This  $2\frac{1}{2}$  ton magnet is mounted on a turntable carriage rolling on a railway and can be moved easily to and from the cryostat by one person.

## The Susceptibility Bridge

The bridge to measure the susceptibility is a d.c. mutual inductance bridge whose circuit is given in Figure 2. The mutual inductance coil around the paramagnetic sample is wound on a bakelite former and consists of two secondaries in opposition separated by a gap of 1", and a primary extending a total length of 5". One secondary is 1" in length, while the other is  $l\frac{1}{2}$ ". The sample is placed inside the shorter secondary at the centre of the former. The longer secondary, near the end of the former serves as a compensator. Another compensator, at room temperature, can be varied continuously from 0 to 4 millihenries. Hence the deflection before calibration can be adjusted easily. In the course of our experiments several susceptibility coils were wound with approximately the same number of turns. Reference to Figure 2 can be supplemented by the following data on the susceptibility coils. S, had about 3000 turns and S, about 3600 turns of No. 40 B & S S.S.C. copper wire which at room temperature had a total d.c. resistance of  $\simeq$  1,600 ohms. The primary had about 600 turns of No. 36 B & S D.S.C. copper wire with a room temperature resistance of  $\simeq$  75 ohms.

### B Gamma Ray Detection Equipment

Scintillation counters were used for the detection of the gamma radiation. The necessary equipment consists of NaI crystals, photomultipliers, cathode followers, linear amplifiers, amplitude discriminators, pulse height analysers and scalers. The radiation is recorded simultaneously in two directions as the temperature of the radioactive specimen varies; hence two separate channels are used as shown in the block diagram given in Figure III.

The NaI (TI) scintillation crystal, the photomultiplier with its potential divider, and the cathode follower form a portable unit. The crystal is  $l\frac{1}{2}$  inch in diameter, 1" long, and was obtained ready mounted from Harshaw Co. It is held in optical contact on a RCA 6342 photomultiplier by Dow Corning Fluid 200. The phototubes were magnetically shielded against stray fields by a Mu metal tubing and later by Conetic-Fermetic tubing. The high voltage supply was a commercially available type manufactured by Technical Measurements Corporation (HV 4A). The potential is applied to the cathode, the dynodes and the anode through a chain of resistors. Cathode followers designed for negative pulses were used.

The pulses from the cathode follower were fed into a linear pulse amplifier through low impedance cables. The amplifiers have been built following closely the circuit and the layout of the commercially available Linera Amplifier Model 218 of Atomic Instrument Co. It consists of two separate three stage amplifiers with negative feedback loops. The gain is



FIGURE 3 BLOCK DIAGRAM OF THE COUNTER ARRAY

controlled at the input by a potentiometer providing an adjustment of the signal between 50% and 100% of its maximum value. A coarse gain control follows which gives roughly steps of 2. The gain of the amplifier is 6,000 for a rise time of some 0.7 microsecond and a pulse duration of 5 microsecond. Some modifications of the original circuit have been made and detailled circuit diagrams are given in the thesis of G.L.J. Lamarche (1956). The filaments on all tubes have been set at a D.C. potential of 40 volts with respect to the chassis. The signal at the output is a positive pulse with amplitude between 0 and 100 volts. This signal is fed to an amplitude discriminator and/or to a pulse height analyzer. The amplitude discriminator is the usual Schmidt trigger circuit. The output from the discriminator is also a positive pulse with constant amplitude of 40 volts. Since in general Berkeley scalers were used and these will accept only negative pulses, the pulses are differentiated before being fed to the scaler. The single channel pulse height analyzers were the commercially available Model 510 manufactured by Atomic Instrument Company. The scalers were Berkeley Decimal Scalers (Models 100, 2105, and 2001) but Atomic Instrument Co. Model 101A Scale of 64 scalers were also used.

The simultaneous use of a discriminator and pulse height analyzer with a total of 4 scalers enable us to observe the anisotropy of two different gamma rays in a single run. In some experiments the entire electronic equipment was duplicated by borrowing various components from other groups

in our department. This enabled us to accumulate more data and better statistics in each run. A permanent duplicate electronic set up is being assembled.

The electronic equipment operates on a standard regulated 1 kilowatt power supply (Stabiline Voltage Regulator made by Superior Electric Corp.).

The scalers were turned on and off manually. Since counting periods of  $\frac{1}{2}$  minute up to several minutes were used, the slight error in turning two scalers on and off simultaneously that this procedure may introduce is negligible.

A pair of water cooled, air-core Helmholtz coils was constructed. These coils are operated in parallel and produce a maximum magnetic field of 1,000 gauss at the center of a 3 inch gap with a current of 15 amperes flowing through each. The dimensions of each coil are the following: Inner Diameter  $4 \frac{1}{2}$ , Outer Diameter 8  $\frac{1}{2}$ , Width 3". They consist of approximately 1,100 turns of No. 16 B & S enamelled copper wire, each layer separated by strips of 1 mm. thick bakelite and the whole is encased in a water tight brass case. The coils fit closely around the tail of the outer dewar 2  $\frac{1}{2}$ " in diameter. Prior to and during a run the current was passed through the coils continuously so that the system was in thermal equilibrium and the current constant.

The stray magnetic field produced by the coils at the photomultipliers will completely disturb their operation. This difficulty is solved by (a) removing the phototubes from the strong magnetic field region, (b) by magnetic shielding,

and (c) by the use of a bucking coil.

The photomultipliers were placed about 8 inches from the scintillation crystals and a lucite pipe provides a path for the light. The lucite rods, 1 1/2" in diameter, are well polished and in good optical contact with the photomultipliers and the crystals. The lucite rods are rigidly mounted with a minimum of contact at the points of support. Besides the Mu metal or Fernetic-Conetic tubing additional magnetic shielding was obtained by placing two concentric cylinders of mild steel around each phototube. The cylinders extend about two inches beyond the front of the phototube, they are 1/4 and 1/8 inch thick each, and are separated by a thin brass sheet.

The above arrangement still does not provide adequate shielding for the phototube in the direction of the field. In this case a bucking coil consisting of one layer of enamelled copper wire was wound around the outer steel cylinder and the current adjusted until the effect of the stray field on the counting rate was approximately corrected. Due to the presence of the steel cylinders inside the bucking coil the adjustment of the current through the bucking coil is less critical. A change of about 10% in this current does not affect the counting rate by more than 1% once the current has been adjusted. The circuits of the bucking coil and the Helmholts coils are placed in parallel; hence a change in the D.C. generator voltage will cause both to vary proportionately.

The detector units and the Helmholtz pair are mounted on a turntable which is placed on a carriage rolling

on rails; hence the assembly can be moved easily and quickly around the dewar, allowing the counting to start not later than 30 seconds after the end of the demagnetization. Alignment of the detectors with respect to the sample was done visually prior to the experiment using some distant objects as reference points. The alignment is estimated to be accurate within some  $5^{\circ}$ .

# CHAPTER III NUCLEAR ORIENTATION EXPERIMENTS WITH Pr<sup>142</sup> AND Yb<sup>175</sup> NUCLEI IN PARAMAGNETIC SINGLE CRYSTALS

Historical Remark:

The research described in this chapter was initiated by Dr. J.L.G. Lamarche while working as a graduate student in this laboratory at the suggestion of Dr. J.M. Daniels. At that time a liquid air cooled solenoid capable of producing a maximum field of 14 to 15 kilogauss was used in this laboratory for adiabatic demagnetization. This cumbersome set up not only limited the temperature range for investigations but rendered the accumulation of statistical data a most laborious procedure. Nevertheless preliminary measurements on Pr<sup>142</sup> in zero external field had been carried out down to a temperature of 0.005° K. These failed to show any reliable anisotropy greater than 1%. Further extensive measurements of the 396 and 282 kev  $\gamma$ -rays of  $Yb^{175}$  were performed down to a temperature of  $0.005^{\circ}$  K in zero external field, and preliminary observations of both &-rays with an external field of 180 gauss parallel to the trigonal axis were carried out down to a temperature of 0.009° K. These measurements indicated no anisotropies greater than 1%.

When the large water-cooled electromagnet mentioned in Chapter II became available the collection of more accurate statistical data became much easier and the attainment of lower temperatures became possible. It was decided to repeat this work and extend the range of investigation to 0.003<sup>°</sup> K.

The results reported in this chapter are based entirely on this new series of measurements carried out by the author.

#### Part I

# Nuclear Orientation of Pr<sup>142</sup>

### Introduction:

The magnetic hyperfine structure method of orienting nuclei has been established by Bleaney et al (1954) and has already proved useful in establishing details of nuclear decay schemes and in evaluating nuclear magnetic moments (e.g. Grace and Halban 1952). As part of a program to exploit the potentialities of such experiments, we have oriented  $Pr^{142}$  in cerium magnesium nitrate by this method and have observed and measured an anisotropy in the emission of the 1.57 mev  $\mathcal{X}$ -ray which occurs in the decay of this nucleus. A value of the magnetic moment of the  $Pr^{142}$  nucleus has been deduced from these measurements.

# Experimental:

The experimental technique which we used is essentially that described in detail by Bleaney et al (1954) and we mention the features pertiment to this experiment. A solution of a few milligrams of praseodymium nitrate in heavy water was irradiated in the B.E.P.O. pile at Harwell to an activity of some 10 millicuries. It was then brought to Vancouver by C.P.A.'s transpolar flight, and the active solution was poured into a saturated solution of about 10 grams of cerium magnesium nitrate. Single crystals were then grown from this solution in a vacuum dessicator over concentrated sulphuric acid.

Because of the short half life of the isotope special care must be taken to accelerate the growth of the crystals.

This was done by preparing beforehand several small well formed crystals of cerium magnesium nitrate. These are then used as seeds from which large crystals can be easily and quickly obtained in the radioactive saturated solution. We found it possible to obtain within less than 18 hours some 20 well formed single crystals with a total weight of about 4 grams and a total counting rate of about 100/second in the counting apparatus with the scintillation crystals placed at a distance of 10 cm from the source.

The crystals which are flat plates of trigonal symmetry were glued with parallel crystallographic orientation on a strip The strip of mica was tautly suspended by short nylon of mica. threads in the glass sample holder which is then sealed and mounted in the cryostat. The detectors are aligned with respect to the plane of the mica by taking distant objects in the laboratory as reference points. The crystals were cooled by adiabatic demagnetization from an initial field of about 20 kilogauss and temperatures of 1.3°K to temperatures of about 3x10<sup>-3</sup>oK. After demagnetization, the magnet was removed and two scintillation counters placed in position round the specimen in some 20 seconds. One scintillation crystal was placed along the trigonal axis of the radioactive crystals, about 10 cm. from the source, and the other was placed at a similar distance in a direction at right angles to this axis. The pulses due to gamma rays of energy greater than 1 Mev were counted. During the period when the crystals warmed up from the low temperature attained on demagnetization to the helium bath







FIGURE 4

ę

DECAY SCHEME of  $Pr^{142}$ 

temperature of  $1.3^{\circ}$  K, from 10 to 20 minutes according to the conditions prevailing during an experiment, the counting rate was measured in the two counters, and the temperature of the crystals was measured using a mutual inductance and a ballistic galvanometer (Chapter II p. 29, Bleaney et al 1954). After the active crystals had warmed to  $1.3^{\circ}$ K, the counting rate was observed for a while to test the stability of the counters, and for normalization purposes. In the second series of experiments an external field of a few hundred gauss was applied to the radioactive crystals by placing Helmholtz coils around the dewar with the field along the trigonal axis. When these coils were used the scintillation crystals were coupled to the photomultipliers shielded from the stray field as described in Chapter II.

### Decay Scheme

The decay scheme of 19.2 hour  $Pr^{142}$  has been studied by various workers, including Gideon et al (1949), Jensen et al (1950), Bartholomew and Kinsey (1953), Polm et al (1954) and Sterk et al (1955). The decay scheme suggested by Polm et al (1954) is shown in Figure 4.  $Pr^{142}$  decays to Nd<sup>142</sup> in two branches: a beta of 2.166 Mev to the ground state and a much less intense beta of 0.586 Mev to the only low energy excited level of Nd<sup>142</sup> followed by a 1.57 Mev gamma ray transition to the ground state. The arguments for this decay scheme are, briefly, as follows. Nd<sup>142</sup> is an even-even nucleus; its ground state therefore is O+. The 2.166 Mev X-ray has



log ft = 7.8, and the first special shape appropriate to a beta transition with  $\Delta I = 2$ , yes; the spin and parity of  $Pr^{142}$  are thus 2-. The other beta transition has log ft = 7.1 and allowed shape; it is therefore suggested that it is first forbidden with  $\Delta I = 0$  or  $\pm 1$ , yes. Since the first excited states of nearly all even-even nuclei so far measured have spin and parity 2+, the excited state of Nd<sup>142</sup> in this scheme is assigned spin and parity 2+, and the  $\chi$ -ray is assumed to be E2.

### Results

The absolute temperature of the radioactive crystals was obtained from the magnetic susceptibility measurements, using the relationship given by Daniels and Robinson (1953). The Curie-Weiss  $\Delta$  for our specimen was determined by comparing the measured value of the magnetic temperature T<sup>\*</sup> after demagnetization with the value calculated from the initial magnetic field and the initial temperature. Its value was 2.6 millidegrees which is a reasonable value according to Daniels and Robinson (1953).

We can define the anisotropy parameter  $\mathcal{E}$  by the relation:  $\mathcal{E} = \left( \begin{array}{c} \mathbf{I}_{\perp} - \mathbf{I}_{\prime\prime} \right) / \mathbf{I}_{\prime}$ 

where I  $\eta$  and I  $\perp$  are the normalized counting rates in directions parallel and perpendicular respectively to the trigonal axis of the crystals. Values of  $\mathcal{E}$  for the same temperature range, but from different demagnetizations, were averaged to improve statistics.



