

NUCLEAR MAGNETIC RESONANCE FIELD CYCLING INVESTIGATION OF IRON DOPED
INDIUM PHOSPHIDE, SULPHUR DOPED INDIUM PHOSPHIDE AND SILICON DOPED
GALLIUM ARSENIDE

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By

ADRIAN HABANYAMA

1989

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I SOLEMNLY DECLARE THAT THIS THESIS REPRESENTS
ORIGINAL WORK WHICH HAS NOT BEEN SUBMITTED FOR
A DEGREE AT THIS OR ANY OTHER UNIVERSITY.

SIGNATURE:

A handwritten signature in black ink, appearing to be 'H. S. ...', written over the dotted line of the signature field.

DEDICATION

I sacredly dedicate this work to my father and all those
with whom I share memories of 25 Iris.



ABSTRACT

III-V semiconductors and their alloys are by no means simple and have some rather subtle properties. Therefore their increasing commercial exploitation has stimulated phenomenal growth in the research effort devoted to studying their defects and radiation effects.

NMR spectroscopy has become firmly established as one of the major methods available for structure determination and for obtaining physico-chemical information about atomic dynamics. Recent years have seen several major developments of the technique, one of which is NMR field-cycling.

This work was part of a recently established and on-going NMR field-cycling research programme on semiconductors, in the physics department at the University of Surrey in Guildford, U.K. It is the first ever, series of investigations attempting a systematic study of III-V semiconductors using field-cycling. The Technique of field cycling is however well established for quadrupolar studies in many other materials. It is very sensitive in contrast to NMR line shape techniques and shows great development potential. Positive results were obtained in this investigation. These are presented in chapter Five.

PREFACE

Scope of the thesis

The first chapter is a general introduction, including an account on the purpose of the investigation. Chapter two, gives the physical properties of pure and doped indium phosphide and gallium arsenide. In this chapter, a number of reproduced theoretical and experimental diagrams are included, as these are necessary to support the text. For non-standard diagrams, all sources are indicated in the figure-captions. The third chapter attempts to draw together the basic theory that is of relevance to the investigation. The chapter is deliberately leaned heavily on standard NMR material, this being the first purely NMR based thesis presented to the department. Chapter four explains the instrumentation, measurement technique and other experimental aspects of the investigation with occasional digression into theoretical considerations which were inevitable. In the fifth chapter, the experimental results are presented and an attempt made to systematically discuss the spectral information. Chapter six, gives a largely theoretical general discussion of the observed spin behaviour in terms of the concept of spin temperature and the density matrix. In this chapter, a degree of repetition of certain mathematical developments, given in other texts, was unavoidable to achieve clarity, although they are undoubtedly not as authoritatively dealt with as elsewhere. The last chapter outlines the established phenomena and gives some conclusive remarks.

Units

Almost all equations are written in SI rationalized units. When CGS units are used, as in Eq. (3.63), this is indicated in brackets. However, when referring to numerical values in the text or in diagrams, whatever units that seem most appropriate to the quantity described are used. Thus magnetic field induction is frequently quoted in Gauss, optical absorption co-efficients in cm^{-1} etc., since this is the most widely used convention.

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GLOSSARY OF SYMBOLS

Subscripts :	n = nuclear; e = electron;
	p = hole; L = longitudinal;
	T = transverse
Superscripts :	$\pm$ = ionized; integer superscript
	= nuclear species; decimal number superscript
	= reference number

$\vec{A}$	hyperfine (electron-nuclear) interaction tensor
$\langle A \rangle$	expectation value of observable A
$\vec{B}$	magnetic induction field (magnetic flux density)
$\vec{B}_0$	static magnetic field of an NMR spectrometer
$\vec{B}_1$	RF magnetic field perpendicular to $\vec{B}_0$



B_{NMR}	field at which measurement is made in NMR field cycling
c	speed of light in vacuum
e	magnitude of electronic charge
E	electron energy eigen value
E_g	band gap energy
$\vec{F}$	force due to a magnetic field
$\mathcal{H}$	Hamiltonian operator - its nature being indicated in the text
h	value of plank's constant
$\vec{I}$	Nuclear spin operator
I_x, I_y, I_z	components of $\vec{I}$
I	spin quantum number associated with $\vec{I}$
I_+	nuclear spin raising operator
I_-	nuclear spin lowering operator
J	general angular momentum quantum number associated with the operator $\vec{P}$
K	linear optical absorption co-efficient
$\vec{k}$	electron wave vector
k_B	Boltzmann's constant
k_o	linear optical extinction co efficient
$\vec{M}(t)$	macroscopic magnetization of a spin system
M_o	equilibrium macroscopic magnetization of a spin system in the presence of B_o

$M_x, M_y, M_z,$	components of macroscopic magnetization
m_I	eigen value associated with I_z (or magnetic projection quantum number)
m_p	value of proton mass
N	total number of nuclei in a macroscopic sample
N_+	total number of nuclei in the spin $+\frac{1}{2}$ state, in a macroscopic sample
N_-	total number of nuclei in the spin $-\frac{1}{2}$ state, in a macroscopic sample
n	population difference between spin-up and spin-down nuclear states
$\vec{P}$	general angular momentum operator
P_x, P_y, P_z	components of $\vec{P}$
P_n	probability of occupation of state n
$P_{a \rightarrow b}$	probability of transition from state a to state b
Q_A	nuclear quadrupole moment of nucleus A
$q(r)$	coulomb electric field gradient per unit charge
$\vec{S}$	electron spin operator
S_+	electron spin raising operator
S_-	electron spin lowering operator
T_1	longitudinal or spin-lattice relaxation time
T_2	transverse or spin-spin relaxation time
t_p	pulse duration
t_{prep}	preparation time in field cycling
t_{switch}	switching time in field cycling

T_L	lattice temperature
T_s	spin temperature
W	transitional probability per unit time
β	temperature parameter - subscripts indicate its nature
γ	magnetogyric ratio - subscripts indicate its nature
$\delta(r)$	Dirac delta operator or function
$\vec{\mu}$	magnetic dipole moment
μ	magnitude of magnetic dipole moment or mobility - subscripts indicate the nature
μ_B	Bohr magneton
μ_N	nuclear magneton
ν_i	Larmor precession frequency of nucleus i
ρ	conductivity or density matrix - the distinction being made in the text
$(1 - \sigma_A)$	Sternheimer anti shielding factor of nucleus at point A
$\vec{\tau}$	torque exerted on a spin magnetic moment
ψ	total wave function of a system
ω	angular frequency

CHAPTER ONE

INTRODUCTION

1.1 The Compounds In P and Ga As

Indium phosphide and gallium arsenide belong to a group of simple compounds formed between elements of groups III and V of the periodic table. This class of what are referred to as III-V compounds, constitute the best understood class of compound semiconductors as opposed to the elemental semiconductors of which the best known, silicon and germanium, are the most extensively used semiconductors. There are many other semiconductors of interests in the III-V group such as In Sb, In As, Ga Sb, Al Sb and Ga P.

1.1.1 Indium Phosphide

Indium phosphide is a dark grey substance with a tarry lustre. It crystalizes in the zinc blend structure where an indium atom is tetrahedrally bonded to four phosphorus atoms. It is a very highly reactive substance and is sometimes difficult to work with. It's melting point is 1070°C. It begins to oxidize in air upon heating at about 500°C and dissociation in vacuum begins at approximately 750°C.

This compound is one of the most promising semiconductors from the standpoint of practical application. It is of interest in being the only member of the group III-V semiconductors for which transistor action has been reported, that is in which minority carrier injection has been observed. Its forbidden

energy gap is 1.43 eV at 0°K. It displays an appreciable rectification effect and can also be used as a material for amplification devices. Its optical properties are also very interesting.

1.2 Gallium Arsenide

Gallium arsenide is a dark grey substance with a violet line and a tarry lustre. Like indium phosphide, it crystalizes in the zinc blend structure. It has a dielectric constant of 11.1, specific gravity 5400 kg/m³ and a melting point $1237 \pm 3^\circ\text{C}$. The compound is stable under ordinary conditions of atmospheric moisture and oxygen. Upon heating in air, it begins to oxidize at 600°C and dissociation in vacuum begins at 850°C.

Gallium arsenide is a semiconductor with a great technological future. Its forbidden gap width, which is 1.52 eV at 0°K, is closer to the wave length of the maximum of solar radiation than that of silicon. For this reason it is used as a material for solar batteries, in which solar energy is directly converted into electrical energy by means of the photo voltaic effect.

The compound displays good rectification effect. Its electrical conductivity and hall constant are practically totally independent of temperature in the range of 1.5 to 300°K which makes it suitable for electronic use. This feature is due to the fact that the substance is in a degenerate or metallic state when heavily doped, i.e. with an electron

concentration of $n = 10^{17} - 10^{18} \text{ cm}^{-3}$.

1.1.3 The Constituent Elements

Indium has two isotopes that possess spin ($I = 9/2$), ^{115}In and ^{113}In with natural abundance 95.72% and 4.28% respectively. A wide range of investigations of solids or melts of indium metals, alloys, and salts have been undertaken. Several theoretical studies of indium NMR properties have been reported. The large quadrupole moments of ^{115}In and ^{113}In , and the low receptivity of the latter, probably accounts for the scarcity of chemistry-oriented NMR studies of these isotopes.

Gallium also has two isotopes ^{69}Ga and ^{71}Ga ; these possess spin ($I = 3/2$) and have a more balanced natural abundance of 49.6% and 50.4% respectively. ^{71}Ga has the higher receptivity and narrower relative line width. This indicates that it is the more favourable isotope for direct NMR observation in spite of the adverse natural abundance. However, resonance of both isotopes can readily be studied and is reported in this work. The relaxation properties of the gallium nuclei and the relatively small number of compounds studied have resulted in little information being available on NMR properties. However, NMR has proved to be a very useful technique for studying the solid state properties of gallium compounds.

The only significantly abundant natural isotope of phosphorus is Phosphorus - 31 (^{31}P). It is a spin ($I = 1/2$) nucleus. The observation of its NMR spectra is relatively

easy and consequently there is a huge mass of data in the literature. There are, however, two major difficulties; firstly phosphorus compounds are generally reactive and secondly, no suitable compound has been established for general studies on the NMR properties of the nucleus.

Arsenic has been little studied by NMR, which is surprising in view of its 100% natural abundance as ^{75}As , which has a reasonably high magnetic moment. The lack of interest in this nucleus can only be partly traced to its quadrupolar properties, but a moderate increase in the use of ^{75}As NMR is apparent. The ^{75}As nucleus has been used for NMR applications in solid state physics^{1, 1}.

1.2 Applications of InP and Ga As

In transistor development, fabrication can be from any semiconductor having an energy gap wide enough that the thermally excited concentration of minority carriers is reasonably low at the desired temperature of operation. A material with an indirect gap, such as silicon or germanium, is however preferred because the lifetime of excess minority carriers is normally longer in such a material since the strong direct recombination process is not active. Therefore attention is not paid to details of the energy bands in this case.

However, more recently, detailed knowledge and understanding of band structure has become increasingly important in the design and analysis of semiconductor devices. With the invention and

development of tunnel diodes, injection lasers, Gunn effect oscillators and other such devices which tend to be more directly based on complex band structure characteristics for their operation, it has become necessary to pay more attention to details of the energy bands in selecting and improving materials for fabrication. Peculiarities of band structure are in fact what make possible some of the operations of these newer devices. In view of this, InP and Ga As are becoming of increasing importance in device fabrication, where they exhibit useful characteristics that are not present in the more widely used elemental semiconductors, silicon and germanium.

2.1 Tunnel Diodes

The highest performance tunnel diodes are generally made from Ga As, which is a direct gap semiconductor, but Si and Ge have also been used.

A tunnel diode consists basically of a pn junction between heavily doped p- and n-type regions. Its current - voltage characteristics include a negative resistance region, which is what makes it a useful device. Fig. 1.1 shows an energy band diagram for a tunnel diode.

When a forward bias voltage is applied across the junction,

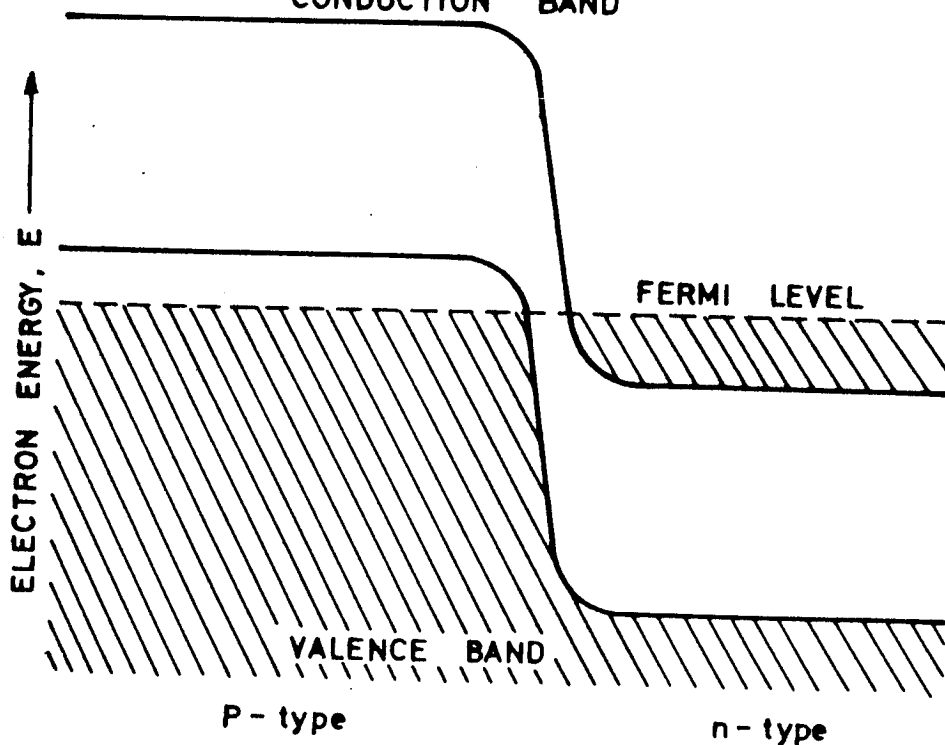


Fig. 1.1 The energy band diagram for a tunnel junction with zero applied bias voltage. The shaded area represents filled electron states.

making the p-type region positive with respect to the n-type region, the Fermi level on the n side rises above that on the p side and electrons are then able to "tunnel" by the quantum mechanical process from the conduction band on the n side through the "barrier" into the valence band on the p side. This tunneling current first increases with increasing applied voltage, but it then decreases to zero as the bottom of the n-side conduction band rises above the top of the p-side valence band so that no further tunneling can occur. This decreasing current with increasing voltage corresponds to the range of negative resistance. During the tunneling process an electron does not change its energy. At still higher forward bias voltage, the normal diode diffusion current rises significantly hence restoring a positive slope in the current-voltage characteristic curve. Under a reverse bias voltage, the tunneling current of electrons from the p side valence band to the n side conduction

band will in principle, increase without limit.

For high performance of a tunnel diode, the main criterion is that it be made from a semiconductor having a direct energy gap (like Ga As) although it is possible also to fabricate reasonably good tunnel diodes from indirect gap materials (like Si and Ge). A direct gap permits a tunneling transition without change of the k vector of the electron, which is more probable than if the gap were indirect, and the direct transition consequently leads to the highest possible tunneling current.

GaAs as tunnel diode material for radiation detection can operate at higher temperatures than those made of germanium or silicon. This is because of its larger forbidden gap with a width of 1.52 eV as to 0.744 eV and 1.17 eV for germanium and silicon respectively.

2.2 Injection Lasers

Injection laser action has been observed in a number of well-known direct gap semiconductors but only a material with a gap width corresponding to the desired laser emission wave length is useful. Emphasis has been placed on the development of Ga As alloys such as $\text{Ga}(\text{As}_{1-x}\text{P}_x)$ as laser materials having a designable output wavelength.

A semiconductor laser structure is essentially a p-n junction diode which can be made to emit coherent radiation as a laser, under conditions of high primary current. An injection laser diode is similar to a tunnel diode in that it is made from rather heavily doped material. The energy band diagram for such a diode is therefore similar to that of Fig. 1.1, but in this case the geometry of the diode must be arranged to



provide a cavity within which the emitted radiation can bounce back and forth in order to be amplified by means of stimulated emission. Laser action is achieved by applying a high forward bias voltage to the pn junction to inject many electrons from the n side into the p side and holes in the opposite direction. This produces an inversion region in which the conduction band electron and valence band hole populations are very high, so that strong recombination occurs, the emitted quanta, which correspond to the energy width across the band gap, travel back and forth through this region stimulating emission of additional quanta hence the lasing. Fig. 1.2 shows a schematic diagram of a p-n junction laser structure.

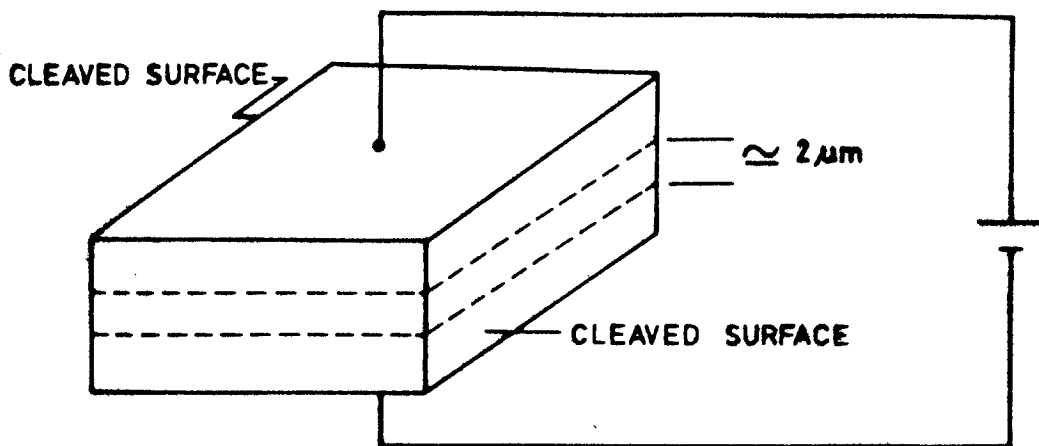


Fig.1.2 The p-n junction laser structure. The two cleaved parallel faces have high reflectivity and serve for a resonator. (The structure is made of a single crystal).

2.3 Gunn Effect

The Gunn effect has been observed only in such semiconductors as InP, Ga As and Cd Te which satisfy the band

structure requirement discussed below.

It was found that high frequency oscillations of voltage across a sample are produced under conditions of high dc bias in certain few semiconductor materials. This effect can be employed to realize a device which is a high frequency electrical oscillator, in the micro wave region.

This effect results from a transfer of carriers from a small effective mass band minimum to higher lying, higher effective mass minima as the carriers gain energy from the strong applied electric field. The carrier mobility is much lower in the subsidiary band minima in this case, so that the excited carriers cannot maintain their energy and they consequently fall back down to the lower minimum. This is a situation of instability and negative resistance which gives rise to the observed oscillations. Only those semiconductors having subsidiary band minima at an attainable energy above a low effective mass absolute band minimum would be feasible materials.

.3 Purpose of Doping with Fe, S or Si

The question of why iron and sulphur are used as dopants for indium phosphide and silicon for gallium arsenide is one that can be answered in a variety of ways, depending on the context within which the question arises. From the academic point of view, these doped samples have stirred up a great deal of interest. Electron nuclear double resonance (ENDOR) investigations have been carried out and this work has been published ^{1, 2}. Electron spin resonance (ESR) studies have also been carried out and great promise is evident in NMR studies as is apparent from the results of this work and work reported in recent papers ^{1, 3}. ENDOR and ESR are just other methods of spectroscopy. As regards industrial interest, since indium phosphide and gallium arsenide are becoming of increasing industrial value and the field of semiconductors being so diverse, these particular dopants may well have been found preferentially applicable in certain regards, of high technological interest.

The dopants are not, however, unique for InP and Ga As. For example, the elements cadmium and zinc could act as acceptors in either one of the two compounds while selenium could be used as a donor. These impurities introduce extra allowed levels in the band gap of the semiconductors. Sulphur and silicon introduce shallow donor levels in InP and Ga As respectively, this being referenced to the edge of the conduction band. Iron introduces a deep acceptor level in In P, the impurity level in this case lies roughly in the middle of the

InP band gap.

Purpose of the Investigation

Many NMR techniques are being developed to study interactions in solids. The particular technique used here is NMR field cycling which has been used to study quadrupolar interactions in organic compounds and the quantum mechanical tunneling of methyl groups at low temperature. A few studies have been undertaken for the study of III-V semiconductors, using more traditional NMR methods based on careful analysis of the NMR line shapes. These were confined to measurements of interactions (mainly quadrupolar) of III-V nuclei around defects and impurities but since only a small fraction of these nuclei are within a few coordination shells of an impurity site, the impurity related spectral features were masked by the features due to the larger fraction of nuclei more distant from the impurity site. Work has also been done to study the impurity atoms directly, but in this case too, the signal was not large enough for decisive analysis.

The aim of this investigation was to use NMR field cycling to produce impurity related spectral features in InP : Fe, InP : S and Ga As : Si, thereby being able to analyse the dopant impurity centres. It is hoped that the results can be interpreted in terms of quadrupolar and hyperfine enhanced Zeeman energy level cross-coupling around the impurities and possibly distinguish between deep and shallow band gap states.

CHAPTER TWO

PHYSICAL PROPERTIES OF INDIUM PHOSPHIDE AND GALLIUM ARSENIDE

As mentioned in the first chapter, indium phosphide and gallium arsenide are inorganic crystalline solids composed of atoms arranged in regular periodic arrays. The atoms are held together in the crystal lattice primarily by covalent bonding, in which valence electrons are shared between adjacent atoms to form each bond. There is also some minor ionic contributions to their inter atomic bonds unlike in the elemental semiconductors such as silicon and germanium that are entirely covalently bonded. The semiconducting properties of all these crystals depend only on the valence electrons, including their energy band structure. Concern is really with the outer shell electrons of the atoms because the inner shell or core electrons are localized mainly around the nucleus as in an isolated atom and hence do not contribute directly to the physical properties of interest. The physical semiconducting properties also greatly depend on the band structure of the higher conduction band states into which electrons can be excited.

Crystal Structure

As mentioned in the first chapter, InP and Ga As crystalize in the zinc blend cubic structure. The cubic nature of the structure arises when a basis of two atoms, belonging to different

species e.g. In and P is considered per lattice point. The atomic arrangement in this structure is shown in Fig. 2.1 for indium phosphide. This structure is the same as the diamond structure, in which the elemental semiconductors silicon and germanium crystallize, except that the immediately adjacent directly bonded atoms are of different species. For example, in In P, an In atom is directly tetrahedrally bonded to four P atoms.

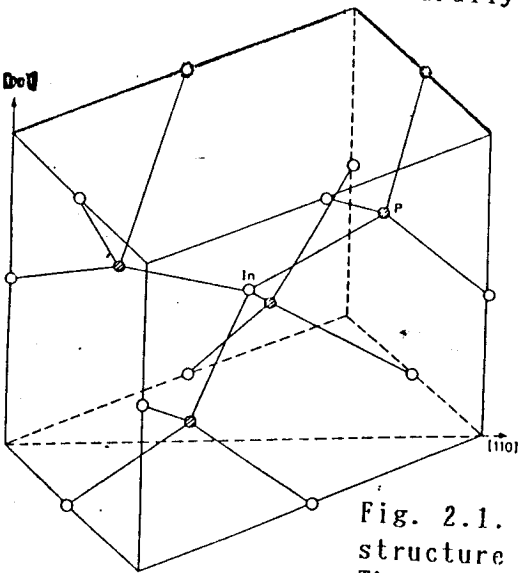


Fig. 2.1. The zinc blend cubic structure of Indium phosphide. The shaded circles represent phosphorus atoms while the unshaded ones represent indium atoms.

It is easy to explain the tetrahedral bonding mechanism in the elemental semiconductors. For example, silicon has the outer-shell electronic structure $3s^2 3p^2$, i.e. it has a filled K- and L- shell; in the M-shell, the s-subshell is filled but the 3p-atomic orbital needs four electrons to be filled. By accepting and sharing four electrons from four other silicon atoms it will obtain six electrons in its 3p-orbital, and form four covalent bonds. This is shown in Fig. 2.2 below.

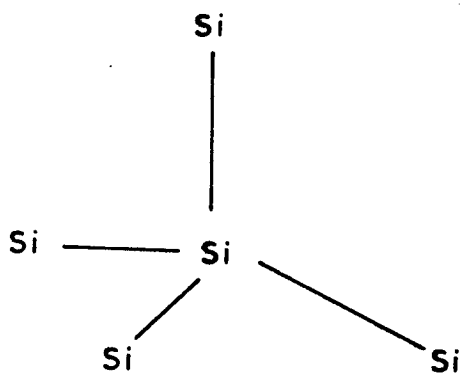


Fig. 2.2 Valence structure in pure silicon.

This simple explanation can however not be given for the zinc blend structure. For example in InP, this is clear from the outer shell electronic structures of In and P which are $5s^2 5p^1$ and $3s^2 3p^3$ respectively. i.e. the indium atom needs five electrons to fill the p-orbital in the N shell or needs to lose the single 5p-electron and the two 5s - electrons to achieve the Krypton structure. The phosphorus atom on the other hand needs three electrons to fill the p-orbit of the M-shell hence obtaining the Argon structure, this is clearly not achievable through an entirely covalent tetrahedral bonding net work. The actual nature of the bonding in such solids (including zinc blend [Zn S] itself) has, in fact, long been a matter of some debate. The electronegativity difference between indium and phosphorus is not so great as to suggest bonding of an entirely ionic nature. Most chemists have in fact, by invoking the concept of resonance, described this bonding as being partially covalent, hence partially ionic.

The concept of resonance (in chemistry) accounts for the fact that the valence structures drawn for some of the polyatomic ions are ambiguous. For example, structural investigations show that all three valence structures for the carbonate ion (CO_3^{2-}), shown in Fig. 2.3 are valid.

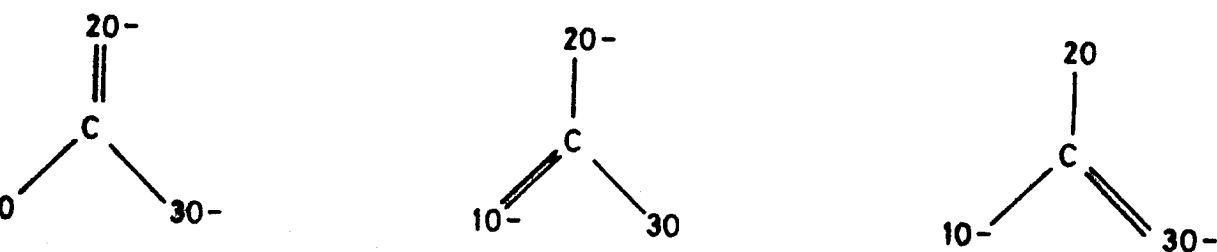


Fig. 2.3 Alternative or canonical valence structures for CO_3^{2-} . The numbers 1, 2 and 3 refer to positions (After D.R. Stranks, M.L. Hefferman, K.C. Leedow, P.T. McTigue and G.R.A. Withers: Chemistry, a structural view, Cambridge University Press, Chapter 9 (1979)).

The striking feature is that a carbonate ion never has one double and two single bonds, but rather has three identical

bonds which are intermediate in character between single and double. Furthermore, in this case, each oxygen will bear just two-thirds of a negative charge. This true state of the ion is said to be a resonance hybrid of the three equivalent structures, any one of the three equivalent forms is referred to as a canonical structure.

It can safely be assumed that at liquid Helium temperature, the iron impurity atoms in indium phosphide are in their ground state. Electron spin resonance (ESR) shows that this state is achieved by iron at an indium lattice site, by contributing three electrons to the covalent bonds. The iron would effectively be electrically neutral in this case. It is found that the impurity atoms being studied both in InP and Ga As preferentially occupy a group III lattice site rather than a group V site or an interstitial position. At an interstitial position, iron would be a charged ion Fe^{3-} , which would give an electric field gradient that is about 500 times larger than that due to Fe at an In site. This large field gradient is not experimentally evident at liquid helium temperature hence ruling out interstitial occupation.

Fig. 2.4 shows a silicon impurity atom substituting at a gallium site, with four arsenic nearest neighbor atoms and twelve gallium next - nearest neighbor atoms.

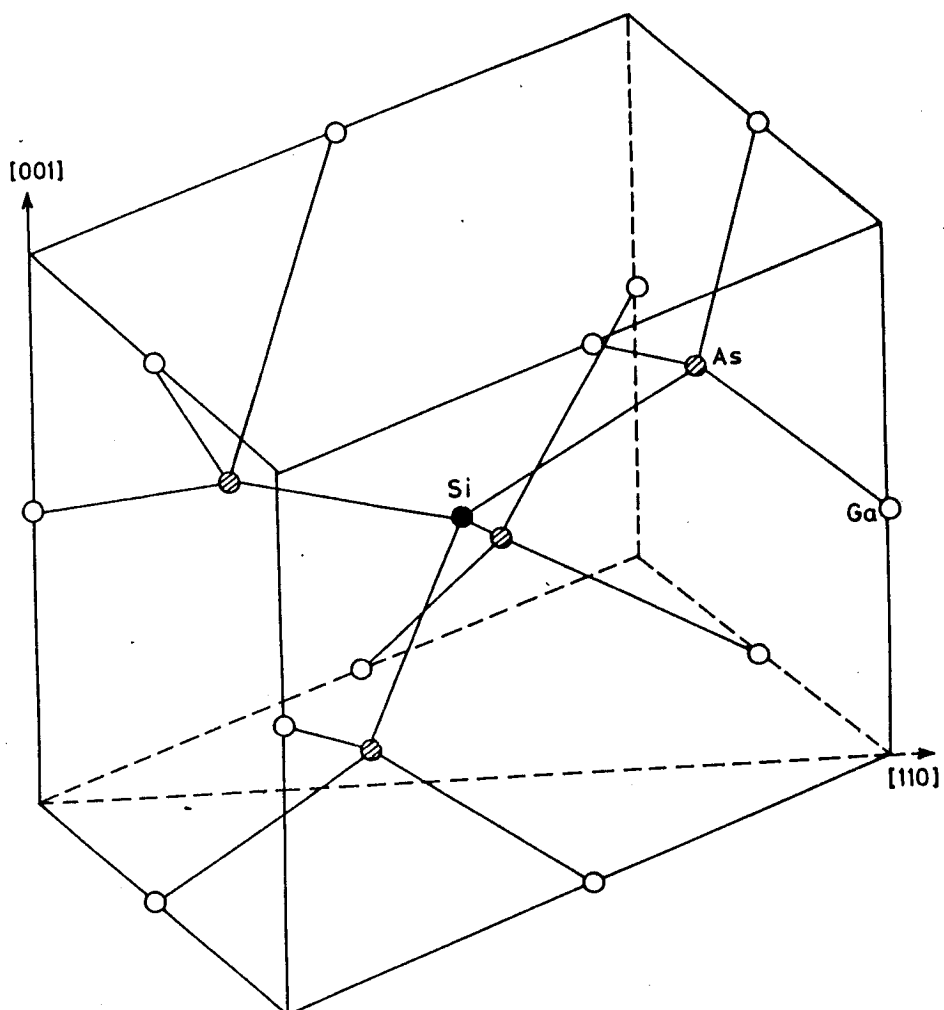


Fig. 2.4 The zinc blend structure of Ga As, showing the substituted Si surrounded by 4 nearest As neighbors and 12 Ga next-nearest atoms.

2.2 Band Structure

Extensive experimental and theoretical studies on the electronic energy band structures of semiconductors have given a very comprehensive knowledge of the band structures in the range covering the energy gap and the edges of the valence and conduction bands, the energy region over which the electronic transitions involved in the characteristic semiconductor phenomena occur.

It is possible, in principle to calculate the electronic energies in a semiconductor crystal, since the nature of the forces involved is well known. However, the complexity of taking into account the interactions of the great number of particles constituting the crystal, has made it necessary in practice to resort to simplifying approximations. Combined theoretical and experimental methods have produced very accurate results for the well known semiconductors.

Three different methods have been used to contribute to the the determination of the valence and conduction band energy curves of these semiconductors, these are:

1. Theoretical calculation of the band structure using an assumed crystal potential and any of several possible approaches in the calculation. This method is beset with great computational difficulties and has not yet been capable of producing results accurate enough for the reliable quantitative prediction of all the experimental parameters.

2. A combination of group theory and perturbation theory to predict the possible forms of the band structure for the particular crystal lattice involved; also to determine the shapes of the energy curves accurately in the vicinity of points of high symmetry within the Brillouin zone.
3. Specific experiments to study the possible form of bands permitted according to group theory, to measure energy gaps, and to determine the energy curve shapes near band edges for comparison with the predictions of perturbation theory.

In group theory, the symmetry operations of a crystal comprise a special type of group known as a space group and the zinc blend structure has such a space group.

All operations of the space group of a crystal commute with the one-electron Hamiltonian of that crystal given in Eq. (2.1) for a one dimensional case.

$$\mathcal{H} \Psi(x) = \left(\frac{p^2}{2m} + V(x) \right) \psi = E \Psi(x) \quad (2.1)$$

where $\mathcal{H}$ represents the Hamiltonian, p the electron linear momentum, m its mass and E the energy eigen value.

As a result, it can be shown that the electron energy must have the symmetry of the crystal in $\vec{k}$ - space: i.e. $E(\vec{k})$ is invariant under any of the group operations performed in $\vec{k}$ - space. Inversion

symmetry is an operational constituent of the diamond structure space group. A crystal with a center of inversion symmetry can be inverted into itself by the operation $\vec{r} = -\vec{r}$, where $\vec{r}$ is the position of a point in the crystal with respect to that center. It is clear that the diamond structure exhibits inversion symmetry about a point mid way between two adjacent directly bonded atoms.

The occupation of adjacent sites by different atoms in the zinc blend lattice results in an absence of the inversion symmetry. This difference between the two closely related crystal types leads to certain small fundamental differences between the energy band structures of elemental semiconductors such as Si and Ge and the III-V compound semiconductors.

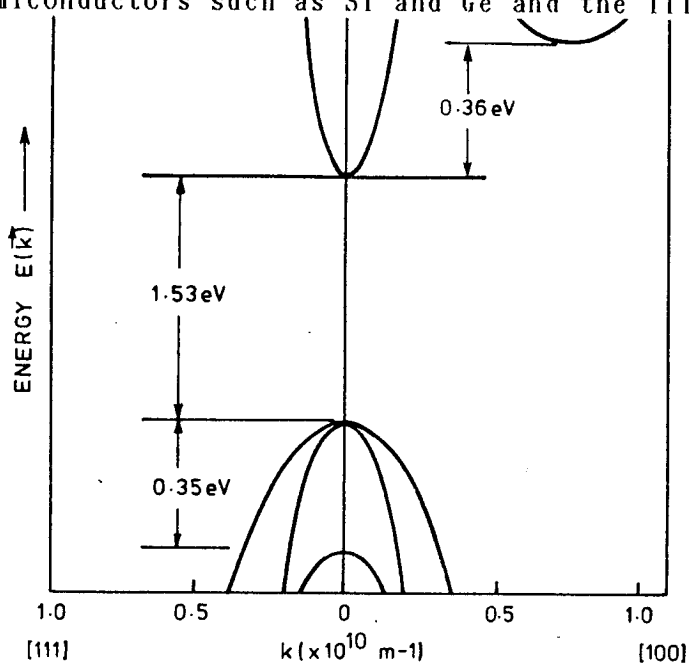


Fig. 2.5 The $E(\vec{k})$ curves of Ga As in the [111] and [100] direction, showing a relatively high effective mass subsidiary band minimum at 0.368 V above the low effective mass absolute band minimum. The important energy differences are indicated as obtained experimentally at 4K.

A plot of energy $E(\vec{k})$ versus wave vector along the [111] and

[100] direction in the band gap in Ga As is shown in Fig. 2.5. These are theoretical $E(\vec{k})$ curves but the indicated energy differences between band extrema are experimentally determined. As can be seen from Fig. 2.5, this is a direct gap semiconductor and there is a relatively sharp low effective mass conduction band minimum at $\vec{k} = 0$. This band is non parabolic at higher energies, which is characteristic of most of the III-V compounds. Ga As along with In Sb form the best known two compounds of the III-V group in terms of band structure. The band structures of these two semiconductors are generally representative of all the III-V compounds and for that reason I include Fig. 2.6 which shows an energy versus wavevector diagram of In Sb along [111] and [100] as in Ga As. This figure shows the complex theoretically determined structure of the valence band edge, resulting from the lack of inversion symmetry combined with the spin-orbit interaction. This detailed valence band structure has not actually been clearly observed experimentally in any of the III-V compounds except possibly indium antimonide (In Sb) and indium arsenide (In As), because it involves such small energy differences.

A complex valence band edge structure similar to that shown in Fig. 2.6 is predicted for Ga As, from group theory considerations (lack of inversion symmetry) and considerations of the spin-orbit interaction. This is not shown in Fig. 2.5 because it has never been experimentally verified.

