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Neutron Scattering Studies of $\text{RENi}_2\text{B}_2\text{C}$: Magnetic Structures
and Lattice Dynamics

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MASTER

Neutron scattering studies of $RENi_2B_2C$: Magnetic structures and lattice
dynamics

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Neutron scattering techniques have been used to study the magnetic structure and lattice dynamical properties of various members of the recently discovered $RENi_2B_2C$ family, where RE stands for a rare-earth element. The magnetic structures of superconducting $DyNi_2B_2C$, $ErNi_2B_2C$, $HoNi_2B_2C$, and non superconducting $TbNi_2B_2C$ have been determined as a function of temperature, in the $2 - 300$ K temperature range. In the superconducting compounds we have long range magnetic order coexisting with superconductivity, and we have discovered some very interesting magnetic structures. In particular, sinusoidally modulated magnetic structures with similar wavevectors along the a^* direction are present in all of the above compounds with the exception of $DyNi_2B_2C$. In the Tb compound we have, in addition to the incommensurate antiferromagnetic structure, the development of a small ferromagnetic component which is probably responsible for the absence of superconductivity.

The low-lying phonon dispersion curves of superconducting $LuNi_2B_2C$ ($T_c \approx 16.6$ K) and $HoNi_2B_2C$ ($T_c \approx 8.1$ K) have also been determined along the $[\xi, 0, 0]$ and $[0, 0, \xi]$ high symmetry directions, using inelastic neutron scattering techniques. The most interesting result of these studies is the discovery of pronounced soft phonon behavior for the acoustic and first optical Δ_4 $[\xi, 0, 0]$ branches at wavevectors close to

the zone-boundary point G_1 . This shows that the electron-phonon interaction is very strong and causes an incipient lattice instability, a behavior typical of strongly coupled conventional superconductors. Both the incommensurate magnetic structures and the soft phonon behavior seem to be influenced by common nesting features of the Fermi surface of the rare-earth nickel boride carbides, as band theoretical calculations suggest.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ix
CHAPTER 1. INTRODUCTION	1
Crystal Structure	3
Macroscopic Measurements	3
Theoretical Studies	7
Dissertation Organization	8
CHAPTER 2. ELEMENTS OF NEUTRON SCATTERING THE-	
ORY	11
Neutron Scattering Cross Sections	12
Nuclear Scattering	14
Coherent Scattering	20
Nuclear Scattering by Crystalline Solids	22
Elastic Scattering	24
One-Phonon Scattering	26
Magnetic Scattering	27
Elastic Scattering from Magnetically Ordered Crystals	29
Antiferromagnetic, Spiral and Sinusoidal Magnetic Structures	31
Connecting Theoretical Results with Experiment	33

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CHAPTER 3. EXPERIMENTAL TECHNIQUES	36
Neutron Sources	36
Monochromatic Neutron Beams	38
Neutron Counters	39
Neutron Spectrometers	40
Measuring Phonon Dispersion Relations	42
CHAPTER 4. MAGNETIC STRUCTURE OF DyNi₂B₂C	46
Abstract	46
Introduction	46
Experiment	48
Results and Discussion	51
Acknowledgements	54
References	55
CHAPTER 5. MAGNETIC STRUCTURE OF ErNi₂B₂C	57
Abstract	57
Introduction	57
Experimental Details	59
Results and Discussion	60
Acknowledgements	66
References	67
CHAPTER 6. MAGNETIC STRUCTURE OF TbNi₂B₂C	68
Abstract	68
Introduction	69
Experimental Details	70

Results and Discussion	73
References	78
CHAPTER 7. MAGNETIC PAIR BREAKING IN $\text{HoNi}_2\text{B}_2\text{C}$. . .	80
Abstract	80
Introduction	80
Experimental Details	82
Results and Discussion	83
Acknowledgements	89
References	89
CHAPTER 8. SOFT PHONONS IN SUPERCONDUCTING	
$\text{LuNi}_2\text{B}_2\text{C}$	92
Abstract	92
Introduction	93
Experiment	95
Results and Discussion	97
Acknowledgments	101
References	102
CHAPTER 9. CONCLUSIONS	104
BIBLIOGRAPHY	106
CHAPTER A. STRUCTURE FACTORS FOR OSCILLATORY	
MAGNETIC STRUCTURES	110
APPENDIX B. THE EXTINCTION PROBLEM	113