The results of the measurements are shown in Figures 5 and 6 in which  $\mathcal{E}$  is plotted as a function of 1/T. Figure 5 is for the case where an external magnetic field of 320 gauss is applied parallel to the trigonal axis of the crystals. This field strength was chosen after preliminary measurements did not show any appreciable difference between results obtained using fields of 160, 250 and 400 gauss along this axis. In each figure the solid curve is the curve of the form  $\xi = a/T^2$  which best fits the data. For zero external magnetic field a = 4.95x  $10^{-70}$  K<sup>-2</sup>, for an external field of 320 gauss <u>a</u> = 18.7 x  $10^{-70}$  K<sup>-2</sup>. These results may be compared with those obtained at Oxford in a similar experiment with Pr<sup>142</sup> in certain magnesium nitrate (Johnson 1958). From their published curves we can estimate the value of <u>a</u>. In the case of zero external field <u>a</u> =  $8.7 \times 10^{-7} \text{oK}^{-2}$ . Since this value is larger than ours by a factor of about 1.7 the agreement is somewhat poor. In the case of an external magnetic field of 300 gauss where  $\underline{a} = 22 \times 10^{-7} \text{oK}^{-2}(\text{Oxford})$  the agreement is quite good. The value of the nuclear magnetic moment of Pr<sup>142</sup> is estimated from the latter curve as shown below. The Oxford group also observed that the anisotropy did not increase at a given temperature in external fields larger than 300 gauss.

The possibility was considered that bremsstrahlung from the 2.166 Mev (3-ray could be counted as 3-rays and reduce the observed anisotropy. Calculations based on formulae in Siegbahn (1955) showed that this effect is negligible.

The threshold of the discriminator was set at 1 Mev to get a good counting rate. In this case one must consider the reduction of anisotropy due to scattered gamma rays. Such a calculation was made by Bleaney et al (1954) for the case of  $\operatorname{Co}^{60}$  in an apparatus which is essentially similar to ours. It was found that this correction is quite negligible for values of  $\mathcal{E}$  as low as 0.04, and we have therefore ignored it. It is very unlikely that the lifetime of the gamma emitting state is greater than about  $10^{-13}$  seconds (Weisskopf's formula predicts a lifetime of  $10^{-14}$  second for an El transition, and  $10^{-12}$  second for an E2 transition) hence loss of anisotropy due to precession in the crystalline fields can be discounted.

## Discussion:

The double nitrates  $M_2Mg_3(NO_3)_{12}^{24} H_2^{0}$  where M is one of La,Ce, or Pr, are isomorphous and form mixed crystals in all proportions. The paramagnetic resonance spectrum of the stable isotope,  $Pr^{141}$ , as an impurity in lanthanum magnesium nitrate, has been observed by Cooke and Duffus (1955), who assigned to this ion the spin Hamiltonian:

$$\begin{aligned} & \oint P = g_{||} \beta H_z S_z + A S_z I_z + A_x s_x + A_y S_y & \dots (1) \\ & \text{where } g_{||} = 1.55 \quad A = 0.077 \text{ cm}^{-1} \\ & \Delta = A \text{verage } \sqrt{\Delta_{\chi}^2 + A_y^2} \approx 0.04 \text{ cm}^{-1} \\ & S = 1/2 \qquad I = 5/2 \end{aligned}$$

and the z-axis is the trigonal axis of the crystals. The Pr<sup>+++</sup>

ion has an even number of electrons, and hence the energy levels need not be doublets (Kramer's theorem). However the symmetry of the double nitrate crystal is such that the ground state is an accidental doublet. Strains and other distortions can cause a splitting of this doublet, and it has been suggested that this is the origin of the  $\Delta$ -term. There is no unique value of  $\Delta$  , a different value being appropriate for each ion, but an "average" value of  $\Delta$  can be assigned.  $\Delta$  is probably structure-sensitive. The most general spin Hamiltonian with trigonal symmetry has terms  $g_{\perp}\beta(H_xS_x + H_yS_y)$  and B  $(S_xI_x + S_yI_y)$  in addition to those in equation (1). To the accuracy of published measurements, both g  $_{L}$  and B are zero. In the case where S = 1/2, g<sub>1</sub> = B = 0 and  $\Delta$  = 0, magnetic interactions between the ions do not affect the angular distribution of gamma rays (Daniels 1957). In this case also, an external magnetic field applied along the z-axis has no effect on the angular distribution (Daniels 1957).

Case a) If the decay scheme is  $2 \xrightarrow{0} 2 \xrightarrow{2} 0$  (i.e. the  $(3 - \nu)$  pair carries off no angular momentum) the normalized intensity distributions  $I_m(\theta)$  for the various m-states of the parent nucleus are:

$$I_{0}(\theta) = 5/16 \pi (1 - \cos^{4} \theta)$$

$$I_{2}(\theta) = 5/16 \pi (1 - 3 \cos^{2} \theta + 4 \cos^{4} \theta) \dots (2)$$

$$I_{0}(\theta) = 5/16 \pi (6 \cos^{2} \theta - 6 \cos^{4} \theta)$$

Case b) If the decay scheme is  $2 \xrightarrow{1} 2 \xrightarrow{0} 0$ (i.e. the  $(3 - \nu)$  pair carries off one unit of angular momentum) the normalized intensity distributions are:

$$I_{0}(\theta) = 5/16 \pi (1 - \cos^{2}\theta + 2/3 \cos^{4}\theta)$$

$$I_{2}(\theta) = 5/16 \pi (1/2 + 5/2 \cos^{2}\theta - 8/3 \cos^{4}\theta) \dots (3)$$

$$I_{0}(\theta) = 5/16 \pi (1 - 3 \cos^{2}\theta + 4 \cos^{4}\theta)$$

We may calculate the polar diagram as a function of temperature from the relation:

$$I(\Theta) = \sum_{m} W_{m}I_{m}(\Theta) \qquad \dots \qquad (4)$$

where  $W_m$  are the temperature dependent relative populations of the substates m. In a state of thermal equilibrium we may assume a Boltzmann distribution consequently:

$$W_{\rm m} = \frac{e^{-E_{\rm m}/kT}}{\sum_{\rm m} e^{-E_{\rm m}/kT}} \qquad \dots \qquad (5)$$

where  $E_{m}$  is the energy of a nucleus in substate m.

If the energy  ${\rm E}_{\rm m}$  is small relative to kT we may expand the numerator

$$e^{-E_{m}/kT} = 1 - E_{m}/kT + E_{m}^{2}/2k^{2}T^{2}$$
 .... (6)

and we may neglect terms of higher order.

In the absence of an external field the energy levels are given from the Hamiltonian equation (1) by:

$$E_{m} = \pm 1/2 \sqrt{(A m)^{2} + \Delta^{2}} \dots (7)$$

where m in the nuclear magnetic quantum number and takes on the values 2,1,0,-1,-2.

If we define the anisotropy by  $\xi = \frac{I(\pi/2) - I(0)}{I(\pi/2)}$ the calculation yields for case a)

$$\mathcal{E} = \frac{3 A^{2} / {}_{16} k^{2} T^{2}}{1 + \Delta^{2} / {}_{8} k^{2} T^{2} + 5 A^{2} / {}_{16} k^{2} \overline{\tau}^{2}} \sim \frac{3 A^{2}}{16 k^{2} \overline{\tau}^{2}} \dots (8)$$

and for case b)

$$\mathcal{E} = \frac{3A^{2}/_{32}k^{2}\tau^{2}}{1+\Delta^{2}/_{8}k^{2}\tau^{2}} \simeq \frac{3A^{2}}{32k^{2}\tau^{2}} \dots (9)$$

If  $\Delta$  and A are small relative to kT this procedure is valid. However since the anisotropy is appreciably increased in the presence of an external field along the trigonal axis these approximations are quite suspect.

We therefore proceed to investigate the behaviour of the energy levels when a magnetic field is applied along the trigonal axis (i.e. the z-axis). The energy levels are then given by:

$$E_{m} = \pm \frac{1}{2} \sqrt{(g_{\parallel}\beta H + Am)^{2} + \Delta^{2}} \qquad \dots (10)$$

If we used the approximation given in equation (6) the expressions (8) and (9) would then contain an additional term in  $(g_{\mu}\beta H)^2$  in the denominator and would be less valid. We note that as  $(g_{||} (\beta H))$  increases relative to a and  $\Delta$  the energy levels become separated and the separation between the different m-states approaches the full value of A/2. This corresponds to the separation in zero field with  $\Delta = 0$ . For instance if we assume  $g_{||} (\beta H = 2A)$ , and  $\Delta \simeq A$ , we obtain levels at  $\pm 3.04A$ ,  $\pm 2.55A$ ,  $\pm 2.06A$ ,  $\pm 1.58A$ , and  $\pm 1.12A$ .

Since the measurements with magnetic fields greater than 320 gauss did not indicate any increase in the anisotropy at a given temperature we assume that in a magnetic field of 320 gauss the levels have attained the full separation of A/2. We may then proceed in the following manner. Let  $\pm E_m = \pm E_0 + mA/2$  where  $E_0$  is some constant energy term. We then expand the numerator in equation (5)

$$e^{\pm E_m/kT} = e^{\pm E_0/kT + mA/2kT} \simeq e^{\pm E_0/kT} \left[1 + \frac{mA}{2kT} + \frac{1}{8} - \frac{mA}{kT}^2\right]$$
.... (11)  
where we neglect higher order terms. Since  $|E_0| > A/2$  we may  
neglect the terms containing the factor  $e^{-E_0/kT}$  and we note  
that the factor  $e^{E_0/kT}$  cancels out. Hence we calculate I ( $\Theta$ )  
of equation (4) and obtain for the anisotropy defined above

the following expressions:

Case a) 
$$\mathcal{E} = \frac{3 \ A^2}{16 \ k^2 T}$$
 .... (12)

$$E = \frac{3 - 1}{32 \text{ k T}} \qquad \dots \quad (13)$$

From the anisotropy measured in a field of 320 gauss and equations (12) and (13) we determine the hyperfine structure

constant A/k. We find

Case a)  $A/k = 0.0032^{\circ}K$ 

Case b)  $A/k = 0.0045^{\circ}K$ 

If we assume that  $\Delta = 0$ , upon substitution of these values for A/k into the appropriate expression given in equations (8) and (9) we note that this does not introduce appreciable reduction of the anisotropy for values of T as low as  $0.005^{\circ}$ K. For instance the denominator becomes 1.13 and 1.23 in case a) and b) respectively at this temperature. The decrease of the anisotropy in zero field must then be attributed to the term in  $\Delta$ . We may estimate the magnitude of the term  $\Delta$  required to reduce the anisotropy to the zero field measurements using the exact expression for I ( $\Theta$ ) and calculating the anisotropy  $\varepsilon$  at various temperatures for ' several values of  $\Delta$ . These calculations show that a  $\Delta \simeq 10A$ and  $\simeq$  7A gives a good fit to our results for case a) and case b) respectively.

From the values of A/k determined above we may estimate the nuclear magnetic moment of  $Pr^{142}$ . Since the field on the praseodymium nucleus is due to the 4f electron shell, independent of the isotope, this field is  $H = A_{141} I_{141} / I_{141} = A_{142} I_{142} / I_{142}$ . For the stable isotope  $Pr^{141}$  the values are known

 $M_{141} = 3.8 \text{ n.m.}, A_{141} = 0.077 \text{ cm}^{-1} = 0.111^{\circ}\text{K}$
It is then a simple matter to substitute into these formulae to find  $\mathcal{M}_{142}$ . The result is:  $\mathcal{M}_{142} = 0.11$  nuclear magnetons if the  $(3 - \nu)$  pair carries off no angular momentum, or  $\mathcal{M}_{142} = 0.15$ nuclear magnetons if the  $(3 - \nu)$  pair carries off one unit of angular momentum.

## Part II

# Nuclear Orientation Experiments with Yb<sup>175</sup>

#### Introduction

To further exploit the potentialities of orienting nuclei by the magnetic hyperfine structure method we performed experiments to orient Yb<sup>175</sup> as an impurity in cerium magnesium nitrate. When these investigations were started, it was discovered that a group at Oxford were preparing to align this isotope. At that time, very little was known about the effect of interactions between neighbouring paramagnetic ions on the angular distribution of gamma rays from an assembly of aligned nuclei, except that such effects could be large (Grace et al 1954). In addition, only one isotope, Co<sup>60</sup>, had been aligned in more than one crystalline environment (Bleaney et al 1954, Ambler et al 1953). Since the Oxford group planned to orient  $Yb^{175}$  in the ethylsulphate lattice, and we planned to align it in the double nitrate lattice, it was thought that these investigations might complement each other and yield information about the effects of interactions. The results of the investigations at Oxford have been published (Grace et al 1957) and are indeed very different from ours.

# Experimental

The technique used to orient the ytterbium was exactly the same as that used to orient praseodymium described in Part I of this chapter.

The starting material for these investigations was  $Yb_2O_3$  separated by the ion exchange method, and supplied to ' us by Dr. F.H. Spedding of the Ames Institute. One milligram was irradiated in the NRX pile at Chalk River, to an activity of about 5 millicuries. On receipt of the irradiated sample, the quartz capsule was crushed under about 20 cc. of water contained in a platinum crucible. A special jig was used for this operation. About six drops of concentrated sulphuric acid were added, and the whole was evaporated to dryness, first on a sand bath and afterwards under a heat lamp. The residue was then dissolved in about 20 or 30 cc. of water. This solution was filtered into a beaker and about 15 cc. of saturated solution of cerium magnesium nitrate was added. Crystals were grown from seeds placed in this solution in a vacuum dessicator over sulphuric acid.

The double nitrates of the rare earths exist only for the rare earths from La to Gd, and ytterbium magnesium nitrate does not exist as such. However, some ytterbium does go into the crystal lattice. After a crystal was removed from the solution, it was washed with distilled water to remove any solution from its surface, and dried with filter paper, to preclude the possibility that the activity is due to a layer of dried off solution on the surface. The crystals were generally clear enough for the observer to see that they contained no large inclusions of solution. On one occasion, a sample of  $Yb_2O_3$ became contaiminated in the irradiation, and the solution from which the crystals were grown emitted a gamma ray of about



FIGURE 8 Yb<sup>175</sup> 396 keVy -RAY Upper graph - Zero external field. Middle graph - fields along the trigonal axis. Lower graph - fields perpendicular to the trigonal axis.