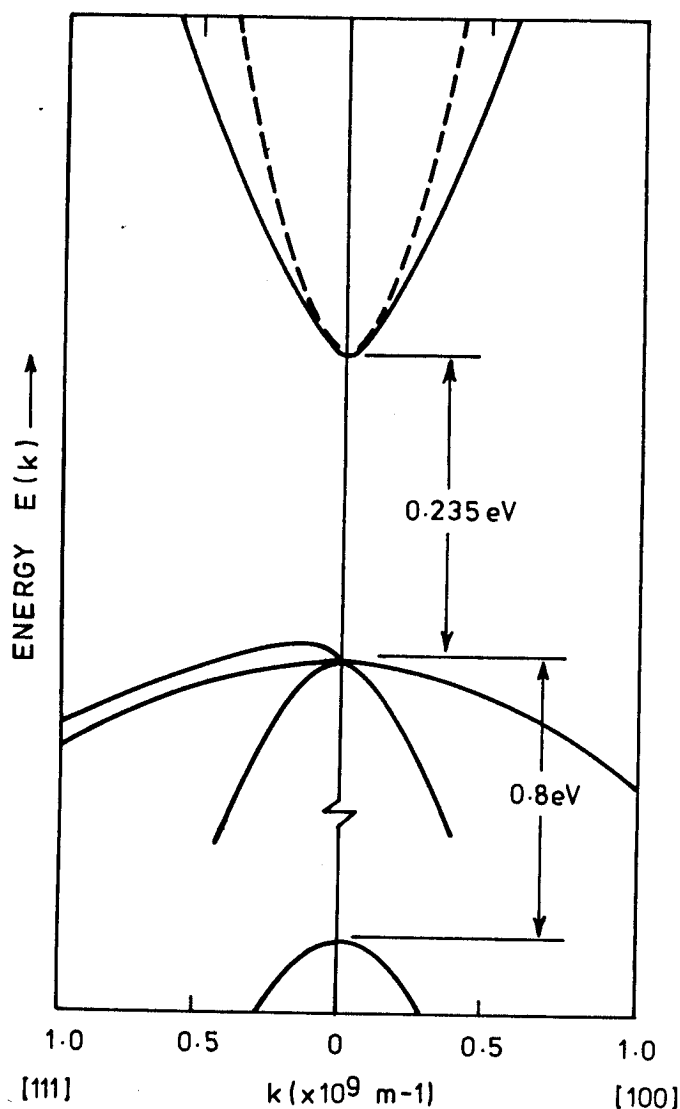


Fig. 2.6 The theoretical $E(k)$ curves of In Sb in the [111] and [100] directions, indicating the band gap energy and the valence band spin-orbit splitting energy. These are determined mainly from optical experiments at 4 K. Also shown is the complex structure of the valence band edge. The dashed curve represents the shape the conduction band would have if it were parabolic with a constant effective mass equal to the $k = 0$ measured value.

Fig. 2.5 shows a relatively high effective mass subsidiary [100] conduction band minimum at an attainable energy

(0.36 eV) above the low effective mass absolute [000] conduction band minimum, a condition required for the oscillatory mechanism in the Gunn effect.

The application of hydrostatic pressure causes a volume change in a sample which in turn changes the band structure. In particular the minima in the conduction band and maxima in the valence band shift in energy. In general the amount of the shift in different minima will be different so that, in a material like Ga As, it is possible to alter the relative energies of the conduction band minima quite considerably. The use of hydrostatic compression provides one of the most convincing pieces of evidence to show that the origin of the Gunn effect is electron transfer between [000] and [100] conduction band minima. By the application of pressure the [100] valleys are lowered to and eventually below the central minimum. At the same time, the Gunn effect oscillations become successively less pronounced and eventually the effect vanishes.

The occurrence of the Gunn effect in In P confirms a similarity in conduction band structure with Ga As. In P (along with most other III-V semiconductors), although not as well established in terms of band structure as Ga As and In Sb, is believed to have a valence band structure with the general qualitative characteristics indicated in Figs. 2.5 and 2.6, including the detailed band edge structure shown for In Sb in Fig. 2.6.

2.3 Electrical Properties

2.3.1 Indium Phosphide

For a long time In P was typically obtained with a carrier concentration of $n \sim 10^{17} \text{ cm}^{-3}$. The mobilities at this sample purity are $\mu_e = 3400 \text{ cm}^2/\text{V sec}$ at 290 K and $\mu_p = 50 \text{ cm}^2/\text{V sec}$ at the same temperature. Relatively recently, considerably purer samples have been obtained with a carrier concentration $n = 6 \times 10^{15} \text{ cm}^{-3}$ and an electron mobility of $5000 \text{ cm}^2/\text{V sec}$. μ_e and μ_p stand here for electron and hole mobility respectively, as described in the list of symbols.

Looking at the specific case of Fe-doped In P, as mentioned earlier the Fe is a deep acceptor with an energy level located near the centre of the In P band gap. **Electron:** concentration, conductivity and mobility at approximately 290K are $n = 2.3 \times 10^{-7} \text{ cm}^{-3}$, $\rho = 7.6 \times 10^7 \Omega \text{ cm}$ and $\mu_e = 2.9 \times 10^3 \text{ cm}^2/\text{V sec}$ ^{2.4} respectively.

In view of the above values, this impure sample of In P is referred to as semi-insulating. The energy difference between the Fe level and the conduction band edge is found to be 0.65 eV. Sulphur in In P:S, being a shallow level donor, is likely to increase the electron concentration in the conduction band, especially at temperatures around 290 K and above. However, the electron mobility is likely to be reduced by the presence of the

impurity, as is the case in In P: Fe (as explained at the beginning of this section). The question of whether the increased electron concentration in In P : S results in an increased conductivity can be answered by theoretical analysis of the electron transport properties in the sample or through experimental observation. However, for a heavily doped or degenerate sample, as is required in tunnel diodes, the conductivity is greatly increased because this is essentially a metallic state.

3.2 Gallium Arsenide

Gallium arsenide ordinarily has electron mobility in the range 400-8500 cm²/V sec and hole mobility in the range 200-400 cm²/V sec. The electrical conductivity and Hall constant are practically totally independent of temperature in the range from 1.5K to 300K for electronic samples of gallium arsenide. This is due to the fact that the substance is in a degenerate state (i.e. metallic) with an electron concentration of

$n = 10^{17} \rightarrow 10^{18} \text{ cm}^{-3}$. Silicon in Ga As : Si increases the electron concentration, being a shallow level donor.

The electron effective mass in both Ga As and In P increases with increases in external magnetic field at low temperatures. This was deduced from cyclotron resonance data^{2,2}.

There is a change in electrical resistance, referred to as piezoresistance, of any conductor on the application of hydrostatic pressure. Ga As and In P are no exceptions and this is essentially

due to the change in volume on compression which in turn changes the band structure as discussed in Section 2.2.

2.4 Optical Properties

Macroscopically, the optical properties of any medium can be fully specified by two quantities:

the refractive index n_0 and the extinction coefficient k_0 . These two quantities are defined by a set of equations of the form

$$E_y = E_{y0} \exp \left\{ -i\omega \left[t - \frac{z}{c} (n_0 + ik_0) \right] \right\} \quad (2.2)$$

which describes the electric field component in the y-direction of a transverse electro magnetic wave propagating in the z-direction through a medium described by n_0 and k_0 . ω is the angular frequency and c the velocity of light in a vacuum. Similar expressions apply to the other components of the electromagnetic wave.

During transmission of radiation through the bulk of a sample, the radiation intensity, I_r , which is proportional to the square of the amplitude, falls off with distance through the sample as

$$I_r = I_r(0) \exp (-Kz) \quad (2.3)$$

where K is called the absorption coefficient.

Comparing (2.3) with (2.2) shows that

$$K = \frac{2K_0\omega}{c} = \frac{4\pi K_0}{\lambda} \quad (2.4)$$

where λ is the wave length of the radiation. It follows therefore

that if the refractive index and absorption coefficient of a medium are known, then its optical properties are fully specified, macroscopically.

4.1 Indium Phosphide

Indium phosphide has a refractive index of 3.0. Fig. 2.7 shows the absorption spectrum of Fe-doped In P. A broad absorption band extending from the absorption edge to an energy in the vicinity of 0.7 eV is evident for Fe-doped In P samples. The intensity of this absorption increases with decreasing electron concentration, that is, with decreasing occupation of the Fe acceptor levels. This behaviour indicates that the absorption is primarily due to electronic transitions from the valence band to the Fe levels. Transitions are evidently possible from these Fe levels to the conduction band as well, since the absorption band does not completely disappear even for an n-type sample, in which all the Fe levels are occupied. An n-type sample can be obtained by co-doping with Sn (tin) which is a donor.

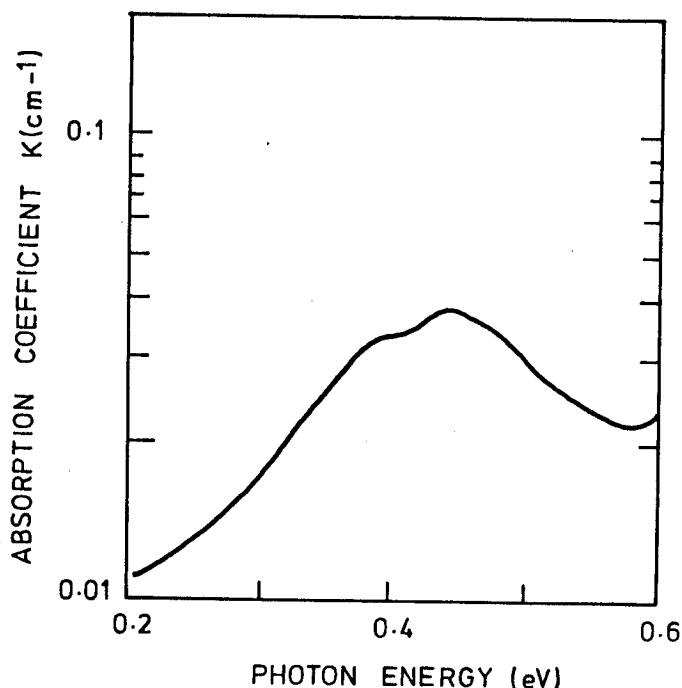


Fig. 2.7 Experimental optical absorption spectrum of InP: Fe at 300K. (After G.W. Iseler; Properties of In P doped with Fe, Cr or Co. Inst. Phys. Conf. Ser. No. 45: Chapter 2, 1978).

2.4.2 Gallium Arsenide

The index of refraction of Ga As is 3.2.

In the lattice vibrational spectrum of a three-dimensional crystal, there is more than one optical branch unlike in the case of a one-dimensional model considering only longitudinal oscillations of atoms. In a three-dimensional crystal there are in addition, two transverse oscillations per longitudinal oscillation but these two transverse oscillations are degenerate with each other in a cubic crystal and hence appear on the same optical branch. Fig. 2.8 is a reproduction of an experimental lattice vibrational or phonon spectrum of Ga As at 296K.

Branches are shown for the two wave vector directions $[100]$ and $[111]$. $k_{\max}$ is the value of the wave vector k at the

Brillouin zone boundary

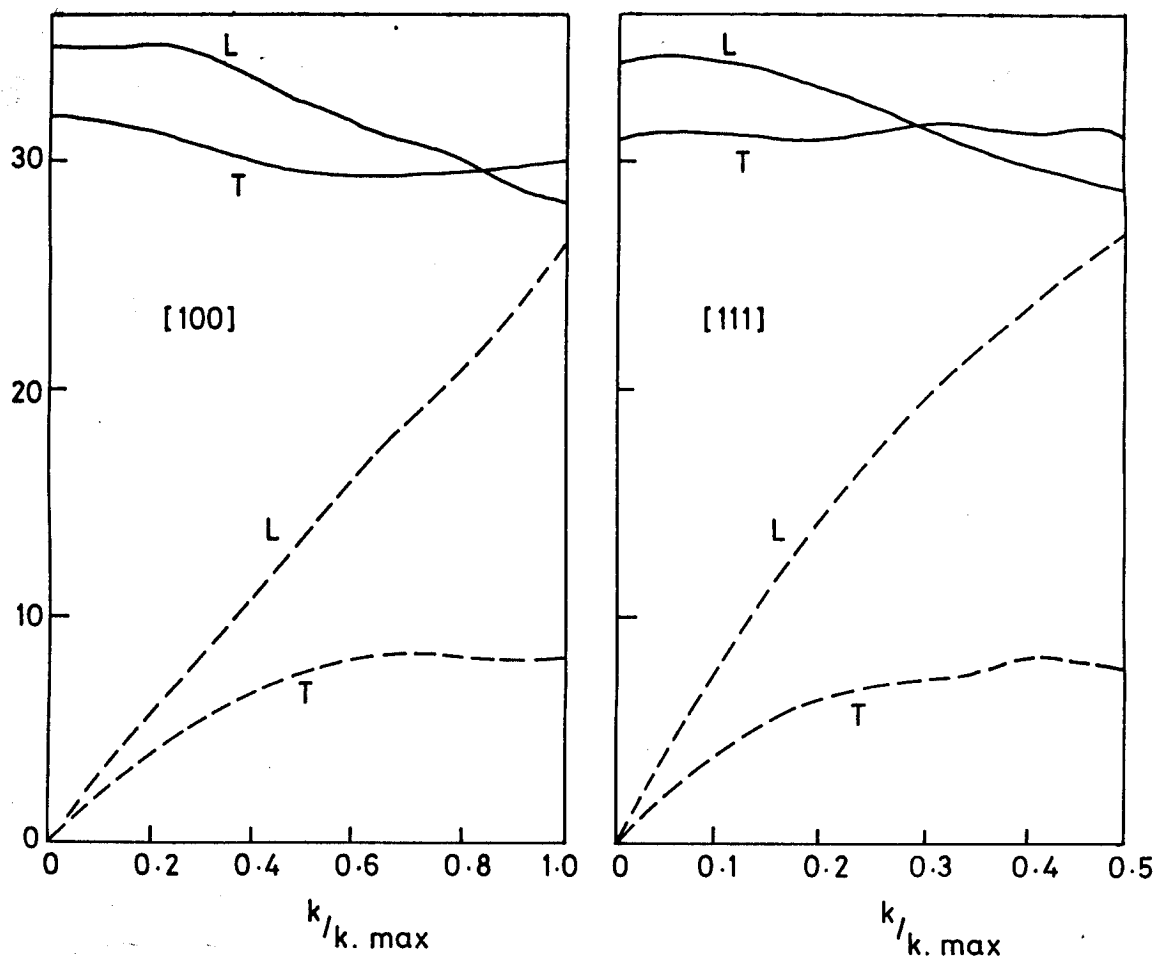


Fig. 2.8. Lattice vibrational spectrum of gallium arsenide at 296K. The broken lines represent the acoustic branches. L stands for the longitudinal modes of vibration while T the transverse (doubly degenerate). (After G. Dolling and J.L.T. Waugh: Lattice Dynamics p. 19 Pergamon. 1965).

The Ga As phonon spectrum of Fig. 2.8 is like that of a purely covalent crystal like Si apart from the more pronounced splitting between transverse and longitudinal optical branches which even, persists up to $k = 0$ where degeneracy is expected on symmetry grounds. This splitting is characteristic of partially ionic crystals including InP and is due to Coulomb forces resulting from the ionic nature. This shape effect

appears to diminish as k increases and the lack of degeneracy at the edge of the first Brillouin zone is not due to the coulomb splitting but is typical of compound semiconductors as a result of the different atomic masses of the constituent atoms e.g. Ga and As atoms in Ga As. Due to the ionic binding character in compound semiconductors, atomic oscillations in the optical phonon mode may be excited by electromagnetic radiation.

When the p side of a pn junction is made positive, current is carried by a flow of electrons into the p material where there are already free holes in equilibrium and conversely holes flow into the n side. Recombination can then take place and optical emission occurs. Ga As is a direct gap semiconductor, therefore radiative recombination is highly probable. In Ga As pn junctions, with the p side positive, junctions made with low p and n impurity concentrations show strong emission at low temperatures due to exciton annihilation. When high impurity doping concentrations ($>10^{18}\text{cm}^{-3}$) are used, however, exciton formation is no longer possible as the conductivity of the material is too high and emission is primarily due to band - impurity transitions. Frequently the emission is due to transitions from the conduction band to impurity band-acceptor levels. Emission is confined to a thin layer, a few μm thick, on the P side of the junction due to the injection of electrons. The peak of this emission shifts to higher photon energies as the current through the junction is increased until, at a

critical current, the emission peak sharpens considerably and laser action or lasing begins.

The shift with current of the peak emission to higher photon energies indicates that the density of electrons in the conduction band of the p material is rising. As the band is filled up, so the 'centre of gravity' of the electron distribution moves to higher energies in the band hence creating a larger average energy difference relative to the acceptor levels in the band gap down to which the electrons fall during radiation emission.

The lifetime of minority carriers is one of the key material parameters affecting the performance of semiconductor devices including solar cells.

In semiconductors, lifetime limitations are brought about by; radiative recombination (e.g. exciton annihilation), non-radiative recombination (e.g. phonon creation) and Auger recombination. The latter mechanism has been known to be of significance primarily in low-energy-gap semiconductors. It can however dominate the overall recombination under certain conditions in Ga As. Fig. 2.9 shows a schematic presentation of Auger recombination in p-type Ga As. A recombining electron and hole (1 and 2) transfer the released energy E_g directly to a second hole (3), which changes its energy position by $E = E_g$ to the final state 3'. The

probability of Auger recombination increases with increasing hole concentration and temperature, whereas the probability of radiative and non-radiative recombination decreases with increasing temperature and hence exhibits a different dependence on carrier concentration.

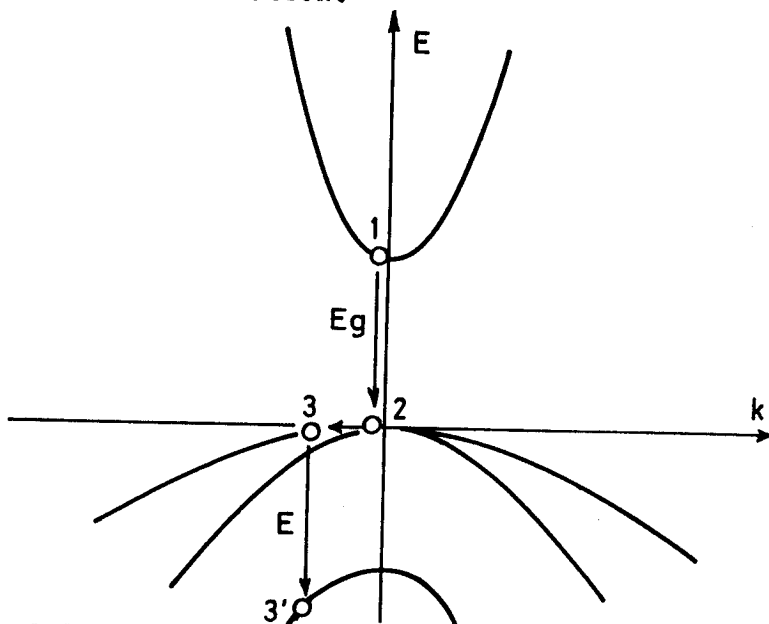


Fig . 2.9. Schematic representation of Auger recombination process in p-type Ga As. (After L. Jastrzebski, J. Lagowski, H.C. Gatos and W. Walukiewicz. Inst. Phys. Conf. Ser. No. 45: Chapter 5. 1978).

The effect of Auger recombination on the conversion efficiency of solar cells is phenomenologically described by introducing a critical temperature, T_c , above which the lifetime of holes decreases exponentially with temperature. The probability of Auger recombination, and thus the critical temperature, depends significantly on the semiconductor band structure. In InP the probability of Auger recombination is smaller than in Ga As. Therefore T_c in InP is expected to be higher than in Ga As cells. InP appears to be superior to Ga As as a material for solar cells working at elevated temperatures.

CHAPTER THREE

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY AND RELATED THEORY

Basic NMR Theory

The magnetic properties of nuclei were first postulated by Pauli^{3.1}. The phenomenon of nuclear magnetic resonance (NMR) has been effectively exploited by Rabi and his co-workers^(3.2, 3.3). Since the discovery of nuclear magnetic resonance in condensed matter (e.g. water and paraffin wax) by Purcell^{3.4} and Bloch^{3.5} this phenomenon has been interesting to chemists and physicists. The theory of NMR is presented in many text-books^(3.6, 3.7, 3.8)

Nuclear Spin And Its Quantization

Any isolated particle is assumed to have an intrinsic angular momentum in addition to its possible orbital motion (in terms of a quantum mechanical description). This intrinsic angular momentum of the particle, called its spin angular momentum P , is quantized according to the formula (similar to that of orbital angular momentum):

$$P = \hbar [J(J + 1)]^{1/2} \quad (3.1)$$

where $\hbar = h/2\pi$, h is the Planck's constant and J is a quantum number or simply "the spin" of the particle. For a proton or a neutron J equals to $\frac{1}{2}$.

The concept of spin angular momentum is applied also to a system of particles, e.g. an atomic nucleus. The spin of an atomic nucleus other than hydrogen (^1H) is the resultant of the spins of its constituent nucleons. The magnitude

of the nuclear spin angular momentum of such nuclei is given by

$$P = \hbar [I(I + 1)]^{1/2} \quad (3.2)$$

where I is the spin quantum number of the nucleus, which may be integral, half-integral or zero.

For nuclei other than hydrogen (^1H) the spin angular momenta of the individual nucleons couple together with their orbital-type angular momenta to give the observed total spin angular momentum of the nucleus. Nuclei with an even mass number and an even charge number have zero spin (e.g. ^{12}C , ^{16}O , and ^{28}Si). Nuclei with an even mass number but an odd charge number have integral spin [e.g. ^{10}B ($I=3$) and ^{14}N ($I=1$)] . Nuclei with an odd mass number have half-integral spins [e.g. ^{11}B ($I=3/2$), ^{17}O ($I=5/2$) and ^{29}Si ($I=1/2$)] . Thus, the nuclei of different elements and different isotopes of the same elements differ in spin angular momentum. This fact may be traced to details of the internal construction of nuclei. Since NMR depends on the existence of nuclear spin, nuclei with $I = 0$ do not show any direct effects and for most purposes may be ignored.

The quantization of angular momentum implies quantization of energy. Each energy state of a particle or nucleus is specified also by the appropriate quantum numbers.

Spin angular momentum, being a vector property, has to be specified by magnitude as well as direction for a full description. This is done, in quantum-mechanical terms by using a set of values of another quantum number m_l , called a magnetic projection quantum number, such that the component of angular momentum P_z along any chosen axis assumed in the z direction is

$$P_z = \hbar m_l \quad (3.3)$$

From quantum mechanics it is known that there are $2l + 1$ allowed values of m_l , i.e.

$$m_l = l, l-1, l-2, \dots, -l \quad (3.4)$$

Since the component cannot be greater than the vector itself (Fig. 3.1).

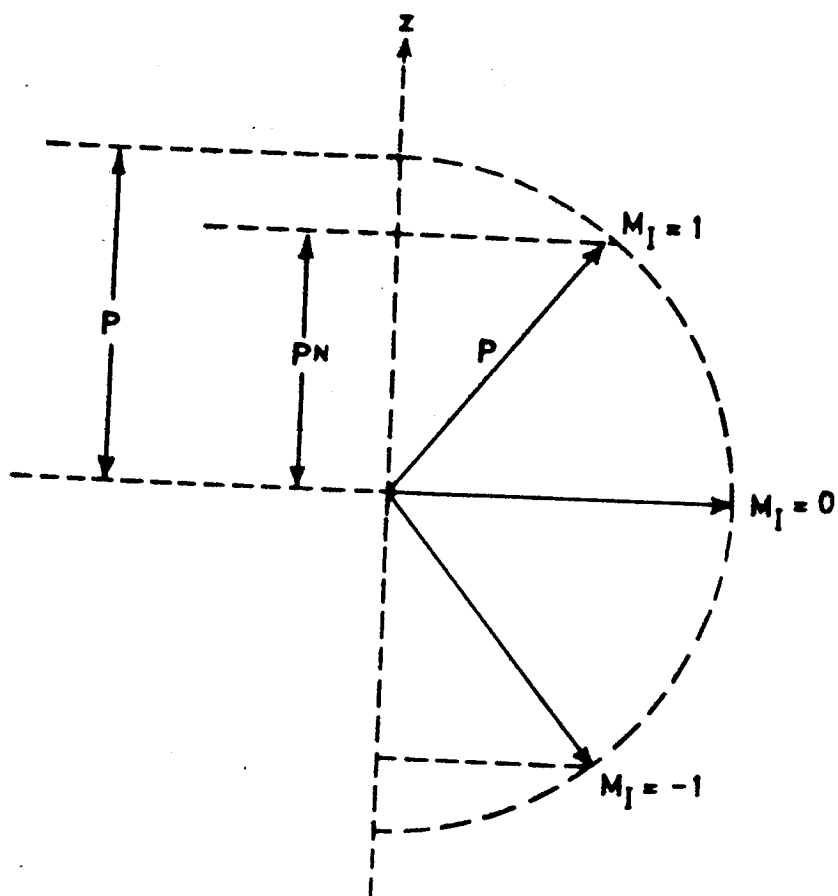


Fig. 3.1. Spin angular momentum vector, P and its possible orientations in space for $l=1$.

In the absence of a magnetic field all these states of the nucleus with different m_l 's but the same l value have the same energy. However, when a magnetic field of strength B_0 is applied in a direction defined as z , transitions between nuclear spin energy levels, which are no longer degenerate, give rise to the phenomenon of NMR.

Nuclei with spin quantum numbers greater than $\frac{1}{2}$ also possess electric quadrupole moments. This results in lifetimes

for their nuclear magnetic states in solution which are normally much shorter than those for spin $\frac{1}{2}$ nuclei. The NMR absorption lines of $I > \frac{1}{2}$ nuclei are therefore generally broad by virtue of the uncertainty principle and not so readily studied as those for $I = \frac{1}{2}$ nuclei. For some purposes such nuclei may be regarded as effectively non-magnetic.

3.1.2 Nuclear Magnetic Moments

Any motion of a charged body has an associated magnetic field. This phenomenon also occurs on an atomic scale. When electrons or nuclei possess angular momentum, there is a magnetic moment. Since angular momentum is quantized on this scale, so are magnetic moments. The nuclear magnetic moment $\vec{\mu}$ is given by

$$\vec{\mu} = \frac{g_N \mu_N}{\hbar} \vec{P} \quad (3.5)$$

where $\mu_N = eh/4\pi m_P$ is the nuclear magneton ($5.05095 \times 10^{-27} \text{ JT}^{-1}$). m_P being the mass of a proton and g_N is the nuclear g-factor which takes into account the quantum mechanical effects. The equation allows the nuclear g-factor to be either positive or negative, where a negative g-factor implies that the spin magnetic moment is anti-parallel to the angular momentum as for the electron. Usually nuclear magnetic moments are described in terms of magnetogyric ratios, γ , defined as the ratio of the magnetic moment to the angular momentum taking explicit account of the sign of the relationship

$$\vec{\mu} = \gamma \vec{P} \quad (3.6)$$

From equations (3.5) and (3.6)

$$\gamma \hbar = g_N \mu_N \quad (3.7)$$

Therefore the magnitude of the nuclear magnetic moment is given by

$$\mu = g_N \mu_N [I(I+1)]^{1/2} = \gamma \hbar [I(I+1)]^{1/2} \quad (3.8)$$

1.3 Nuclei In A Magnetic Field

When a magnetic field of strength B_0 is applied in a direction defined as z , a magnetic moment $\vec{\mu}$ would have an associated energy U given in classical terms by

$$U = -\vec{\mu} \cdot \vec{B} = -\mu_z B_0 \quad (3.9)$$

where μ_z is the z -component of $\vec{\mu}$. Quantum mechanically

$$\mu_z = g_N \mu_N m_I = \gamma \hbar m_I \quad (3.10)$$

Thus

$$U = -\gamma \hbar m_I B_0 \quad (3.11)$$

In this case there are $(2I + 1)$ non-degenerate energy levels, corresponding to the $2I + 1$ values of m_I (Fig. 3.2).

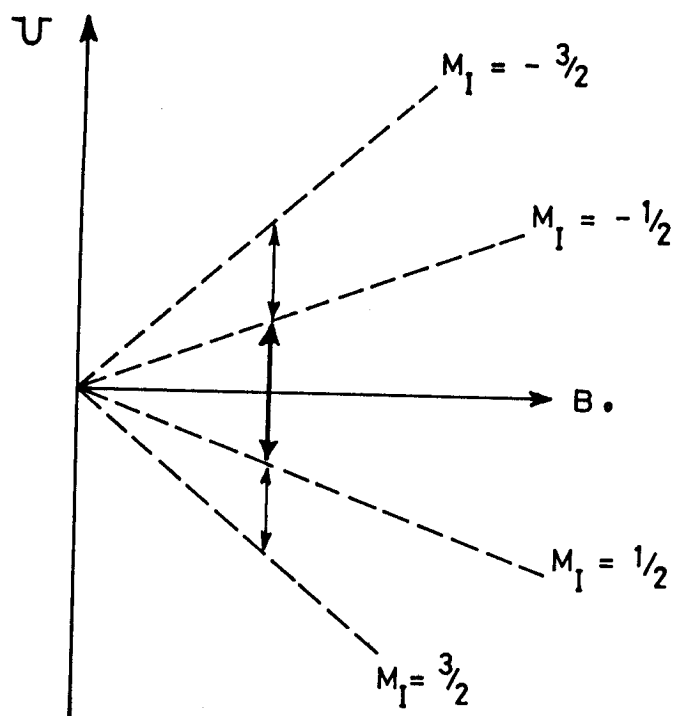


Fig 3.2. The nuclear spin energy levels for a nucleus with $I = 3/2$ (e.g. ${}^7\text{Li}$, ${}^9\text{Be}$, ${}^{11}\text{B}$, ${}^{23}\text{Na}$, ${}^{33}\text{S}$, ${}^{39}\text{K}$, ${}^{69}\text{Ga}$, ${}^{71}\text{Ga}$, ${}^{75}\text{As}$) as a function of the magnetic field B_0 . The transitions obeying the selection rule $\Delta M_I = \pm 1$ for a particular value of B_0 are indicated.

Spectroscopy may be defined as the interaction between matter and electromagnetic radiation such that energy is absorbed or

emitted according to the condition $\Delta E = h \nu$, ΔE being the energy difference between the initial and final states

NMR involves the magnetic energy of nuclei when they are placed in a magnetic field, and the transitions occur in the radio wave frequency region.

There are four basic concerns for the NMR spectroscopists i.e.

1. Obtaining spectra and developing the techniques used.
2. Evaluating the nuclear magnetic parameters from the spectra.
3. Interpreting or predicting these parameters using physical or theoretical models.
4. Applying the knowledge gained to problems of chemical interest such as structure determination and evaluation of kinetic or thermodynamic data.

The energy of an isolated nucleus in a magnetic field B_0 (applied in the z-direction) is given by Eq. (3.11). The energy levels corresponding to the $2I + 1$ values of m_I are each separated by $|\gamma \hbar B_0|$. It is clear that in principle, transitions may be induced between these levels by the use of appropriate electromagnetic radiation. Thus for NMR transitions of a single nucleus

$$h \nu = |\gamma \hbar B_0 \Delta m_I| \quad (3.12)$$

$$\nu = | (\gamma/2\pi) B_0 \Delta m_I | \quad (3.13)$$

The selection rule governing such transitions is

$$\Delta m_I = \pm 1, \text{ therefore}$$

$$\nu = |\gamma/2\pi| B_0$$

This is known as the Larmor frequency as explained in the next section. Since the resonance frequency is proportional to the applied magnetic field, either ν or B_0 may be varied in order to achieve resonance. Magnetic fields in the range 0-2.5T and frequencies in the range 0-24MHz were used in this case.

4 Larmor Precession

An alternative approach to NMR, which is of great illustrative use, is to consider the classical motion of a magnetic moment in a uniform magnetic field B_0 , under the condition of constant total energy. Nuclei with spin $\frac{1}{2}$, such as protons (^1H), are often described in terms of tiny bar magnets for certain classical treatments but because of their small size and the fact that they are always in a state of motion, their behaviour differs in some ways from the ordinary behaviour of macroscopic bar magnets. When placed in a magnetic field the spinning nuclei do not all obediently flip over and align their magnetic moments in the field direction. Instead, like gyroscopes in a gravitational field, their spin axes undergo precession about the field direction. This could be

explained as follows:

The torque $\vec{\tau}$, exerted on a spin magnetic moment $\vec{\mu}$ in a constant field of intensity B_0 and in the z-direction is

$$\vec{\tau} = \vec{\mu} \times \vec{B} = B_0(\mu_y \hat{i} + \mu_x \hat{j}) \quad (3.15)$$

This torque only has components along the x- and y-directions i.e. it produces turning moments about the x-axis [Fig. 3.3 (d)]. The torque therefore tends to align the magnetic moment along the magnetic field as in an ordinary magnet, but since there is no component of torque in the z-direction or no turning effect about the z-axis, whatever rotational motion originally present in the xy plane is unaltered [Fig. 3.3 (b)], resulting in a net rotational motion of the spin direction

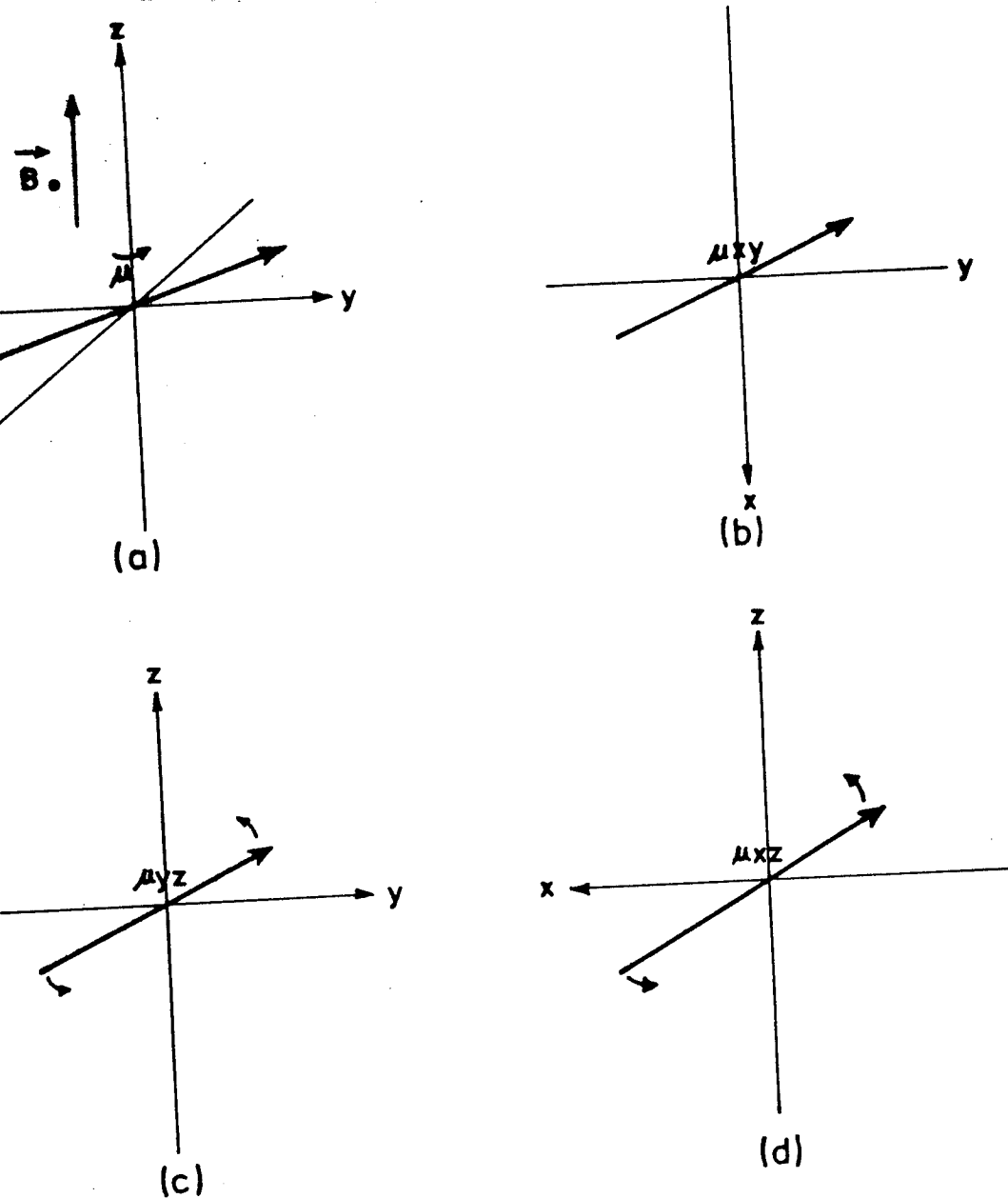


Fig. 3.3. (a) shows a three dimensional illustration of a magnetic moment μ in the field B_0 . (b) shows a view of the same magnetic moment with the positive z-axis pointing out of the paper. (c) the positive x-axis pointing out of the paper (d) the positive y-axis pointing out of the paper. The curved arrows show the direction of any turning effect

of μ in a cone with its axis along B_0 as shown in Fig. 3.4.

Such motion is known as Larmor precession.

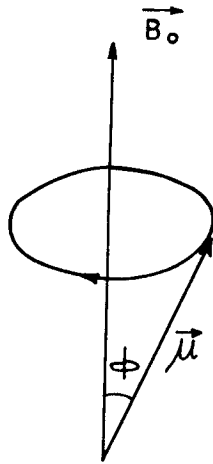


Fig. 3.4 Larmor precession about a static field $\vec{B}_0$ of a magnetic moment $\vec{\mu}$ making an angle ϕ with the field direction.