700 kev energy, yet this gamma ray was completely absent from the crystals grown from this solution. In this way we are sure that the ytterbium does go into the crystal lattice; it is most reasonable to assume that it goes into a rare-earth position, although there is no direct evidence for this. The specific activity of the crystals was about 1/30 that of the solution.

#### Decay Scheme:

The principal features of the decay scheme of Yb<sup>175</sup> are shown in Figure 7. This decay scheme has been studied by a variety of investigators de Waard (1955), Akerlind et al (1955), Marty (1955), Mize et al (1955a, b), Cork et al (1956) and has been analyzed theoretically by Chase and Wilets (1956). We shall therefore assume that the decay scheme is established correctly.

During the irradiation of natural ytterbium, three isotopes are formed, 4.2 day  $Yb^{175}$ , 32.4 day  $Yb^{169}$ , and 6.7 day Lu<sup>177</sup>. However, about 10 times as much  $Yb^{175}$  as  $Yb^{169}$  or Lu<sup>177</sup> is produced (Cork et al 1950) and the 396 kev **X**-ray of  $Yb^{175}$  has a greater energy than any other from any of the three isotopes.  $Yb^{169}$  has a X-ray of 300 kev, but this is less intense than the 282 kev X-ray of  $Yb^{175}$ .

#### Results:

Measurements were made on both the 396 kev  $\checkmark$ -ray and also on the 282 kev  $\checkmark$ -ray; for the former a bottom cut discriminator was used, set to pass the photopeak of the 396 kev  $\checkmark$ -ray; for the latter a single channel kicksorter was





FIGURE 9 Yb<sup>175</sup> 282 keV y - RAY Upper graph - no external magnetic field. Middle graph - fields along the trigonal axis. Lower graph - fields perpendicular to the trigonal axis. used, set to pass only the photopeak of this  $\checkmark$ -ray. Measurements were made with zero external magnetic field, with fields of 260, 380, 510, and 700 gauss parallel to the trigonal crystalline axis, and with fields of 60, 100, and 160 gauss perpendicular to this axis. In no case was any significant anisotropy of  $\checkmark$ -radiation observed at any temperature. The results for the 396 kev  $\checkmark$ -ray are shown in Figure 8 and the results for the 282 kev  $\checkmark$ -ray in Figure 9.

From measurements of the anisotropy of these two  $\checkmark$ -rays from Yb<sup>175</sup> oriented in ytterbium ethylsulphate, Grace et al (1957) deduced a value for the magnetic moment of Yb<sup>175</sup>; it is 0.15 ± 0.04 nuclear magnetons; the sign is not known. The 396 kev  $\checkmark$ -ray and the 282 kev  $\checkmark$ -ray are both M2 with a small admixture E1. The experiments so far carried out do not give consistent values for the mixing ratios of these  $\checkmark$ -rays (Grace et al 1957).

#### Discussion:

No one has observed paramagnetic resonance in Yb<sup>+++</sup> in the double nitrate lattice, hence the spin Hamiltonian is not known. An estimate of the constants in the spin Hamiltonian was made. Since the details of these calculations are presented elsewhere (J.L.G. Lamarche 1956) we will only indicate the general procedure and the results.

We assume that the crystalline field acting on the ytterbium ion is the same as that acting on the cerium ion; the coefficients for the expansion of this field in a series of spherical harmonics are given by Judd (1955a). We assume that the formula given by Elliott and Stevens (1953a) for the radius of the 4f shell,

$$r^{n} \propto (2 - 55)^{-n/4}$$
 .... (1)

is applicable in the case of Yb<sup>+++</sup>. Using these values of crystal field parameters and ionic radii, we can work out an energy matrix for the ytterbium ion using the method and formulae given by Stevens (1952), Elliott and Stevens (1952, 1953a, b), and Judd (1955a, b). The results of these calculations are as follows: whereas the free Yb<sup>+++</sup> ion has J = 7/2 and an eight-fold degenerate ground state, in the double nitrate environment, this degenerate level is split into 4 doublets whose energies are - 2.26, +39.4, +0.4, and -37.5 cm.<sup>-1</sup>. The state with energy -2.26 cm<sup>-1</sup> is the doublet spanned by  $\left|J_{z} = 3/2\right\rangle$  and  $\left|J_{z} = -3/2\right\rangle$ , which lies lowest in the ethylsulphate. The lowest energy level is the one at -37.5 cm<sup>-1</sup>.

$$0.794 | 7/2 \rangle - 0.424 | 1/2 \rangle - 0.435 | -5/2 \rangle = | + \rangle$$
(2)

and

$$-0.794 | -7/2 \rangle - 0.424 | -1/2 \rangle + 0.435 | 5/2 \rangle = | - \rangle$$

# We assume a spin Hamiltonian of the form

$$\mathcal{H} = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A S_z I_z + B (S_x I_x + S_y I_y)$$

$$\dots (3)$$

The g values in this spin Hamiltonian can be obtained from:

$$g_{II} = 2\left|\left\langle +\right| L_{z} + 2S_{z} + \right\rangle = 2\left|\left\langle J\right| | \Lambda | | J \right\rangle \left\langle + | J_{z} + \right\rangle\right| \qquad (4)$$

$$g_{\perp} = 2 |\langle +| L_{x} + 2S_{x} |- \rangle = 2 |\langle J|| |J| ||J| + ||J_{x}|- \rangle |... (5)$$

where the  $\langle J || \wedge || J \rangle$  are constants given for each rare earth.

Thus we find for Yb<sup>+++</sup> in cerium magnesium nitrate:

$$g_{\parallel} = 4.2$$
  $g_{\perp} = 2.9$ 

The extent of the hyperfine structure is given by A I and B I. These can be evaluated by the following formulae:

$$A I = 4 \beta \beta_N M_N \quad (\underline{1}_3) \langle J || N || J \rangle \langle + |J_z| + \rangle \dots (6)$$
$$B I = 4 \beta \beta_N M_N \quad (\underline{1}_3) \langle J || N || J \rangle \langle + |J_x| - \rangle \dots (7)$$

where the  $\langle J || N || J \rangle$  are again constants given for each rare earth. Here again we use our initial assumption to approximate  $r^{-3}$  which for Yb<sup>+++</sup> has the value 91 X 10 <sup>24</sup> Å<sup>-3</sup>. Assuming that the magnetic moment of Yb<sup>175</sup> is 0.15 nuclear magnetons (Grace et al 1957) and dividing by the Boltzmann factor, we obtain

A 
$$I = 0.024^{\circ}K$$
 B  $I = 0.017^{\circ}K$ 

It is true that it is rather optimistic to expect such a calculation to give a result which is quantitatively correct, but unfortunately no better estimate of the properties of the ytterbium ion in this lattice exists. On the basis of these estimates, we should expect to observe nuclear orientation under the conditions of our experiments.

In view of the established fact that sizeable anisotropies of both the 396 kev &-ray and the 282 kev &-ray have been observed from oriented  $\ensuremath{Yb^{175}}$  nuclei (Grace et al 1957), the absence of an anisotropy in zero field in our experiment can be explained by one or more of the following hypotheses:

- (i) The ytterbium ion does not enter the lattice in a rare-earth position.
- (ii) The spin Hamiltonian is isotropic; i.e.  $g_{\parallel} = g_{\perp}$ and A = B.
- (iii) Magnetic interactions in the double nitrate crystal destroy the alignment of the ytterbium nuclei.
  - (iv) The  $\checkmark$ -emitting state is long-lived and precession of the excited Lu<sup>175</sup> nucleus in the internal atomic fields destroys the alignment before the emission of the  $\checkmark$ -ray.

As for the hypothesis (ii), the application of an external magnetic field in any direction should cause an anisotropy of **%**-emission to appear (Gorter 1958; Rose 1949; Ambler et al 1953). Since this does not occur, the possibility of the other hypotheses must also be considered. Hypothesis (111) is certainly applicable in this case. The theory of the effect of interactions has been given by Daniels (1957), and an order of magnitude calculation based on the formulae given there shows that the magnetic interference can be much greater than the forces which tend to orient the nuclei. Naively, the internal field at a rare-earth site is about 30 gauss; this will produce a splitting of the ground state of about  $0.01^{\circ}$ K, whereas the forces which tend to produce spatial orientation are of the order of magnitude of (A - B)**I** I, or about  $0.007^{\circ}$ K. However, the application of an external field larger than the internal field of 30 gauss should cause an anisotropy to appear, and this is not so.

Hypothesis (iv) is quite sufficient to explain our results, and also to explain the difference between our results and those obtained at Oxford. In the spin Hamiltonian for the Yb<sup>+++</sup> ion in the ethylsulphate,  $g_{\perp} = 0 = B$ . Under these circumstances, the angular distribution of  $\checkmark$ -rays is not affected by precession of the  $\checkmark$ -emitting nucleus. This is easily seen, for the angular distribution of  $\checkmark$ -rays is given by an expression of the form

$$\sum_{\tau} g_{\tau} \langle \Psi_{\tau} | r | \Psi_{\tau} \rangle \qquad \dots \qquad (8)$$

where  $g_{\chi}$  is a statistical distribution (e.g., Boltzmann) factor,  $\gamma_{\chi}$  is a wave-function of the ion containing the  $\gamma$ -emitting nucleus, and  $\Gamma$  is an operator which represents the angular distribution of  $\gamma$ -rays (see e.g., Daniels 1957). Because of the axial symmetry of the ion and its environment

in a representation with  $S_{\tau}$  diagonal only the diagonal elements of  $\Gamma$  appear in the result. If there is precession for a time t before the emission of the X-ray,  $\Gamma$  must be replaced by  $\exp\left[+i\mathcal{H}t/\hbar\right] \Gamma = \exp\left[-i\mathcal{H}t/\hbar\right]$ . Now the spin Hamiltonian  $\mathcal{H}$  for ytterbium ethylsulphate is diagonal in this representation and hence the diagonal elements of  $\exp\left[+i\mathcal{H}t/\hbar\right] \Gamma \exp\left[-i\mathcal{H}t/\hbar\right]$  are independent of t. Thus the angular distribution of  $\gamma$ -radiation in ytterbium ethylsulphate is not affected by precession. This is not so for the more general spin Hamiltonian which presumably applies to the double nitrate. It is difficult to estimate the lifetime necessary to wipe out all the anisotropy which should be there. If we take as a rough criterion that the lifetime should be about as long as it would take for the excited  $Lu^{175}$  nucleus to precess in the atomic magnetic field, the result is about 10<sup>-10</sup> seconds. Chase and Wilets (1956) have explained that for both &-rays, the El transition is strongly inhibited, and the lifetime should be about that appropriate to an M2 transition. Weisskopf's formula for the lifetime of a 400 kev M2 emitting state gives  $10^{-8}$  seconds; since the transition in  $Yb^{175}$  is a collective transition, not a single nucleon transition, a lifetime of at least  $10^{-10}$  seconds is more likely. A question arises whether the spin Hamiltonian of the ytterbium ion should be used during the precession, since after the X-emission the electronic configuration should be that of lutecium, which is not magnetic. This depends principally on the lifetimes of the 4f states. These are

probably about  $10^{-6}$  to  $10^{-8}$  seconds, typical lifetimes for optical transitions, and in the absence of further information the use of the ytterbium spin Hamiltonian is justifiable. Thus, it appears that hypothesis (iv) is adequate to explain our results. This conclusion has recently been confirmed by Vartapetian (1957) who measured a lifetime of 3.4 X  $10^{-9}$ seconds for this state.

# CHAPTER IV NUCLEAR ORIENTATION EXPERIMENTS IN ANTIFERRO-MAGNETIC SINGLE CRYSTALS

# Part I

# Nuclear Orientation Experiments with Mn<sup>54</sup> and Co<sup>60</sup> in Antiferromagnetic Single Crystals

# Introduction

It had been suggested by Daunt (1951) and Gorter (1951) that nuclei might be aligned in antiferromagnetic single crystals at low temperatures. At the Néel temperature and at lower temperatures a negative exchange interaction produces an antiparallel ordering of the electronic moments along preferred directions of the crystal lattice. The magnetic hyperfine interaction then at suitably low temperatures should cause an appreciable nuclear alignment.

At the time we initiated the work described in this chapter, the only attempt to detect nuclear orientation in an antiferromagnetic single crystal had been made in Leiden with an undiluted cobalt ammonium sulphate crystal and no effect greater than 1% was reported (Poppema 1954). Although  $Mn^{54}$ (Grace et al 1954) and Ce<sup>141</sup> (Ambler et al 1955, 1956) had been aligned in cerium magnesium nitrate at 0.003°K where an antiferromagnetic transition is believed to occur it was not clear whether the alignment was enhanced or reduced at the Néel temperature. At any rate these measurements did not

yield information on nuclear alignment below the Néel temperature. The negative results of the Leiden group with cobalt ammonium sulphate which has a Néel temperature at  $0.085^{\circ}$ K (Garrett 1951) led us to expect that a substance with a higher transition temperature might be more suitable.

Measurements at about  $1^{\circ}$ K and lower on antiferromagnetic MnF<sub>2</sub> with a transition temperature at  $67^{\circ}$ K indicated the presence of a considerable nuclear specific heat and this substance was proposed as very promising for nuclear orientation (Cooke 1957). Single crystals of MnF<sub>2</sub> are quite difficult to grow however. We decided to try instead another antiferromagnetic salt of manganese which is readily crystallized from the solution. We selected MnCl<sub>2</sub>4H<sub>2</sub>O although its Néel temperature is some orders of magnitude lower than MnF<sub>2</sub>. When these measurements proved successful we tried another salt of manganese, MnBr<sub>2</sub>4H<sub>2</sub>9 in order to confirm this method of orienting nuclei.

The anisotropies observed for the Mn<sup>54</sup> gamma radiation with these crystals required several hours to attain a maximum value. Gradual cooling of the crystal may account for this phenomenon but it may also be due to some extent to long nuclear relaxation times in antiferromagnetic materials. In such a case this method of orienting nuclei would be of little value. Alternatively however nuclear alignment in antiferromagnetic materials might yield information on nuclear relaxation phenomena in this class of substances.

A series of experiments was launched in order to explore the possibilities and general features of nuclear alignment in antiferromagnetic single crystals and also to gain some insight into the nuclear relaxation mechanism in such substances. In this chapter we report on the results of experiments completed to date.

From the large number of antiferromagnetic compounds that are known and have been investigated we selected a few salts of cobalt and manganese for this experimental survey. Cobalt and manganese each have an isotope which is particularly suitable for this type of investigation. The isotopes Co<sup>60</sup> and Mn<sup>54</sup> are readily available, long-lived gamma emitters; they have simple and well known decay schemes and large nuclear magnetic moments. Further the orientation of these nuclei has been well investigated in paramagnetic salts.

Dr. Myer Bloom pointed out to the author that theoretical work predicted a strong dependence of the nuclear relaxation time on the Néel temperature of the antiferromagnetic materials (Van Kranendonk and Bloom 1956). Indeed with all other factors approximately constant for different salts of a given ion  $\mathcal{T} \prec T_N^3$ , where  $\mathcal{T}$  is the nuclear relaxation time and  $T_N$  is the Néel temperature. For this reason we thought it might be informative to investigate salts with transition temperatures differing by some order of magnitude. We list the salts in which nuclear alignment has been studied and is reported in this thesis, with their

Néel temperature.

The question also arose whether nuclear alignment would occur for nuclei of foreign ions incorporated as impurities in the lattice of an antiferromagnetic crystal. A further possibility dependent upon this is that the nuclear relaxation time might be appreciably different for each type of nucleus in a crystal. This would then provide us with a technique to investigate the nuclear relaxation time and to distinguish between this phenomenon and the process of gradual cooling of the crystal lattice. To study this point we incorporated a small amount of  $\operatorname{Co}^{60}$  in single crystals of MnCl 4H 0 and  $\operatorname{MnSiF}_{6}_{2}^{6}$  and made some preliminary measurements with Mn<sup>54</sup> in  $\operatorname{CoCl}_2_{6}_{6}_{0}^{6}$  and  $\operatorname{Co}(\mathrm{NH}_{4})_{2}(\mathrm{SO}_{4})_{2}_{6}_{0}^{6}$ .

The results obtained with single crystals of each salt are presented separately. In each case we give the morphology of the crystal, the Néel temperature, and the preferred axis of antiferromagnetic ordering. In the crystals used in these experiments, with the exception of  $Co(NH_4)_2(SO_4)_26H_2O$ , it is not yet known whether this preferred direction corresponds to only one set of sub lattices.

# Experimental Procedure

Salts in the antiferromagnetic state cannot in general be cooled by adiabatic demagnetization and salts which

are paramagnetic at liquid helium temperatures but undergo an antiferromagnetic transition at lower temperatures will not cool appreciably below the Néel temperature (Ambler and Hudson In the salts we have used the Néel temperature is 1955). either in the liquid helium range or at temperatures that are still relatively high for a significant degree of nuclear alignment to be expected. Hence to study the nuclear alignment well into the antiferromagnetic region external cooling of the antiferromagnetic crystals is required. This was accomplished by placing the single crystals in good thermal contact with a paramagnetic cooling salt. Since it may be cooled to temperatures of the order of 0.01°K by adiabatic demagnetization from moderate values of H/T and has a large specific heat we used potassium chrome alum as the cooling agent.

Two techniques for external cooling have been used in our work. In the simpler and earlier technique the crystals were covered with apiezon oil B and embedded between cylinders of compressed potassium chrome alum powder. This will be referred to as technique A. In the later and more elaborate method some hundred and fifty No. 36 B & S enamelled copper wires with a total surface of about 60 cm<sup>2</sup> were soft soldered to a thin copper disc of 1 cm. diameter. The space between the wires was filled with fine potassium chrome alum powder and apiezon oil B, and the assembly was pressed into a "pill" at some 5 tons/cm.<sup>2</sup> pressure. This produced a cylinder with a flat copper disc at one end. The crystal was then sandwiched between two such pills and the space between was filled with Apiezon N grease. This will be referred to as technique B. This more effective method of cooling a crystal was adopted by the author at the suggestion of Dr. J.C. Wheatley. The first method was used in earlier experiments and when the second arrangement was adopted most of the experiments performed with the first technique were repeated. When the pills containing copper wire were used the magnetic field was removed slowly over some 5 minutes in the adiabatic demagnetization to avoid eddy current heating.

In general one small single crystal of about

0.25 gram weight or less containing 5 to 10 microcuries of radioactive  $Mn^{54}$  and/or  $Co^{60}$  was used. The crystals were grown from seeds some 20 cubic mm. in volume to a size 2 to 3 times greater. This means that the radioactive nuclei were located in the outer layer of the crystal. In all the results presented in this chapter one single crystal was used in the experiment. In the case of  $MnCl_24H_20$  and  $MnBr_24H_20$  containing  $Mn^{54}$  experiments were also performed with the same amount of radioactive material distributed in several small crystals sandwiched between several cylinders of cooling salt in the same assembly. For each experiment we give the approximate dimensions of the crystal used.

Usually the assembly of potassium chrome alum cylinders had a total length of about 8 cm., and a diameter of l.l cm. The temperature of the potassium chrome alum was measured using a mutual inductance and ballistic

galvanometer, as the assembly warmed up after adiabatic demagnetization. The calibration of the magnetic thermometer in the liquid helium range gives an experimental relation between the galvanometer deflection and the magnetic temperature. This is of the form  $\delta = a_0 + a_1/T$ . Readings of the ballistic galvanometer after adiabatic demagnetization give a magnetic temperature  ${\rm T}_{\rm m}$  of the KCr Alum from this relation. On account of demagnetizing effects different values of T<sub>m</sub> may be obtained with specimens of different shapes. The accepted procedure is to determine the magnetic temperature for a spherical specimen where we now denote this magnetic temperature by  $T^*$ . The magnetic temperatures  $T_m$  obtained for a pressed pill assembly can be converted to the temperatures T\* for a spherical specimen when the appropriate correction factor is known using the relation  $T_m + \Delta = T^*$  where  $\Delta$  is the correction factor.

For a specimen ellipsoidal in shape this correction factor may be calculated and the correction factor for a sample of any arbitrary shape may be determined empirically. The correction factor for an ellipsoid of large axial ratio will be approximately equal to that for a cylindrical sample of the same length to diameter ratio. Previous workers in this laboratory have determined a correction factor of  $0.025^{\circ}$ K for a cylindrical pressed pill of KCr Alum with a length to diameter ratio of 7. This is the value we have used throughout our work.

Several workers have studied the relation between the magnetic temperature  $T^*$  and the absolute temperature T of KCr Alum (de Klerk et al 1949, Keesom 1948, Bleaney 1950, Daniels and Kurti 1954, Ambler and Hudson 1954). Although the results differ markedly in the lowest temperature range, agreement is fairly good at higher temperatures. We have adopted the values given by Bleaney (1950) to assign absolute temperatures to the potassium chrome alum in our work.

Recent measurements on external cooling (Miedema et al 1958) in the range between  $0.5^{\circ}$ K to  $0.04^{\circ}$ K have shown that the rate of cooling of a crystal in a set up very similar to technique B, could be described by the relation:

$$\frac{dQ}{dt} = A_1 \left(T_w^2 - T_c^2\right) \qquad \dots \qquad (1)$$

at the higher temperatures and by the relation:

$$\frac{dQ}{dt} = A_2 (T_w^4 - T_c^4)$$
 .... (2)

at the lowest temperatures, and by a combination of these formulae at intermediate temperatures.  $A_1$  and  $A_2$  are parameters determined from the experiment,  $T_w$  and  $T_c$  are the temperature of the warm crystal and the cooling agent respectively.

These relations indicate that as the temperature increases we can expect better correspondence between the temperature of the KCr Alum and that of the antiferromagnetic crystal in our experiments. Since the antiferromagnetic crystal in our experiments contains a radioactive isotope it will be a generator of heat and this will further increase the temperature difference between  $T_w$  and  $T_c$ . At "high" temperatures the following approximation is valid:

where  $\boldsymbol{\mathcal{E}}$  is the gamma ray anisotropy, T is the absolute temperature and a is a constant.

Using this relation we can check the consistency of our temperature assignments. Application of this relation to our data shows that in several cases the anisotropies observed are consistent with the temperatures measured in the range above  $0.05^{\circ}$ K. We may then compare the anisotropies observed in our experiments with those observed with the same isotope in paramagnetic crystals at the same temperatures. From this comparison we may gain some insight into the hyperfine structure coupling in antiferromagnetic crystals.

The gamma ray counters were placed about 10 cm. from the radioactive source. Generally one counter was placed along the axis of preferred direction and the other along some other crystallographic axis perpendicular to the first. The axes chosen are given for each experiment.

The procedure followed in the experiments was the following. The anisotropy and temperature were measured as a function of time from the end of the demagnetization as the potassium chrome alum warmed up. Exchange gas was then introduced in the sample holder to warm the salt to the temperature of the liquid helium bath and a normalization count was taken. The normalization count was taken for intervals of some minutes during about an hour to check the stability of the counters. The curve given in each case is the result of one run. However in each case several runs were made to check the reproducibility of the results.

The results are presented in the figures in the following manner: measurements of the anisotropy and the inverse of the magnetic temperature  $(1/T^*)$  are plotted as a function of time from the end of the demagnetization. Although a larger number of temperature readings were taken in a run than shown, only enough points are given to indicate the variation of temperature with time. The curve of the anisotropy exhibits three main features in succession: a) an increase to a maximum value, b) a levelling off or plateau at this maximum value for a time which in some cases can be of several hours duration, and finally c) a decrease. The increasing portion of the curve may throw some light on nuclear relaxation times. The broad plateau has to date only served to tax the patience of the experimentalist. This could provide however an opportunity for nuclear magnetic resonance investigations on oriented radioactive nuclei (Tolhoek and de Groot 1951, Bloembergen and Temmer 1953, Abragam 1956). Such endeavours are in progress in this laboratory at the time of writing of this thesis and we are indebted to Dr. Myer Bloom for pointing out this possibility to us. The decreasing portion enables us to determine the anisotropy





4. 2



FIGURE 11 DECAY SCHEME OF CO60

versus temperature curve and thus to compare our results with other data. Hence in this region we indicate the absolute temperature of the potassium chrome alum at convenient points.

The presence of the copper wire throughout the KCr Alum will help equalize the temperature throughout the volume of the sample. Nevertheless it is possible that an appreciable heat leak will introduce significant temperature gradients in the length and radius of the KCr Alum specimen thereby rendering the results quantitatively inaccurate. To minimize this source of error we have endeavoured to reduce the heat leak. This of course means that a run will last for several hours and increases the possibility of drift in the electronics, thereby necessitating several check runs.

# Decay Scheme of Mn<sup>54</sup> and Co<sup>60</sup>:

In Figure 10 we present the decay scheme of Mn<sup>54</sup> (Grace et al 1954, Strominger et al 1958). Mn<sup>54</sup> decays by electron capture to an excited state of  $Cr^{54}$  which de-excites by gamma emission to the ground state. The gamma transition was found to be E2 (Grace et al). The ground state of Mn<sup>54</sup> may have either spin 2 or 3. Thus two decay schemes are possible:  $3 \xrightarrow{1} 2 \xrightarrow{2} 0$ , and  $2 \xrightarrow{0} 2 \xrightarrow{2} 0$ .

In Figure 11 we present the main features of the decay scheme of  $\operatorname{Co}^{60}$  (Strominger et al 1958).  $\operatorname{Co}^{60}$  decays by  $\beta$  emission to an excited state of Ni<sup>60</sup> which de-excites by a cascade gamma emission to the ground state. The  $\beta$ - $\nu$  pair carries off one unit of angular momentum and the gamma





 $C_0 Cl_2 \cdot 6 H_2 O$ 



FIGURE

20

FIGURE I2

## General Information

The Néel temperature is 1.6<sup>°</sup>K (Friedberg and Wasscher 1953).

Manganous chloride crystallizes in the monoclinic system and its external morphology is described in Groth (1906) whose nomenclature we use. The external appearance is shown in Figure 12 where the a- and b-planes are also indicated. The a-plane is generally quite pronounced and may be easily identified.  $(3 = 99^{\circ} 25)$ .

According to Gijsman (1957) and Poulis and Gijsman (1958) the direction of easy magnetization is the crystallographic c-axis, and the next preferred axis is the b-axis.

We measured the radiation along these axes hence the anisotropy parameter  $\mathcal{E}$  is given by:

$$\boldsymbol{\xi} = \frac{\mathbf{I}_{b} - \mathbf{I}_{c}}{\mathbf{I}_{b}}$$

where the subscripts refer to the axes.

The crystals used were thin and flat, about 1 mm. thick and with an effective surface of about 1.5 cm<sup>2</sup> each. (We define the effective surface as the total surface of the crystal in direct contact with the copper discs at the end



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of the KCr Alum pills. The area of the sides of the crystal is not taken into account.)

## Results and Discussion

# $Mn^{54}$ in $McCl_24H_20$

Figure 13 shows the result of a run where the anisotropy increases to a plateau. It will be noticed that the manganese nuclei were in fact aligned along the preferred axis (c-axis). The anisotropy requires some 100 minutes to reach a maximum. This particular run was performed using technique A. The experiment was repeated using technique B to cool the crystal. The results were essentially the same and within statistical accuracy neither the rate of growth of the anisotropy nor the maximum value reached were enhanced.