The induced angular velocity of the precession is given by

$$\omega = -\gamma B_0 \quad (3.16)$$

Thus, since $\omega = 2\pi \nu$, the Larmor frequency is given by

$$\nu = |\gamma/2\pi| B_0 \quad (3.17)$$

In nuclear magnetic resonance we often need to apply a weak alternating or rotating field (termed irradiation) perpendicular to the static field B_0 . This is used to induce various nuclear transitions and is very important in pulse methods which will be introduced later in connection with the rotating frame of reference.

If a weak magnetic field $\vec{B}_1$ is added perpendicular to $\vec{B}_0$, it exerts a torque on $\vec{\mu}$, tending to change the angle ϕ as $\vec{\mu}$ precesses. The net effect is a slight wobbling in the precession of $\vec{\mu}$ referred to as nutation.

If, on the other hand $\vec{B}_1$ is not fixed in direction, but is rotating about $\vec{B}_0$ with the same frequency as the precession of $\vec{\mu}$ and in the same direction, its orientation with respect to $\vec{\mu}$ will be constant. Suppose this orientation is such that $\vec{B}_1$ is always perpendicular to the plane containing $\vec{B}_0$ and $\vec{\mu}$ as shown in Fig. 3.5. The torque exerted on $\vec{\mu}$ by $\vec{B}_1$ will in this case consistently be away from $\vec{B}_0$. This is indicated by the curved arrow labeled by an associated force $\vec{F}$. Consequently, a large effect on $\vec{\mu}$ is possible.

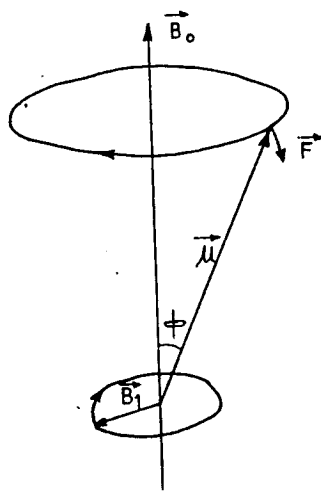


Fig 3.5 The effect of a field $\vec{B}_1$ perpendicular to both $\vec{B}_0$ and $\vec{\mu}$ and rotating at the same frequency and in the same rotational direction as $\vec{\mu}$. $\vec{F}$ is a force associated with the torque exerted on $\vec{\mu}$.

Since changing Φ corresponds to changing the energy of $\vec{\mu}$ in $\vec{B}_0$, this condition in which $\vec{B}_1$ rotates at the same frequency as $\vec{\mu}$ is described as resonance, the frequency ν of the field B_1 required must therefore be equal to the Larmor recession frequency $\nu = |\gamma/2\pi| B_0$, this clearly being in agreement with the quantum mechanical expression for NMR absorption. The energy for the change of Φ is of course derived from the rotating field $\vec{B}_1$, which may be supplied by radio frequency electromagnetic radiation.

3.1.5 The Bloch Equations

The motion of the magnetic moment $\vec{\mu}$, described in the previous section, can be described as caused by a resultant field

$$\vec{B} = \vec{B}_0 + \vec{B}_1 \quad (3.18)$$

The interaction of this applied magnetic field $\vec{B}$ and the magnetic moment $\vec{\mu}$ gives a torque given by

$$\vec{\tau} = \frac{d\vec{p}}{dt} = \vec{\mu} \times \vec{B} \quad (3.19)$$

since by eqn. (3.6) $\vec{p} = \frac{\vec{\mu}}{\gamma}$ therefore

$$\frac{d\vec{\mu}}{dt} = \gamma \vec{\mu} \times \vec{B} \quad (3.20)$$

In treating the experimental observations of nuclear magnetic resonance, it is convenient to adopt the approach of Bloch^{3, 6}, and to consider the assembly of nuclei in macroscopic terms.

A total magnetic moment or magnetization of the sample, $\vec{M}$, can be defined as the resultant vectorial sum per unit volume, of all the individual nuclear magnetic moments $\vec{\mu}$ in an assembly of identical nuclei with magnetogric ratio γ . Therefore over a unit volume

$$\vec{M} = \sum_j \vec{\mu}_j \quad (3.21)$$

Thus by vectorial summation on eqn. (3.20)

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B} \quad (3.22)$$

B_1 can be thought of as a field rotating in the xy plane at angular frequency ω . Thus the components of $\vec{B}$ are

$$B_x = B_1 \cos \omega t \quad (3.23)$$

$$B_y = -B_1 \sin \omega t \quad (3.24)$$

$$B_z = B_0 \quad (3.25)$$

From Eq. (3.22) we get three equations for the time derivative of the components of $\vec{M}$,

$$\frac{d M_x}{d t} = \gamma (M_y B_0 + M_z B_1 \sin \omega t) \quad (3.26)$$

$$\frac{d M_y}{d t} = \gamma (M_z B_1 \cos \omega t - M_x B_0) \quad (3.27)$$

$$\frac{d M_z}{d t} = -\gamma (M_x B_1 \sin \omega t + M_y B_1 \cos \omega t) \quad (3.28)$$

These equations are not complete, since they do not account for the decay or relaxation of M_x and M_y back to their equilibrium values of zero, while M_z returns to its equilibrium

value of M_0 . Assuming these decay processes could be treated as first-order with characteristic times T_2 and T_1 respectively we have

$$\frac{d M_x}{d t} = \gamma (M_y B_0 + M_z B_1 \sin \omega t) - \frac{M_x}{T_2} \quad (3.29)$$

$$\frac{d M_y}{d t} = \gamma (M_z B_1 \cos \omega t - M_x B_0) - \frac{M_y}{T_2} \quad (3.30)$$

$$\frac{d M_z}{d t} = \gamma (M_x B_1 \sin \omega t + M_y B_1 \cos \omega t) - \frac{(M_z - M_0)}{T_1} \quad (3.31)$$

T_1 and T_2 are often called the longitudinal and transverse relaxation times, respectively, since they are the time constants for decay of the components of magnetization along and perpendicular to the field B_0 . They are also referred to as spin-lattice and spin-spin relaxation times for reasons to be explained later.

A clearer insight into the significance of these equations in experimental terms is gained if the frame of reference is changed from fixed axes x , y and z to a set of axes x' , y' and z' imagined to rotate with H_1 , i.e. with angular velocity $-\omega$ about the z -axis. In this rotating frame, which is illustrated in greater depth in section 3.1.7,

both B_0 and B_1 are fixed. M may then be projected on the x , y plane into components $M_{x'}$ and $M_{y'}$, which are along and perpendicular to B_1 , respectively, and will accordingly be in-phase and out-of-phase with B_1 (Fig. 3.6)

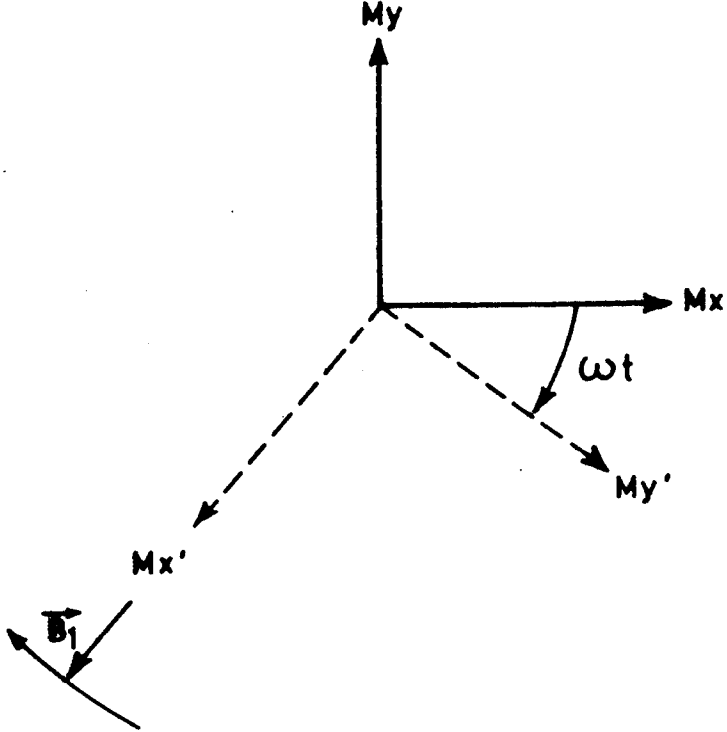


Fig. 3.6. The components of magnetisation M_x and M_y in a fixed plane (referenced to the lab.) and the components $M_{x'}$ and $M_{y'}$ in a plane rotating along with B_1 at the Larmor frequency about the static field B_0 taken as directed out of the paper. $M_{x'}$ and $M_{y'}$ are along and perpendicular to B_1 respectively.

To transform to this new frame

$$M_x = M_{x'} \cos \omega t - M_{y'} \sin \omega t \quad (3.32)$$

$$M_y = M_{x'} \sin \omega t + M_{y'} \cos \omega t \quad (3.33)$$

Substituting these into Eqs (3.29) - (3.31) and putting

$\omega_0 = \gamma B_0$, also noting that

$$M_z = M_{z'} \quad (3.34)$$

we get

$$\frac{d M_x'}{d t} + \frac{M_x'}{T_2} + (\omega_0 - \omega) M_y' = 0 \quad (3.35)$$

$$\frac{d M_y'}{d t} + \frac{M_y'}{T_2} - (\omega_0 - \omega) M_x' + \gamma B_1 M_z = 0 \quad (3.36)$$

$$\frac{d M_z}{d t} + \frac{M_z - M_0}{T_1} - \gamma B_1 M_y' = 0 \quad (3.37)$$

In this case, the terms $(\omega_0 - \omega)$ are a measurement of how far ω is from exact resonance. From Eq. (3.37), it is clear that changes of M_z , which corresponds to changes in energy of the spin system, are associated only with M_y' , the out-of-phase component of the magnetisation (referred to rotation of $\vec{B}_1$) and not with M_x' . It may then be anticipated that absorption signals will be associated with the measurement of M_y' . The component M_x' will be associated with "dispersion - mode" signals. The actual method of observation is discussed in greater detail in section 3.1.9 and in specific instrumental terms in chapter 4.

3.1.6 The Intensity of an NMR Signal

The NMR signal is as a result of the induced current in a receiver coil around the sample holder as shown in Fig. 3.7. **I**t therefore depends on the rate of change of the magnetization rather than the magnetization itself.

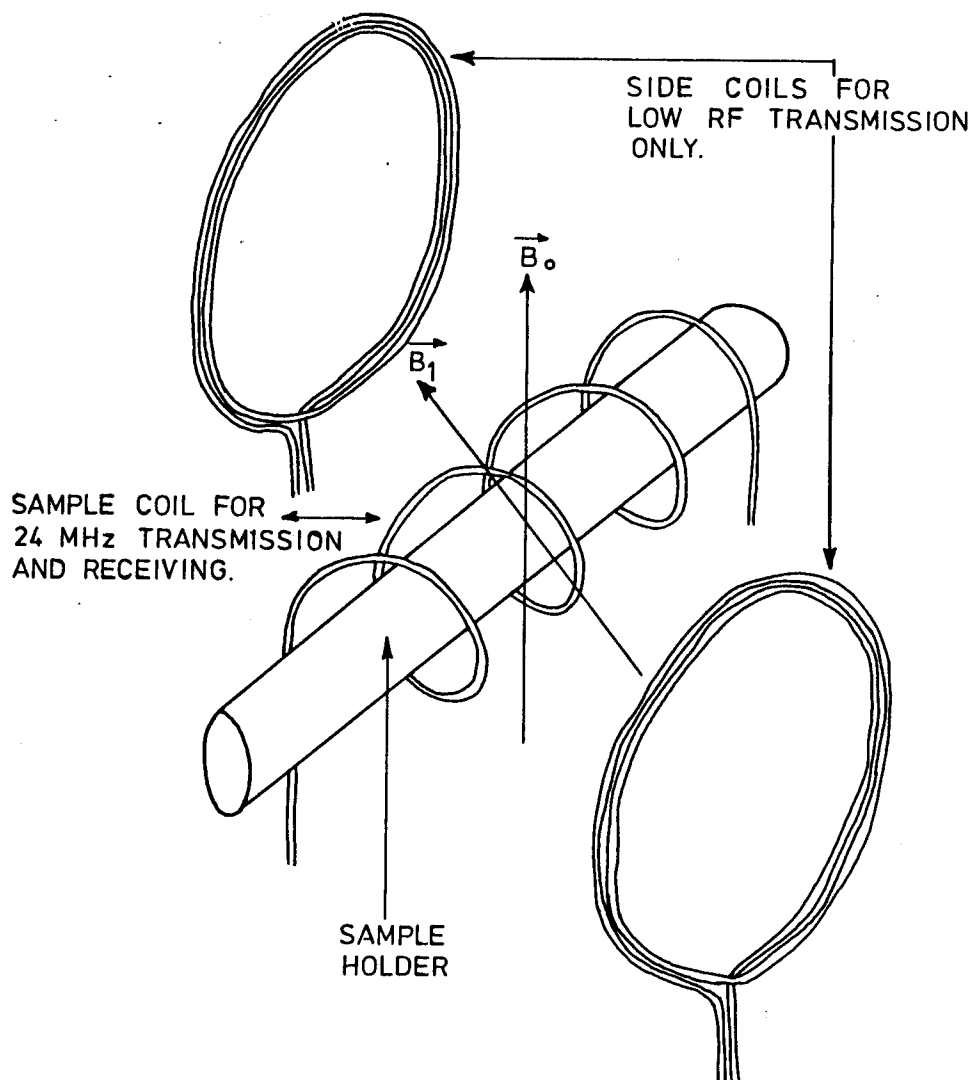


Fig. 3.7. The transmitter and receiver coils on a sample probe, showing the perpendicular fields $\vec{B}_0$ and $\vec{B}_1$.

It is technically difficult (though not intrinsically impossible) to produce a magnetic field rotating in two dimensional space and therefore, as shown in Fig. 3.7, the transitions are caused by a one dimensional alternating magnetic field $\vec{B}_1$, derived from two RF transmission coils. $\vec{B}_1$ is conventionally in the x direction and acts on the component of the spin magnetic moment in that direction. The whole set up of Fig. 3.7 is built at the end of a probe which is inserted into

the core of a superconducting magnet that produces the strong static field $\vec{B}_0$.

In a steady-state NMR experiment the spin system can absorb energy from the radio frequency radiation at a rate which depends on three factors viz:

1. the probability P , per unit time per spin of a transition being induced
2. the population difference between the spin states
3. the energy change appropriate to the transition.

A detailed quantum-mechanical treatment shows that

$$P \propto \gamma^2 B_1^2 g(\nu) \quad (3.38)$$

where $g(\nu)$ is a quantum mechanical energy factor.

In a strong static magnetic field, the population difference between the spin states depends on the temperature of the sample, the lower the temperature the greater the population difference and hence the greater the absorption signal. Since all experiments, in this case, were done at liquid helium temperature (4 K), this suggested the likelihood of a good signal.

3.1.7 The Rotating Frame of Reference

The total magnetic moment or magnetization, $\vec{M}$, of the

sample is the resultant of the individual magnetic moments $\vec{\mu}$ and it therefore has a resultant precession in a magnetic field. It is useful to refer the motion of the magnetization, not to the fixed coordinate system of the laboratory, but to a coordinate system that rotates about $\vec{B}_0$ in the same direction in which the nuclear moments precess. This coordinate system is often called the rotating frame of reference.

If

$$\vec{M} = M_x \mathbf{i} + M_y \mathbf{j} + M_z \mathbf{k} \quad (3.39)$$

then

$$\begin{aligned} \frac{d\vec{M}}{dt} = & \frac{\partial M_x}{\partial t} \mathbf{i} + M_x \frac{\partial \mathbf{i}}{\partial t} + \frac{\partial M_y}{\partial t} \mathbf{j} + M_y \frac{\partial \mathbf{j}}{\partial t} + \frac{\partial M_z}{\partial t} \mathbf{k} \\ & + M_z \frac{\partial \mathbf{k}}{\partial t} \end{aligned} \quad (3.40)$$

$$= \left(\frac{\partial M_x}{\partial t} \mathbf{i} + \frac{\partial M_y}{\partial t} \mathbf{j} + \frac{\partial M_z}{\partial t} \mathbf{k} \right) + \left(M_x \frac{\partial \mathbf{i}}{\partial t} + M_y \frac{\partial \mathbf{j}}{\partial t} + M_z \frac{\partial \mathbf{k}}{\partial t} \right) \quad (3.41)$$

but

$$\frac{\partial \mathbf{i}}{\partial t} = \vec{\omega} \times \mathbf{i}, \quad \frac{\partial \mathbf{j}}{\partial t} = \vec{\omega} \times \mathbf{j}, \quad \frac{\partial \mathbf{k}}{\partial t} = \vec{\omega} \times \mathbf{k} \quad (3.42)$$

where the magnitude of ω gives the angular frequency of rotation of the unit vectors, while the direction of ω is the axis about which the rotation occurs.

Therefore

$$\left(\frac{d\vec{M}}{dt} \right)_{\text{fixed}} = \frac{\partial \vec{M}}{\partial t} + \vec{\omega} \times (M_x \mathbf{i} + M_y \mathbf{j} + M_z \mathbf{k}) \quad (3.43)$$

$$= \left(\frac{d\vec{M}}{dt} \right)_{\text{rot}} + \vec{\omega} \times \vec{M} \quad (3.43)$$

In first equation above, the total derivative represents the overall motion of $\vec{M}$ in the fixed laboratory frame, whereas the



partial derivative represents the explicit dependence of $\vec{M}$ on time in the rotating frame.

But since

$$\left(\frac{d\vec{M}}{dt}\right)_{\text{fixed}} = \gamma \vec{M} \times \vec{B} \quad (3.45)$$

therefore

$$\left(\frac{d\vec{M}}{dt}\right)_{\text{rot}} = \gamma \vec{M} \times \vec{B} - \vec{\omega} \times \vec{M} \quad (3.46)$$

$$= \gamma \vec{M} \times \left(\vec{B} + \frac{\vec{\omega}}{\gamma}\right) \quad (3.47)$$

The term $\vec{\omega} / \gamma$ has the dimensions of a magnetic field and can be considered a fictitious field that arises from the effect of the rotation. Alternatively we can write the equation in terms of an effective field

$$\left(\frac{d\vec{M}}{dt}\right)_{\text{rot}} = \gamma \vec{M} \times \vec{B}_{\text{eff}} \quad (3.48)$$

$$\vec{B}_{\text{eff}} = \vec{B} + \frac{\vec{\omega}}{\gamma} \quad (3.49)$$

Thus the ordinary equation of motion applicable in the laboratory frame is valid in the rotating frame as well, except that in the rotating frame the magnetization appears to be precessing about an effective field $\vec{B}_{\text{eff}}$.

The frame of most interest is one that rotates at about the same frequency of the applied RF field $\vec{B}_1$ since this choice of rotating frame not only results in the simplest treatment but, gives the resonance condition if it also rotates at the Larmor frequency.

8 Magnetization in the Rotating Frame

With the aid of the rotating frame we can explain just how the magnetization behaves during certain types of NMR experiments and see more explicitly the effects of relaxation. Assuming the only field present is $\vec{B}_0$ along the z axis, taking a frame rotating at an angular frequency

$$\vec{\omega} = -\gamma \vec{B}_0 \quad (\text{the Larmor frequency})$$

and

$$\left(\frac{d\vec{M}}{dt_{\text{rot}}} \right) = 0 \quad (3.50)$$

therefore $\vec{M}$ is invariant with time in this rotating frame.

If the field $\vec{B}_1$ is applied in the xy plane and rotates in the laboratory frame at ω rad sec⁻¹. Then in the frame rotating at ω

$$\vec{B}_{\text{eff}} = \vec{B}_0 + \frac{\vec{\omega}}{\gamma} + \vec{B}_1 \quad (3.52)$$

at resonance

$$\vec{\omega} = -\gamma \vec{B}_0$$

therefore

$$\vec{B}_{\text{eff}} = \vec{B}_1 \quad (3.53)$$

Since at resonance B_1 rotates at the same frequency as the frame we can arbitrarily assign it along the rotating x axis designated x' axis.

$$\text{From } \left(\frac{d\vec{M}}{dt_{\text{rot}}} \right) = \gamma \vec{M} \times \vec{B}_1 \quad (3.54)$$

$\vec{M}$ precesses about the x' axis in the rotating frame at resonance.

In a time t (secs) the angle θ through which $\vec{M}$ precesses is given by

$$\theta = \omega' t \quad (3.55)$$

$$= \gamma B_1 t. \quad (3.56)$$

If B_1 is applied for the short period of time

$$t \frac{\pi}{2} = \left(\frac{1}{\gamma B_1} \right) \frac{\pi}{2} \quad (3.57)$$

$\vec{M}$ precesses or is tipped by 90° as shown in Fig. 3.8

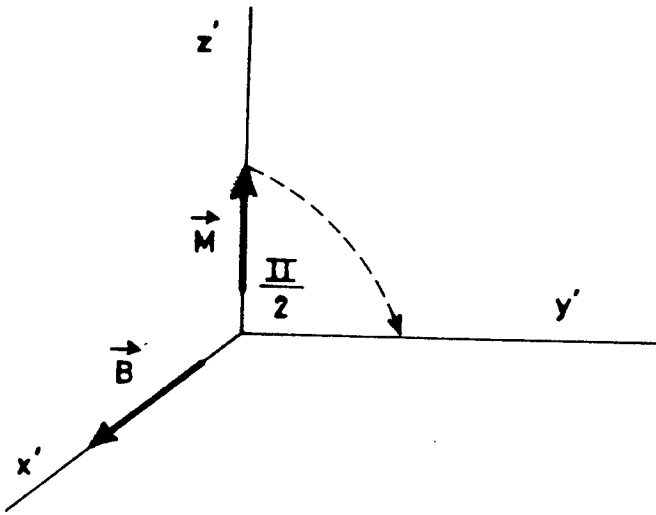


Fig. 3.8 The 90° tipping of magnetization $\vec{M}$ by $\vec{B}_1$ applied for a period $t\pi/2$.

This irradiation (the presence of $\vec{B}_1$ along x' axis) over the short interval $t\pi/2$ is referred to as a 90° pulse, similarly we could have a 180° pulse.

Before the pulse, there is no phase coherence of the moments in the $x'y'$ plane and hence no component of $\vec{M}$ in this plane as shown in Fig. 3.9 (a).

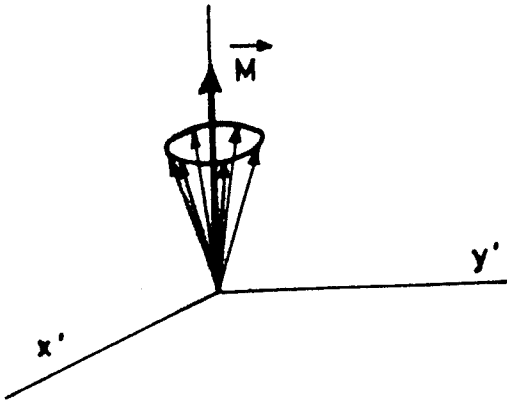


Fig. 3.9(a). The situation before a pulse with no spin phase coherence in $x'y'$ plane hence no component of magnetization in this plane.

As a result of the pulse the moments lie in such an orientation that $\vec{M}$ is generated along y' as shown in Fig. 3.9 (b).

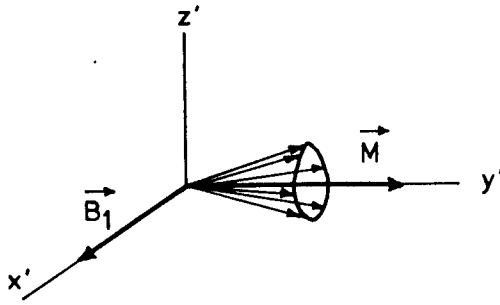


Fig. 3.9 (b). The situation just after a 90° pulse with $\vec{M}$ along the y' axis.

After B_1 is turned off, because of the natural processes that cause nuclei to exchange energy with each other, the moments begin to spread out in the $x' y'$ plane as shown in Fig. 3.9 (c). Thus y' component of magnetization $M_{y'}$ decays with a time constant T_2 .

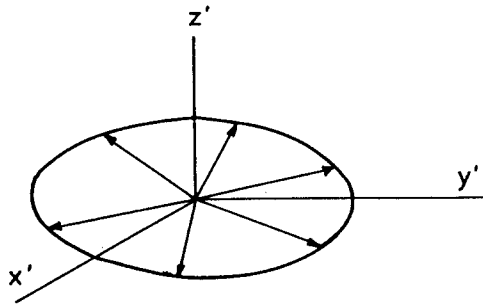


Fig 3.9(c). The spreading out of spin in the $x' y'$ plane resulting in the decay of $M_{y'}$ in a time T_2 .

T_2 here is the same spin-spin relaxation time referred to in connection with the block equations. However, since the magnetic field is not perfectly homogeneous, nuclei in different portions of the sample experience slightly different

values of B_0 , hence precess at slightly different frequencies both faster and slower than the rotating frame. This process too causes M_y to diminish, hence making T_2 shorter, since it causes the nuclei to precess out of phase with each other.

Spin-lattice relaxation also occurs as the nuclear moments lose energy to their surroundings and thus relax, or tip back, towards the z' axis, as indicated in Fig. 3.9 (a). Therefore M_z relaxes towards its equilibrium value of M_0 with time constant T_1 as explained in connection with the block equations. In general

$$T_2 \leq T_1 \quad (3.58)$$

9 Free Induction Decay (FID)

Just after a single 90° pulse, $\vec{M}$ lies entirely along the y' axis as indicated in Fig. 3.9 (b). As transverse relaxation occurs, the change in magnetization in the $x' y'$ plane induces a signal in the receiver coil which as shown in Fig. 3.7, lies in the fixed $x y$ plane. The $x' y'$ plane being equivalent to the $x y$ plane since the z and z' axes coincide. The detector responds to the magnetization which has a fixed phase relation to $\vec{B}_1$ hence which occurs along a fixed axis in the rotating frame in this case the positive y' axis. This is done by phase sensitive detection referenced to the RF. Thus although detection of the signal occurs when no RF is directly applied (after the pulse), the RF reference is applied to the detector

continuously. The detected signal is a pure exponential decay shown in Fig. 3.10(b), this is called the free induction signal or FID signal, since the nuclei precess freely without an applied RF. Since the induced signal depends on the rate of change or time derivative of magnetization, the original magnetization along the y' axis just after the pulse can be obtained by integration of the FID signal. This magnetization along the y' -axis just after the pulse is approximately equal to the magnetization along the z -axis before the pulse. This method of measuring the recovered magnetization is employed in NMR field cycling as is illustrated in chapter 4. It is assumed here that the length of the pulse is short relative to T_1 and T_2 .

Figure 3.10(a) shows a representation of the 90° pulse assuming that the RF is turned on and off so fast that the envelope during irradiation has the shape of a single ripple of a square wave.

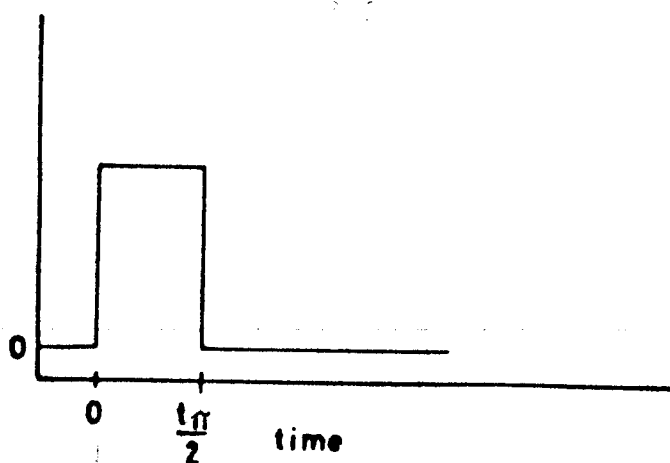


Fig. 3.10(a). The representation of a 90° pulse, assuming a square wave envelope.

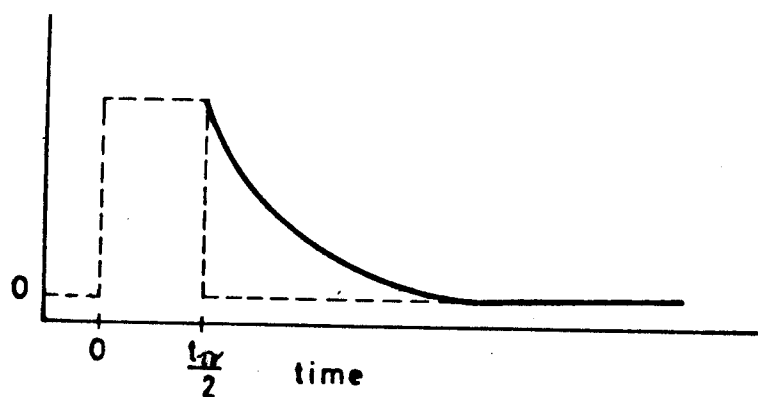


Fig. 3.10(b). The FID signal after a 90° pulse showing the pure exponential nature.

The exponential nature of the FID confirms the assumption made in the derivation of the Bloch equations in section 3.1.5 that the relaxation or decay processes could be treated as first-order i.e. could be represented by first order

differential equations, with decay constants T_2 and T_1 , which when solved would of course give exponentials. The FID only confirms the T_2 case however.

If the RF is slightly different from the Larmor frequency of the nuclei, considering the frame rotating at the radio frequency, then immediately after the 90° pulse $\vec{M}$ can be taken as lying along the y' axis. However, $\vec{M}$ now rotates relative to the rotating frame, and the detector displays not only the exponentially decaying value of M_{xy} but also the interference effects of M_{xy} and the reference frequency alternately coming in and out of phase with each other, a typical response is shown in Fig. 3.10(c).

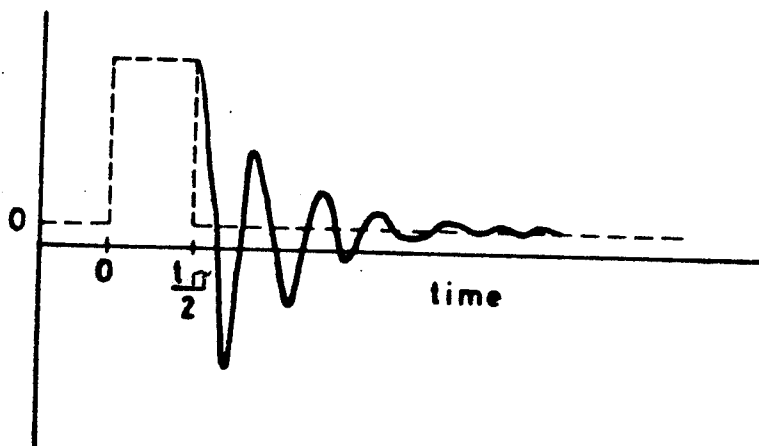


Fig. 3.10(c). A typical off-resonance induction decay response.

The shape of the FID is directly related to Eq. (3.36) for $B_1 = 0$ i.e. free induction. However the integration of the block equation, Eq. (3.31) or the other form of the equation, Eq. (3.37) for $B_1 = 0$ is of more practical importance although not directly related to the FID. From those two equations if $B_1 = 0$ then

$$\frac{dM_z}{dt} = - \frac{M_z - M_0}{T_1} \quad (3.59)$$

Integrating this equation and putting an integration constant such that $M_z = M_0$ as $t \rightarrow \infty$ or $M_z = 0$ at $t = 0$, we get

$$M_z(t) = M_0(1 - \exp(-t/T_1)) \quad (3.60)$$

This expression is used in section 4.4 in relation to the experimental determination of T_1 . The boundary conditions considered here have a specific meaning in that section.

Relaxation mechanisms

In this case, by relaxation mechanisms is meant the mechanisms or interactions by which a system of nuclear spins relaxes when put in a large magnetic field once perturbed from its equilibrium state.

The NMR technique used in this investigation, as mentioned in section 1.4, is NMR field cycling. This is described in detail in section 4.3. Referring to Fig. 4.2 in that section, during the relaxation period of field cycling i.e. at the field B_r , the spins preferably align themselves along the external field but energy changes produced by interactions constituting the relaxation mechanisms disturb them from this state.

It is the dependence of the recovered magnetization on the relaxation field B_r or on the frequency of any irradiation during relaxation that helps to determine the particular relaxation mechanisms involved, hence giving better understanding of the structure and other properties of the sample being studied.

The most prominent relaxation mechanism is the spin-lattice relaxation in which the spins directly lose energy to the lattice. This is explained in detail in terms of the concept of spin temperature and the density matrix in chapter 6.

There are many interactions of interest, one example of which is the interaction termed the dipole-dipole interaction. The two

interactions found to be of greatest relevance here are the quadrupolar interaction and the hyperfine interaction.

In Eq. (3.1) of section 3.1.1 the symbol $\vec{P}$ was used to represent the intrinsic spin angular momentum of any particle in general. This symbol was carried on, as can be seen from Eq. (3.2), to represent the specific case of nuclear spin angular momentum. It will however become necessary in subsequent sections to distinguish between the nuclear spin angular momentum operator which will have the symbol, $\vec{I}$, and the electron spin angular momentum operator which will be represented by $\vec{S}$. The nuclear and electron spin raising and lowering operators are symbolized as I_+ , I_- and S_+ , S_- respectively.

3.2.1. The Quadrupolar Interaction

A charged lattice site at some point "A", like a site occupied by an impurity ion will give out a coulomb electric field and hence a field gradient which when assumed spherically symmetric, is given by

$$eq(r) = \frac{e(1 - \sigma_A)}{2 \pi \epsilon_0 \epsilon_r r^3} \quad (3.61)$$

$(1 - \sigma_A)$ is the Sternheimer antishielding factor which takes into account the electron shielding of the nuclear charge.

ϵ_0 is the permittivity of free space

ϵ_r is the dielectric constant

An electric quadrupole, though unaffected directly by an electric field, interacts with an electric field gradient.

Therefore any nucleus possessing a quadrupole moment and lying at some point "B" within the influence of the field gradient will interact with it.

The hamiltonian of this quadrupolar interaction is

$$\begin{aligned} \mathcal{H} = & \frac{e^2 q(d_o) Q_B (1 - \sigma_B)}{4I(2I - 1)} \{ \frac{1}{2} (3 \cos^2 \theta_B - 1) (3I_z^2 - I(I + 1)) \\ & + \frac{3}{2} \sin \theta_B \cos \theta_B (I_z (I_+ + I_-) + (I_+ + I_-) I_z) \\ & + \frac{3}{2} \sin^2 \theta_B (I_+^2 + I_-^2) \} \quad \begin{array}{l} \text{(Abragam 1983)} \\ \text{(3.62)} \end{array} \end{aligned}$$

where

d_o is the distance from A to B

$eq(d_o)$, the electric field gradient at B due to the charge at A.

Q_B , the nuclear quadrupole moment of the nucleus at B.

θ_B , the angle between the field B_o and the A - B bond.

$(1 - \sigma_B)$, the sternheimer antishielding factor, designed to take care of the distortion from spherical symmetry of the core electrons at B caused by the charge at A.

3.2.2 The Hyperfine Interaction

Hyperfine interaction is basically due to magnetic coupling between electrons and nuclei. As long as the nuclear and electron moments $\vec{\mu}_n$ and $\vec{\mu}_e$ are far enough apart, we expect their interaction to be that of a pair of magnetic dipoles, the Hamiltonian being

$$= \frac{\vec{\mu}_e \cdot \vec{\mu}_n}{r^3} - \frac{3(\vec{\mu}_e \cdot \vec{r})(\vec{\mu}_n \cdot \vec{r})}{r^5} \quad (3.63)$$

(C.G.S)

where $\vec{r}$ is the radius vector from the nucleus to the electron.

The appropriate quantum mechanical expression is obtained by using

$$\vec{\mu} = \gamma h \vec{I} \quad (3.64)$$

After expanding the scalar products and expressing in terms of raising and lowering operators, the hamiltonian can be written in the form

$$= \frac{\gamma_e \gamma_n h^2}{r^3} (A+B+C+D+E+F) \quad (3.65)$$

where the terms A to F, expressed in spherical co-ordinates, can be found in any standard N M R text book. ^(6.3)

Eq. (3.65) is best suited for expressing the hyperfine interaction between an electron and a nucleus of another atom.

Now consider the hyperfine interaction between an electron and a nucleus of the same atom. If $\mathcal{H}$ is averaged over the electron wave function $U(r)$, the effective interaction energy in the s - state is

$$E_0 = - \frac{8\pi}{3} \vec{\mu}_e \cdot \vec{\mu}_n U^2(0) \quad (3.66)$$

where $U(0)$ is the electron wave function in the s-state.