Figure 14 shows the results of a run where the coolant salt was allowed to warm until a definite drop in the anisotropy was observed. It will be noticed that the anisotropy starts to decrease at a temperature of about  $0.12^{\circ}$ K. The crystal in this experiment also contained some Co<sup>60</sup>, hence some of the gamma radiation from the Co<sup>60</sup> was counted in the pulse height analyzer channel set to accept the photopeak of the Mn<sup>54</sup> gamma radiation. Since this background radiation was isotropic within less than 1% the anisotropy observed was correspondingly reduced. The purpose of this experiment was to establish the temperature at which the anisotropy decreased, hence the points plotted in



Mn<sup>54</sup> IN Mn Cl2<sup>:</sup>4 H2O 14 FIGURE

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Figure 14 were not corrected for this background.

In the case where the background is isotropic we may calculate the correct anisotropy from the relation:

$$\xi_{c} = \left(\frac{I_{b} + I_{Bgd}}{I_{b}}\right) \xi_{o}$$

where  $\xi_c$  is the corrected anisotropy,  $\xi_o$  is the observed anisotropy,  $I_b$  is the intensity of radiation from the Mn<sup>54</sup> along the b-axis, and  $I_Bgd$  is the background radiation due mainly to Co<sup>60</sup> radiation. This correction factor may be appreciable since the photopeak of the 842 kev gamma ray of Mn<sup>54</sup> coincides with the Compton plateau from the 1.33 and 1.17 Mev gamma rays of Co<sup>60</sup>. Since  $I_b$  changes with the nuclear alignment of the Mn<sup>54</sup> nuclei, the correction factor will also vary. It may be assumed constant however when small anisotropies are involved since then  $I_b$  changes by a few percent only. Further the crystals are prepared so that  $I_b > I_{Bgd}$ . To determine the correction factor we measure this background relative to the Co<sup>60</sup> count with a Co<sup>60</sup> source. In this experiment the correction factor was  $\simeq 1.45$ .

These experiments indicate that the assembly of nuclei cools only to a temperature of about  $0.12^{\circ}$ K. Experiments described later show that with essentially the same cooling arrangement and with crystals of about the same effective surface to volume ratio the nuclei and therefore the crystal lattice may be cooled to a temperature of  $\simeq 0.06^{\circ}$ K. We may then conclude that the nuclear spin relaxation time of manganese nuclei in this lattice is

several hours at 0.12<sup>°</sup>K. Van Kranendonk and Bloom (1956) give the following expression for the nuclear relaxation time, valid for very low temperatures.

$$\gamma = \underbrace{c \quad e^{T_A/T}}_{T^2} \qquad \dots \qquad (4)$$

where C is a proportionality factor and may be calculated from their paper,  $T_A$  is a measure of the anisotropy energy. This result is based on the spin wave model of antiferromagnetic substances. Assuming only dipole-dipole interaction between the nuclear spins and electronic spins and using their detailed expression for a temperature  $T = 0.1^{\circ}K$  the nuclear relaxation time was estimated to be  $\simeq$  500 hours. The contribution of hyperfine interaction to the nuclear spin relaxation is neglected in these calculations and may be very significant.

Experimental work on the relaxation time of protons in  $\operatorname{CuCl}_2\operatorname{2H}_2$ 0 shows a more rapid increase of  $\gamma$  with decrease of temperature (Hardeman et al 1956) than predicted by this expression. Cooke and Edmonds (1958) report a nuclear spin relaxation time of about 7 minutes at  $0.5^{\circ}$ K in MnF<sub>2</sub> from specific heat measurements. Hence it is not surprising that the nuclear system remains at a temperature of  $\simeq 0.12^{\circ}$ K for several hours even if the crystal lattice is appreciably colder.

An anisotropy of  $\simeq 0.07$  at a temperature of  $\simeq 0.12^{\circ}$ K is comparable to the anisotropy of Mn<sup>54</sup> observed in paramagnetic



cerium magnesium nitrate at this temperature. This is in agreement with the 'expectation that the hyperfine structure coupling of  $Mn^{++}$  is independent of the solid state.

 $Co^{60}$  in MnC<sub>2</sub>4H<sub>2</sub>0

# Results and Discussion

 $\rm Co^{60}$  was introduced as an impurity in single crystals of MnCl\_4H\_0 and the anisotropy of the gamma radiation was measured along the same axis as in the experiment discussed above. Several runs were made and a small anisotropy was measured. The anisotropy averaged for the various runs gives 0.0075± 0.0025. This effect is very small and in such cases some suspicion always remains that it may be spurious. It is conceivable that the cobalt nuclei do not align along the c-axis.

 $MnBr_2^{4H_2^0}$ 

#### General Information:

The Néel temperature is given as  $2.2^{\circ}K$  (Gijsman 1955) and  $2.4^{\circ}K$  (Henry 1954).

This salt crystallizes in the monoclinic system and its external morphology is described in Groth (1906). Its external appearance is very similar to  $MnCl_24H_20$  shown in Figure 12. ( $3 = 99^{\circ}6'$ .

The direction of easy magnetization corresponds to the crystallographic c-axis (Bolger 1955 Gijsman 1955). The



anisotropy parameter is defined as in the experiment with  $\mathrm{MnCl}_{2}\mathrm{^{4}H}_{2}\mathrm{^{0}}$  .

The crystals were bulkier than the MnCl  $_2^{4H}$  0 crystals, and were about 2 mm. thick and had an effective surface of about 1.5 cm<sup>2</sup> each.

#### Results and Discussion

The crystal was cooled using technique A. The measurements were not repeated when technique B was adopted. Figure 15 shows  $\mathcal{E}$  and  $1/T^*$  as functions of time from demagnetization. It is noticed that the anisotropy increases extremely slowly and only reaches a maximum after some 8 hours. Since the Néel temperature for this salt is higher than that for MnCl\_4H\_0 we may attribute this to a longer relaxation time.

$$MnSiF_6H_20$$

# General Information

The Néel temperature is 0.1<sup>o</sup>K (Ohtsubo et al 1958). The crystals are trigonal and grow in hexagonal pillars parallel to the trigonal axis (Groth 1906).

The preferred axis is along the hexagonal axis (Ohtsubo et al 1958).

The anisotropy parameter in these experiments is defined by

$$\mathcal{E} = \frac{\mathbf{I}_{p} - \mathbf{I}_{a}}{\mathbf{I}_{p}} \qquad \dots \qquad (5)$$
where  $I_a$  is the normalized intensity of radiation along the hexagonal axis, and  $I_p$  is the intensity in some arbitrary direction in the hexagonal plane.

The crystal was about 0.15 mm. thick with an effective surface of about 0.8  $\text{cm}^2$ .

## $Mn^{54}$ in $MnSiF_66H_20$

#### Results and Discussion

Figure 16 shows the results of a typical run. It is noticed that the anisotropy grows more rapidly than in the two previous experiments and the maximum corresponds to a temperature of  $\simeq 0.05^{\circ}$ K. In other runs (not shown) the coolant salt was allowed to warm up to T = 0.12°K, i.e. above the Néel temperature of manganese fluosilicate. In Table I we list the values of  $\mathcal{E}$ , T and <u>a</u> (calculated from =  $a/T^2$ ) obtained from these runs.

Table I

		11
T		<u>a</u> x $10^{-4}$
0.045 <sup>°</sup> K	0.205	4.02
0.050	0.187	4.67
0.060	0.154	5.55
0.070	0.113	5.53
0.080	0.083	5.32
0.090	9.063	5.10
0.10	0.047	4.70
0.11	0.039	4.60
0.12	0.032	4.37

The decrease in <u>a</u> at the lower temperatures is probably due to poor thermal equilibrium and the fact that the approximation  $\mathcal{E} = a/T^2$  is no longer valid. It is also noticed that <u>a</u> decreases gradually at higher temperatures. Further runs are in progress to verify this result. At corresponding temperatures the anisotropies measured are smaller by a factor of about 2/3 from those observed with Mn<sup>54</sup> in cerium magnesium nitrate in an external field (600 and 1000 gauss) but 3/2 larger than those observed in zero external field in this salt (Grace et al 1954, Bishop et al 1954).

Paramagnetic resonance investigations of Mn<sup>++</sup> in magnesium fluosilicate, zinc fluosilicate and bismuth magnesium nitrate have been reported (Arakawa 1954, Bleaney and Ingram 1951 a, Trenam 1953). The values of D and A in the spin Hamiltonian of Mn<sup>++</sup> in these different salts are listed in Table II. The temperature at which these measurements were carried out and the dilution are also given.

#### Table II

Salt	T		D cm <sup>-1</sup>	<u>A cm<sup>-1</sup></u>	Dilution
$Bi_{2}Mg_{3}(NO_{3})_{12}24$ H <sub>2</sub> O	20 <sup>0</sup> к	1/3	-0.0215	-0.0090	<b>∫</b> 1/200
-	20 <sup>0</sup>	2/3	-0.0080	-0.0090	t
мgsif <sub>6</sub> бн <sub>2</sub> 0	290		-0.0274	-0.0092	1/20 to 150
ZnSiF <sub>6</sub> 6H <sub>2</sub> 0	20		-0.0134	-0.0091	1/1000

The measurements with magnesium fluosilicate (Arakawa 1954) indicated the presence of six magnetic complexes



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in the unit cell. The six complexes are equivalent but are oriented at an angle of about  $7^{\circ}$  to the hexagonal axis. This contrasts with the measurements on zinc fluosilicate (Bleaney and Ingram 1951a) which indicated one magnetic ion per unit cell. At any rate the distortion involved is too small to account for the reduction in anisotropy. Since the magnitude of the D term in manganese fluosilicate is unknown at present no detailed calculations have been carried out.

# ii) $co^{60}$ in MnSiF<sub>6</sub>6 H<sub>2</sub>0

The results of a typical run are shown in Figure 17. This particular run was carried out after a demagnetization with H/T of 13 Kilogauss/degree K since it was desired to shorten the duration of the experiment. It is noticed that the cobalt nuclei were aligned along the preferred axis. Within statistical accuracy the anisotropy observed for the  $Co^{60}$  radiation is equal to that of the Mn<sup>54</sup> radiation and also exhibits a small decrease in the value of the parameter a at higher temperatures. The anisotropies are considerably larger than any previously measured with Co<sup>60</sup> in any paramagnetic salt at corresponding temperatures. For instance Co<sup>60</sup> polarized in cerium magnesium nitrate with an external field of 400 gauss gives an anisotropy of about 0.1 at 0.05°K compared to 0.18 at 0.05°K in this salt. Bleaney and Ingram (1951b) have studied the paramagnetic resonance of  $Co^{++}$  in zinc fluosilicate and determined the value of A and B in



FIGURE 18

External morphology of Co(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>6H<sub>2</sub>O crystal

in the spin Hamiltonian. It is evident from a comparison of these results with the values of A and B for Co<sup>++</sup> in the zinc Tutton salts and bismuth magnesium nitrate that the spin Hamiltonian does not account for the discrepancy. No attempt has been made to date to explain this large anisotropy.

The runs seemed to indicate that the anisotropy of  $Co^{60}$  increased more rapidly than that of  $Mn^{54}$  in this same lattice (compare Figure 16 and 17). Hence a crystal containing both  $Co^{60}$  and  $Mn^{54}$  was prepared. Preliminary measurements (not shown) with this crystal indicate that the anisotropies increase at the same rate.

## $Co(NH_4)_2(SO_4)_26H_2O$

#### General Information

Cobalt ammonium sulphate is a Tutton salt. The Tutton salts are an isomorphous series with the formula M"  $XO_4$  M'\_2  $XO_4$  6 H\_2O; where M" is a divalent metal of the iron group (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mg), M' is a monovalent metal (K, Rb, Ce, NH4, Tl) and X is one of (S, Se, Cr). The salts form monoclinic crystals whose morphology has been described by Tutton (1905, 1913, 1916). The external appearance is shown in Figure 18, where also the various crystal axes are depicted. The b-axis is perpendicular to the a-c plane; the a and c-axes are inclined at an angle  $\beta \simeq 105^{\circ}$ . The principal axes of magnetic susceptibility are denoted by K<sub>1</sub>, K<sub>2</sub>, and K<sub>3</sub>, and are mutually perpendicular.  $K_1$  and  $K_2$  are respectively the directions of maximum and minimum susceptibility and lie in the a-c plane;  $K_3$  coincides with b. We denote by  $\Psi$  the angle from a to  $K_1$  in the acute angle between a and c. In the b- $K_1$  plane lie the two tetragonal axes denoted by  $T_1$  and  $T_2$ ; each makes the same angle  $\prec$ with  $K_1$ .

There are two divalent cations in the unit cell of the crystal, and each is surrounded by a crystal field of roughly tetragonal symmetry due mainly to a distorted octahedron of six water molecules. One tetragonal axis, say  $T_1$ , (i.e. the axis of distortion of the octahedron) is the mirror-image of the other,  $T_2$ , in the crystallographic a-c plane. The positions of the crystallographic and magnetic axes and of the tetragonal axes are shown in Figure 18.

For the Co<sup>++</sup> ion we have taken  $\Psi = 40^{\circ}$ ,  $\ll = 33^{\circ}$  as given by Garrett (1951).

The magnetic properties of a single crystal of cobalt ammonium sulphate have been extensively studied by Garrett (1951) between 1°K and 0.04°K. He found the Néel temperature to be 0.084°K. From less reliable measurements Malaker (1951) reports a Néel temperature of 0.125°K. Garrett's work also shows that the tetragonal axes are the preferred axes of magnetization in the antiferromagnetic state. The anisotropy parameter may then be defined as:

$$\boldsymbol{\xi}' = \frac{\mathbf{I}_{K_2} - \mathbf{I}_{K_1}}{\mathbf{I}_{K_2}} \qquad \dots \quad (7)$$



where  $I_{K_1}$  and  $I_{K_2}$  are the normalized intensities of radiation along the  $K_1$  and  $K_2$  axes respectively.