This ground state coupling energy can be expressed in terms of a Hamiltonian for the interaction as

$$\mathcal{H}_0 = - \frac{8\pi}{3} \vec{\mu}_e \cdot \vec{\mu}_n \delta(\vec{r}) \quad (3.67)$$

where $\delta(\vec{r})$ is the dirac delta function.

using $\vec{\mu}_e = -\gamma_e \hbar \vec{S}$ and $\vec{\mu}_n = \gamma_n \hbar \vec{I}$

$$\mathcal{H}_0 = \frac{8\pi}{3} \gamma_e \gamma_n \hbar^2 \vec{I} \cdot \vec{S} \delta(\vec{r}) \quad (3.68)$$

For non s-states

$$\mathcal{H} = \frac{\gamma_e \gamma_n \hbar^2}{r^3} \left[\frac{3(\vec{I} \cdot \vec{r})(\vec{S} \cdot \vec{r})}{r^2} - \vec{I} \cdot \vec{S} \right] \quad (3.69)$$

If $\Psi(\vec{r})$ is taken as the general wave function, then the general Hamiltonian will be the sum of the s-state Hamiltonian and the non s-state Hamiltonian averaged over this general wave function, i.e.

$$\mathcal{H} = \int |\Psi(\vec{r})|^2 \left\{ \frac{8\pi}{3} \gamma_e \gamma_n \hbar^2 \vec{I} \cdot \vec{S} \delta(\vec{r}) + \frac{\gamma_e \gamma_n \hbar^2}{r^3} \left(\frac{3(\vec{I} \cdot \vec{r})(\vec{S} \cdot \vec{r})}{r^2} - \vec{I} \cdot \vec{S} \right) \right\} d\tau \quad (3.70)$$

This hamiltonian will clearly be linear in the spin variables I_x, I_y, I_z, S_x, S_y and S_z , i.e. in general

$$\mathcal{H} = A_x I_x S_x + A_y S_y I_y + A_z I_z S_z \quad (3.71)$$

or

$$\mathcal{H} = \vec{S} \cdot \vec{A} \cdot \vec{I} \quad (3.72)$$

where $\vec{A}$ is referred to as the hyperfine tensor.

Eq. (3.72) is generally valid as an expression either for the hyperfine interaction between an electron and a nucleus of another atom or with the nucleus of the same atom, the difference lies in the way of calculating $\vec{A}$.

Double Irradiation

As mentioned in section 3.2, it is the dependence of the spectral variation of the recovered magnetization on either the field B_r (Section 4.3) or the frequency of any irradiation during relaxation (at the field B_r) that helps to determine the particular relaxation mechanisms involved. The process of irradiation during relaxation is termed double irradiation. The radiation in this case is generally of low frequency. This is all explained in greater detail in the preceeding chapters.

Certain simple theoretical implications are inherent in the process of double irradiation that are not entirely obvious. As an

example, for spin $\frac{1}{2}$ nuclei like phosphorous, if the number of nuclei in the two m_I states $+\frac{1}{2}$ and $-\frac{1}{2}$ are specified by N_+ and N_- respectively the total number of spins

$$N = N_+ + N_- \quad (3.75)$$

is constant. Application of an alternating field will cause a change in N_+ and N_- as a result of the transitions induced. The two states are shown in Fig. 3.11.

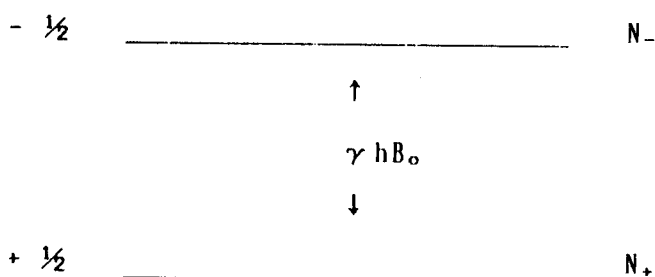


Fig. 3.11. The two energy levels of spin $\frac{1}{2}$ nuclei with separation $\gamma h B_0$ and occupied by N_- and N_+ nuclei respectively.

If the probability per second of inducing the transition of a spin with $m_I = +\frac{1}{2}$ to a state $m_I = -\frac{1}{2}$ is denoted $W_{(+)\rightarrow(-)}$, and that of the reverse transition by $W_{(-)\rightarrow(+)}$, the differential equation for the change of population N_+ can be written as

$$\frac{dN_+}{dt} = N_- W_{(-)\rightarrow(+)} - N_+ W_{(+)\rightarrow(-)} \quad (3.76)$$

From time-dependent perturbation theory, the probability per second $P_{a\rightarrow b}$, that an interaction $V(t)$ induces a transition from a state

(a) with energy E_a to a state (b) with energy E_b is

$$P_{a \rightarrow b} = \frac{2\pi}{h} | \langle b | v | a \rangle |^2 \delta(E_a - E_b - \hbar\omega) \quad (3.77)$$

(An expression equivalent to this can be arrived at through density matrix considerations explained in section 6.2)

It is $V(t)$ that takes into account any interaction mechanisms affecting the system.

Since

$$| \langle a | v | b \rangle |^2 = | \langle b | v | a \rangle |^2 \quad (3.78)$$

it follows that

$$P_{a \rightarrow b} = P_{b \rightarrow a} \quad (3.79)$$

therefore

$$W_{(+)} \rightarrow (-) = W_{(-)} \rightarrow (+) = W \quad (3.80)$$

Eq. (3.76) becomes

$$\frac{dN_+}{dt} = W(N_- - N_+) \quad (3.81)$$

or

$$\frac{dn}{dt} = -2Wn \quad (3.82)$$

where n is the population difference ($n = N_+ - N_-$). The solution of this differential equation is

$$n = n(0) e^{-2\omega t} \quad (3.83)$$

where $n(0)$ is the population difference at $t = 0$. It is clear that if there was an initial population difference, it would eventually disappear under the action of the induced transitions. This situation is referred to as saturation, needless to mention that the total magnetization is zero in this state. This is of course undesirable if one is to obtain a spectrum of radiation frequency against recovered magnetization. Therefore care has to be taken in selecting the length of time of irradiation during the relaxation period. Saturation does however find a useful application in field cycling as explained in section 4.3.

The rate of energy absorption is given by the difference between the energy absorbed by spins, per second, that go from the lower to the upper energy level and that emitted by spins that drop from the upper to the lower energy level;

$$\frac{dE}{dt} = N_+ \hbar \omega - N_- \hbar \omega = \hbar \omega N_n \quad (3.84)$$

Since n approaches zero as ω gets very large, it follows that the resonant absorption of energy would eventually stop.

Even when the irradiation is not set at the resonant or Larmor frequency, we expect to observe a certain small amount of absorption because when a sine wave of frequency ~~say~~ f Hz, is turned on for a short period of time ~~say~~ τ sec, its fourier transform reveals that we not only obtain a frequency component at the frequency f but also components of frequency over the range

$(f \pm \tau^{-1})\text{Hz}$. Hence the shorter the time τ the wider the range. It is the fourier component at the nuclear resonance frequency that is responsible for the absorption. Therefore, where as it is undesirable to choose too long a period of irradiation for fear

of saturation, it should be long enough to give a narrow enough range of fourier components in the frequency domain. This ensure narrow absorption peaks in the spectrum.

CHAPTER FOUR

EXPERIMENTAL DETAIL

4.1 The Samples

The samples used were obtained from large ingots of substrate material. They were single crystal samples measuring 10mm x 5mm x 0.5mm.

4.2 Measurement Technique

Fig. 4.1 shows a block diagram of the instrumentation used for the investigation. This is a type of pulsed NMR spectrometer as opposed to the continuous wave (CW) spectrometer. The pulse NMR receiver system is able to withstand large voltages and recover very quickly from overload, in about 10 micro seconds or faster. The sample circuitry in this type of spectrometer is not only able to handle large RF voltages, between 100-1000 Volts, of very short duration (about 10 micro seconds), but is also able to process the weak nuclear signal in such a way that a high sensitivity is achieved.

4.2.1 The Transmitter System

The transmitter system contains a very stable RF crystal oscillator which runs continuously, this is in the continuous wave mode, at a high frequency of 24 MHz. The gate is an RF switch which is open in the presence of a d c pulse signal from the monostable pulse generator, which in turn, is controlled by the BBC microcomputer. The gate

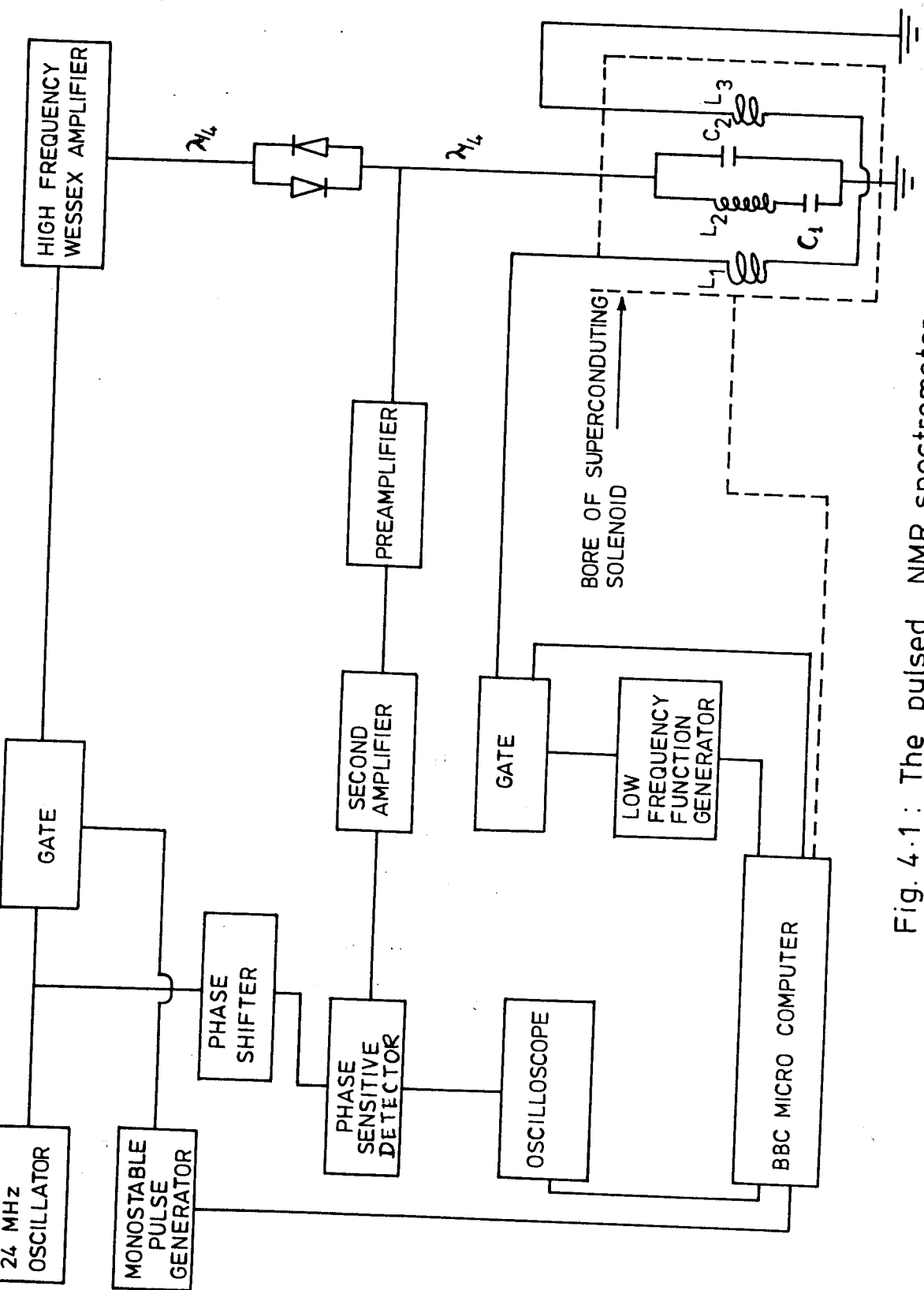


Fig. 4.1 : The pulsed NMR spectrometer.

is closed otherwise. The RF pulses that pass through the gate are amplified by the high frequency Wessex amplifier which is coupled to the sample probe. The amplifier is capable of delivering short (between 1-10 microseconds long) and powerful (between 100-1000 volts) bursts of RF power in such a way that the rise and fall times of the envelope of the RF pulse are short compared with the width.

Since phase sensitive detection is used, the high frequency oscillator also provides a reference output signal. It is of great importance that none of this signal leaks out into the laboratory environment and into the sample coil because neither the amplitude nor the phase of this stray signal can be controlled, resulting in many experimental difficulties in the receiver system.

4.2.2 The Sample Probe

The sample is contained in the RF coil L_2 , which is tuned with capacitors C_1 and C_2 at the Larmor frequency. This is coupled both to the transmitter system and the receiver-detector system. L_2 in this case is used both to transmit $\vec{B}_1$ to the sample, and to receive the nuclear signal or FID after the pulse. $\vec{B}_1$ at the sample must be large compared with the width of the spectrum being studied, which means a $\vec{B}_1$ in the range of 10 to several hundred gauss.

The RF coils L_1 and L_3 are arranged orthogonal to L_2 and are used to provide a $\vec{B}_1$ irradiation at lower frequencies (between 0-800 kHz). Since L_1 and L_3 are orthogonal to L_2 , this $\vec{B}_1$ is in the same plane as that provided by L_2 i.e. in the $x' y'$ plane of the rotating frame. Irradiation by L_1 and L_2 is referred to as double irradiation. This is also computer controlled as can be seen from the figure.

The back-to-back or cross-coupled diodes and quarter-wave ($\lambda/4$) sections of the RF cable are used to optimize the sample circuitry for both intense signals of short duration (the pulse) and for very weak slowly decaying signals (the FID signals).

The sample probe fits into the bore of a superconducting solenoid that provides the strong d c magnetic field $\vec{B}_0$ which is orthogonal to $\vec{B}_1$. This field is very homogeneous and its intensity is computer controlled.

4.2.3 The receiver detector system

The sample must be efficiently coupled to the receiver such that the maximum signal to noise ratio (S/N) is obtained from the nuclear induction signal. The pre amplifier and the sample coil configuration determine the signal to noise ratio of the entire system.

Both the preamplifier and the receiver should have a linear response over a wide voltage range. Since phase sensitive detection is used, no phase information is lost. The phase shifter is used to vary the phase of the reference signal and the detector discriminates heavily against any signal which does not have the same phase and frequency as the reference signal. The major disadvantage of this detection mechanism is the difficulty of eliminating the RF signal leakage at the resonance frequency.

Although its not shown in figure 4.1 (for simplicity) the monostable pulse generator also supplies pulses for triggering the oscilloscope. A triggering pulse is sent to the oscilloscope after any one or series of pulses which control the transmitter depending on when recording is required, this being computer controlled. The oscilloscope is of the digital storage variety such that the FID signal can be stored long enough to be integrated by the computer for a determination of the magnetisation.

Finally, the whole system takes advantage of the time stability of the BBC microcomputer by allowing the computer to regulate the length, spacing and repetition rate of the RF pulse sequences.

4.3 Field Cycling

Field cycling is a technique suitable for the observation of sample response to RF irradiation, laser irradiation and other special effects in a low magnetic field range. The significance of this particular reference to the low field region is made clear at the end of this section.

This cycle begins with a comb of resonant RF pulses at a field B_{NMR} referred to as the NMR field (resonant pulses in the sense that the spectrometer frequency of 24 MHz, which is the frequency of the RF signal within the pulse envelope, is the Larmor frequency at the field B_{NMR} .) These serve to saturate the NMR signal (to destroy the magnetization in the sample) and ensure that the starting conditions are always the same for each cycle.

The sample is then quickly brought down to the starting relaxation field, B_r , of a range to be studied. The nuclear spin system is allowed to recover for a short length of time at this field and finally the field is returned to the NMR field value, where a single 90° pulse, as described in section 3.1.9, is used to measure the amount of magnetization recovered. The cycle is then repeated and a range of fields B_r is scanned to produce a spectrum of the recovered magnetization as a function of the relaxation field.

Each cycle or the whole experiment is preceded by a period of high preparation field, B_{prep} , which simply generates more magnetization or "cools" all the nuclear spins of different species in the sample.

The significance of this becomes apparent in chapter 5.

The preparation time, t_{prep} , was typically set from 2 to 5 minutes, which was long enough to generate a considerable amount of magnetization in the sample. The switching time, t_{switch} , was kept short to avoid relaxation during the switch. This was from 8 to 15 seconds depending on the extent of the difference between the fields B_{NMR} and B_r . The relaxation time, t_{relax} , was of course kept short compared to the spin lattice relaxation time to avoid measuring equilibrium magnetization throughout the experiment. This was set at anything from zero to 2.5 seconds. The sample was kept at liquid helium temperature throughout the investigation. The signal to noise ratio varied from experiment to experiment but was roughly in the range of 100 to 1 which was reasonably good for this particular investigation. The magnet stability was better than 1 in 10^5 per hour and the field reproducibility following switching was also better than 1 in 10^5 .

RF excitation may be introduced during the relaxation stage of the cycle as indicated at B_r , in Fig. 4.2. This is referred to as double irradiation as explained in section 3.3.

Frequency scans were also obtained in which the relaxation field, B_r , was kept constant for each cycle, while the RF double irradiation frequency was varied to cover the spectral frequency range of interest.

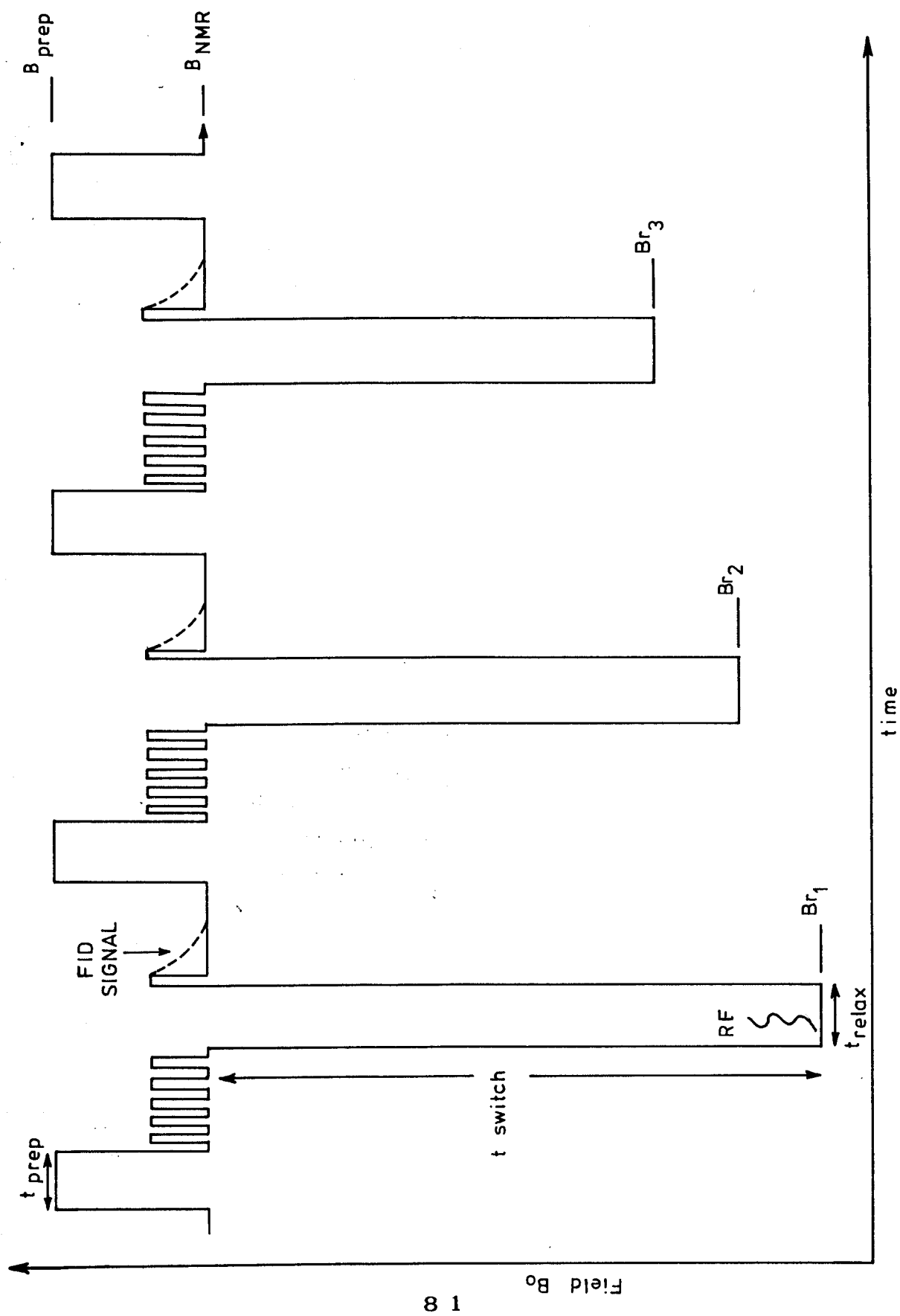


Fig. 4.2: The field cycling sequence.

As stated earlier, the measurement of recovered magnetization is done at the field B_{NMR} using a single resonant 90° pulse. This pulse consists of a short burst of 24 MHz irradiation and the field B_{NMR} is the field for which 24 MHz is the Larmor frequency for the particular nuclear species being studied. Therefore depending on how one sets the value of B_{NMR} , it is possible to measure the "partial" recovered magnetizations in the nuclei of different species, more or less independently, provided their Larmor frequencies are well spaced.

Furthermore, where as all spins of different nuclear species are "cooled" during preparation at the field B_{prep} , the pulses used for saturation after the preparation are resonant pulses for one particular nuclear species, hence they only saturate nuclear spins of that particular species while the rest remain cool. This point reflects the importance of the preparation, in that these "cool" spins could then act as a heat sink for the saturated or "hot" spins during relaxation at the field B_r . And should the "hot" spins appear to lose energy to these "cool" spins faster than they do to the reservoir lattice (a phenomenon which is loosely referred to as cross-relaxation in the next chapter) then some form of coupling between the "hot" and "cool" nuclear spins would be suggested. This is explained in more depth in terms of spin temperature in section 6.3.

Although as discussed earlier, it can be said that the different nuclear species in a sample can be observed independently using

field cycling, this should not be taken to imply that the spins of different species are not coupled by any interaction mechanism.

Field cycling is suitable for investigation in the low field region as indicated at the beginning of this section. The advantage being that although the interaction mechanisms (which are effectively relaxation mechanisms) being studied take effect during relaxation at the low field B_r , the actual measurements are carried out at the high fields B_{NMR} , hence effectively amplifying the signal.

1.4 Experimental Determination of Spin-Lattice Relaxation Time, T_1

A procedure similar to that used in field cycling was employed for the experimental determination of the values of T_1 . During the relaxation period of field cycling, Eq. (3.60) applies because as in section 3.1.9. we have here a situation where $B_1 = 0$, as long as there is no double irradiation. Furthermore we would also assume in this case that $M_z = M_0$ as $t \rightarrow \infty$ and of course $M_z = 0$ at $t = 0$ i.e. after saturation.

Going through the procedure of field cycling but this time keeping the relaxation field B_r constant, We could measure the

recovered magnetization as a function of the time within which the system is allowed to relax at the field B_r , i.e. the relaxation time, T_1 . This is done for a series of values of t to produce a graph of M_z versus t . This graph is then extrapolated to obtain the "saturation value" of $M_z(t)$ for very large values of t , i.e. the value

of M_o .

From Eq. (3.60) it is clear that

$$\ln \frac{M_o - M_z(t)}{M_o} = -\frac{1}{T_1} t \quad (4.1)$$

therefore using the value of M_o obtained from the extrapolation explained above and taking the values of $M_z(t)$ and t obtained, the straight line graph of $\ln \frac{M_o - M_z(t)}{M_o}$ versus t can be

obtained, from the gradient of which the value of T_1 is evaluated.

CHAPTER FIVE

EXPERIMENTAL RESULTS AND DISCUSSION

Results of T_1 Measurements

Table 5.1 shows values of the spin-lattice relaxation time T_1 measured at various angles of orientation of the magnetic field B_1 . This being relative to the (100) plane of the iron doped indium phosphide crystal. The experimental method used to measure T_1 was explained in section 4.4. This table refers to InP : Fe which has a cubic structure, hence the T_1 values were almost symmetric between the angles $0^\circ - 45^\circ$ and $45^\circ - 90^\circ$. Despite the large values of error, it can conclusively be said that the table shows an increase in length of T_1 with the angle.

Table 5.1. The spin lattice relaxation time T_1 , measured as a function of the angle between the [100] plane of the crystal lattice and the magnetic field B_0 .

ANGLE OF ORIENTATION (degrees)	T_1 (Seconds)	LEAST SQUARE FIT ERROR (Seconds)
0	549	± 67
7	669	± 189
15	724	± 208
22	749	± 151
30	773	± 109
37	801	± 20
45	868	± 22

The error was obtained from the standard deviation in the Least Square Fit approximation of the experimental straight line $\ln [(M_0 - M(t))/M_0]$ versus time described in section 4.4. All symbols are explained in that section.

This error is evidently very large, which reflects the difficulty in obtaining accurate experimental values of long T_1 . This difficulty is due to the electrical noise in the system despite the 1 in 10^5 per hour field stability and a good field reproducibility.

Field Cycling Results (without double irradiation)

5.2.1 Cross-relaxation in InP : Fe

Fig. 5.1 shows a phosphorous field scan of InP : Fe without double irradiation. The spectrum shows a distinct narrow peak in the low field region. This peak is very reproducible, as can be seen in the more sensitive scan of Fig. 5.2. The peak was seen to be around 50 Gauss for all angles of orientation (of the sample) considered. For all the spectra in this chapter, the angle of orientation is 0° unless indicated otherwise.

Fig. 5.3 and 5.4 show spectra obtained at angles of orientation 15° and 30° respectively. The peak diminishes rapidly in intensity with increased angle probably due to the increased high field spin lattice relaxation time.

The peak is thought to be either due to quadrupolar interaction around the impurity atoms or hyperfine interaction, both of which are illustrated later, on a quantitative basis. This suggestion is based on the fact that the peak should be due to coupling between the phosphorous and indium energy levels. At the start of a cycle, the Indium (say) is cold and the phosphorous hot, following saturation. Relaxation at a field where the transition energies are the same causes magnetisation transfer and hence the peak, this is proved by double saturation which is discussed later.

Sun, 15 Jan 19A7.00:28:20 ; 1.FCDAT,INP-155
RELAXATION TIME 1 secs
SWITCHING TIME 8 secs
PREPARATION TIME 2.5 mins
PREPARATION FIELD 250

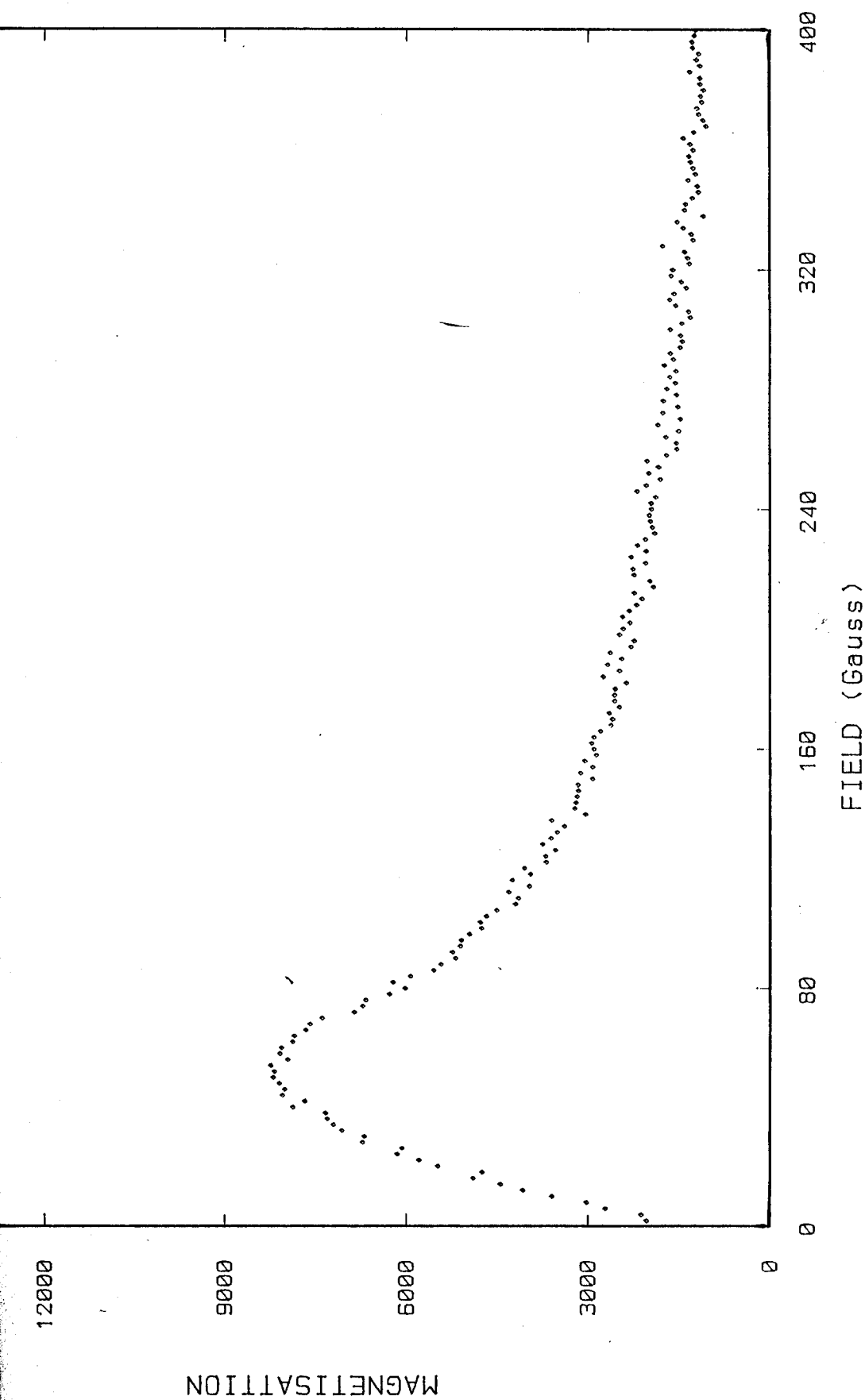


Fig.5.1 Phosphorus field scan of InP: Fe without double-irradiation. Magnetization being in arbitrary units.

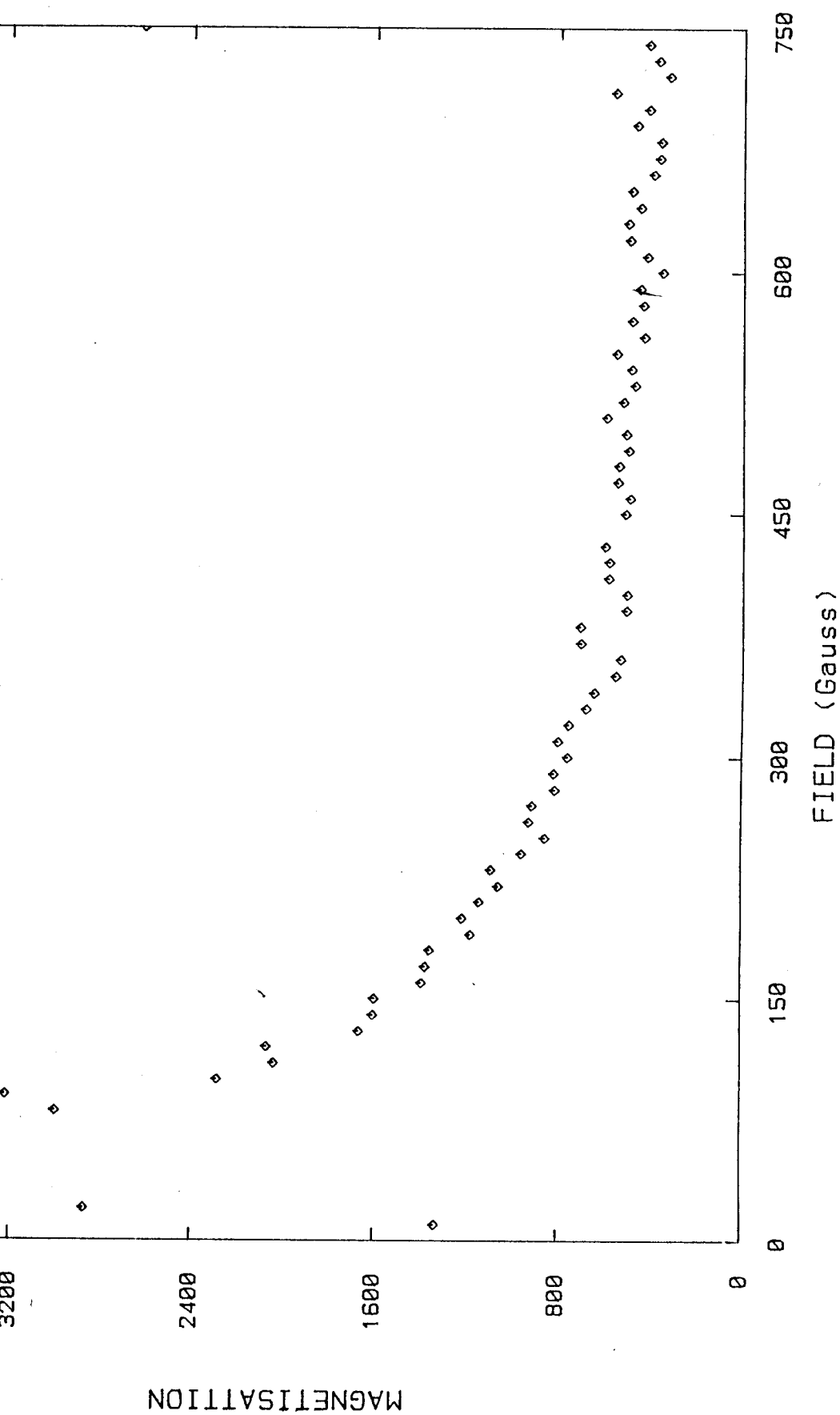


Fig. 5.2. Phosphorus field scan of InP:Fe without double-irradiation.