The crystal was about 3 mm. thick and had an effective surface of about 1.2 cm<sup>2</sup>.

#### Results and Discussion

The results of a run are shown in Figure 19. The results show that the anisotropies observed are about equal to those measured in experiments with  $Co^{60}$  in paramagnetic Tutton salts at the corresponding temperatures. We may then conclude that the effective field at the nucleus is not significantly modified in the antiferromagnetic state for this salt.

The magnetic field for adiabatic demagnetization was applied parallel to the a-axis, hence perpendicular to the b-axis (K<sub>3</sub> axis) and at an angle of  $\simeq 40^{\circ}$  to the K<sub>1</sub> axis. The entropy removed is given by the relation:

 $S/R = -y \tanh y + \ln \cosh y$  .... (8)

where

$$\mathbf{y} = \frac{H}{2kT} \mathbf{\lambda}_{1}^{2} \quad g_{1}^{2} + \mathbf{\lambda}_{2}^{2} \quad g_{2}^{2} + \mathbf{\lambda}_{3}^{2} \quad g_{3}^{2} \qquad \dots \quad (9)$$

 $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  being the direction cosines of the applied field relative to the principal axes of either set of ions. The principal ionic g-values were found from resonance experiments (Bleaney and Ingram 1949) to be 6.2 (along a tetragonal axis), 3.0 and 3.0.

In our experiments  $H/T \simeq 1.5 \times 10^4$  gauss/degree. We then calculate y = 1.96 which yields a value of S/R = 0.60for the entropy removed. From the curve of S/R versus T given in Garrett (1951) this indicates a cooling of the cobalt ammonium sulphate crystal to  $\simeq 0.055^{\circ}$ K upon adiabatic demagnetization. It appears from our results (see Figure 19) that the system of nuclei required a few minutes to cool to this temperature. As we mentioned earlier, the Leiden group reported negative results (within 1%) from an attempt to detect nuclear orientation of  $Co^{60}$  in a single crystal of this salt (Poppema 1954). Considering the initial values of H/T used for adiabatic demagnetization and Garrett's values of S/R versus T, their crystal was certainly cooled to temperatures below 0.05°K (they claim final temperatures between 0.02°K and 0.04°K). However insufficient details are given in their report (Poppema 1954) to assess fully the meaning of their experiment.

To clarify the situation we investigated the anisotropy as a function of time from demagnetization and of the sysceptibility of the specimen with  $Co^{60}$  in a single crystal of cobalt ammonium sulphate embedded between two pressed pills of cobalt ammonium sulphate. The temperature of the cobalt ammonium sulphate pills should be about  $0.055^{\circ}$ to  $0.060^{\circ}$ K after demagnetization. The magnetic field was parallel to the K<sub>1</sub> axis of the single crystal, hence it should be a few millidegrees colder immediately after demagnetization. We have observed an anisotropy of about 0.035 which seems to appear immediately after demagnetization and decreases to about 0.02 as the susceptibility of the specimen reaches a Our crystal also contained some  $Mn^{54}$  and for this maximum. isotope we observed an anisotropy of  $\simeq$  0.07 decreasing to  $\simeq$  0.04 at the susceptibility maximum. A similar experiment with manganese fluosilicate has been performed. A single crystal of  $MnSiF_66H_0$  containing  $Mn^{54}$  was embedded between two pressed pills of  $MnSiF_6 6 H_2 0$  powder. The assembly was cooled by adiabatic demagnetization from initial values of H/T ~ 15 Kilogauss/degree. In two runs the susceptibility after demagnetization was practically constant for two The anisotropy  $\boldsymbol{\xi}$  observed during this period was hours. also constant with a value  $\simeq$  0.035. In a third run the anisotropy was measured after the susceptibility had shown a small but definite increase to a constant value. The anisotropy observed at this constant value was also 🛥 0.035. It is not known at present whether  $MnSiF_66H_20$  cools appreciably below 0.1°K upon adiabatic demagnetization. These experiments show that nuclear alignment occurs when a substance with a low Néel temperature is cooled by adiabatic demagnetization.

#### General Information

 $CoCl_2 6H_2 O$  crystallizes in the monoclinic system, and its external morphology has been described by Groth

 $Co Cl_2 \cdot 6H_2O$ 



FIGURE 2I Susceptibility of CoCl<sub>2</sub>6H<sub>2</sub>O versus temperature in powder and in single crystal.

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(1906). The external appearance is shown in Figure 20 where the a- and c- planes are also indicated.  $(3 = 122^{\circ}19)$ .

The salt was found to become antiferromagnetic at about 3°K from susceptibility measurements of the powder (Haseda and Kanda 1957). From susceptibility measurements with several large crystals we determined roughly the preferred axis of magnetization. These measurements indicate that the preferred axis is perpendicular to the crystallographic c-plane (i.e. the axis perpendicular to the cleavage plane). The results of these measurements are shown in Figure 21 where  $\mathcal{S}$ , the galvanometer deflection is proportional to the susceptibility  $\chi$ , according to the relation  $\mathcal{S} = a_0 \chi + a_1$  ( $a_0$  and  $a_1$  are constants for any one curve but may be different for each curve).

With respect to the c-plane we define the anisotropy parameter by

$$\xi = \frac{I_p - I_A}{I_p} \qquad \dots \qquad (10)$$

where  $I_A$  is the normalized radiation intensity in the direction perpendicular to the c-plane and Ip is the normalized intensity in some arbitrary direction in the c-plane. The crystal was about 3 mm. thick with 1.0 cm<sup>2</sup> effective surface.

#### Results and Discussion

## $Co^{60}$ in $CoCl_2 6H_2 0$

Figure 22 shows the results of a typical run. The anisotropies are appreciably smaller than those observed with



co<sup>60</sup> at corresponding temperatures in paramagnetic crystals. It is conceivable that there are more than one magnetic ion per unit cell with different orientations. The susceptibility and anisotropy measurements would then given an effect averaged over these sets of ions. Work is in progress in this department under the direction of Dr. Myer Bloom to investigate the proton resonance in the paramagnetic and antiferromagnetic states of this salt. It may be that the preferred direction is actually at an appreciable angle to the c-axis. Our determination of the preferred axis was only approximate and we did not measure the susceptibility for intermediate angles to the c-plane. Greater accuracy in this respect was not attempted since the main purpose of this experiment was to determine whether the cobalt nuclei would show an alignment in an antiferromagnetic salt of cobalt with a relatively high Néel temperature and to estimate the temperature to which these nuclei might easily be cooled.

 $Mn^{54}$  in  $CoCl_26H_20$ 

Figure 22 shows the results of a typical run. The anisotropies are corrected for the background radiation from the  $Co^{60}$  in the sample according to the relation:

$$\mathcal{E}_{M_{n}} = \mathcal{E}_{Mn}^{1} + \left(\mathcal{E}_{Mn}^{1} - \mathcal{E}_{Co}^{1}\right) - \frac{I_{Co}}{I_{Mn}} \qquad \dots \qquad (11)$$

where  $\xi_{Mn}^{1}$  and  $\xi_{Co}^{1}$  are the observed anisotropies for the Mn<sup>54</sup> and Co<sup>60</sup> respectively, I<sub>Co</sub> and I<sub>Mn</sub> are the normalized

intensities of radiation in the plane from the  $Co^{60}$  and  $Mn^{54}$  respectively. We assumed the ratio  $I_{Co}/I_{Mn}$  was constant in applying this correction although it will vary a few percent with temperature.

The  $\mathrm{Co}^{60}$  anisotropy is too small to enable us to draw any conclusions with respect to the relative rate of cooling of the different isotopes. It is noticed that the  $\mathrm{Mn}^{54}$  anisotropy is equal to that observed at corresponding temperatures in cerium magnesium nitrate in an external field of 600 gauss (Bishop et al 1954).

#### Part II

## <u>Nuclear Orientation Experiments</u> with I<sup>131</sup> and Br<sup>82</sup> in Antiferromagnetic Single Crystals

#### Introduction

Recent investigations of the nuclear magnetic resonance of  $F^{19}$  in  $MnF_2$ ,  $CoF_2$ , and  $FeF_2$  have shown a hyperfine structure interaction to exist between the fluorine nuclei and the magnetic electrons (Shulman and Jaccarino 1956, 1957, 1958; Jaccarino et al 1957; Jaccarino and Shulman 1957; Baker and Hayes 1957). The free fluorine ion  $(2s^2 2p^6)$  is diamagnetic and can have no hyperfine interaction with the  $F^{19}$  nucleus. However, in a paramagnetic and antiferromagnetic solid the surrounding ions may alter the ground state ion configuration and a hyperfine interaction can result. It has been shown that these interactions depend upon the spin orientation of the magnetic ion.

There are several mechanisms which might create paramagnetism at the fluorine site. The two most apparent are; the transfer of an electron from the fluorine ion and the formation of covalent bonds between the two ions. Both mechanisms have been invoked to explain the results of nuclear magnetic resonance of  $F^{19}$  in various substances. This electron transfer also provides a likely mechanism for indirect or super exchange interaction between the magnetic ions in the antiferromagnetic state (Anderson 1950, Cooke 1957). In either case the unpaired electron remaining on the  $F^-$  ion with spin parallel or antiparallel to that of the paramagnetic ion produces a relatively large field at the fluorine nucleus and hence a hyperfine structure coupling if the nucleus has a magnetic moment. The alignment of the spin of the unpaired electron is coupled to the alignment of the paramagnetic ion. In  $MnF_2$  below the Néel temperature the  $Mn^{++}$ spins are antiferromagnetically ordered with the spins  $S_{a} = \pm 5/2$  respectively parallel and antiparallel to a crystal axis. As the temperature is lowered and the magnetization approaches saturation in each sublattice the alignment of the unpaired electron of the fluorine ion becomes more complete. From their measurements of the F<sup>19</sup> resonance at temperatures from 1.3°K to 20°K Jaccarino and Shulman estimate that the hyperfine splitting parameter A/k is of the order of 16 x  $10^{-4}$  cm<sup>-1</sup>.

A hyperfine structure interaction has also been reported for the chlorine ion in certain tightly bound magnetic complexes such as  $[Ir \ Cl_6]$  -- in potassium chloroiridate  $K_2Ir \ Cl_2$ , and ammonium chloroiridate  $(NH_4)_2IrCl_2$  (Griffiths and Owen 1954; Griffiths et al 1953; Cooke 1957) which become antiferromagnetic at  $3.3^{\circ}K$  and  $2.1^{\circ}K$  respectively (Cooke 1957). This hyperfine coupling has also been interpreted in terms of a similar mechanism of electron transfer between the diamagnetic and paramagnetic components (Stevens 1953).

If a hyperfine structure interaction exists for the chlorine and bromine nuclei in  $MnCl_24$  H<sub>2</sub>O and  $MnBr_24$  H<sub>2</sub>O through one of the mechanisms mentioned above then at







FIGURE 44 DECAY SCHEME OF

suitably low temperatures, say 0.01 °K, we might expect an appreciable orientation of these nuclei along the preferred direction of antiferromagnetic ordering in single crystals of these salts. Bromine has a gamma emitting isotope, Br<sup>82</sup>, hence orientation of this nucleus may be detected by measuring the anisotropy of the radiation. Further Br is known to have a fairly large nuclear magnetic moment of 1.6 nuclear magnetons, (Green et al 1957). Chlorine does not have any suitable isotopes for this type of measurement however stable iodine enriched with gamma emitting 1<sup>131</sup> which has also a large nuclear magnetic moment of 2.56 nuclear magnetons (Fletcher and Amble 1958) may be introduced as an impurity at the chlorine sites in  $MnCl_24$  H<sub>2</sub>O and at the bromine sites in MnBr<sub>2</sub>4 H<sub>2</sub>0. For these reasons we have thought it worthwhile to measure the gamma ray distribution from  $I^{131}$ in single crystals of  $MnCl_24$  H<sub>2</sub>O and  $MnBr_24$  H<sub>2</sub>O and of  $Br^{82}$  in MnBr<sub>2</sub>4 H<sub>2</sub>0.

In Figure 23 we show the decay scheme of  $I^{131}$  and in Figure 24 the decay scheme of  $Br^{82}$ .

#### Procedure and Results

 $I^{131}$  in MnCl<sub>2</sub>4 H<sub>2</sub>O and MnBr<sub>2</sub>4 H<sub>2</sub>O

 $I^{131}$  was produced by neutron bombardment of tellurium metal in the Chalk River Reactor in the reaction  $Te^{130}$  (n,  $\checkmark$ )  $Te^{131} \xrightarrow{\beta} I^{131}$ . After chemical separation  $I^{131}$ is commercially available in NaI in basic solution of NaHSO<sub>3</sub>. One cubic centimeter of this dilute solution containing

l millicurie of  $I^{131}$  activity was poured into l cc. of saturated solution of MnCl<sub>2</sub>4 H<sub>2</sub>O or MnBr<sub>2</sub>4 H<sub>2</sub>O. A crystal seed some 20 cubic millimeter in volume was placed in the saturated solution and allowed to increase to double the original size. The crystal was carefully rinsed with distilled water and dried with filter paper. It was noticed that only a small fraction of the specific activity could be introduced in the crystal. To check that this activity did not reside in a thin film on the surface of the crystal we weighed a crystal and measured its activity. Then some of the outer layer was dissolved, the crystal was weighed again after drying and its activity was measured. The activity remaining in the crystal corresponded fairly well with the volume of its residual active layer.

When the  $I^{131}$  and its chemical carrier are mixed with the saturated solution of manganous chloride (or manganous bromide) a fine suspension forms in the liquid. After the liquid was passed through a filter paper and this suspended material removed it was noticed that a larger portion of the  $I^{131}$  activity remained on the filter paper than in the residual solution. A small amount of this fine suspension later appeared in the solution as the crystal grew. It is then possible that the  $I^{131}$  activity in the crystal is actually included in this fine suspension and merely becomes trapped in the body of the crystal as it grows. The procedure outlined above was repeated with MnBr<sub>2</sub>4 and H<sub>2</sub>0 and

the same disturbing phenomenon observed.

The crystal was embedded with Apiezon oil B between two pressed pills of K Cr Alum and mounted in the cryostat. After adiabatic demagnetization we counted the 368 kev gamma ray using both a low cut discriminator to pass the photopeak of this gamma ray and pulses of higher energy, and a single channel kicksorter to accept only the photopeak of this gamma ray. The activity was measured simultaneously along the b-axis and along the c-axis.

Several runs with I<sup>131</sup> in MnCl<sub>2</sub>4 H<sub>2</sub>O and MnBr<sub>2</sub>4 H<sub>2</sub>O single crystals failed to indicate any anisotropy greater than 0.5%. In Table III we list the temperature of the K Cr Alum after demagnetization and its temperature at the time exchange gas was allowed in the sample; as well as the time elapsed while the KCr Alum warmed up from the initial to the final temperature for each run. The formula of the crystal used is also given.

## $\operatorname{Br}^{82}$ in MnBr<sub>2</sub>4 H<sub>2</sub>0

One cc. of saturated solution of  $MnBr_2^4 H_2^0$  in a quartz ampoule was irradiated to an activity of 5 millicuries of  $Br^{82}$  in the neutron flux of the B.E.P.O. pile at Harwell. It was then brought to Vancouver by C.P.A.'s transpolar flight. The active solution was transferred to a small beaker and a crystal seed of  $MnBr_2^4 H_2^0$  20 cubic mm. in volume was placed in this solution and allowed to grow to twice its original volume. After rinsing and drying the crystal was



embedded with Apiezon oil B between two pressed pills of KCr Alum and mounted in the cryostat.

As can be seen from Figure 24 the decay scheme of  $Br^{82}$  is quite complex. We measured the five most intense gamma rays; e.g., 1.45, 1.30, 1.03, 0.77, 0.56 mev. These are represented by a double line in Figure 24. We used a bottom cut discriminator to count the gamma ray of highest energy and a single channel kicksorter set at the photopeak of each lower gamma ray in succession. A typical spectrum is shown in Figure 25 where the counting rate is plotted against the voltage setting of the pulse height analyzer.

Br<sup>82</sup> has a half life of 35 hours. In order to obtain adequate statistics for each gamma ray and to eliminate preparing a second sample we performed all the measurements using two separate duplicate electronic systems and operated continuously until the activity of the sample had died out. This was made possible by enlisting the assistance of Mr. H. Schneider, a graduate student in this laboratory who assembled the second system of electronics and alternated with the author in conducting the experiments.

In Table III we list the results under the X-ray observed, the initial and final temperature of the K Cr Alum, and the time elapsed while the alum warmed up from the initial to the final temperature. No anisotropy greater than 0.005 was observed for any of the X-rays.

#### Discussion:

Although there is a strong possibility that the iodine did not replace the chlorine or bromine ions in our crystals, the negative results obtained can be attributed to two main causes. The method used for cooling the crystals was certainly crude and it is very doubtful that temperatures even as low as 0.05°K were obtained. If there is a hyperfine structure coupling for  $Br^{82}$  and  $I^{131}$  in these salts and it is of the same magnitude as that measured for F<sup>19</sup>, temperatures lower than 0.05°K would be required for a significant anisotropy to appear. Further nuclear relaxation times of the order of 30 sec. at 4.2°K and 90 sec. at 1.3°K were observed for  ${\rm F}^{19}$  in  ${\rm MnF}_9$  (Jaccarino and Shulman 1957, Jaccarino and Walker 1958). It is possible that even if the crystal lattice were cooled to temperatures of the order of 0.05°K and lower, significant anisotropies would require an impractically long time to develop.

### CHAPTER V NUCLEAR ORIENTATION EXPERIMENTS IN FERROMAGNETIC SUBSTANCES

#### Introduction:

The Oxford group established that nuclear orientation could be produced in a ferromagnetic substance by measuring the anisotropy of Co<sup>60</sup>, in a single crystal of cobalt metal (Grace et al 1955, 1957). We undertook to investigate nuclear orientation in binary alloys of ferromagnetic substances in order to determine whether a hyperfine structure coupling occurred in both components of such a binary alloy and to obtain thereby some information on the electronic configuration in ferromagnetic alloys. In preparation for this project the author used a radioactive single crystal of Cobalt metal to acquire experience with techniques of cooling metallic samples to temperatures well below 0.05 K. In the course of this work a significant discrepancy was noticed between the anisotropy measured at a given temperature and the results reported by the Oxford group (Grace et al 1957). In part I we describe the investigations with  $co^{60}$ in a cobalt single crystal and in part II we discuss the project and describe the preliminary work on nuclear orientation in a ferromagnetic binary alloy.

#### Part I

# Nuclear Orientation of Co<sup>60</sup> in a Cobalt Metal Single Crystal Experimental Procedure and Results:

A single crystal of cobalt metal, rectangular in shape, 0.13 x 0.13 x 0.30 cm. in size, was prepared by Dr. Peter Myers in the metallurgy department of this university and placed at our disposal. This single crystal was irradiated to an activity of 3 microcuries in the neutron flux of the Chalk River Reactor.

In all experiments with this crystal the anisotropy is defined with respect to the hexagonal axis by the relation:

$$\mathcal{E} = \frac{I_{Plane} - I_{Axis}}{I_{Plane}}$$

where I<sub>Axis</sub> and I<sub>Plane</sub> are respectively the normalized intensities of radiation in the direction parallel to the hexagonal axis of the crystal and in any arbitrary direction parallel to the basal plane.

In a preliminaty experiment the crystal was wetted with glycerine and embedded between two pressed pills of K Cr Alum. The whole sample was cooled by adiabatic demagnetization and observations made as the sample warmed up. With this crude arrangement a maximum anisotropy  $\simeq 0.05$ was observed. From measurements using a similar arrangement the Oxford group reported a maximum anisotropy  $\simeq 0.015$ (Grace et al 1955).



surface. Square dots indicate Oxford results at corresponding temperatures.

To improve the cooling of the crystal it was mounted on a copper strip in the following manner. The crystal was inserted in a small hole cut in the middle of a copper strip and this assembly was copper plated together. The strip of copper was 3 cm.long, 1 cm. wide and 0.08 cm. thick, i.e. the total cooling surface was about 6 cm<sup>2</sup>. This strip of copper was sandwiched between two half cylinders of pressed K Cr Alum powder and the space between filled with a sludge of K Cr Alum and glycerine. The sample was mounted in the cryostat with the thin edge of the copper strip parallel to the demagnetizing field in order to avoid eddy currents. The results of two typical runs are shown in Figure 26 and 27.

In Figure 26 the anisotropies expected from the Oxford results at the measured temperatures of the K Cr Alum are indicated by square dots. It is noticed that the anisotropies we observed are 3 to 4 times larger than the former. Unfortunately we have performed only two runs like that shown in this figure. Further it was realized only after the nature of the crystal had probably been altered that the cooling surface provided (6 cm.<sup>2</sup>) was certainly inadequate. Dr. J.C. Wheatley during a visit to our laboratory indicated to the author that the Oxford group had provided some 200 cm<sup>2</sup> of cooling surface by linking several hundred fine copper wires to their crystal. Using this superior arrangement they obtained the results shown in Figure 26 (Grace et al 1957) and a maximum anisotropy  $\simeq$  0.15 (Kurti 1957) at the lowest temperatures.



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In the experiment shown in Figure 27 the cooling salt upon demagnetization failed to cool to the temperature expected from the initial value of H/T. This probably occurred because not enough exchange gas was present to conduct away the heat of magnetization. In this run and others similar to it we were endeavouring to reduce the final heat leak by using a very small amount of exchange gas (say 0.15 microns) during the magnetization of some 5 to 10 minutes in order to leave very little residual gas after pumping for 20 to 25 minutes. When adequate exchange gas was used the result of the previous figure was obtained. The results shown in Figure 27 are given to show that the cobalt crystal could not have been cooled to a temperature lower than 0.05°K since the cooling salt itself did not cool below this temperature. This run and the others like it also confirm that the anisotropies observed are appreciably larger than those reported by the Oxford group in the same temperature range.

The cobalt single crystal was then heated for some ten minutes at about  $1000^{\circ}$ C and quenched to room temperature.

With the same cooling and mounting arrangement described above new observations were made on the single crystal. The results of such a run are shown in Figure 28. A comparison of the results shown in Figure 26 and 28 indicates that the anisotropy is now reduced by a factor of about 2.5 at the equivalent temperatures.



It was thought at the time that the drastic heat treatment had in some way ruined our cobalt single crystal. Dr. J.C. Wheatley's visit to our laboratory referred to above occurred at this time and upon his suggestions we proceeded to improve the cooling of our crystal. Several arrangements were attempted and the techniques which yielded the best results were the following:

(a) The crystal was copper plated in a copper strip 1.5 cm x 1.0 cm. x 0.08 cm in size. To this assembly we soft soldered some two hundred 36 B & S enamelled copper wires with a total surface of about 150 cm<sup>2</sup>. Fine K Cr Alum powder was introduced between the wires and wetted with Apiezon oil B. This assembly was pressed together to a pressure of 3 tons/cm. The results of a run with this set up are shown in Figure 29 where the square dots again indicate the anisotropies expected according to the Oxford work. (b) In another series of experiments we soft soldered the crystal and copper strip assembly mentioned in (a) to a copper sheet 10 cm by 12 cm. and 0.005 cm thick. This sheet was folded into parallel strips and K Cr Alum powder wetted with Apiezon oil B introduced between the folds. This assembly was then pushed tightly into a lucite container. The results of a run with this arrangement are shown in Figure 30 where the square dots again indicate anisotropies according to the Oxford group.

It is noticed that the anisotropies now measured are still somewhat larger than the Oxford values by a factor



of  $\simeq$  1.6 in Figure 29 and about 1.4 in Figure 30 although they are appreciably smaller than those observed with the untreated crystal at equivalent temperatures.

The maximum anisotropies reached in Figures 29 and 30 are respectively  $\simeq$  0.12 and  $\simeq$  0.10. Several runs with the arrangements described in (a) and (b) confirmed these values. The Oxford group has reported a maximum anisotropy of 0.15 (Kurti 1957). The difference between our values and the Oxford one may still be due to the superior cooling technique used by the Oxford group. However other aspects may be more significant in the explanation of this difference. The Oxford cryostat and solenoid enable this group to demagnetize from H/T values of about 30 as compared with H/T values of 16 in our case. In our experiments with samples containing large amounts of copper wire and copper foil we have never been able to reach the Curie temperature, say  $T^* \simeq 0.033^\circ$ , of K Cr Alum. The temperatures reached after adiabatic demagnetization with arrangements (a) and (b) were only  $T^* \simeq 0.05^{\circ} K$ and  $T^* \simeq 0.06^{\circ} K$  (see Figures 29 and 30). We may attribute this failure to eddy current heating in the copper since with our initial H/T values we should attain the Curie temperature and indeed we usually reach this temperature with a sample consisting only of K Cr Alum. Samples with larger surfaces of copper wire or foil cooled to temperatures higher than those indicated above and in all experiments with samples containing copper wire or foil the final temperatures reached


by adiabatic demagnetization depended on the time taken to remove the field. It is to be expected that eddy current effects would be less appreciable using a solenoid as at Oxford since in this case the field is parallel to the length of the wires or foils hence the flux intersects the smallest area of metal.

#### Discussion

It is convenient to discuss the various measurements of the anisotropy of Co<sup>60</sup> in cobalt metal in terms of the parameter "a" in the relation  $\mathcal{E} = a/T^2$ . This approximation is certainly valid at the "high" temperatures range where it is applied in these experiments.

The Oxford work yields a value  $a = 1 \times 10^{-4} \text{ deg}^2$ (This value has recently been corrected (Kurti 1958) and the recent data gives  $a = 0.79 \times 10^{-4} \text{ deg}^2$ . The revised value came to our attention after Figures 26, 29 and 30 were printed and the points shown in these figures correspond to the value  $a = 1 \times 10^4 \text{ deg}^2$ .)

Our measurements on the crystal after heat treatment give a value  $a = 1.5 \times 10^{-4} \text{ deg}^2$  and from measurements on the crystal before heat treatment we may assign a value  $a_{\min}$ ,  $3 \times 10^{-4} \text{ deg}^2$ .

Khutsishvili (1957) has observed anisotropies of 0.10 to 0.15 in the temperature range  $0.08^{\circ}$  to  $0.05^{\circ}$  K. This would yield values of a  $\simeq 4 \times 10^{-4}$  to 6 x  $10^{-4}$  deg<sup>2</sup>. (Although this paper contains scant information of the experimental details and is often neglected in the literature it does confirm our view that results on Co<sup>60</sup> in Cobalt metal are ambiguous).

The nuclear specific heat of cobalt metal has been measured by Heer and Erickson (1957), Heer (1958) and Arp et al (1957). The data of Heer and Erickson (1957) and Heer (1958) give:

$$\frac{C T^2}{R} = 4 \times 10^{-4} \qquad \dots (1a)$$

those of Arp et al (1957) give:

$$\frac{C T^2}{R} = 6.2 \times 10^{-4} \qquad \dots (1b)$$

where C/R is the specific heat per mole and R is the gas constant. From these results we may derive a value of  $a = 1.4 \times 10^{-4}$  and  $2.17 \times 10^{-4} \text{ deg}^2$  as follows: If we assume that the Hamiltonian for a cobalt atom in the hexagonal cobalt metal structure is similar to that for the cobalt ion in the crystalline electric field of axial symmetry in cobalt salts we may write as a first approximation:

$$\mathcal{H} = A S_z I_z + B (S_x I_x + S_y I_y) \qquad \dots \qquad (2)$$

The specific heat can then be written (Bleaney 1950):

$$\frac{C T^2}{R} = (A_{59}^2 + 2 B_{59}^2) \quad I (\underline{I + 1}) = 4 \times 10^{-4} \dots (3)$$

where I is the nuclear spin of cobalt 59.