Sat, 27 Feb 1988.08:35:56 ; 1.FCDAT.INP-117
RELAXATION TIME 2 secs
SWITCHING TIME 8 secs
PREPARATION TIME 3.5 mins
PREPARATION FIELD 138

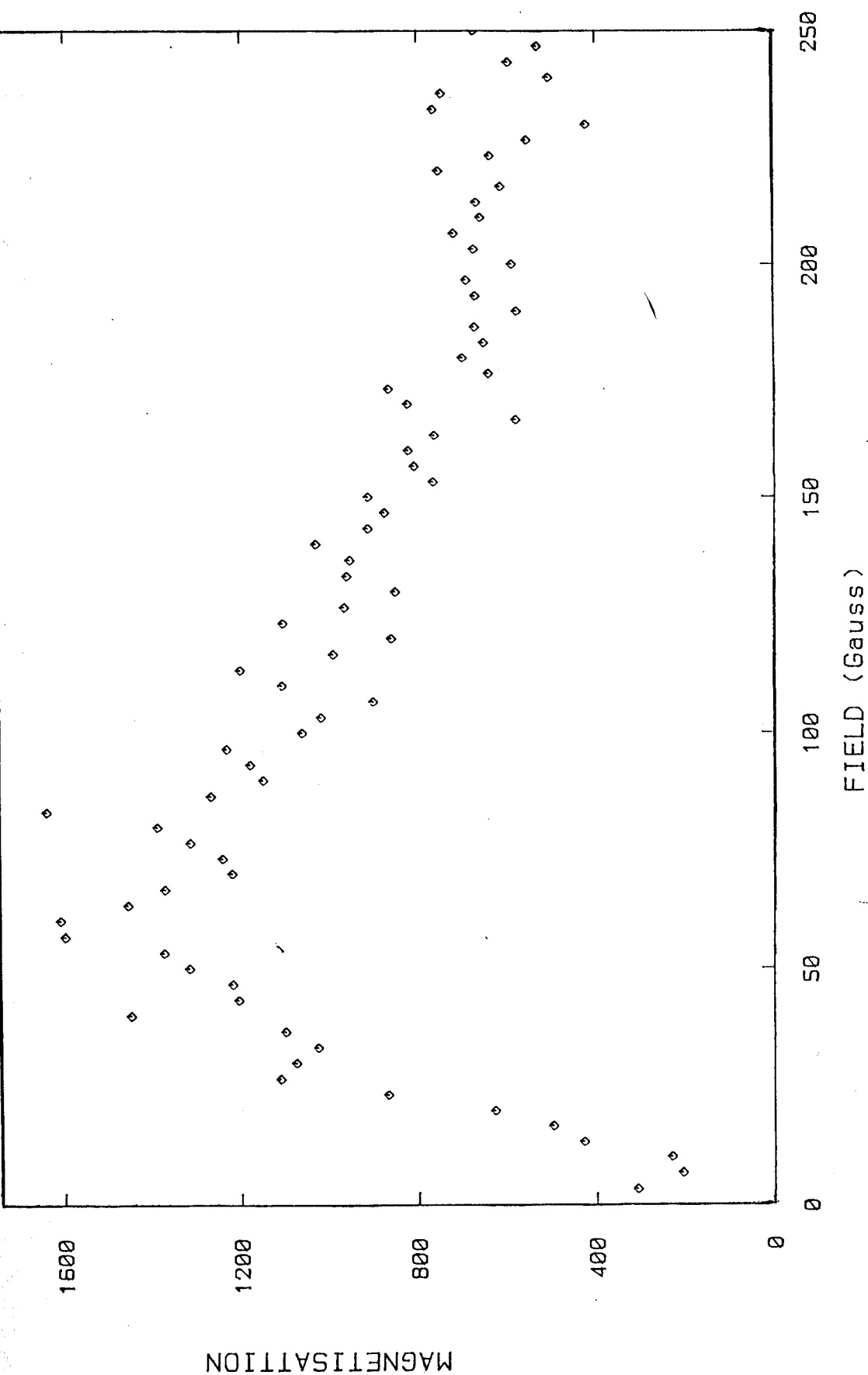


Fig.5.3 Phosphorus field scan of InP:Fe
at angle of orientation 150

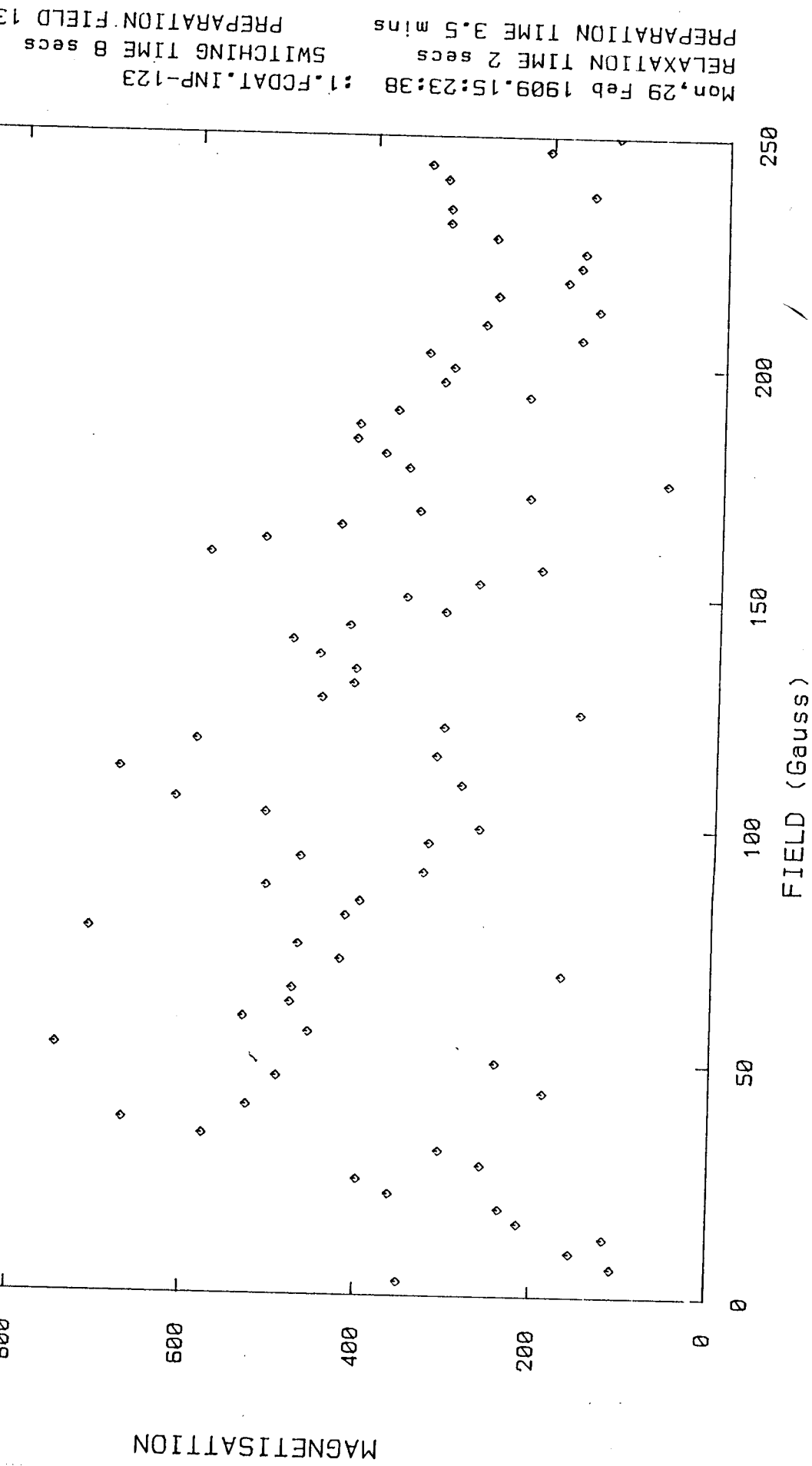


Fig.5.4 Phosphorus field scan of InP:Fe
at angle of orientation 30° .

For $\text{InP} : \text{Fe}$, the Fe impurity site is almost neutral as the impurity electrons are strongly localised, resulting in a deep electron level in the band gap (by impurity electron, is meant, an electron from an impurity atom, that may occupy the impurity level in the band gap of the semiconductor). Consequently, the magnetic hyperfine interaction due to the impurity electrons is likely to dominate the quadrupolar interaction as the impurity site is essentially neutral.

As shown in Chapter 3, the Hamiltonian for the combined symmetric Hyperfine and Zeeman interaction is,

$$\mathcal{H} = \mu_B g \mathbf{S} \cdot \mathbf{B} + \gamma_n \mathbf{B} \cdot \mathbf{I} + A \mathbf{I} \cdot \mathbf{S} \quad (5.1)$$

(symmetric in the sense that all components of the hyperfine tensor are assumed equal to the scalar Factor A),

where the first two terms are ^{the} electron and nuclear Zeeman terms in that order. μ_B is the Bohr magneton and g the electron g -factor. All other symbols are as explained in Chapter 3.

At high fields

$$B \gg A \quad (5.2)$$

The hyperfine term can then be considered as a small perturbation on the Zeeman term. In this case the states $|I m_I S m_S\rangle$ can be taken as approximate eigenstates of the system, resulting in an interaction energy of the form

$$E \simeq \mu_B g B m_S + \gamma B m_I + \text{hyperfine term} \quad (5.3)$$

The hyperfine term to a first order shift, by the time independent perturbation theory, is

$$\langle I m_I S m_S | A I \cdot S | I m_I S m_S \rangle = A m_I m_S \quad (5.4)$$

This is a diagonal term, suggesting that we get pure states at high fields.

At low fields

$$A \gg B \quad (5.5)$$

In this case the hyperfine term assumes considerable significance, hence the states $|I m_I S m_S\rangle$ can no longer be considered eigenstates since, as shown in Chapter 4. The hyperfine Hamiltonian can be expressed in terms of raising and lowering operators I_+ , S_+ , etc. in such a way that the states $|I m_I S m_S\rangle$ can not be eigenstates. We therefore get mixed states at low fields.

The matrix elements for the combined hyperfine and zeeman interactions were evaluated numerically and the Hamiltonian matrices diagonalised. The resulting energy levels for indium are shown in Fig. 5.5. Since indium is a spin $(9/2)$ nucleus, the Hamiltonian matrix is sixty by sixty.

The hyperfine factor A was assumed to be equal to 75 MHz for phosphorus and 15 MHz for indium, values obtained from Electron - nuclear double resonance (Endor) measurements of similar materials like Ga:P Mn^{5+} . Endor is a type of spectroscopy as is NMR and ESR (electron spin resonance).

This diagram, as predicted earlier shows pure states at high fields and mixed states at low fields. It clearly shows that the hyperfine interaction splits the zeeman energy levels. In the case of indium this is from ten to sixty non degenerated levels, hence creating conditions for possible cross coupling between the two nuclear species. These are conditions under which, for a particular field, the energy spacing between two indium levels (between which a transition is allowed) is approximately equal to a corresponding phosphorous energy difference.

To place the suggestion that the observed peaks are due to hyperfine interaction on a more quantitative footing, I adopt a method developed by Dr. P.J. McDonald (my

supervisor). This is a new approach in the process of improvement and was included in a paper^{5.2}, unpublished at the time of writing.

For the zeeman/hyperfine Hamiltonian, an expression for the nuclear spin transition energies has been obtained by Van Engelen, using second order perturbation theory. This expression is used here both for phosphorous and indium spin transitions, the two being equated for an estimate of the cross coupling fields. The validity of this approach is strictly limited to high fields but the method is used here as an extrapolation to lower field values permitting more quantitative analysis.

As explained earlier, for Fe in In P : Fe, the impurity electron for the neutral defect site is localised and hence the hyperfine dominance. Cross coupling occurs approximately at fields satisfying

$$\begin{aligned} & \frac{\gamma_p B}{2\pi} + m_s A_p - \frac{(s(s+1) - m_s^2 + m_s(2m_p - 1))A_p^2}{2g\mu_B B} \\ & = \frac{\gamma_{In} B}{2\pi} + m_s A_{In} - \frac{(s(s+1) - m_s^2 + m_s(2m_{In} - 1))A_{In}^2}{2g\mu_B B} \end{aligned} \quad (5.6)$$

where all symbols and subscripts have their usual meanings.

This equation is quadratic in B and when solved, for all the allowed values of m_p , m_{In} and m_s , gives the results of

Table 5.2.

As expected, most of these values lie in the low field region, the lowest being 3.6×10^{-4} Tesla. We do however get clusters of rather large field values where coupling is predicted, the largest being 6.3 Tesla. These haven't as yet been observed or fully explained on the basis of the available spectral data, except to say that their small relative occurrence reflects a correspondingly small significance in terms of the observable spectral transitions.

Table 5.2. Possible cross-coupling field values induced by the Zeeman/hyperfine interaction in InP : Fe, as predicted by second order perturbation theory.

POSSIBLE CROSS COUPLING MAGNETIC FIELD VALUES (Tesla)			
-3.559E - 4	6.347E0	-9.186E-3	1.278E0
-4.003E - 4	6.347E0	-1.278E0	9.186E-3
-4.448E - 4	6.347E0	-1.278E0	9.142E-3
-4.893E-4	6.347E0	-1.278E0	9.098E-3
-5.338E-4	6.347E0	-1.278E0	9.055E-3
-5.782E-4	6.347E0	-1.278E0	9.011E-3
-6.227E-4	6.347E0	-1.278E0	8.967E-3
-6.672E-4	6.347E0	-1.278E0	8.923E-3
-7.117E-4	6.347E0	-1.278E0	8.879E-3
-2.134E-3	3.810E0	-1.278E0	8.835E-3
-2.178E-3	3.810E0	-3.810E0	2.489E-3
-2.223E-3	3.810E0	-3.810E0	2.445E-3
-2.267E-3	3.810E0	-3.810E0	2.401E-3
-2.312E-3	3.810E0	-3.810E0	2.356E-3
-2.356E-3	3.810E0	-3.810E0	2.312E-3
-2.401E-3	3.810E0	-3.810E0	2.267E-3
-2.445E-3	3.810E0	-3.810E0	2.223E-3
-2.489E-3	3.810E0	-3.810E0	2.178E-3
-8.835E-3	1.278E0	-3.810E0	2.134E-3
-8.879E-3	1.278E0	-6.347E0	7.117E-4
-8.923E-3	1.278E0	-6.347E0	6.672E-4
-8.967E-3	1.278E0	-6.347E0	6.227E-4
-9.011E-3	1.278E0	-6.347E0	5.782E-4
-9.055E-3	1.278E0	-6.347E0	5.338E-4
-9.098E-3	1.278E0	-6.347E0	4.893E-4
-9.142E-3	1.278E0	-6.347E0	4.448E-4
	1.278E0	-6.347E0	4.003E-4
	1.278E0	-6.347E0	3.559E-4

On the other hand, spin diffusion transferring magnetisation from nuclei near an impurity to more distant nuclei, may be less efficient at high field.

5.2.2 Cross-relaxation in InP : S

Fig. 5.6 shows a phosphorous field scan of InP : S without double irradiation, the angle of orientation was 0° . The spectrum clearly shows a peak an

Sat Jun 1988.16:03:53 : 1.FCDAT.INP-S-21
 RELAXATION TIME 1 secs
 SWITCHING TIME 8 secs
 PREPARATION TIME 2 mins
 PREPARATION D 255

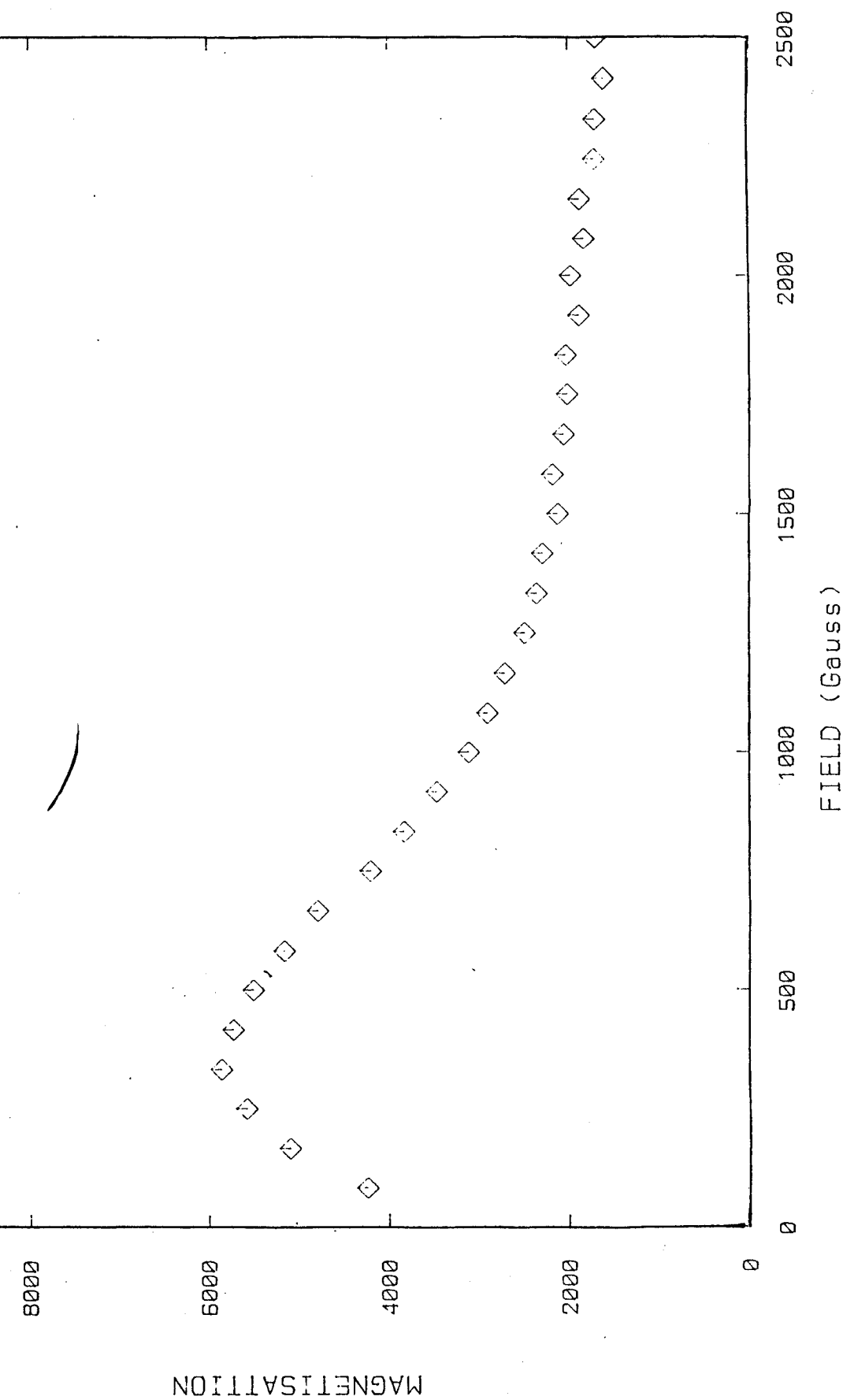


Fig.5.6. Phosphorus field scan of InP:S
 without double-irradiation.

order of magnitude (10x) broader than the one observed in the InP : Fe.

If we consider the sulphur impurity at an indium site, the impurity electron is diffuse, i.e. is at a shallow level. Hence the site is not neutral but has a charge +e, the quadrupole interaction is expected to be significant around this charged site. The hyperfine interaction on the other hand is of negligible importance on account of the impurity electron not being localised.

The electric field gradient due to the remaining nuclear charge at the impurity site is assumed to be spherically symmetric and given by

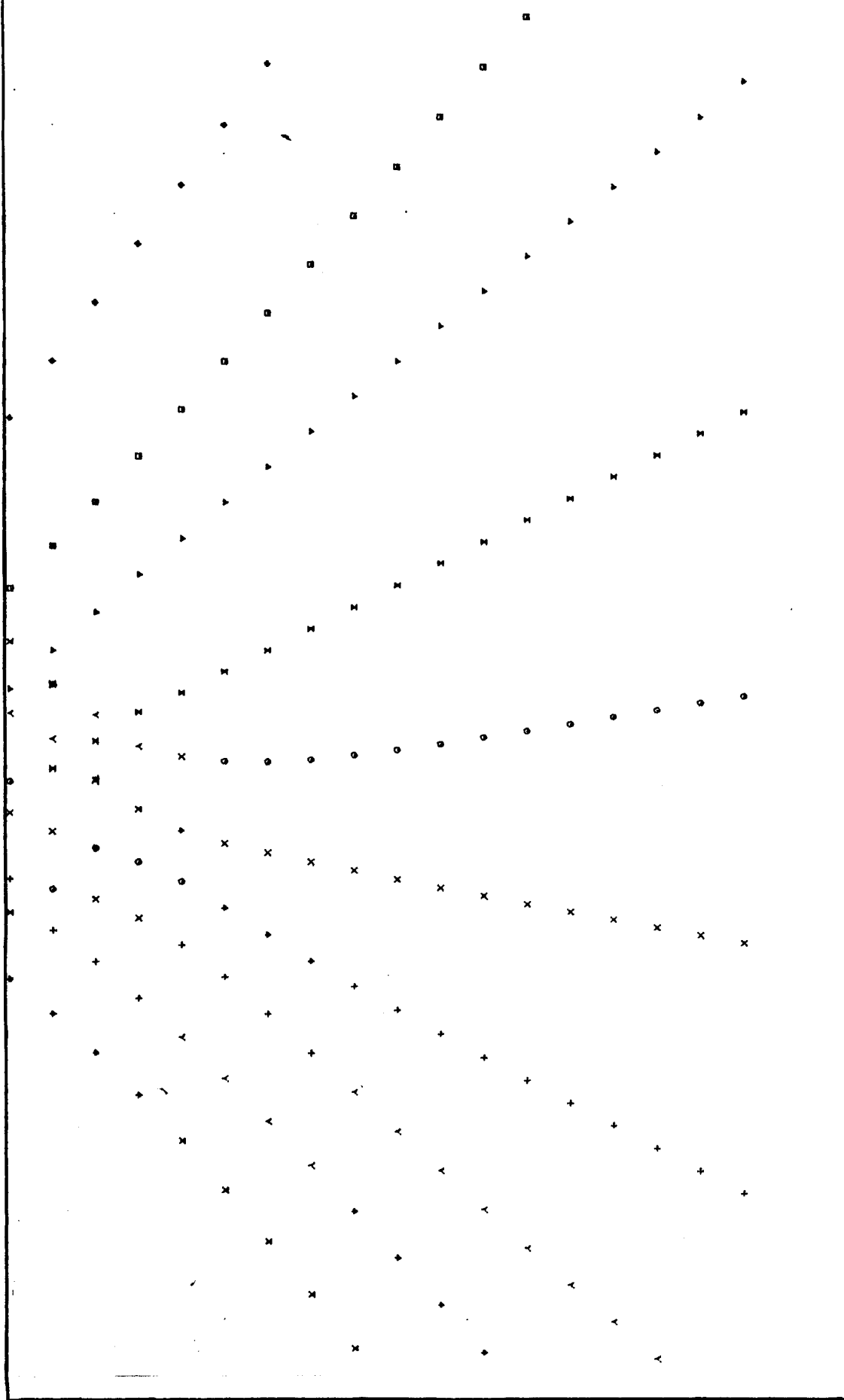
$$eq(r) = \frac{e(1 - \sigma_s)}{2\pi E_0 E_r r^3} \quad (5.7)$$

where all symbols are as explained in Chapter 3 and similarly the hamiltonian for the zeeman quadrupole interaction is

$$\begin{aligned} \mathcal{H} = & - \gamma_{In} h B I_z + \frac{e^2 q(d_0) Q_{In} (1 - \sigma_{In})}{4I(2I - 1)} \{ \\ & \frac{1}{2} (3 \cos^2 \theta_{In} - 1) (3I_z^2 - I(I+1)) + \frac{3}{2} \sin \theta_{In} \cos \theta_{In} (\\ & I_z(I_+ + I_-) + (I_+ + I_-) I_z) \\ & + \frac{3}{2} \sin^2 \theta_{In} (I_+^2 + I_-^2) \} \end{aligned} \quad (5.8)$$

this of course being only applicable to the indium nuclei since phosphorous is a spin $\frac{1}{2}$ nucleus with zero quadrupole

ENERGY (arbitrary units)



FIELD (arbitrary units)

Fig.5.7. The combined quadrupole and Zeeman energy levels for indium as a function of the applied magnetic field.

moment.

The matrix elements for this interaction were evaluated and diagonalised numerically, the result of which is shown in Fig. 5.7.

Table 5.3. Possible zeeman/quadropole induced, cross-coupling field values in InP :S as predicated by second order perturbation theory

POSSIBLE CROSS COUPLING MAGNETIC FIELD VALUES (Tesla)	
1.36600825E-3	1.66628019E-2
5.2669844E-3	1.72861912E-2
-9.97054057E-3	1.5980144E-2
-1.34941542E-2	1.34941542E-2
-1.5980144E-2	9.97054057E-3
-1.72861912E-2	5.2669844E-3
-1.66628019E-2	-1.36600825E-3

Although the quadrupole interaction does not split the ten zeeman levels as in the hyperfine, it alters the field dependence of zeeman levels significantly.

Field cycling cross-coupling occurs when the energy of phosphorous transitions equal the energy of indium transitions around the Fe impurity. Using similar considerations as in section 5.2.1, based on second order perturbation theory, cross coupling occurs at fields closely satisfying the condition

$$\frac{\gamma_P B}{2\pi} = \frac{\gamma_{In} B}{2\pi} - \frac{3e^2 q(d_I) Q_{In}(2I_{In}-1)}{8I_{In}(2I_{In}-1)h} \quad (5.9)$$

Q_P being equal to zero.

d_I is the Fe - In bond length

This equation is solved for a series of fields in the range 0 to 2000 Gauss, the result of which is shown in Table 5.3. As expected the field values extend to higher fields than in InP : Fe excluding the very high field clusterings. However, they do not extend as far as the observed peak and clearly, more theoretical work directed to explaining this is required.

If indeed the observed peak is due to cross-coupling between the two nuclear species then by saturating both species before each cycle we would expect the peak to disappear. This is because by saturating a single species we made that species 'hot' while the other remained 'cold' and hence acted as a reservoir for energy transfer, which would not be achieved if both species were hot.

Sat, 11 Jun 1988, 18:50:33 ; 1.FCDAT, INP-S-22
 RELAXATION TIME 1 secs
 SWITCHING TIME 8 secs
 PREPARATION TIME 2 mins
 PREPARATION FIELD 25

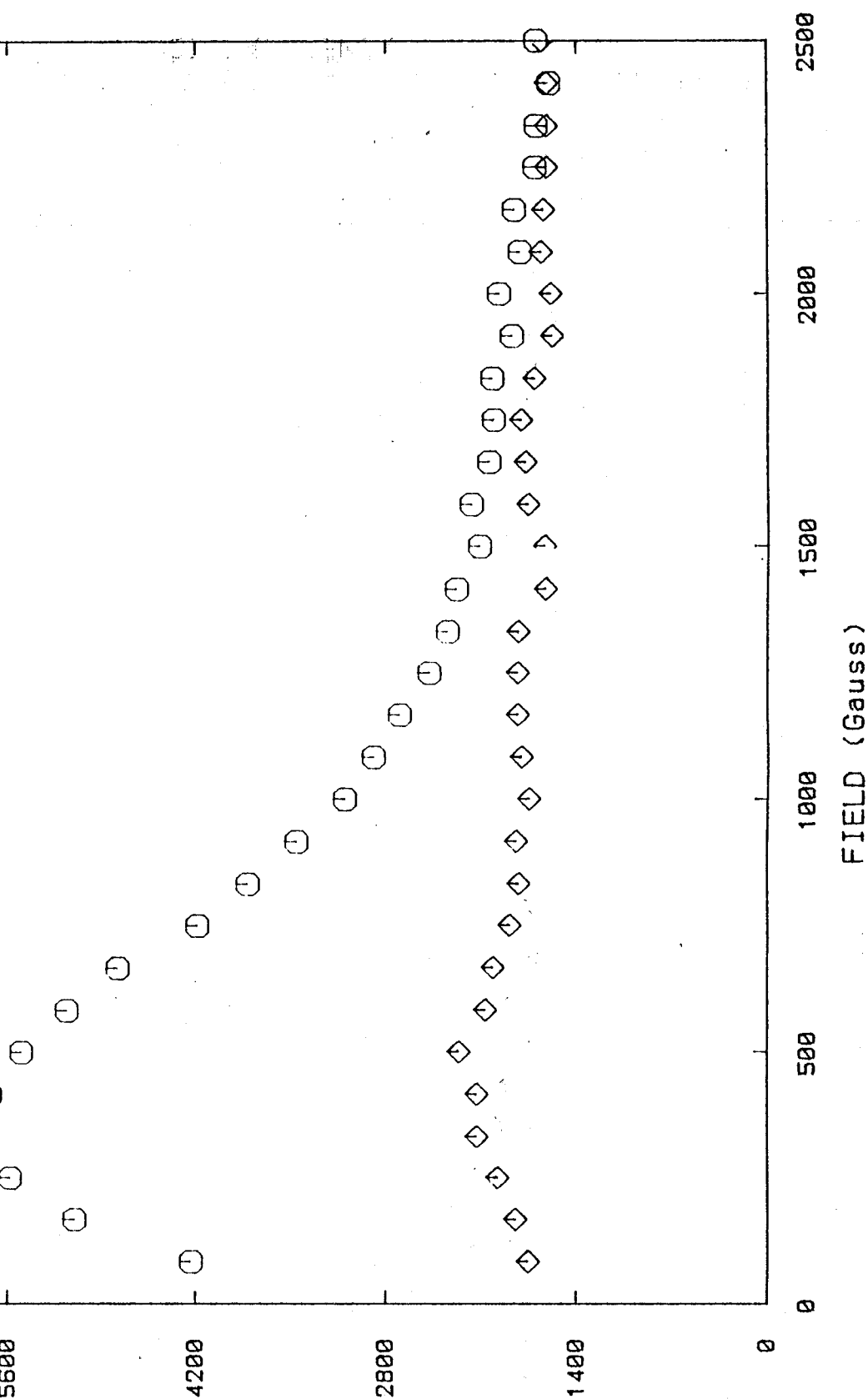


Fig. 5.8

Fig.5.8. Selective saturation in InP:S.

MAGNETISATION

1.04

Sat, 11 Jun 1988.18:50:33 :1.FCDAT.INP-S-22
 RELAXATION TIME 1 secs
 SWITCHING TIME 8 sec
 PREPARATION TIME 2 mins

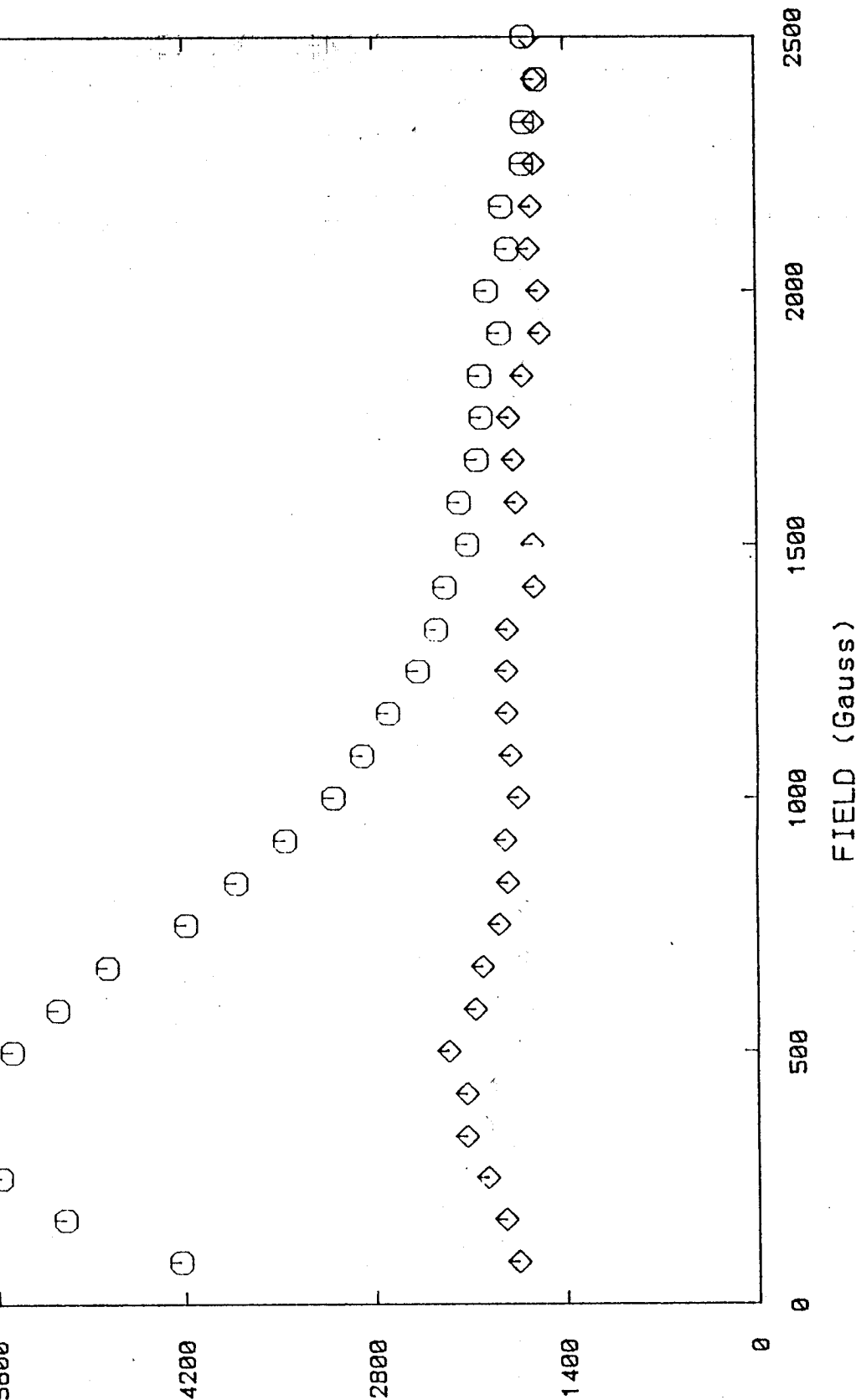


Fig.5.8. Selective saturation in InP:S.

Fig. 5.8

MAGNETISATION

1.04

Sun, 05 Jun 1988. 15:34:20 : 1.FCDAT.GA-SI-4
RELAXATION TIME 1 secs
PREPARATION TIME 2 mins
SWITCHING TIME 11 secs
PREPARATION FIELD 18336 G

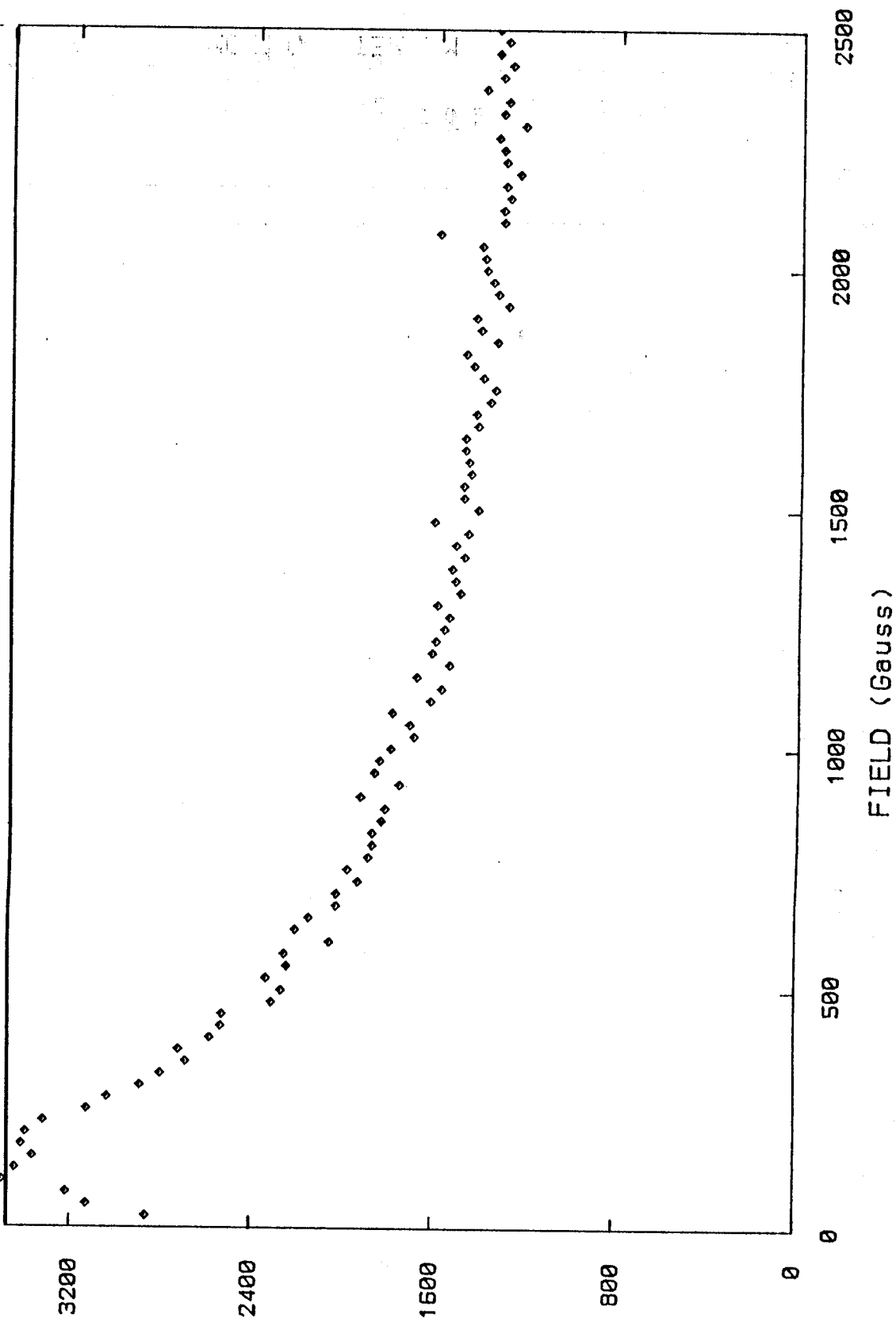


Fig.5.9. Cross-relaxation without double irradiation in GaAs:Si.

This experiment was carried out and the result was Fig. 5.8. The upper graph was obtained with phosphorous saturation alone, while the second one was a result of the saturation of both nuclear species.

The small hint of a peak in the lower graph was probably due to Indium - 113 which was not saturated and has a natural occurrence of 4.28%, while indium - 115 which was saturated has 95.72% occurrence.

5.2.3 Cross-Relaxation in Ga As : Si

Fig. 5.9 shows the cross-relaxation peak (without double irradiation) in Ga As : Si. Here again, we observe a relatively broad peak pointing more to the quadrupole than to the localised hyperfine interaction. The silicon impurity substituting for a Ga atom introduces a shallow defect level. The impurity electron is diffused, and the hyperfine interaction can be ignored.

As in the In P : S field cycling cross-coupling should occur at fields satisfying the condition

$$\frac{\gamma_{As}B}{2\pi} - \frac{3e^2q(d_o)Q_{As}(2m_{As} - 1)}{8I_{As}(2I_{As} - 1)h} = \frac{\gamma_{Ga}B}{2\pi} - \frac{3e^2q(d_i)Q_{Ga}(2m_{Ga} - 1)}{8I_{Ga}(2I_{Ga} - 1)h} \quad (5.10)$$

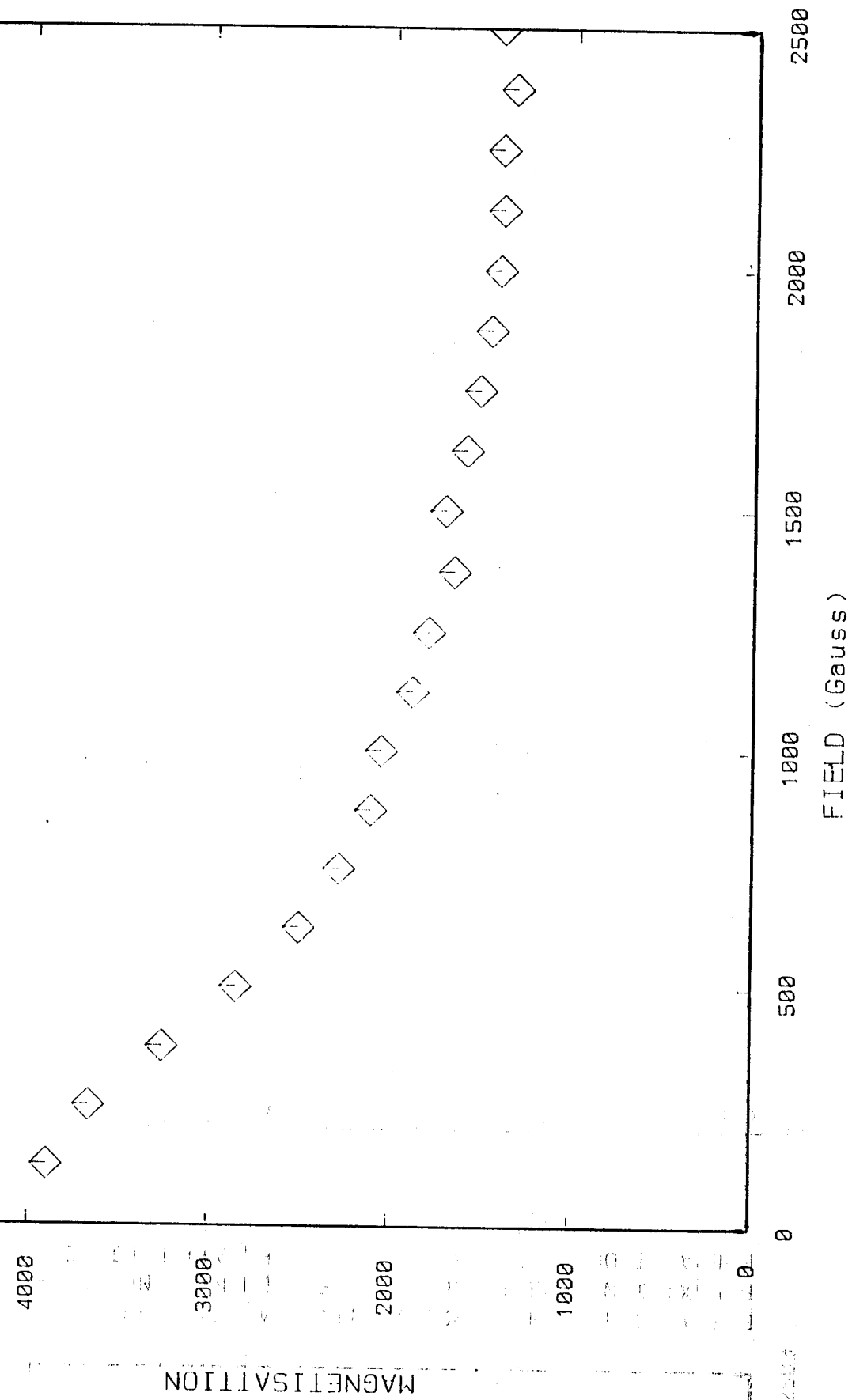


Fig510. Ga-69 field scan in Ga As: Si.

Fri, 10 Jun 1988, 14:22:57 : 1.FCDAT.GA-SI-9
 RELAXATION TIME 1 secs
 SWITCHING TIME 11 secs
 PREPARATION TIME 2 mins
 PREPARATION FIELD 3279

Fr, 10 Jun 1988.15:32:20 ; 1.FCDAT.GA-SI-10
RELAXATION TIME 1 secs
PREPARATION TIME 2 mins
SWITCHING TIME 11 secs
PREPARATION FIELD 32793

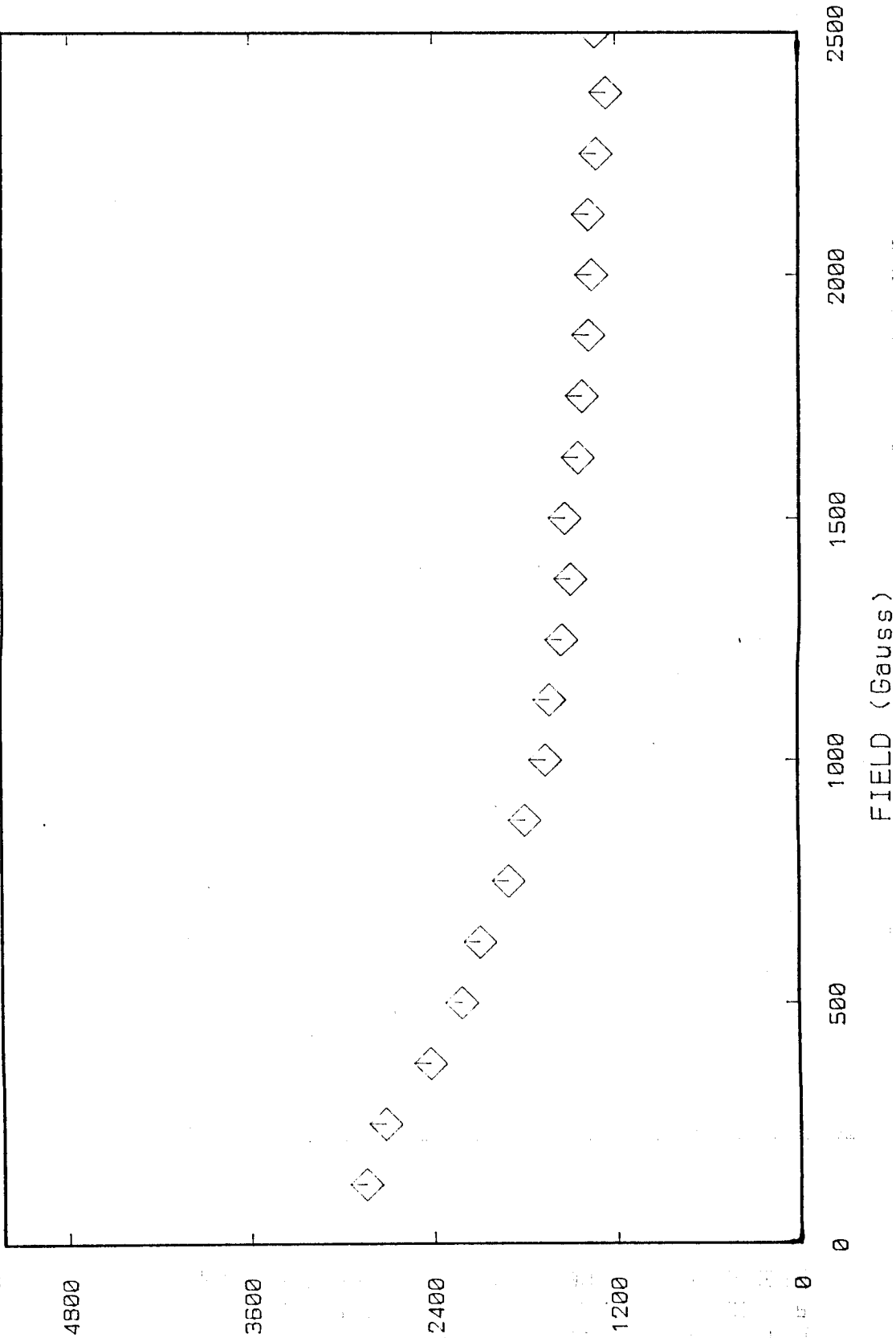


Fig.5.11. Ga-69 field scan in Ga As: Si with Arsenic saturation.

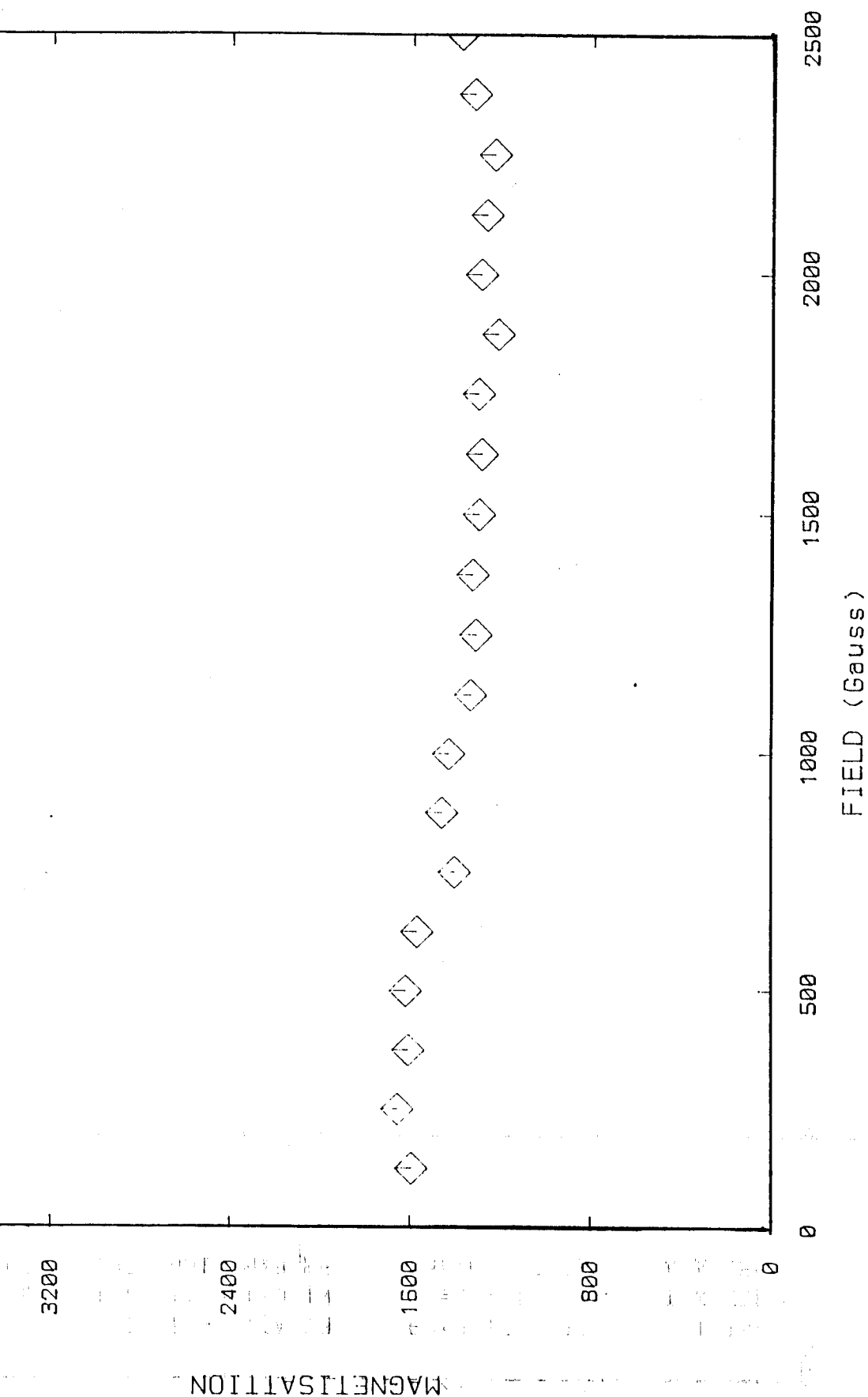


Fig.5.12. Ga As: Si field scan of Ga-69
with Ga-71 and Arsenic saturation.

Fri, 10 Jun 1988.17:45:29 :1.FCDAT.GA-SI-11
RELAXATION TIME 1 secs
SWITCHING TIME 11 secs
PREPARATION TIME 2 mins
PREPARATION FIELD 32793

Table 5.4. Possible zeeman/quadrupole induced, cross-coupling
1 1 0
field values in Ga As : Si as predicted by second order
perturbation theory.

POSSIBLE CROSS COUPLING MAGNETIC FIELD VALUES (Tesla)	
1.365E-1	0.000E0
1.504E-1	4.5441E-4
1.653E-1	0.000E0
1.084E-1	-1.228E-1
1.151E-1	-1.151E-1
1.228E-1	-1.084E-1
0.000E-0	-1.653E-1
-4.541E-4	-1.504E-1
0.000E0	-1.365E-1

Table 5.4 shows a range of fields satisfying this condition and clearly shows consistency with the observed spectrum.

Gallium, as mentioned earlier, exists in two naturally occurring isotopes i.e. Gallium - 69 (50.4%) and Gallium - 71 (49.6%). Fig. 5.11 shows a Ga - 69 scan with Arsenic saturation and in Fig. 5.12, Gallium - 71 is also saturated. Fig. 5-10 shows an ordinary Ga - 69 scan performed under exactly the same conditions as the other two. Successive reduction in peak height is observed in these three spectra as would be expected.

5.3 Field Cycling Results (with double irradiation)

5.3.1 Double Irradiation of In P : Fe

Fig. 5.13 shows a frequency scan at 70E-3 T. A more sensitive frequency scan of the same nature as shown in Fig. 5.14.

In these two scans it can be seen that all prominent minima appear at the theoretical Larmor frequencies for both nuclear species. Certain minima are observed which correspond to a double flip or even triple flip of the nuclei, i.e.

$\Delta m = 2$ and $\Delta m = 3$, where Δm is the difference between the magnetic projection quantum numbers of the two states before and after the transition. Certain minima were seen to be broader than others, which probably was due to a superposition of two minima corresponding to appropriate "orders" of transition in the two nuclear species.

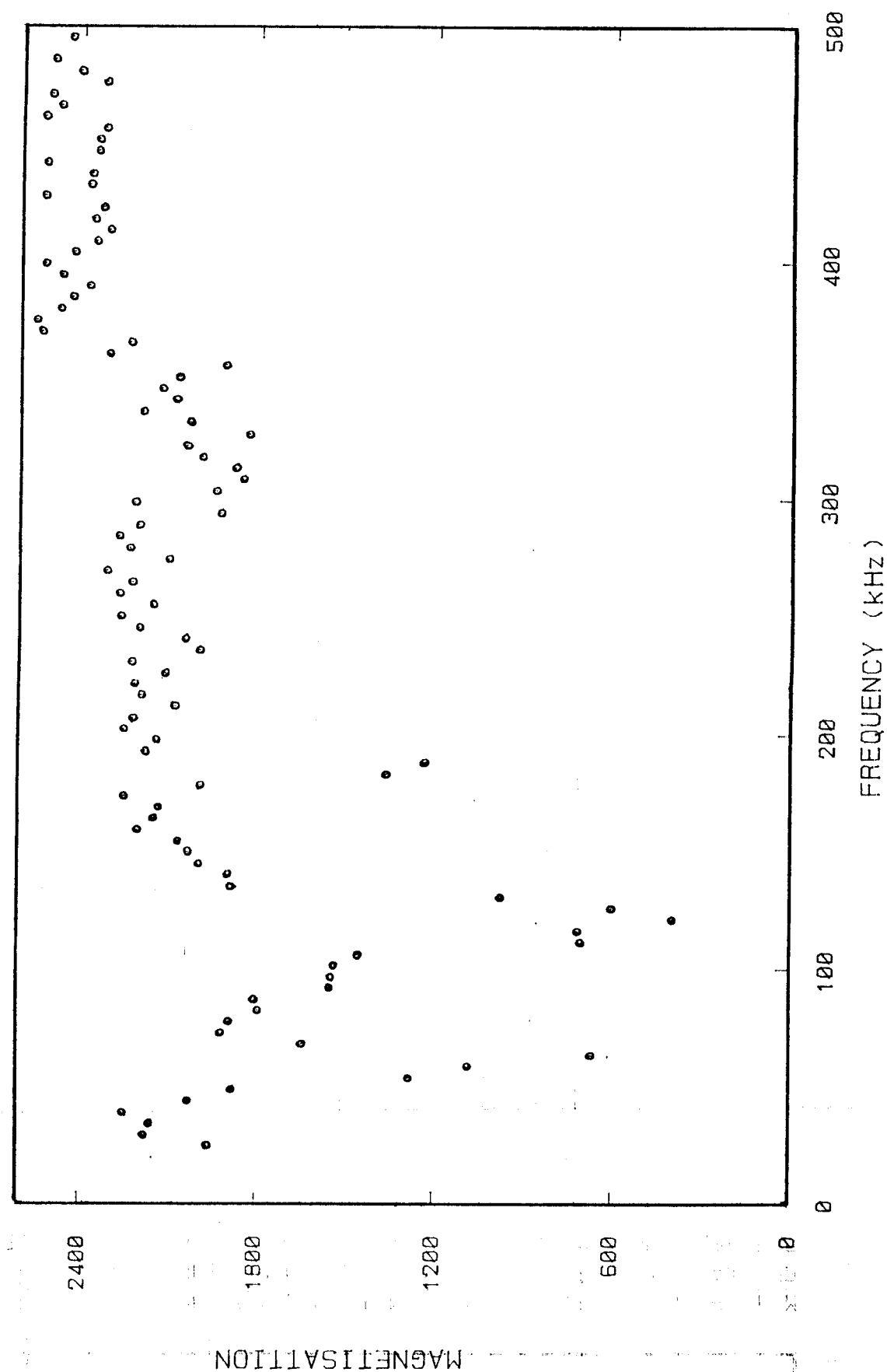


Fig.5.13. Phosphorus frequency scan of InP: Fe with double irradiation. Constant magnetic field 70G.

Mon, 15 Feb 1988, 16:55:10 ; 1.FCDAT, INP-105
 RELAXATION TIME 2 secs
 SWITCHING TIME 8 secs
 PREPARATION TIME 2 mins
 PREPARATION FIELD 13995.5

MAGNETISATION

1 1 3

3200
2400
1600
800
0

0 40 80 120 160 200
FREQUENCY (kHz)

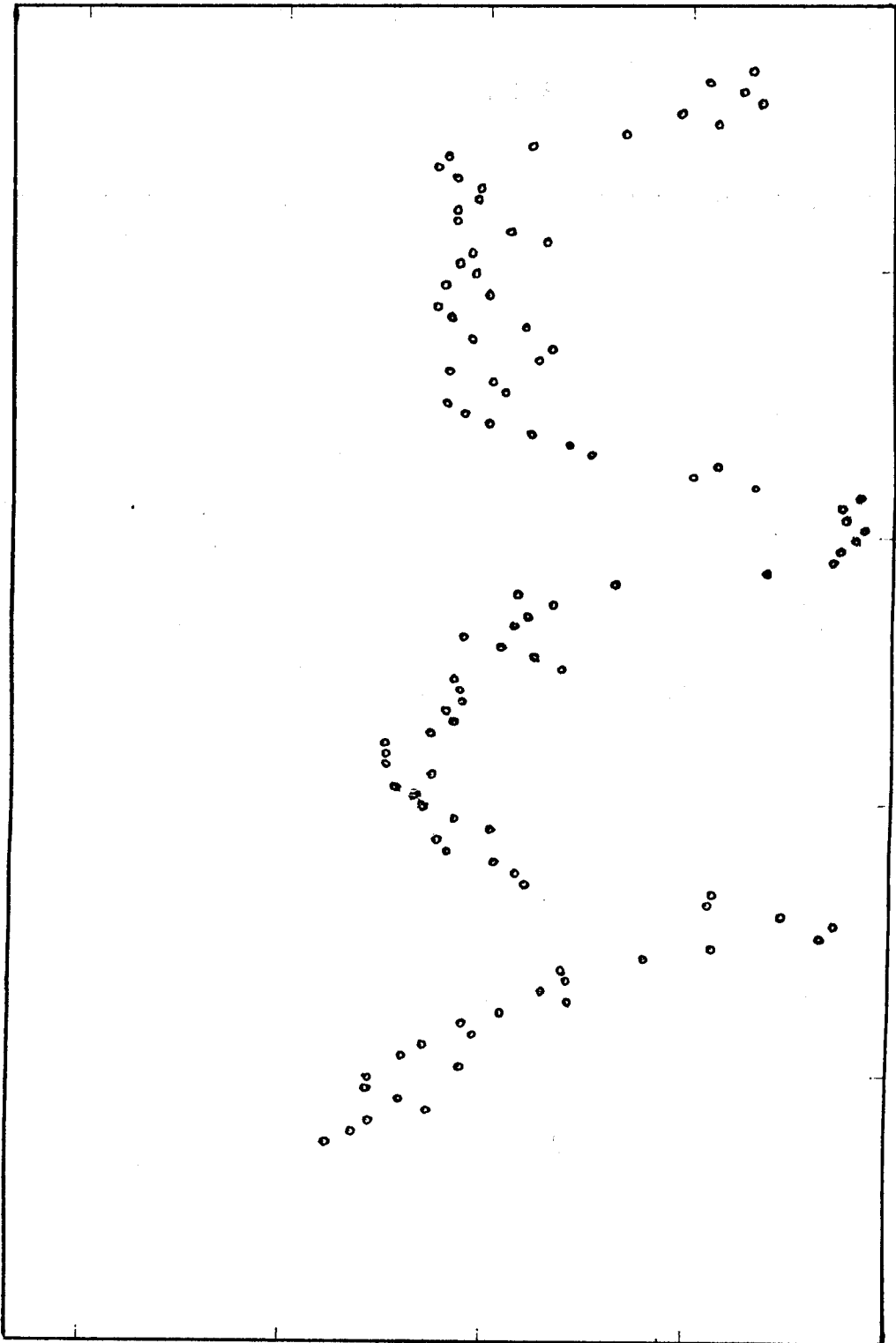


Fig.5.14. Phosphorus frequency scan of InP:Fe with double-irradiation. Constant magnetic field 70G.

Sun, 14 Feb 1988.10:54:07 ; 1.FCDAT.INP-103
RELAXATION TIME 2 secs
SWITCHING TIME 8 secs

PREPARATION TIME 3.5 mins

PREPARATION FIELD 14002

Sun, 28 Feb 1988.00:48:46 : 1.FCDAT.INP-119
 RELAXATION TIME 2 secs
 SWITCHING TIME 8 secs
 PREPARATION TIME 4 mins
 PREPARATION FIELD 13808 G

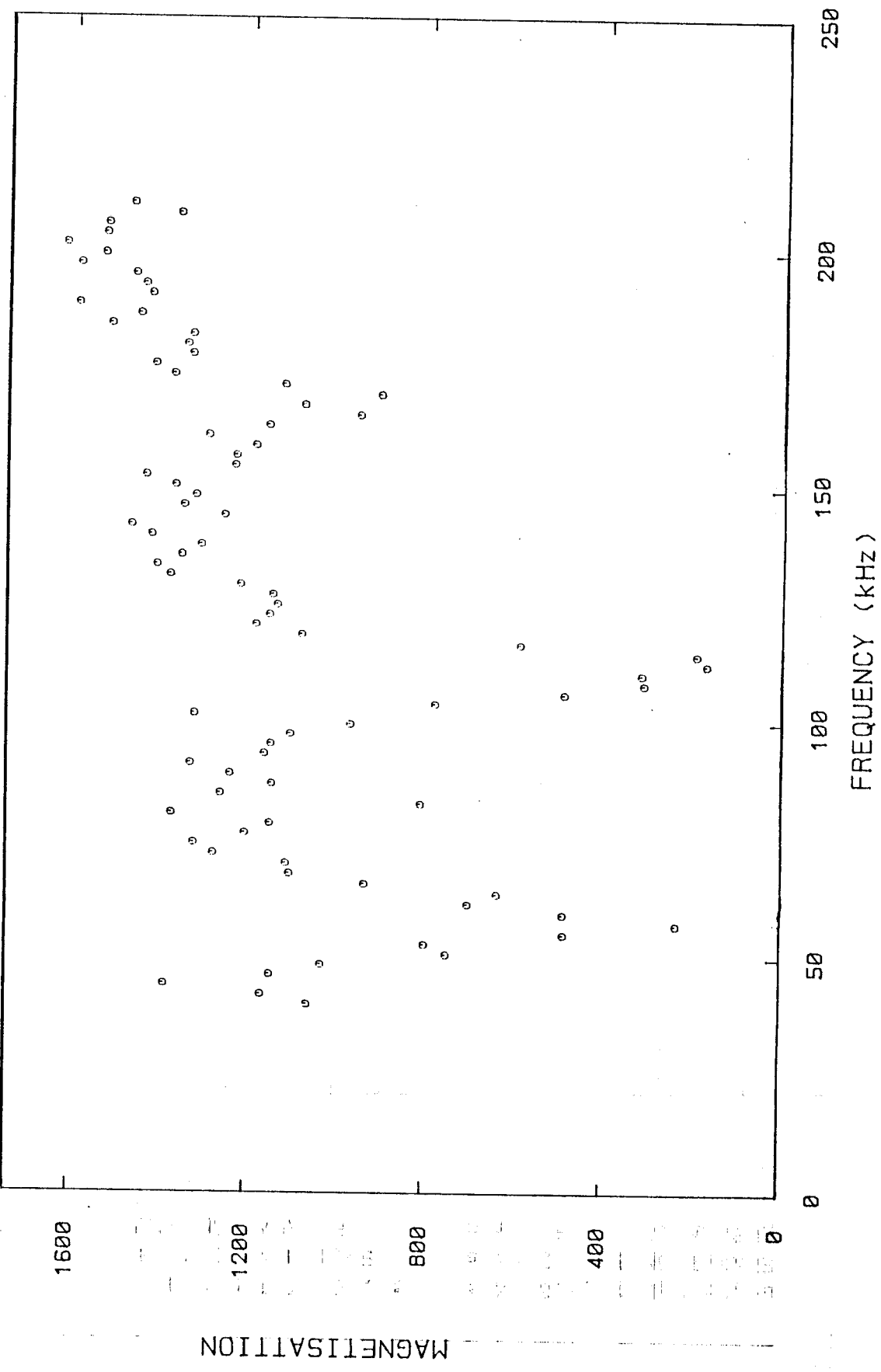


Fig.5.15. Phosphorus frequency scan of InP:Fe with
 double-irradiation at angle of orientation 15° .

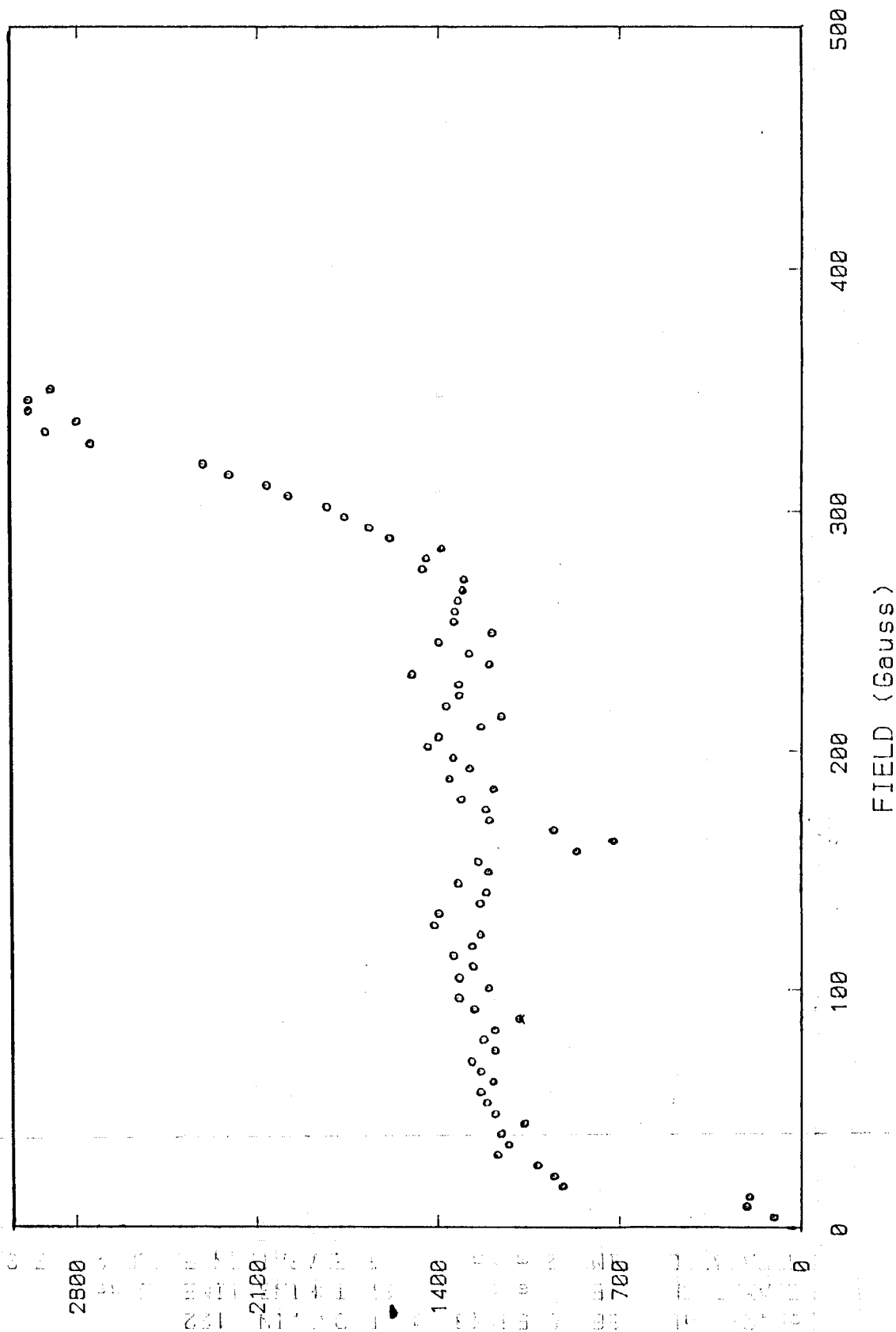


Fig.5.16. Indium field scan of InP:Fe with double-irradiation at angle of orientation 30° . Double-irradiation frequency 150 k Hz.

Mon, 29 Feb 1988 06:58:48 : 1.FCDAT.INP-122
RELAXATION TIME 2 secs
SWITCHING TIME 15 secs
PREPARATION TIME 2 mins
PREPARATION FIELD 25527
INVENT DATE 14

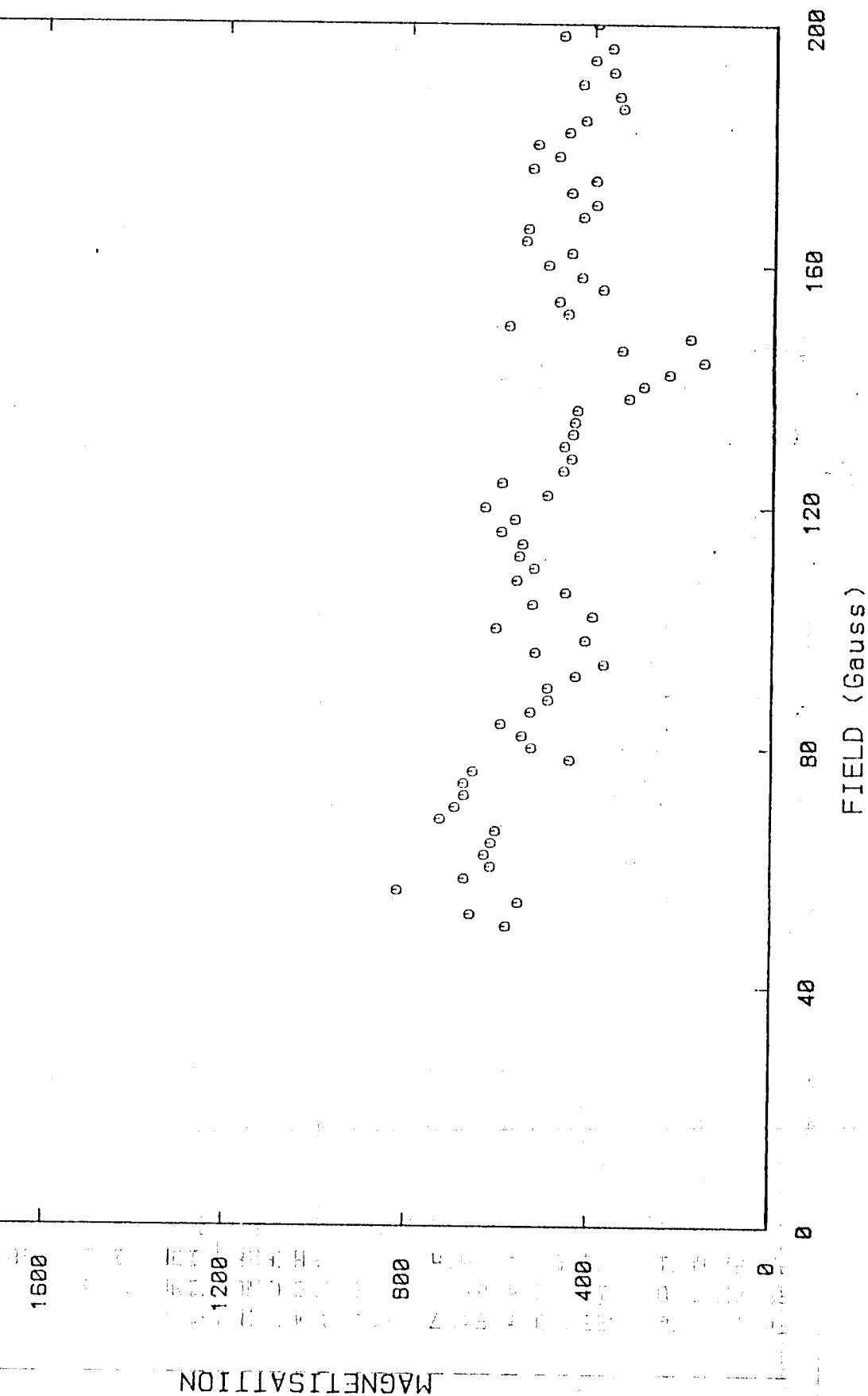


Fig.5.17. Phosphorus field scan of InP:Fe with double-irradiation at angle of orientation 45° . Double-irradiation frequency 250 k Hz.

Fr, 19 Feb 1988.09:55:37 #1.FCDAT.INP-114
 RELAXATION TIME 2 secs
 SWITCHING TIME 8 secs
 PREPARATION TIME 3.5 mins
 PREPARATION FIELD 138

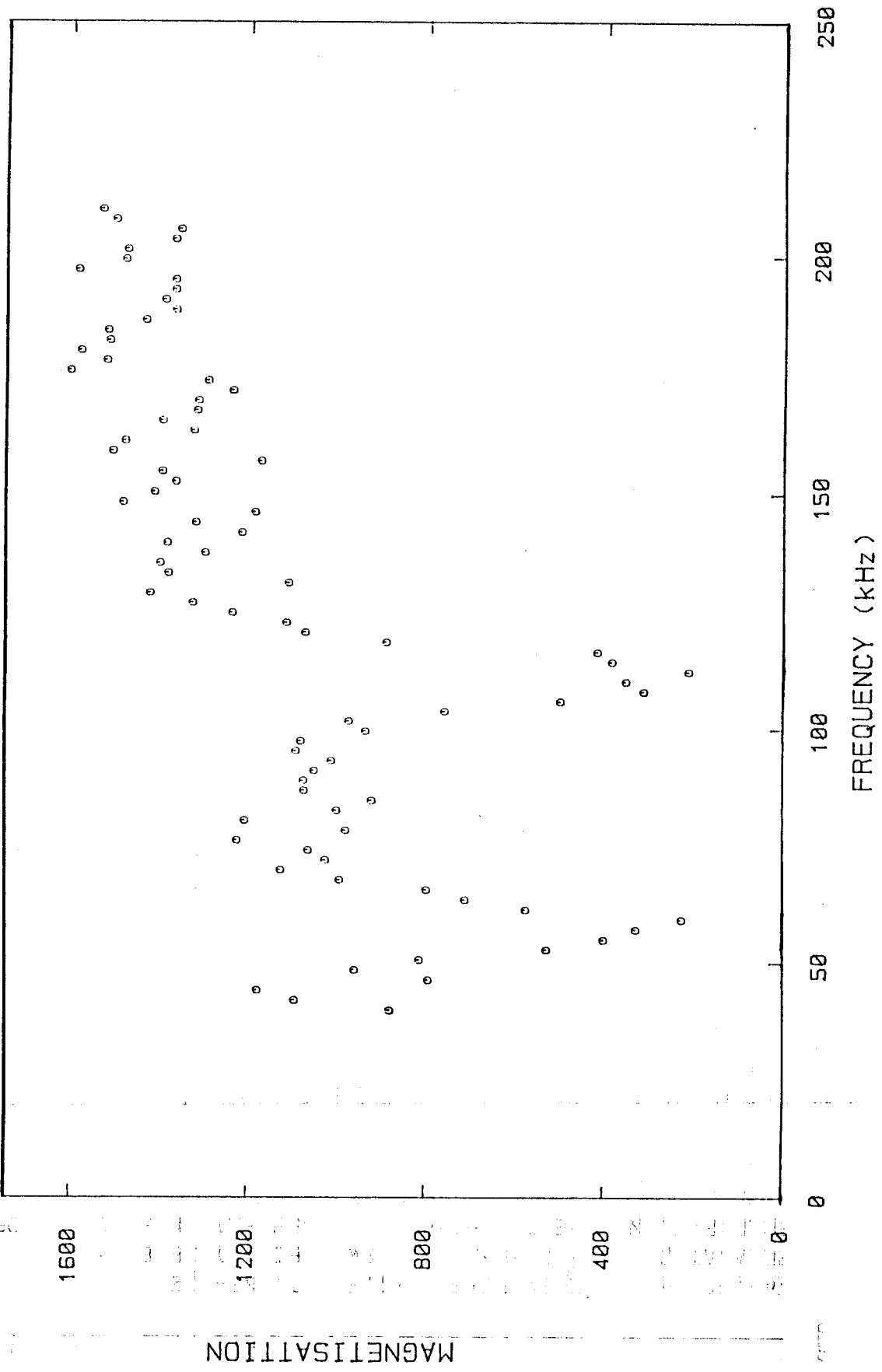


Fig.5.18. Phosphorus frequency scan of InP:Fe with double-irradiation at angle of orientation 90° . Constant magnetic field 64G.