Also using this Hamiltonian we may calculate the polar diagram hence the anisotropy expected for Co<sup>60</sup> gamma rays at "high" temperatures. This calculation gives:

$$\mathcal{E} = \left(\frac{A_{60}^2 - B_{60}^2}{k^2 T^2} \right) \qquad \dots \qquad (4)$$

If we assume that  $A^2 >> B^2$  and drop the B terms then we obtain:

$$\frac{C T^2}{R} \simeq A_{59}^2 \quad (\frac{21}{16}) \simeq 4 \times 10^{-4} \text{ deg}^2 \text{ and } 6.2 \times 10^{-4} \dots (5)$$

and

$$\mathcal{E} \simeq \frac{(A_{60}^2)}{k^2 T^2} \qquad (\frac{39}{28}) \qquad \dots \quad (6)$$

Since we can assume the field at the nucleus to be the same for the cobalt isotopes in cobalt metal, from the relations  $M_{59}$  H<sub>eff</sub> = 1/2 A<sub>59</sub> I<sub>59</sub> and  $M_{60}$ H<sub>eff</sub> = 1/2 A<sub>60</sub>I<sub>60</sub> we obtain A<sub>60</sub> = 0.572 A<sub>59</sub>. The value of A<sub>59</sub> may be calculated from equation (5) hence the value of A<sub>60</sub> is known and upon substitution into equation (6) we obtain the result  $\boldsymbol{\varepsilon} = 1.4 \ge 10^{-4}/T^2$  and 2.17  $\ge 10^{-4}/T^2$ .

We offer the following qualitative explanation of these results.

Hexagonal cobalt is formed from face-centeredcubic cobalt by a transformation on cooling below a temperature of 417<sup>°</sup> C. This transformation is seldom if ever complete and the structure of any particular specimen is often a mixture of face centred-cubic and close-packed-hexagonal forms (van Arkel 1939). For instance Edwards and Lipson (1942), found about equal proportions of the cubic and hexagonal phases in a sample that had been annealed at  $1,100^{\circ}$  C for 5 days and then at about  $380^{\circ}$  C for 1 week. Also small completely cubic single crystals of cobalt have been observed (Edwards and Lipson 1942).

Even in the close packed hexagonal structure some face-centered cubic ordering is present and this is referred to as a stacking fault. (Edwards and Lipson 1942, Wilson 1942, Houska and Averbach 1958, Troiana and Tokich 1948). The presence of these faults may be described in the following way. Close-packed structures are made by piling up closepacked planes of atoms in three different relative positions. We may refer to these positions as A, B, C. In proper hexagonal close-packing only two of the positions are used so that the succession of planes may be represented by ABABAB .... or BCBCBC .... or CACACA .... In the face centered cubic all three positions are used and the succession of planes may be represented by ABCABCA .... A close packed hexagonal structure in which a fault occurs may then be represented by the sequence ABABCBC .... In the sample mentioned above Wilson (1942) found on the average one fault in every 14 planes of atoms. In a sample heated quickly into the facecentred cubic region  $(600^{\circ} \text{ C})$  and ice-quenched, Houska and Averbach (1958) also found one fault in every ten planes of the hexagonal cobalt.

It is quite probable then that after heat treatment our crystal contained a large proportion of the face-centeredcubic phase. It would then appear from our results that the presence of this phase reduces the anisotropy. This seems quite likely for in such a structure (e.g. iron) the body diagonals are the preferred axes of orientation of the domains and isotropic radiation would be expected in this case. We do not know how "perfectly" hexagonal our crystal was prior to heat treatment and the phase composition of our crystal since it was subjected to heat treatment has not yet been determined although work is in progress in this direction. If we assume, as seems reasonable, that the crystal was initially more hexagonal than after heat treatment we can state that the constant "a" for a perfect or nearly perfect close packed hexagonal crystal should be of the order or greater than  $3 \times 10^{-4}$  deg<sup>2</sup>. This implies of course that the crystal used by the Oxford group for their investigations did not have a perfect hexagonal composition.

This explanation seems to receive confirmation from the results reported by Khutsishvili (1957). It is inferred from this paper that the Russian group used fine cobalt powder embedded in the cooling salt. The domains were polarized by a large external magnetic field. It is known that grinding a cobalt specimen to a fine powder will produce small particles of perfect or almost perfect close packed hexagonal composition (Houska and Averbach 1958).

Further if we accept the analysis given above of the nuclear specific heat data of Heer and Erickson (1957), Heer (1958) and Arp et al (1957) we may then conclude that their specimen contained a proportion of the face-centeredcubic phase. This means that in the Hamiltonian given in equation (2) the terms A and B are decreased. In other words the hyperfine coupling depends on the crystal phase in which the atom finds itself.

At any rate our results indicate that the data on nuclear orientation in cobalt metal is at present ambiguous and should be further investigated in conjunction with x-ray analysis before conclusions may be drawn on the hyperfine structure coupling in the metal (Marshall 1958) and the contribution of the polarization of the conduction electrons to the effective field at the nucleus. Such studies are being pursued in this laboratory.

#### Part II

## Nuclear Orientation Experiments with Mn<sup>54</sup> in Ferromagnetic MnBi

#### Introduction:

In single crystals of ferromagnetic alloys with hexagonal structure the domain magnetization is generally parallel to the hexagonal axis or in the basal plane perpendicular to this axis. Hence the unpaired electron spins are aligned parallel or perpendicular to this axis. Since these unpaired electrons produce a magnetic field at the atomic nuclei when the system is cooled to temperatures of about 0.1° to 0.01°K, the nuclei will also be oriented parallel or perpendicular to the hexagonal axis. If the nuclei are gamma-emitting isotopes this orientation can be detected by an anisotropic emission of the radiation. Measurements of the anisotropy then yield information on the field produced at the nuclei by the ferromagnetic electrons and hence on their "location". Such observations with hexagonal ferromagnetic crystals of binary alloys should indicate whether the electrons are localized, in which case only one component nucleus may show orientation, or ionized into a band, in which case both may show orientation. The ultimate object of this project was therefore to ascertain whether the ferromagnetism should be described by a localized Heitler-London-Heizenberg model, or a collective Slater-Stoner model.

#### Procedure:

In face-centered cubic and body-centered cubic ferromagnetic crystals the preferred directions of domain magnetization are generally parallel to the body diagonals of the cube or parallel to the cubic axes (e.g. nickel and iron). These are then not particularly suitable for nuclear orientation experiments. Since in ferromagnetic crystals of hexagonal structure the nuclei may align parallel to one axis or in a definite plane we confined our attention to this group. A search of the literature for ferromagnetic binary compounds of hexagonal structure composed of elements with gamma emitting isotopes of adequately long half-lives produced a list of promising alloys; e.g. MnBi, MnTe, MnSb, CrTe, FeBe. Attempts were made to obtain single crystals of these compounds by slow cooling of the melt, in temperature gradient furnaces of various design. Numerous trials with several of these alloys produced only polycrystalline specimens from which single crystals could not be separated.

Special attention was given to the compound MnBi. It is an intermetallic compound with a hexagonal, NiAs, crystal structure and a high magnetic anisotropy (Guillaud 1943). It is most easily magnetized along the hexagonal axis until the temperature is reduced below 85°K. Below this temperature it is most easily magnetized parallel to the basal plane (Guillaud 1943, Bozorth 1951). Its Curie temperature has been found to be about 360°C (Guillaud 1943, Heikes 1955). The gamma emitting isotopes Mn<sup>54</sup> and Bi<sup>207</sup> are

very long-lived and readily available.

At the time this project was undertaken it was known that single crystals of the required size had been produced elsewhere by a special technique (Adams et al 1952, Adams This technique required thorough mixing of the 1957). reacting components by rotation, diffusion of the melt through the walls of the crucible and subsequent crystallization on the outside walls of the crucible. We attempted to duplicate this experiment with crucibles of the same composition as those used in the original work and others of various composition but without success. Two single crystals of some 10 cubic mm. volume each prepared by this method were placed at our disposal by Dr. E.A. Adams. We tried to induce sufficient  $Mn^{54}$  and Bi<sup>207</sup> radioactivity in these crystals by bombardment in the gamma ray beam of the U. of Sask. betatron for 3 months. However the activity induced was much too weak for our purpose. Recently single crystals of MnBi have been prepared by slow cooling of the melt (Ellis et al 1957) but before this work came to our attention we had abandoned this approach for the one described below.

Experiments elsewhere have established that polycrystalline specimens of MnBi when annealed at a temperature of 300 °C for about 90 hours in a magnetic field (e.g. 8000 gauss) form an aggregate of small oriented crystals with their preferred axis of magnetization parallel to the applied field (Roberts 1955, Williams et al 1957a, 1957b). Hence an assembly of crystallites prepared in this way has been found

to be equivalent to a single crystal (Williams et al 1957b). The formation of this parallel arrangement has been attributed to a recrystallization of the MnBi in the magnetic field (Boothby 1958).

Some MnCl<sub>2</sub> containing Mn<sup>54</sup> dissolved in a few drops of distilled water was dried by gentle heating on a thin disc of manganese weighing about 1 gram. This was then placed in a molybdenum container and melted in an induction furnace for a few seconds. The manganese now containing  $Mn^{54}$  was separated from the molybdenum container, ground to a fine powder (200 mesh) and thoroughly mixed with fine Bismuth powder (100 mesh) in a proportion of 45 atoms of manganese to 55 atoms of bismuth. The reason for the excess bismuth is that the reaction does not go to completion and even single crystals contain some free bismuth phase have been observed (Ellis et al 1957). When studying the Mn<sup>54</sup> radiation it is of course desirable not to have any unreacted manganese in the specimen although unreacted bismuth should not alter the results. The mixed powders were placed in a quartz container and sintered at 750°C for 12 hours, then placed for some 30 hours in a small furnace at 310°C between the poles of an electromagnet producing a field of 12 kilogauss at the sample. (This procedure was adopted by the author on the basis of the work of Roberts (1955). Our procedure is similar to the technique of Williams et al (1957b) which seems to give better results but which only came to our attention later.)

A rod shaped piece weighing about 1.5 gram was cut from this specimen and copper plated in a copper strip 2.5 cm long, 1 cm wide and 0.08 cm thick thereby providing a cooling surface of some 5 cm<sup>2</sup>. This assembly was embedded with glycerine between two half cylinders of pressed K Cr Alum powder and mounted in the cryostat.

#### Results and Discussion:

To investigate qualitatively whether our specimen behaved as a single crystal we performed the following test. The long dimension of our MnBi sample (0.7 cm.) corresponded to the hexagonal axis of the oriented crystals, i.e. the axis along which the external magnetic field had been applied. The specimen was mounted so that it could rotate freely and placed in dewars with unsilvered tails. The sample was positioned with its "hexagonal" axis perpendicular to an external field and at room temperature the torque on the sample aligned this axis parallel to the field of 5 kilogauss. We cooled the specimen slowly to liquid air temperature with the field on. The temperature was determined approximately by measuring the resistance of a copper coil placed in the dewar. As the sample cooled the angle between the "hexagonal" axis and the magnetic field increased and at a temperature of about 80°K (corresponding to zero magnetic anisotropy) this axis had adopted a direction perpendicular to the field. The sample was then cooled to liquid helium temperature at which temperature a MnBi single crystal magnetizes preferentially

in the basal plane. Rotating the magnet some 20 degrees caused the sample to twist a few degrees to retain its alignment perpendicular to the field.

The amount of Mn<sup>54</sup> at our disposal when this sample was prepared was unfortunately inadequate and we obtained only some 30 counts per second in our counting apparatus. Numerous runs with this sample failed to show any significant anisotropy (greater than 2%).

Since the technique used when this sample was prepared differed from that of Williams et al (1957b) it is possible that in our specimen the crystallites were not all well oriented in a parallel direction. Further in our specimen an appreciable proportion of unreacted manganese may have been present. We found subsequently that a specimen prepared by sintering at 750°C for some 12 hours contained as much as 40% non-magnetic component. The presence of some Mn<sup>54</sup> in this non-magnetic material would give an isotropic radiation distribution and reduce any observable anisotropy.

Since we expect the nuclei to align in any arbitrary direction in the basal plane any anisotropy present would then be reduced by a factor of 1/2 compared to that expected for  $Mn^{54}$  with alignment along one axis. The domains should however align parallel when an external field of adequate strength is applied in some direction parallel to the basal plane. Measurements of the radiation distribution with an external field of 100 gauss along the basal plane also failed to show any significant anisotropy.

At any rate the effective cooling surface for such a relatively large amount of material was certainly inadequate. For these reasons we view the results obtained as inconclusive. It is proposed to repeat these measurements with a more active sample prepared according to the procedure of Williams et al (1957b) and using a much larger cooling surface. Some 207 70 microcuries of Bi are available in our laboratory and it is also intended to investigate the distribution of the radiation from this isotope in a sample prepared and mounted in a similar manner.

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FIGURE / VACUUM SYSTEM





FIGURE 3 BLOCK DIAGRAM OF THE COUNTER ARRAY



FIGURE 7



# FIGURE 4







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282 keV y - RAY



# FIGURE TO DECAY SCHEME OF Mn 54



DECAY SCHEME OF CO<sup>60</sup> FIGURE 11



FIG 20

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FIGURE 14  $Mn^{54}$  IN  $Mn Cl_2 4 H_2O$ 



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 $C_0 C_1 \cdot 6 H_2 O$ 

# $\varkappa$ of POWDER

5

4

3

δ

2

0 0.2

о O

0

0.4

0

0

Ò

0

0.6

 $\frac{V_{T}}{T}$ 

0

0

0.8

0.2

0

#### II to c - AXIS X





0 0

0 0



FIG 21

 $\perp$  to c - AXIS  $\boldsymbol{\chi}$ 

0<sup>0000</sup>000

0000000 0

8.0