Wed, 31 Feb 1909, 01:57:32 ; 1.FCDAT.INP-130
 RELAXATION TIME 2 secs
 SWITCHING TIME 8 secs
 PREPARATION TIME 3.5 mins
 PREPARATION FIELD 13800

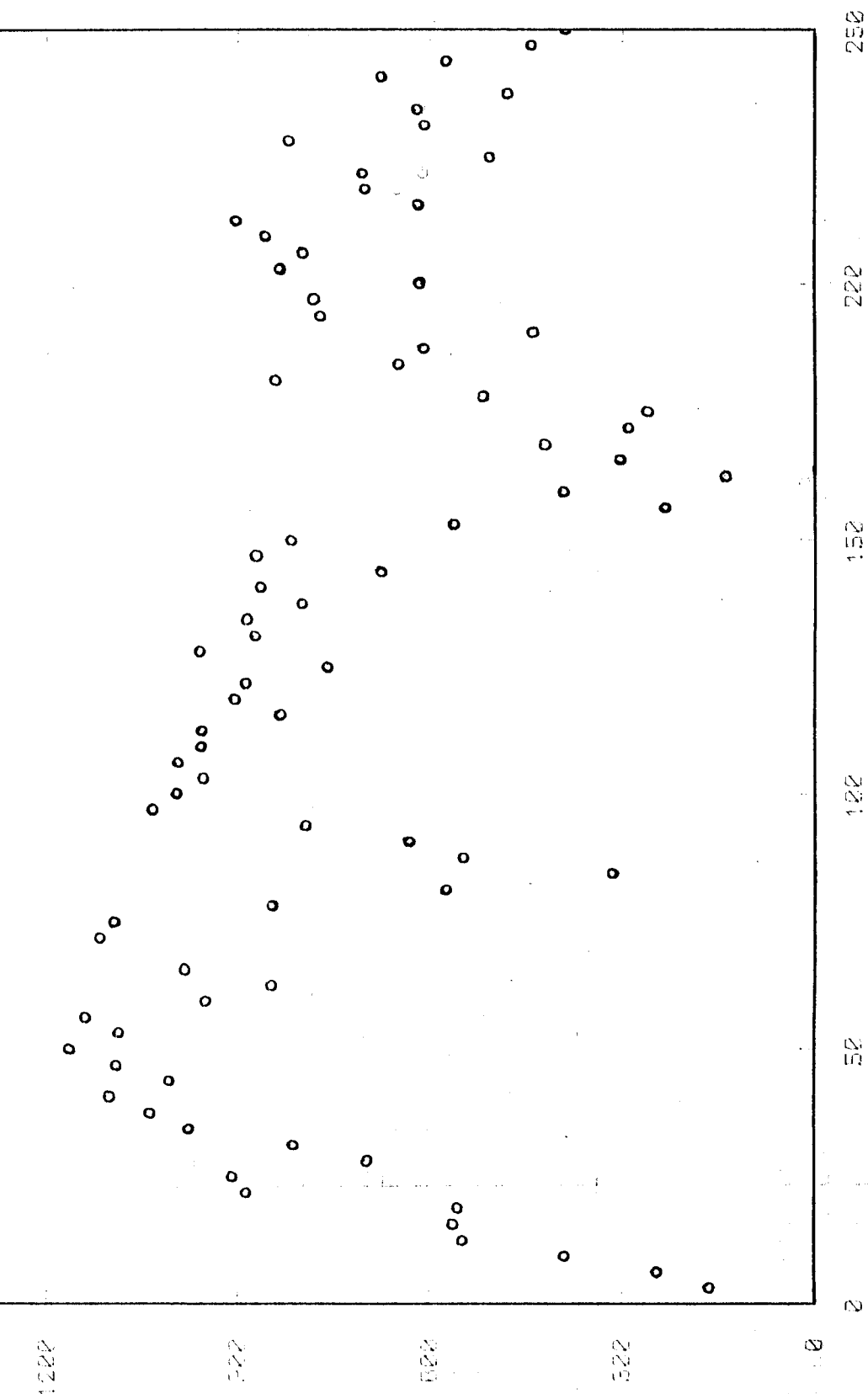


Fig.5.19. Phosphorus field scan of InP:Fe with double-irradiation at angle of orientation 90° . Double-irradiation frequency 150 k Hz.

Time, 30 Feb 1969, 20:22:25 #1, FODAL, IN-129
 RELAXATION TIME 2.000 S SWEEPING TIME 8.000 S
 PREPARATION TIME 8.000 S

The spectra of Fig. 5.13 and 5.14 are for phosphorus scans but as seen, the minima observed are due to indium transitions. This suggests a coupling between the two nuclei. This coupling and the flip transitions referred to earlier are explained later.

Figs. 5.15 through to 5.19 show field and frequency scans at various angles of orientation of the sample. The intensity of these minima was seen to be dependent on the angle. There is a general reduction of intensity as the angle increases from zero, to 45° and a gradual restoration as it increases from 45° to 90° , this is clearly due to the change in spin-lattice relaxation time which follows a similar pattern.

It was hoped that double irradiation scans of this sort would identify cross coupling transitions, by enhancing some transitions with irradiation. The holes in the InP : Fe spectra ~~did~~ appeared at bulk matrix nuclei resonance fields. More interesting effects were seen in InP : S.

5.3.2 Double Irradiation in InP : S

Figs 5.20 and 5.21 show the spectra of three different double-irradiation field scans at the frequencies of 900 kHz and 1 MHz respectively.

Sun, 12 Jun 1988, 10:06:17 : 1.FCDAT.INP-S-23
 RELAXATION TIME 1 secs
 PREPARATION TIME 2 mins
 SWITCHING TIME 8 secs
 PREPARATION FIELD 25000 G
 ACQUITT ATTIC

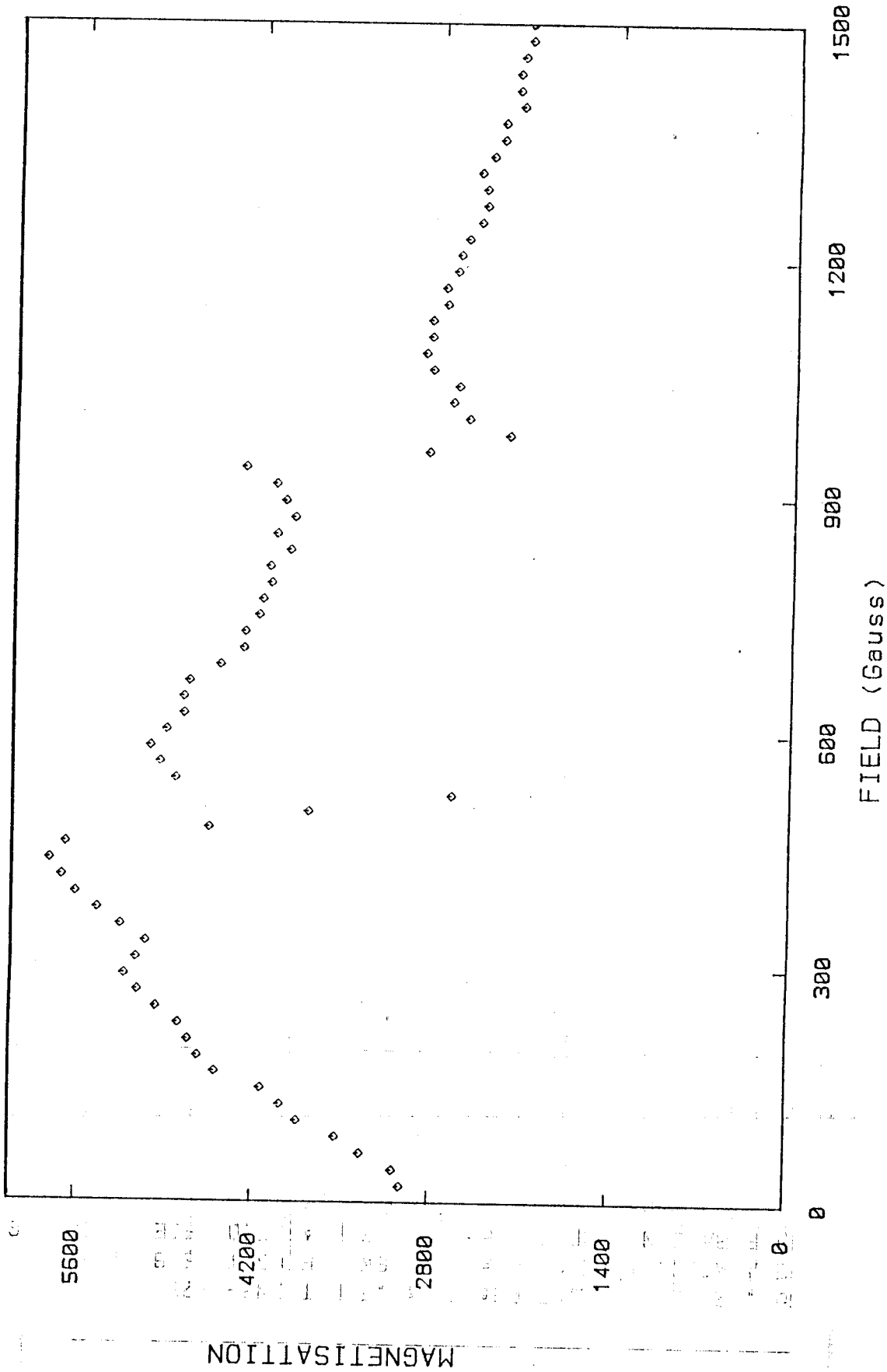


Fig.5.20. Phosphorus field scan of InP:S with
 double-irradiation.
 Double-irradiation frequency 900 k Hz.

MAGNETISATION

1 2 1

8000

6000

4000

2000

0

300

600

900

1200

1500

FIELD (Gauss)

Fig.5.21. Phosphorus field scan of InP:S with double-irradiation.
Double-irradiation frequency 1 M Hz.

Sat, 18 Jun 1988, 10:45:12 ; 1.FCDAT.INP-S-34

RELAXATION TIME 2 secs

SWITCHING TIME 8 secs

PREPARATION TIME 2 mins

PREPARATION FIELD 25000

INVEST 50000

Mon, 13 Jun 1988. 13:19:02 #1.FCDAT.INP-S-26
RELAXATION TIME 2 secs
SWITCHING TIME 8 secs
PREPARATION FIELD 250

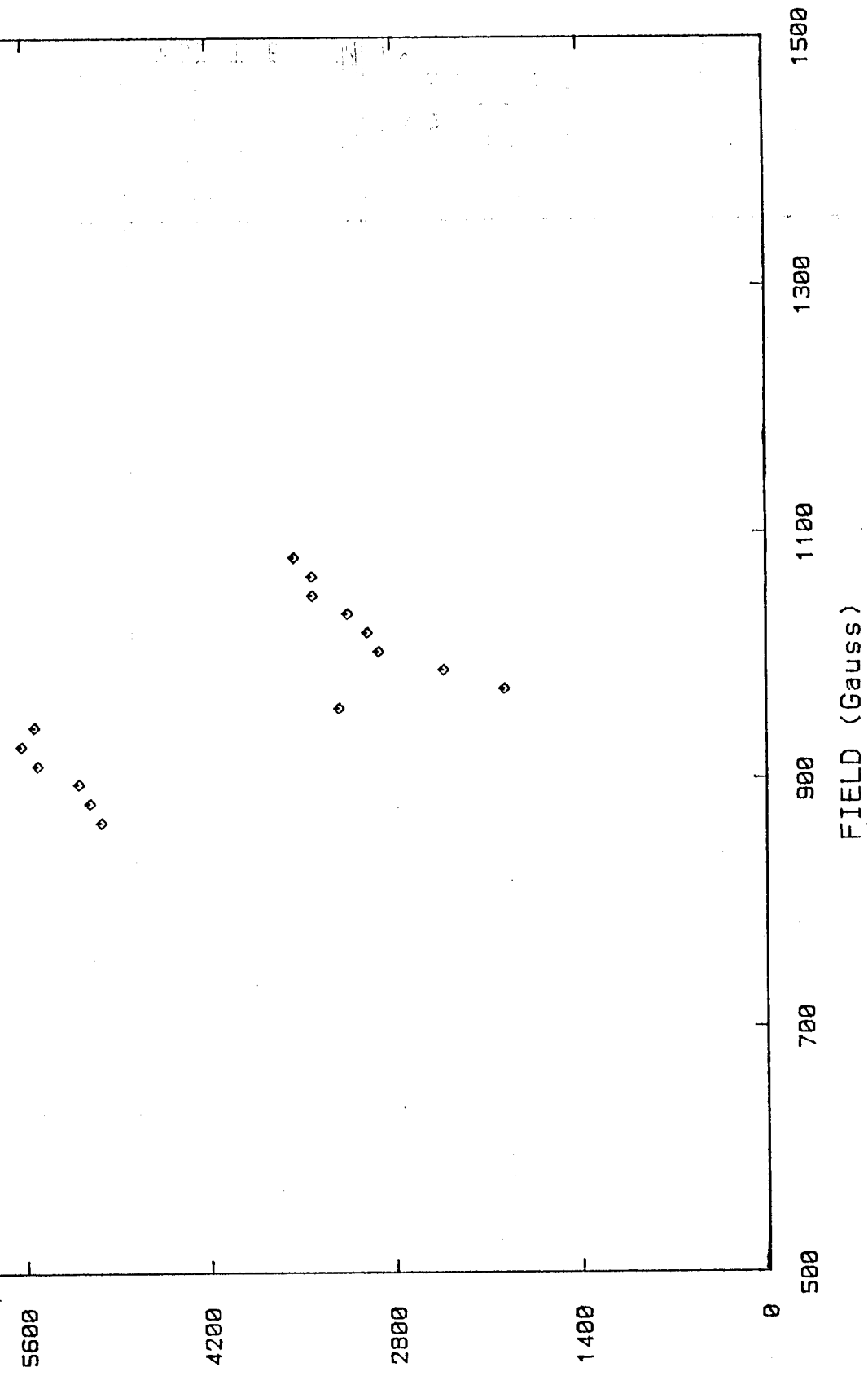


Fig.5.22. Phosphorus field scan of InP:S with double-irradiation.
Double-irradiation frequency 200 k Hz.

MAGNETISATION

1 2 2

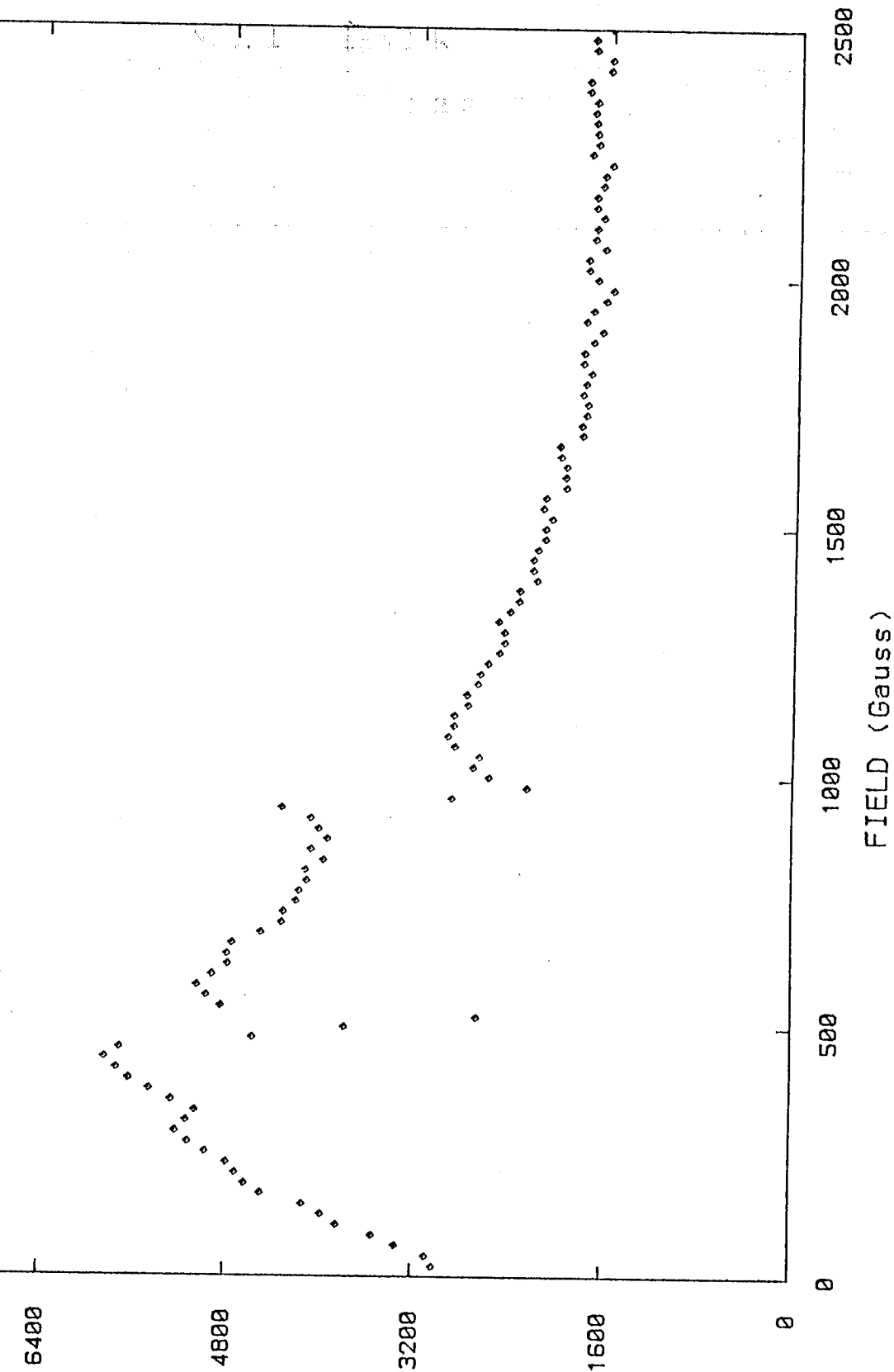


Fig.5.23. Phosphorus field scan of InP:S with double-irradiation.

Double-irradiation frequency 900 k Hz.

Sun, 12 Jun 1988, 10:06:17 : 1.FCDAT.INP-5-23
 RELAXATION TIME 1 secs
 SWITCHING TIME 8 secs
 PREPARATION TIME 2 mins
 PREPARATION FIELD 25000

These give a result very much similar to that observed in the InP : Fe except for the sudden rise in magnetisation on the low field side of the In $\Delta m = 1$ hole, observed around 950 Gauss. This feature was readily reproducible as can be seen from the two figures.

Fig 5.22 is the spectrum of a close-up scan of this feature. No explanation has, as yet, been given for this effect except to say that it could be some form of localised effect due to the quadrupole interaction discussed.

Fig. 5.23 is included to show that the cross-relaxation region is very wide for this sample and although, as expected, the magnetisation (recovered at lower field) relaxes towards zero relatively quickly, a considerable amount of magnetisation is nonetheless retained at zero field. This is probably due to bulk effects and the fast ultra low-field spin-lattice relaxation. A different approach to explaining this observation is given in section 6.1 (in terms of the concept of spin temperature).

5.4 High Pressure Field Cycling in InP : S

Figs 5.24 through to 5.27 show phosphorus field scans with double irradiation, carried out at a pressure of about 2 k bars on the sample but at different successive times.

Wed, 08 Jun 1988. 14:23:32 : 1.FCDAT.INP-S-P1
 RELAXATION TIME 1 secs
 SWITCHING TIME 8 secs
 PREPARATION TIME 2 mins
 PREPARATION FIELD 2500

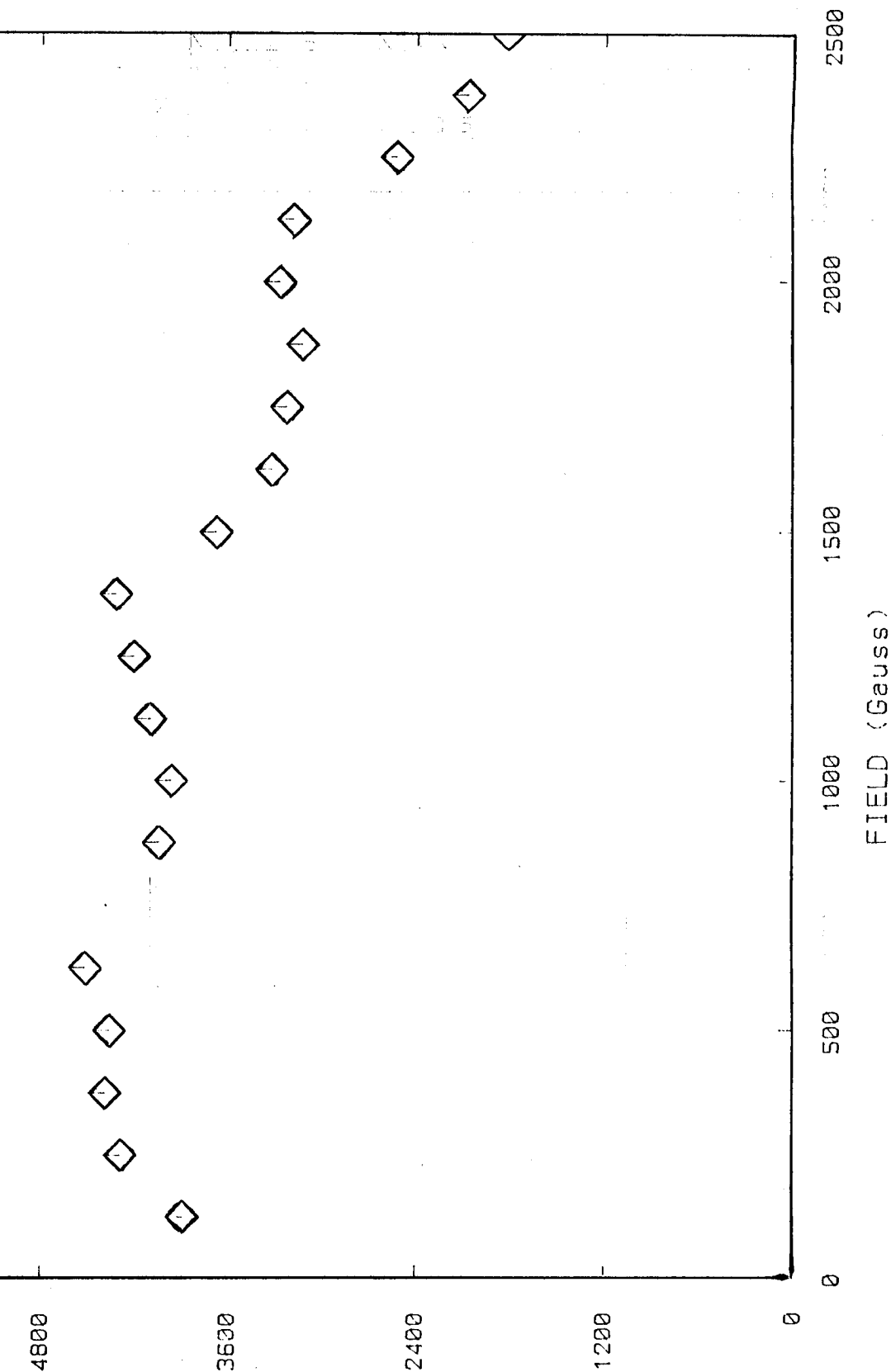


Fig. 5.24. Phosphorus field scan of InP:S with double-irradiation at 2 k bars.
 Double-irradiation frequency 900 k Hz.

MAGNETISATION

Wed, 08 Jun 1988.15:55:26 ;1.FCDAT.INP-S-P2
 RELAXATION TIME 1 secs
 SWITCHING TIME 8 secs
 PREPARATION TIME 2 mins
 PREPARATION FIELD 25000

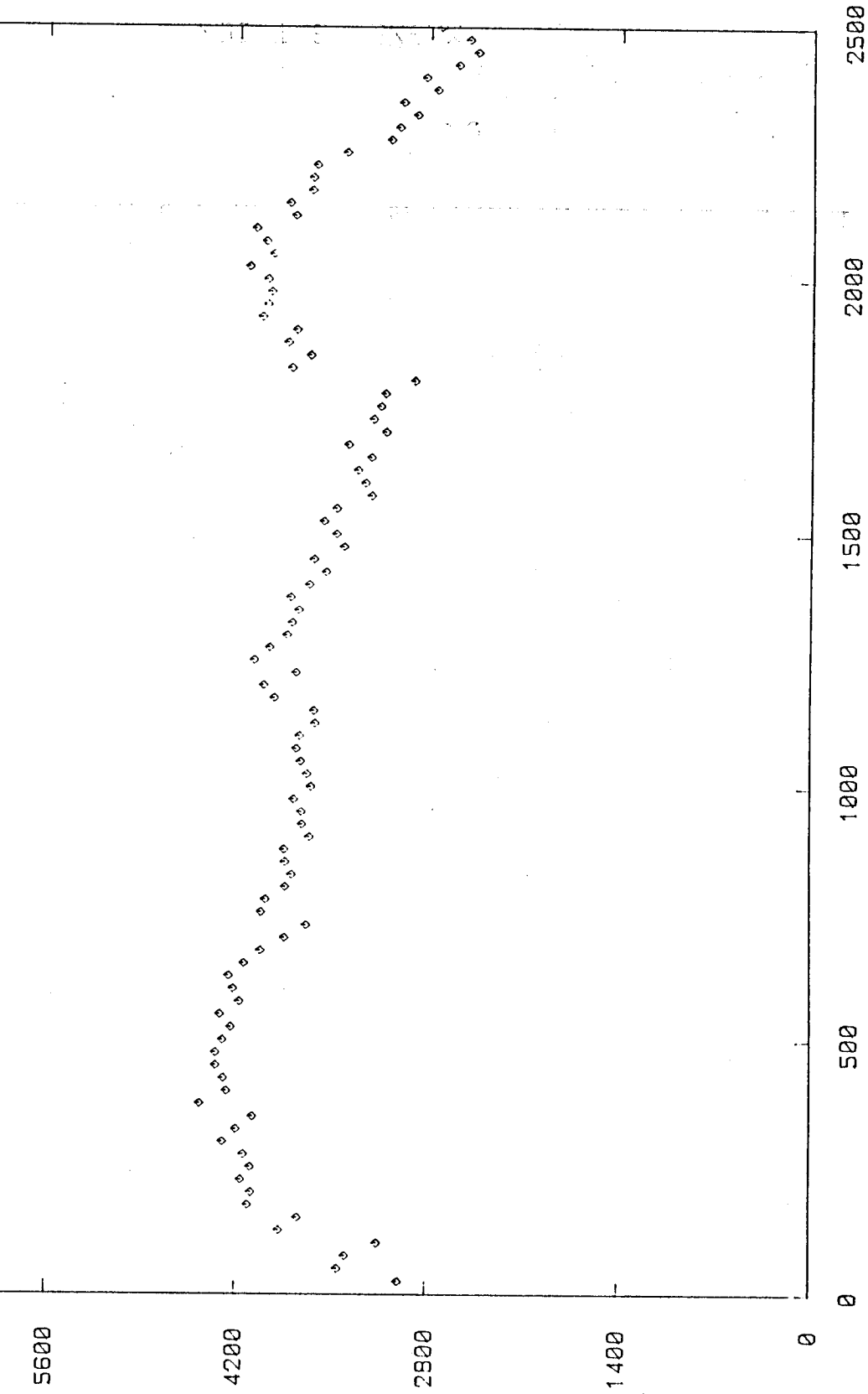


Fig.5.25. Phosphorus field scan of InP:S with double-irradiation at 2k bars.
 Double-irradiation frequency 900 k Hz.

9 1 2 6
 MAGNETISATION
 PREPARATION FIELD 25000
 PREPARATION TIME 2 mins
 SWITCHING TIME 8 secs
 RELAXATION TIME 1 secs
 ;1.FCDAT.INP-S-P2

Thu, 09 Jun 1988, 09:32:58 : 1.FCDAT.INP-S-P4
 RELAXATION TIME 1 secs
 SWITCHING TIME 8 secs
 PREPARATION TIME 2 mins
 PREPARATION FIELD 25000

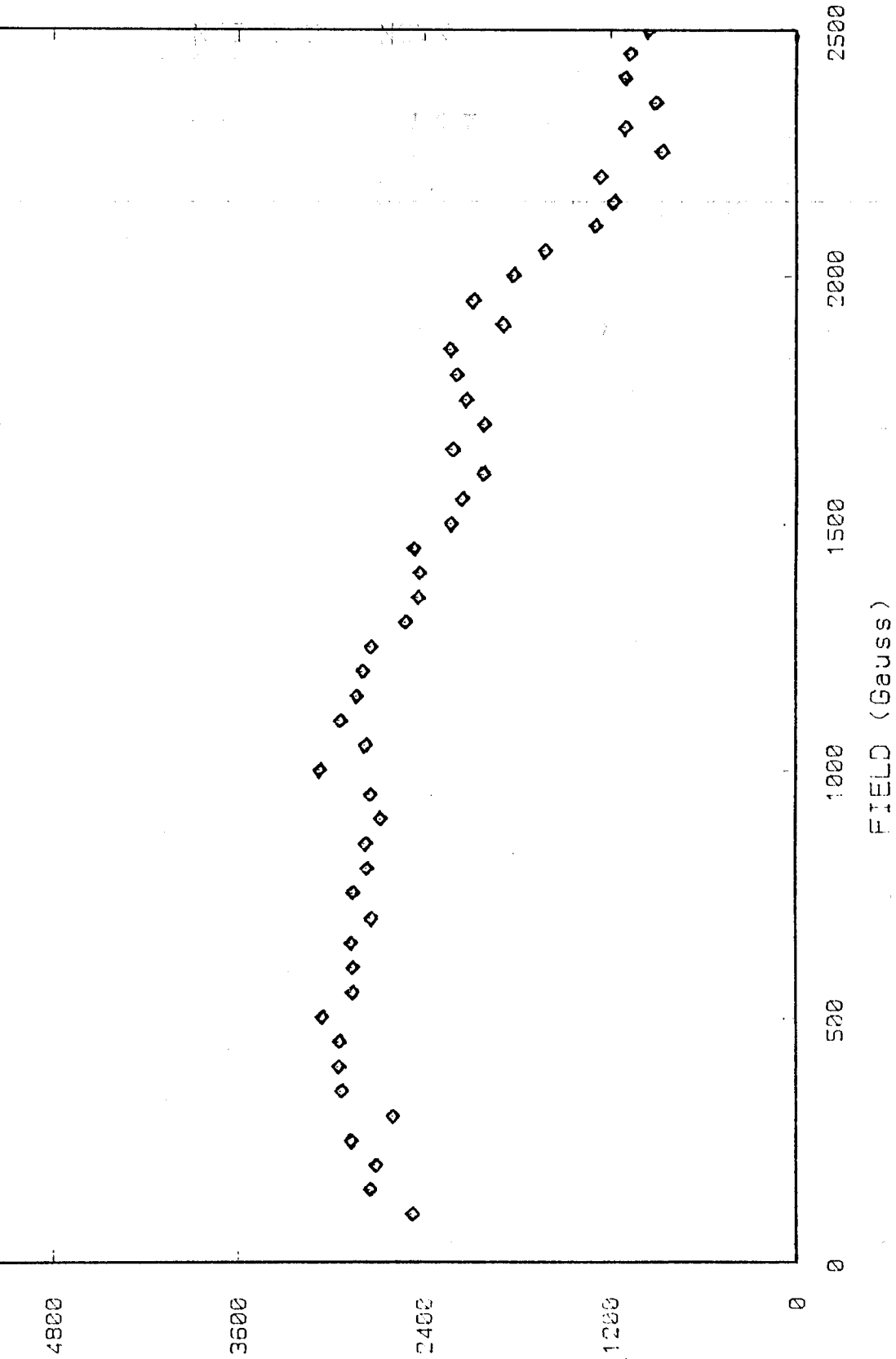


Fig.5.26. Phosphorus field scan of InP:S with double-irradiation at 2k bars.
 Double-irradiation frequency 900 k Hz.

1 2 7
 MAGNETISATION
 PREPARATION FIELD 25000
 PREPARATION TIME 2 mins
 RELAXATION TIME 1 secs
 SWITCHING TIME 8 secs
 Thu, 09 Jun 1988, 09:32:58 : 1.FCDAT.INP-S-P4

Thu,09 Jun 1988.12:06:23 :1.FCDAT.INP-S-P5
 RELAXATION TIME 1 secs
 SWITCHING TIME 8 secs
 PREPARATION TIME 2 mins
 PREPARATION FIELD 25000

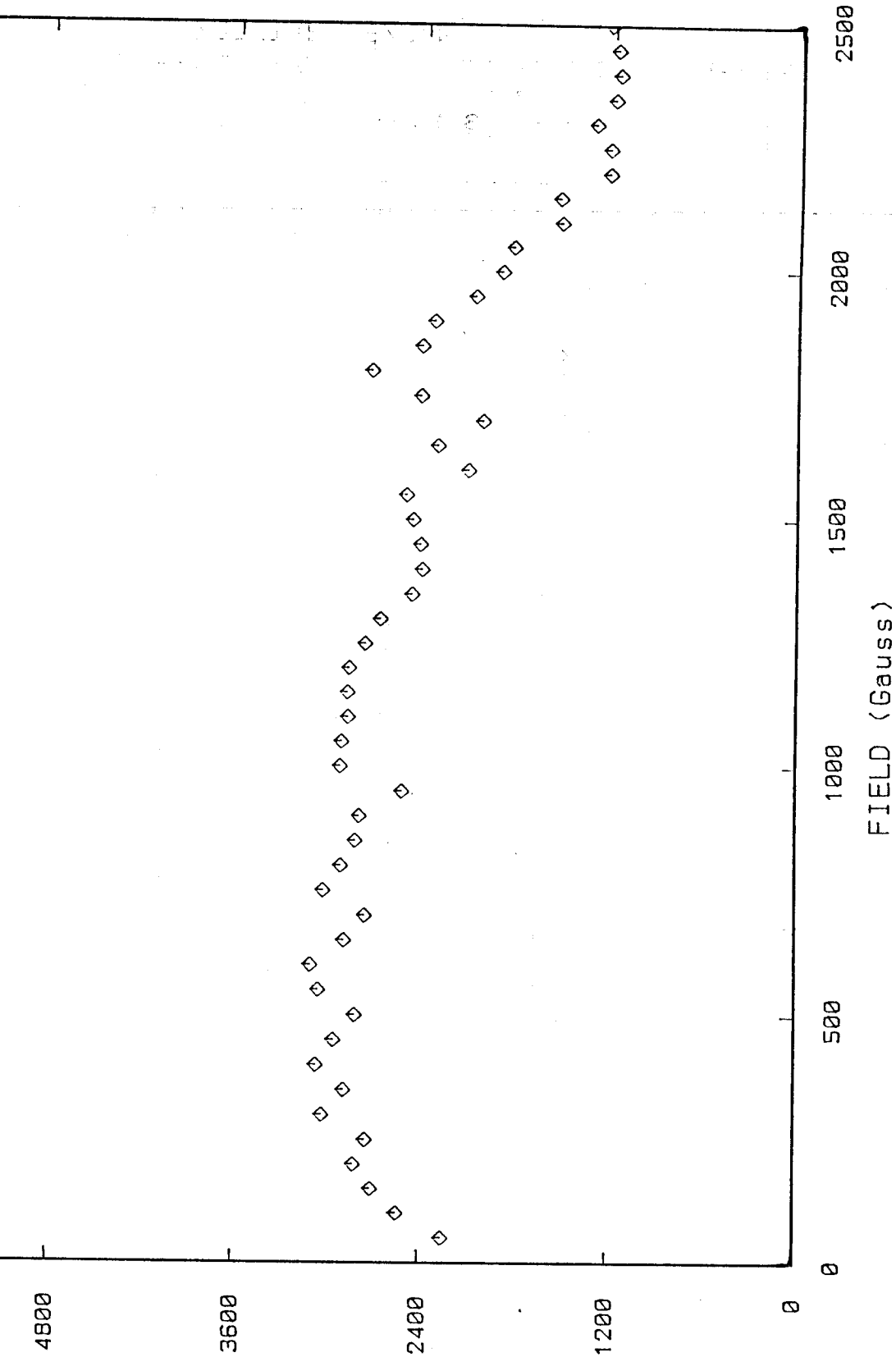


Fig.5.27. Phosphorus field scan of InP:S with double-irradiation at 2k bars.
 Double-irradiation frequency 900 k Hz

8 2 1 1
 128
 MAGNETISATION

A marked broadening of the quadrupole peak (by about a factor of two) is observed which could be as a result of some change to the band structure inherent at such a high pressure, or simply a shift in the fermi level.

A hump-like feature is observed at around 2000 Gauss and seems to shift towards the lower field region rather linearly with time as is apparent from the four spectra. This may be due to decreasing pressure resulting from a leaky bomb (high pressure vessel). These scans are at a very early stage in the investigation.

CHAPTER SIX

GENERAL DISCUSSION IN TERMS OF THE CONCEPTS OF SPIN TEMPERATURE AND THE DENSITY MATRIX

For the discussion of most of the field dependent phenomena that are studied using magnetic field cycling, the concepts of the spin temperature and the density matrix are of such paramount importance that one tends to feel that a discussion of field cycling is incomplete without their being mentioned. This discussion is strictly a part of the NMR related theory of chapter 3 but some of the experimentally observed spin phenomena like zero field magnetization and cross-relaxation are accounted for so naturally in this approach that it seemed a premature inclusion before chapter 5. However, only a simple general discussion is given here.

It must be mentioned that the concept of the density matrix, in particular (which assumes the existence of spin temperature for certain approximations) is a growing theoretical approach. To actually relate it directly and in detail to the localized interactions suggested by the observed spectra (e.g. hyperfine and quadrupolar) is non trivial but nonetheless very interesting.

1 Relaxation in Terms of Spin Temperature

As mentioned in section 4.3, the different nuclear species in a sample, can be observed independently using field cycling, as

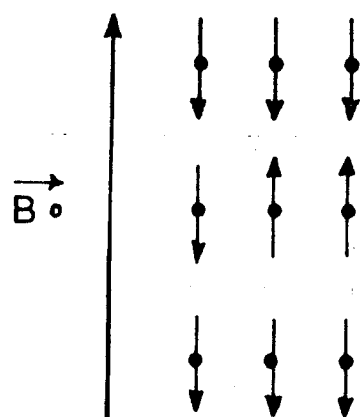
long as they resonate at well spaced frequencies. This leads to the suggestion that the identical spins of a particular nuclear species could, under certain conditions, be treated as a single macrosystem while the rest of the lattice acts as a heat bath.

Considering a system of N non-interacting identical nuclear spins placed in the static field $\vec{B}_0$. Assuming these are spin $\frac{1}{2}$ nuclei, as in the case for phosphorus, the spins will precess in a general direction either parallel or anti parallel to the field $\vec{B}_0$.

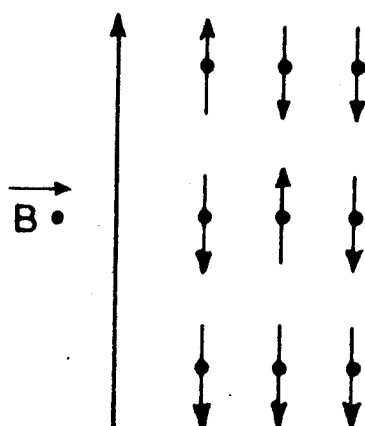
If n spins are oriented parallel to the field ($M_I = \frac{1}{2}$) and the remaining $(N-n)$ antiparallel ($M_I = -\frac{1}{2}$), the energy of the system is given by

$$E(n) = n \left(\frac{-\gamma \hbar B_0}{2} \right) + (N-n) \left(\frac{\gamma \hbar B_0}{2} \right) = (N-2n) \frac{\gamma \hbar B_0}{2} \quad (6.1)$$

Fig. 6.1 shows two different microstates for a two-dimensional model with $N=2$, both of which correspond to the same macrostate $n = 2$. The two microstates are distinct physically different states because the two nuclei with "spin up" are located at different lattice sites in the two cases



(a)



(b)

Fig. 6.1. (a) and (b) show two different microstates, for an array of 9 spin $\frac{1}{2}$ nuclei, both corresponding to the same macrostate $n = 2$. (After F. Mandl, *statistical physics*, J. Wiley & son (London, 1971)).

Clearly all microstates of the same macrostate give the same total energy. The number of microstates with energy $E(n)$ is given by the number of ways in which n sites can be selected, out of the total of N sites, at which 'up-spins' are placed, all other sites having 'down-spins'. This number is

$$\Omega_1(n) = \binom{N}{n} = \frac{N!}{n!(N-n)!} \quad (6.2)$$

Taking an energy interval $\delta E < \gamma h B_0$, the interval contains only one energy level and since $\Omega_1(n)$ gives the number of microstates with the same energy $E(n)$, it follows that $\Omega_1(n)$ is the statistical weight of the macrostate with energy $E(n)$.

As a measure of the disorder of a system in a given macrostate, the entropy is given by

$$S = k_B \ln \Omega_1 \quad (6.3)$$

where k_B is the Boltzmann's constant.

At thermal equilibrium, by definition, the absolute temperature is given by

$$\frac{1}{T} = \frac{\partial S}{\partial E} \quad (6.4)$$

So far, this only goes to show that the concept of temperature has natural occurrence for a spin system under the simplifying conditions and assumptions stated in this section.

Assuming that the lattice acts as a heat bath and that the combined total energy of the spin system and the lattice

has a constant value E_0 . If the spin system possesses a discrete set of energy levels E_n , then the probability P_n , that the spin system will be in a state with energy E_n will be proportional to the number of lattice states $\Omega_2(E_L)$ compatible with this energy level. Since

$$E_0 = E_n + E_L, \quad (6.5)$$

one can write

$$P_n = \text{const. } \Omega_2(E_0 - E_n), \quad (6.6)$$

The entropy of the heat bath is given by

$$S_2(E_0 - E_n) = k_B \ln \Omega_2(E_0 - E_n). \quad (6.7)$$

Therefore

$$P_n = \text{const. } \exp[S_2(E_0 - E_n)/k_B] \quad (6.8)$$

The average energy of the lattice is very large compared to that of the spin system. Therefore

$$E_n \ll E_0 \quad (6.9)$$

In view of this, expanding the function $S_2(E_0 - E_n)$ into a Taylor series about E_0 , yield

$$S_2(E_0 - E_n) = S_2(E_0) - E_n \frac{\partial S_2(E_0)}{\partial E_0} + \frac{1}{2} E_n^2 \frac{\partial^2 S_2(E_0)}{\partial E_0^2} + \dots \quad (6.10)$$

By definition

$$\frac{\partial S_2(E_0)}{\partial E_0} = \frac{1}{T_L} \quad (6.11)$$

where T_L is the temperature of the lattice. Ignoring all terms of order higher than one and substituting equ. 6.11 into 6.2 gives

$$P_n = \text{const.} \exp\left(-\frac{E_n}{k_B T_L}\right) \quad (6.12a)$$

where the term $eS_z(E_0)/k_B$ goes as part of the constant.

For normalization of the probability

$$P_n = \frac{1}{Z} \exp\left(-\frac{E_n}{k_B T_L}\right) \quad (6.12b)$$

where

$$Z = \sum_m \exp\left(-\frac{E_m}{k_B T_L}\right) \quad (6.13)$$

is the partition function.

Eqs. (6.12a, b) assume of course that the spin system is in thermal equilibrium with the lattice. However, vast progress in solid state physics, and particularly in interpreting the behaviour of spin systems arose from realising that for any other non-equilibrium states, it is equally valid to say that the probability of the spin system being in a state with energy E_n is given by

$$P_n = \frac{1}{Z} \exp\left(-\frac{E_n}{k_B T_s}\right) \quad (6.14)$$

This formally assigns a temperature T_s to the spins, called the spin temperature, which is not necessarily equal to the lattice temperature. Such a state in which thermal equilibrium is disturbed occurs in the presence of a varying external field.

However, Eq. (6.14) is only valid when the spins are in

equilibrium with each other (although not with the lattice) and this suggests a similar condition for the validity of a spin temperature.

If an expression is obtained for the time rate of change of spin temperature, it is likely to give some further insight into the relaxation of a spin system.

To do this, let $\mathcal{H}$ be the Hamiltonian of the system with eigen values E_n and let these energies be measured from a reference such that

$$\sum_n E_n = 0 \quad (6.15)$$

Then

$$\text{Tr } \mathcal{H} = 0, \quad (6.16)$$

which is a condition fulfilled for the zeeman interaction.

The average energy of the system is

$$\bar{E} = \sum_n P_n E_n \quad (6.17)$$

Then $\beta_s = 1/k_B T_s$ (the spin temperature parameter), (6.18)

$$\frac{d\bar{E}}{dt} = \frac{d\bar{E}}{d\beta_s} \frac{d\beta_s}{dt} \quad (6.19)$$

$$\frac{d\bar{E}}{d\beta_s} = \frac{d}{d\beta_s} \sum_n P_n E_n \quad (6.20)$$

$$\text{and } P_n = \frac{1}{Z} e^{-\beta_s E_n} \quad (6.21)$$

Assume the temperature to be high enough so that $\beta \cdot E_n \ll 1$.

$$Z = \sum_n e^{-\beta \cdot E_n} = \sum_n (1 - \beta \cdot E_n + \frac{\beta^2 E_n^2}{2!} + \dots) \quad (6.22a)$$

By Eq. (6.15), the second term in the expansion vanishes. Neglecting all other higher order terms, Z becomes equal to the total number of states

$$Z = N \quad (6.22b)$$

Using Eq. (6.20),

$$\frac{d\bar{E}}{d\beta} = -\frac{1}{N} \sum_n E_n^2 e^{-\beta \cdot E_n} \quad (6.23a)$$

or, by neglecting all high order terms of the exponential

$$\frac{d\bar{E}}{d\beta} \simeq -\frac{1}{N} \sum_n E_n^2 \quad (6.23b)$$

Substituting this into Eq. (6.19)

$$\frac{d\beta}{dt} = -N \frac{1}{\sum_n E_n^2} \frac{d\bar{E}}{dt} \quad (6.24)$$

To evaluate $\frac{d\bar{E}}{dt}$, we write

$$\frac{d\bar{E}}{dt} = \frac{d}{dt} \sum_n P_n E_n = \sum_n \frac{E_n dP_n}{dt} \quad (6.25)$$

If W_{mn} is the probability per second that the lattice induces a transition of the system from m to n then

$$\frac{dP_n}{dt} = \sum_m (P_m W_{mn} - P_n W_{nm}) \quad (6.26)$$

therefore

$$\frac{d\bar{E}}{dt} = \sum_{mn} (P_m W_{mn} - P_n W_{nm}) E_n \quad (6.27a)$$

$$\frac{d\bar{E}}{dt} = \frac{1}{2} \sum_{mn} (P_m W_{mn} - P_n W_{nm}) E_n + \frac{1}{2} \sum_{mn} (P_n W_{nm} - P_m W_{mn}) E_m \quad (6.27b)$$

$$\frac{d\bar{E}}{dt} = \frac{1}{2} \sum_{mn} (P_m W_{mn} - P_n W_{nm}) (E_n - E_m) \quad (6.27c)$$

By Eq. (6.21) it is clear that

$$P_n = P_m e^{(E_m - E_n)\beta_s} \quad (6.28)$$

when the system is in thermal equilibrium with the lattice (when $T_s = T_L$),

$$P_m W_{mn} = P_n W_{nm} \quad (6.29a)$$

$$W_{mn} = \frac{P_n}{P_m} W_{nm} \quad (6.29b)$$

$$W_{mn} = W_{nm} e^{(E_m - E_n)\beta_L} \quad (6.29c)$$

where $\beta_L = 1/(k_B T_L)$, the lattice temperature parameter substituting Eqs. (6.28) and (6.29c) into Eq. (6.27c),

$$\frac{d\bar{E}}{dt} = \frac{1}{2} \sum_{mn} P_m W_{mn} [1 - e^{(E_m - E_n)(\beta_s - \beta_L)}] (E_n - E_m) \quad (6.30a)$$

By expanding the exponential and ignoring the high order terms, one obtains

$$\frac{d\bar{E}}{dt} \simeq \frac{1}{2} \sum_{mn} P_m W_{mn} (E_n - E_m)^2 (\beta_s - \beta_L) \quad (6.30b)$$

and

$$P_m = \frac{1 - \beta E_m}{N} + \dots \simeq \frac{1}{N} \quad (\text{for } \beta E_m \ll 1) \quad (6.31)$$

Using Eq. (6.31) in Eq. (6.30b) and substituting Eq. (6.30b) into Eq. (6.24), yields

$$\frac{d\beta_s}{dt} = (\beta_L - \beta_s) \frac{[\frac{1}{2} \sum_{mn} W_{mn} (E_m - E_n)^2]}{\sum_n E_n^2} \quad (6.32a)$$

As expected, when the spin temperature equals the lattice temperature i.e. $\beta_s = \beta_L$, the spin temperature remains constant i.e. $\frac{d\beta_s}{dt} = 0$

This equilibrium condition is to be achieved in a time equal to the spin lattice relaxation time hence

$$\frac{d\beta_z}{dt} = \frac{\beta_z - \beta_{\text{eq}}}{T_1} \quad (6.32b)$$

where

$$T_1 = \frac{\sum E_n^2}{\frac{1}{2} \sum_{mn} W_{mn} (E_m - E_n)^2} \quad (6.33)$$

which gives an alternative expression for the spin lattice relaxation time. W_{mn} could be evaluated using time dependent perturbation theory or density matrix considerations.

It is clear from Eq. (6.32b) that it is the spin-lattice relaxation mechanism which tends to make the spin temperature equal the lattice temperature. Steady state irradiation establishes a spin temperature which is higher than the lattice temperature. This implies that, left to themselves, the spins will rapidly achieve a state of thermal equilibrium consistent with the energy content and any other quasi-invariant of the system.

Through rapid reduction of the applied field, spin systems can acquire a spin temperature much lower than that of the lattice. This implies that they can preserve a significant amount of magnetization even though the external field is very small or even zero. This was a feature observed in Fig. 5.23.

6.2 Behaviour of a Spin System in terms of the density matrix

The hypothesis of spin temperature is based on the observation that the spin system behaves in the same way as thermodynamical systems for which the arguments leading to the concept of temperature have experimentally proved to be valid. One such argument is that the spins maintain an equilibrium among themselves (though not necessarily with the lattice). This is not always valid, (as will be seen later), for example it is only after a time longer than T_2 that it is valid to speak of the existence of a spin temperature after a 90° pulse.

When the spin temperature concept breaks down, the technique of the density matrix becomes very useful. It allows the discussion of both T_1 and T_2 processes in a natural way.

Consider a system consisting of one isolated nucleus in the static magnetic field $\vec{B}_0$. If $\Psi(t)$ is the time dependent wave function of this system, then the expectation value $\langle A \rangle$ of some operator A is

$$\langle A \rangle = \langle \Psi | A | \Psi \rangle \quad (6.34)$$

If Ψ is expanded in a complete set of orthonormal functions U_n which are time-dependent, then

$$\Psi = \sum_n C_n U_n \quad (6.35)$$

so that

$$\langle A \rangle = \sum_{n,m} C_m^* C_n \langle m | A | n \rangle \quad (6.36)$$

Since Ψ varies with time so must the C_n 's.

As the wave function Ψ varies, the coefficients $C_m^* C_n$ will vary, hence the expectation value $\langle A \rangle$ will be a function of time. However the matrix elements $\langle m | A | n \rangle$ will remain the same in time, the 'expectation weight' of these element is determined by the product $C_m^* C_n$ at any given time. These products $C_m^* C_n$ can be easily arranged in the form of a matrix for all values of m and n . It is convenient to express the matrix $C_n C_m^*$ as the representation of some operator P . i.e.

$$C_n C_m^* = \langle n | P | m \rangle \quad (6.37)$$

Therefore

$$\langle A \rangle = \sum_{n,m} \langle n | P | m \rangle \langle m | A | n \rangle \quad (6.38)$$

As an example, if A is the operator for the x-component of magnetization M_x .

$$\langle M_x \rangle = \sum_{n,m} \langle n | P | m \rangle \langle m | M_x | n \rangle \quad (6.39a)$$

But

$$\langle M_x \rangle = \int \Psi^*(t) M_x \Psi(t) dt \quad (6.39b)$$

For an isolated nucleus in a static field $\vec{B}_0$, and for a particular value of m .

$$\Psi_m(t) = U_m e^{-i(\hbar) E_m t} \quad (6.40)$$

where E_m are the eigen values,

$$E_m = -\gamma \hbar B_0 m \quad (6.41)$$

The most general time-dependent solution, for all m values is

$$\Psi(t) = \sum_{m=-l}^{+l} a_m e^{-(i/\hbar) E_m t} U_m \quad (6.42)$$

Using

$$M_x = \gamma \hbar I_x \quad (6.43)$$

and Eq. (6.42) in Eq. (6.39b) gives

$$\langle M_x \rangle = \sum_{m, m'} \gamma \hbar a_m^* a_m e^{(i/\hbar) (E_m - E_{m'}) t} \langle m' | I_x | m \rangle \quad (6.44)$$

$$\text{where } \langle m' | I_x | m \rangle = \int U_{m'}^* I_x U_m d\tau \quad (6.45)$$

$$\text{Now } I_x = \frac{1}{2} [I_+ + I_-] \quad (6.46)$$

where I_+ and I_- are the raising and lowering operators.

Since

$$I_+ U_m = \sqrt{l(l+1) - m(m+1)} U_{m+1} \quad (6.47a)$$

and

$$I_- U_m = \sqrt{l(l+1) - m(m-1)} U_{m-1} \quad (6.47b)$$

the matrix elements $\langle m' | I_x | m \rangle$ vanish unless $m' = m \pm 1$, in which case

$$E_{m'} - E_m = \pm \gamma \hbar B_0 \quad (6.48)$$

The expansion (6.44) for a spin $\frac{1}{2}$ nucleus like phosphorous is

$$\begin{aligned} \langle M_x \rangle = & \gamma \hbar a_{\frac{1}{2}}^* a_{-\frac{1}{2}} e^{-(i \gamma B_0 t)} \langle \frac{1}{2} | I_x | -\frac{1}{2} \rangle \\ & + \gamma \hbar a_{\frac{1}{2}}^* a_{\frac{1}{2}} e^{(i \gamma B_0 t)} \langle -\frac{1}{2} | I_x | \frac{1}{2} \rangle \end{aligned} \quad (6.49a)$$

Since $\langle \frac{1}{2} | I_x | -\frac{1}{2} \rangle$ is the complex conjugate of $\langle -\frac{1}{2} | I_x | \frac{1}{2} \rangle$,

$$\langle M_x \rangle = 2 \gamma \hbar \text{Re} [a_{\frac{1}{2}}^* a_{-\frac{1}{2}} e^{-i \omega_0 t} \langle \frac{1}{2} | I_x | -\frac{1}{2} \rangle] \quad (6.49b)$$

where $\omega_0 = \gamma B_0$

The matrix element can easily be evaluated using Eq. (6.46) and Eqs. (6.47a, b) to give

$$\langle \frac{1}{2} | I_x | -\frac{1}{2} \rangle = \frac{1}{2} \quad (6.50)$$

The a 's can be expressed in terms of two real positive quantities b and d and two other real quantities χ and β which can either be positive or negative as follows

$$a = b e^{i\chi} \quad (6.51)$$

$$c = d e^{i\beta} \quad (6.52)$$

where $b^2 + d^2 = 1$ for the normalization of the wave function. This gives

$$\langle M_x \rangle = \gamma \hbar b d \cos (\chi - \beta + \omega_0 t) \quad (6.53a)$$

If the same derivation is used for the y and z components of magnetization the result is

$$\langle M_y \rangle = -\gamma \hbar b d \sin (\chi - \beta + \omega_0 t) \quad (6.53b)$$

$$\langle M_z \rangle = \gamma \hbar \frac{(b^2 - d^2)}{2} \quad (6.53c)$$

The three equations show that the expectation values $\langle M_x \rangle$ and $\langle M_y \rangle$ oscillate in time at the frequency ω_0 with the same maximum amplitude, while $\langle M_z \rangle$ is independent of time.

This is clearly a quantum mechanical interpretation of Larmor precession. Moreover, the frequency $\omega_0 = \gamma B_0$ is exactly the Larmor frequency.

Comparing Eq. (6.44) to Eq. (6.39a), it is clear that

$$\langle n | P | m \rangle = a_n^* a_m e^{(i/\hbar)(E_n - E_m)t} \quad (6.54)$$

For the spin $\frac{1}{2}$ nucleus considered earlier, these matrix elements can be evaluated by substituting the appropriate

and putting

$$E_{\frac{1}{2}} - E_{-\frac{1}{2}} = \hbar \omega_0 \quad (6.55)$$

the four matrix elements obtained are

$$\langle \frac{1}{2} | P | \frac{1}{2} \rangle = b^2 \quad (6.56a)$$

$$\langle -\frac{1}{2} | P | -\frac{1}{2} \rangle = d^2 \quad (6.56b)$$

$$\langle \frac{1}{2} | P | -\frac{1}{2} \rangle = b d e^{i(x - \beta + \omega_0 t)} \quad (6.56c)$$

$$\langle -\frac{1}{2} | P | \frac{1}{2} \rangle = b d e^{i(\beta - x - \omega_0 t)} \quad (6.56d)$$

The diagonal elements ($n = m$) give the probabilities of occupation of the various states, the total probability $b^2 + d^2$ being equal to one.

The appearance of x , β and ω_0 in the expressions for the off-diagonal suggests that they are closely related to the components of magnetization perpendicular to the static field since these three parameters appear in Eqs. (6.53a) and (6.53b) but not in Eq. (6.53c) which represents the component parallel to $\vec{B}_0$.

If the spins in a sample are assumed to be non-interacting, each spin can be taken as a system. This has been the assumption throughout the discussion in this section. The spins can then be treated as an ensemble of systems. An average expectation value for the whole ensemble can then be computed.

Consider the expectation value of the x-component of magnetization again. Since the wave function $\Psi(t)$ in equation 6.39a will vary from system to system, the matrix elements $\langle n | P | m \rangle$ will also vary, but the matrix elements $\langle m | M_x | n \rangle$ will be the same for similar nuclei. From Eq. (6.39a), if a bar is used to denote an ensemble average, then

$$\overline{\langle M_x \rangle} = \sum_{n,m} \overline{\langle n | P | m \rangle} \langle m | M_x | n \rangle, \quad (6.57)$$

If the matrix $\overline{\langle n | P | m \rangle}$ is a representation of some other operator ρ i.e.

$$\overline{\langle n | P | m \rangle} = \langle n | \rho | m \rangle \quad (6.58)$$

Then matrix $\langle n | \rho | m \rangle$ is referred to as the "density matrix".

It is easy to show, using the time dependent Schrodinger equation, that the differential equation obeyed by the density matrix in terms of the Hamiltonian $\mathcal{H}$ of the system is

$$\frac{d\rho}{dt} = \frac{i}{\hbar} [\rho, \mathcal{H}] \quad (6.59)$$

$\mathcal{H}$ is assumed identical for all members of the ensemble.

The above equation is the quantum mechanical form of Liouville's theorem describing the time rate of change of density at a fixed point in phase space. Therefore the density matrix is the quantum mechanical equivalent of the classical density ρ of points in phase space.

In a static field, the hamiltonian $\mathcal{H}_0$ is independent of time and Eq. (6.59) can be solved to give

$$\rho(t) = e^{-(i/\hbar)\mathcal{H}_0 t} \rho(0) e^{(i/\hbar)\mathcal{H}_0 t} \quad (6.60)$$

In terms of the eigenfunctions of the Hamiltonian U_n , the density matrix elements are given by

$$\langle n | \rho(t) | m \rangle = \int U_n^* e^{-(i/\hbar)\mathcal{H}_0 t} \rho(0) e^{(i/\hbar)\mathcal{H}_0 t} U_m d\tau \quad (6.61a)$$

$$\langle n | \rho(t) | m \rangle = \int (e^{(i/\hbar)\mathcal{H}_0 t} U_n)^* \rho(0) e^{(i/\hbar)\mathcal{H}_0 t} U_m d\tau \quad (6.61b)$$

Using $\mathcal{H}_0 U_n = E_n U_n$ and the power series expansion of the exponential operator

$$\langle n | \rho(t) | m \rangle = e^{(i/\hbar)(E_m - E_n)t} \langle n | \rho(0) | m \rangle \quad (6.61c)$$

This equation shows that the off-diagonal elements oscillate harmonically in time. This means that if these off-diagonal elements do not vanish, then the average magnetization perpendicular to the static field for a group of non-interacting spins will be an observable property of the ensemble which will oscillate in time.

The diagonal elements are generally given by

$$\langle m | \rho(t) | m \rangle = \langle m | \rho(0) | m \rangle \quad (6.62)$$

and when the spins are in thermal equilibrium, i.e. when the concept of spin temperature is valid, then these elements are simply given by the population of eigen states as described by the spin temperature T_s .

That is

$$\langle m | \rho | m \rangle = \frac{e^{-E_m/kB T_s}}{z} \quad (6.63)$$

where z is the partition function.

However, in quantum theory, any experiment that counts the number of spins in various m states will find a statistical distribution not related to temperature.

Therefore assuming quite generally, as in the case of the single spin, that

$$C_n = a e^{i x_n} \quad (6.64)$$

where a_n 's are real and positive but x_n are real functions of time and can be positive or negative,

$$\langle m | \rho | n \rangle = \overline{\langle m | \rho | n \rangle} \quad (6.65a)$$

$$\langle m | \rho | n \rangle = C_m C_n^* \quad (6.65b)$$

$$\langle m | \rho | n \rangle = a_m a_n e^{i(x_m - x_n)} \quad (6.65c)$$

At equilibrium, by the hypothesis of random phases, the phases x_m and x_n have all values of equal probability causing the elements to be time independent. By Eq. (6.61c), it is only the diagonal terms that are independent of time, implying that the off-diagonal terms and hence the transverse components of magnetisation vanish at thermal equilibrium. One can artificially create situations where the density matrix is non-diagonal. For instance, after a 90° pulse, one obtains a net magnetisation at right angles to the external field, which corresponds to off-diagonal elements.

6.3 Double irradiation in terms of the density matrix and spin temperature.

During double irradiation apart from the strong static field $\vec{B}_0$, there is the time-variational field $\vec{B}_1$. Therefore the equation of motion of the density matrix will have a Hamiltonian consisting of not only the large time-independent interaction $\mathcal{H}_0$ as in Eq. (6.59), but also a much smaller time-dependent

term $\mathcal{H}_1(t)$, i.e.

$$\frac{d\rho}{dt} = \frac{i}{\hbar} [\rho, \mathcal{H}_0 + \mathcal{H}_1] \quad (6.66)$$

The solution when $\mathcal{H}_1$ is zero is given by Eq. (6.60). Assume that in the presence of $\mathcal{H}_1$, the solution would take a similar form i.e.

$$\rho(t) = e^{-(i/\hbar)\mathcal{H}_0 t} \rho'(t) e^{(i/\hbar)\mathcal{H}_0 t} \quad (6.67)$$

where $\rho'(t)$ is expected to change slowly with time.

Substituting Eq. (6.67) into Eq. (6.66) gives

$$-\frac{i}{\hbar} [\mathcal{H}_0, \rho] + e^{-(i/\hbar)\mathcal{H}_0 t} \frac{d\rho'}{dt} e^{(i/\hbar)\mathcal{H}_0 t} = \frac{i}{\hbar} [\rho, \mathcal{H}_0 + \mathcal{H}_1] \quad (6.68)$$

This can be simplified to give

$$\frac{d\rho'}{dt} = \frac{i}{\hbar} [\rho', \mathcal{H}_1(t)] \quad (6.69)$$

$$\text{where } \mathcal{H}_1 = e^{i\mathcal{H}_0 t/\hbar} \mathcal{H}_1 e^{-(i/\hbar)\mathcal{H}_0 t} \quad (6.70)$$

This is a canonical transformation which in actual fact gives the interaction representation. Eq. (6.70) expresses the fact that if $\mathcal{H}_1$ were zero, then ρ' would be constant in time.

This equation can be solved and used to find the probability per second of transitions between any two states, taking into account the interaction mechanisms involved. This as remarked earlier, is a non trivial task and rather beyond the scope

of the investigation at this level. However, an expression
(6.3)
has been obtained elsewhere for a general interaction say
 $V(t)$, which agrees with the time dependent perturbation theory.

During double irradiation, the phenomenon that has been loosely referred to as cross-relaxation, arises because the spins of the two different nuclear species appear to exchange energy with one another faster than they do with the lattice. The spin temperature of both nuclear subsystems evolves towards a common value under the effect of what is essentially an off-diagonal perturbation. Double flip-flops between neighbouring spins of different species, in which the zeeman energy is nearly conserved, occur at integral multiples of the Larmor frequencies of either nuclear species. The small energy imbalance is taken up by the internal energy of the spin systems. This flip-flop process is induced by spin-spin terms of the form $I_{+}^{(1)} I_{-}^{(2)} + I_{-}^{(1)} I_{+}^{(2)}$, where the superscripts are used to distinguish between the operators relating to different nuclear spin species. This is a possible explanation for the observation illustrated in section 5.3 that a transition corresponding to the resonance of some nuclear species is observable in the scans of the other nuclear species of interest.

CHAPTER SEVEN

CONCLUSION

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It was firmly established despite the error involved, that the value of the spin lattice relaxation time T_1 for InP:Fe increases with increasing angle between the [100] plane of the crystal lattice and the static magnetic field $\vec{B}_0$, this being for angles from 0° to 45°. For angles above 45° up to 90°, the relaxation time T_1 decreased with increase in angle of orientation. This phenomenon was established for all three samples InP : Fe, InP : S and Ga As : Si although it was for InP : Fe that sufficient data was obtained for the compilation of a table (Table 5.1). This orientational dependence of T_1 was undoubtedly a major contributing factor to the reduction of the signal to noise (S/N) ratio for spectra obtained at successively increasing angles of orientation between 0° and 45° i.e. Fig. 5.3 and 5.4 which were obtained at angles of orientation 15° and 30° respectively. Spectra obtained at 45° had such a low signal to noise ratio that it seemed quite pointless to include them.

The spectral results can be interpreted in terms of cross-coupling of matrix nuclei (constituent nuclei of the semiconductor excluding impurity) using a spin-Hamiltonian with zeeman-quadrupole and zeeman/hyperfine terms. It was hoped, as pointed out in section 1.4 that the deep and shallow band gap levels could be distinguished. It is shown that this can easily be done, e.g. in InP : Fe, the Fe impurity, which introduces a deep electron level in the band gap,

has strongly localised impurity electrons resulting in an almost neutral impurity site, as explained earlier. This suggests a dominance of the hyperfine over the quadrupolar interaction. From a qualitative theoretical treatment it is seen that the hyperfine interaction does, in fact, predict a narrow peak in the low field region. Furthermore, the width of this theoretically predicted peak agrees with the spectral peak obtained experimentally. As pointed out earlier however, there are high-field transitions predicted theoretically that have not been observed experimentally. For InP : S and Ga As : Si, the impurity introduces a shallow band gap level, the impurity electron is more mobile exposing a net positive charge due to the impurity nucleus. This suggests a dominance of the quadrupole interaction over the hyperfine interaction. The same theoretical treatment as for InP : Fe based on second order perturbation theory, but this time applied to quadrupolar rather than hyperfine interaction, shows that the quadrupolar interaction predicts a much broader peak than the hyperfine^{interaction}. This is in good agreement with the experimental results.

A numerical evaluation of the matrix elements of the zeeman/hyperfine spin-Hamiltonian and diagonalization reveals the fact that the hyperfine interaction splits the zeeman levels. This is shown in the energy fan diagram of Fig. 5.5. A similar treatment for the zeeman/quadrupolar interaction alters the field dependence of the zeeman levels, this being mostly pronounced in the low field region (Fig. 5.7), in fact the region where the spectral peaks were observed. This perturbation on the zeeman levels enhances cross coupling between the two nuclei as explained earlier.

The effect of irradiating the sample with low frequency ν during the recovery period (double irradiation) was to enhance some cross coupling transitions. Holes in the spectra were observed at nuclear zeeman transitions corresponding to $\Delta m_I = 1, 2$ and 3 i.e. at the matrix nuclei resonance fields (or frequencies), at twice the resonance field etc.

The fact that the two matrix nuclear-species of interest are coupled was established by the double irradiation investigations in which a hole corresponding to the resonance of one nuclear species is observed in the scans of the other nuclear species.

There is a sudden rise in recovered magnetization on the low field side of the indium $\Delta m_I = 1$ transition at 950 Gauss (Fig. 5.20). Work in interpreting this readily reproducible feature is still going on.

From a theoretical point of view, the approach introduced in section 5.21 (developed by Dr. P.J. McDonald) for a quantitative interpretation of the spectral information is undoubtedly very effective in as far as the prediction of possible transitions is concerned. This approach however, only gives the fields at which transitions are allowed and the next step would probably be to work out the "relative weights" of these field dependent transitions. That is, to find the probability per second of a transition being induced by hyperfine or quadrupole interaction, either by time dependent perturbation theory or the density matrix, as a function of the magnetic field. This would be important in analysing the spectral information in two ways:

- (1) In explaining why certain transitions that are predicted by theory were not observed. For example, it was argued in section 5.2.1 that an explanation as to why the predicted high field transition clusters were not observed experimentally is that their small relative occurrence in Table 5.2, reflects a corresponding small significance in terms of the observable spectral transitions. A more likely explanation however is that the probability of these high field transitions may simply be too low for concrete observation.
- (2) In explaining certain localized spectral features like the anomalous magnetization rise near the indium $\Delta m_I = 1$ transition. The fact that there is a sudden increase in transition probability in this

particular field region is established. on account of the reproducibility of the feature, the point of interest would be to identify the responsible interaction.

A step was made in the high pressure field cycling of III-V semiconductors and the results showed distinct structure, with a good signal to noise ratio. This promising start indicates that this may well become a major area of research in the future.

On the whole, NMR field cycling has been demonstrated as a new spectroscopic technique for conventional III-V semiconductors.

The apparent break through of this technique as opposed to the more traditional line shape methods is firstly due to the fact that direct measurement of low field phenomena using NMR is difficult because of the low magnetisation intensity that is attainable. A substantially improved sensitivity is achieved using field cycling because the measurement itself is done in an entirely different and higher field region. It is for this reason that rapid switching is of vital importance as remarked in section 4.3. Secondly, spin diffusion transfers magnetization between nuclei both near to and distant from an impurity, in this way involving all nuclei in the sample for a particular measurement, hence giving a strong defect-related signal.

Finally, I should mention that it is one of the great triumphs of the quantum theory that it describes not only simple 'elementary particle' systems but also the complex many-body systems of which a solid is made, with its great wealth of properties. This investigation has therefore been important because it deepens the understanding of the solids studied in terms of quantum mechanics and is a good example of experimental science.

REFERENCES

1 5 7

CHAPTER ONE

- 1.1 E. Kanegsberg, B. Pass and H.Y. Carr, Phys. Rev. Lett. 23, 572 (1969).
- 1.2 W. Teuerle and A. Hausman: ENDOR - Investigations of Iron Doped Ga As and Ga P, Physik B 23. 11-14 (1976).
- 1.3 P.J. McDonald, E.P. O'Reilly and A. Habanyama: A new defect spectroscopy for III-V semiconductors, 15th International conf., Defects in semiconductors, Budapest (1988).
- 1.4 Robin K. Harris and B.E. Mann, NMR and the periodic table. University of East Anglia. Academic press (1978).

CHAPTER TWO

- 2.1 G.W. Iseler: Properties of InP doped with Fe, Cr or Co. Lincoln laboratory, MIT. 02173 USA (1978)
- 2.2 S.D. Smith, S. Nudelman and S.S. Mitra: article on optical properties of solids. Plenum Press (1977)

- 2.3 D.R. Stranks, M.L. Heffernan, K.C. Leedow, P.T. McTigue and G.R.A. Withers: Chemistry, a structural view, Cambridge University Press (1979)
- 2.4 G. Dolling and J.L.T. Waugh: Lattice dynamics, Pergamon (1965)

CHAPTER THREE

- 3.1 W. Pauli, Naturwissen Schoften 12, 741 (1924)
- 3.2 I. Rabi, S. Millman, P. Kusch and J.P. Zacharios, Phys. Rev. 55, 526 (1939)
- 3.3 J.B.M. Kellogg, I. Rabi, N.F. Ramsay and J.R. Zacharios, Phys. Rev. 56, 728 (1939).
- 3.4 E.M. Purcell, H.C. Torrey, and R.V. Pound, Phys. Rev. 69, 37 (1946)
- 3.5 F. Bloch, W.W. Hansen and M.E. Packard, Phys. Rev. 69, 127 (1946).
- 3.6 F.A. Borey: Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York (1969).
- 3.7 R.M. Lynden-Bell, R.K. Harris: Nuclear Magnetic Resonance Spectroscopy, Thomas Nelson and Sons, London (1969)
- 3.8 F. Bloch, Phys. Rev. 70, 460 (1946).
- 3.9 C. Kittel, Introduction to Solid State Physics, John Wiley and Sons, New York, (Chapter 16) (1976).

- 3.10 L. Jastrzebski, J. Lagowski, H.C. Gatos and W. Walukiewicz.
Inst. of Phys. Conf. Ser. No. 45 (1978)
- 3.11 R.J. Elliot and A.f. Gibson : An introduction to solid state
physics and its applications (MacMillan, London, 1978) (Text book).
- 3.12 Karlheinz Seeger: semiconductor physics, third Ed. Springer -
Verlag (1985)

CHAPTER FIVE

- 5.1 P. Van Engelen : Electron-nuclear double resonance of Ga
in Mn-doped Ga P, Phys. Rev. B 22 3144-3151 (1980).
- 5.2 P.J. McDonald : A nuclear magnetic resonance field cycling
investigation of chromium and silicon doped gallium
arsenide, 7660, 6170 R Guildford U.K. (1988) (unpublished).

CHAPTER SIX

- 6.1 F. Mandl : Statistical physics, Dept. of theoretical phys.
University of Manchester (London, wiley, 1971).
- 6.2 F.O. Zelaya, Ph.D thesis, University of Nottingham, (1984,
unpublished).
- 6.3 C.P. Slitcher, Principles of magnetic resonance, University
of Illinois, Harper and Row (1963).

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