LIST OF FIGURES

Figure 1.1:	The crystal structure of the $RENi_2B_2C$ family. Ho can be replaced by any rare-earth element. (After Reference 53) . . .	4
Figure 1.2:	The low-temperature resistivity of $HoNi_2B_2C$. (After Reference 24)	5
Figure 1.3:	Temperature dependence of the specific heat for $HoNi_2B_2C$. (After Reference 24)	6
Figure 1.4:	The calculated generalized susceptibility along the a^* direction for $LuNi_2B_2C$. (After reference 30)	9
Figure 2.1:	Typical scattering experiment.	13
Figure 2.2:	Coordinates of neutron and nuclei. (Adapted from reference 31)	16
Figure 2.3:	Bragg scattering.	25
Figure 2.4:	Vectors used in describing magnetic scattering.	30
Figure 2.5:	Example of antiferromagnetic structure. (After reference 32)	32
Figure 2.6:	Rotating crystal method.	34
Figure 2.7:	Example of a rocking curve.	35
Figure 3.1:	Thermal neutron distribution at 300 K	37
Figure 3.2:	Production of a monochromatic neutron beam.	38

Figure 3.3:	Diagram of the HB3 triple axis spectrometer at the HFIR reactor.	41
Figure 3.4:	Diagram in reciprocal space showing three different positions along a constant- Q scan, for fixed final energy.	44
Figure 3.5:	Example of a constant- Q scan.	45
Figure 4.1:	Susceptibility measurements for $H \parallel c$ (circles) and $H \perp c$ (squares). The insert shows the temperature variation of the susceptibilities.	50
Figure 4.2:	Typical neutron diffraction scans, along c^* , at 19 K and 5 K . Four monitors correspond to a counting interval of approximately 3.6 sec.	52
Figure 4.3:	Temperature dependence of the intensity of the (001) magnetic reflection.	53
Figure 5.1:	Reciprocal space plane showing the points associated with nuclear scattering (filled circles), and the first- and third-order satellites (shaded circles) associated with the modulation wave vector $k = 0.553a^*$	61
Figure 5.2:	Temperature dependence of the (1.447, 0, 0) satellite for increasing (filled triangles) and decreasing (open triangles) temperature.	62

Figure 5.3:	(a) Field dependence at 5.5 K of the (0.553,0,0) satellite and (200) nuclear reflection for increasing (filled triangles) and decreasing (open triangles) fields along the b axis. (b) Field dependence of the (0.553,0,0) satellite at 5.5 K for increasing field along the c axis.	65
Figure 6.1:	Temperature dependence of the measured magnetization of a $TbNi_2B_2C$ single crystal.	72
Figure 6.2:	Typical scans along the $[h01]$ and $[h00]$ symmetry directions. The satellites of the $(h0l)$ reflection are denoted $(h0l)_n^\pm$ where the superscript + (or -) means that the magnetic wave vector is added (or subtracted) from the reciprocal point of the reflection, and the subscript n is the order of the satellite. . .	74
Figure 6.3:	Temperature dependence of the first, $(101)^+$, and third, $(\bar{1}01)_3^+$, order satellites. The data with open (filled) symbols were taken with increasing (decreasing) temperature.	76
Figure 6.4:	Temperature dependence of the relative change, $\Delta I = I - I_0$, of the (006) nuclear reflection, I_0 stands for the intensity at 16 K	77

- Figure 7.1: (a) One quadrant of the $h0l$ reciprocal space plane showing the points associated with nuclear scattering (filled circles) and the commensurate antiferromagnetic Bragg points (open circles); (b) the first- and third-order satellites associated with the modulation wave vector $\mathbf{K}_1 = 0.915\mathbf{c}^*$ (shaded circles); (c) the satellite positions associated with the modulation wave vector $\mathbf{K}_2 = 0.585\mathbf{a}^*$ 84
- Figure 7.2: Temperature dependence of (a) the (003) commensurate antiferromagnetic peak (filled ellipse) and the (101) nuclear Bragg peak (open rectangles); (b) the first- (open ellipse) and third-order (filled ellipse) satellites associated with the modulation wave vector $\mathbf{K}_1 = 0.915\mathbf{c}^*$; (c) the $\mathbf{K}_2 = 0.585\mathbf{a}^*$ magnetic satellite; and (d) the upper critical field H_{c2} (Ref. 11) determined via temperature-dependent magnetization measured parallel (open rectangles) and perpendicular (filled ellipse) to the tetragonal c axis. Lines are intended as guides to the eye. 86
- Figure 8.1: Room temperature acoustic and lowest lying optical phonon dispersion curves of $\text{LuNi}_2\text{B}_2\text{C}$ along the $[\xi 00]$ and $[00\xi]$ symmetry directions. The lines are intended as guides to the eye. The size of the symbols is a measure of the estimated uncertainties in the measured frequencies. 99
- Figure 8.2: The Δ_4 $[\xi 00]$ branches at 295 K and 10 K. The lines through the 10 K points are intended as guides to the eye. 100

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CHAPTER 1. INTRODUCTION

The study of the interaction between superconductivity and magnetic order has continuously occupied scientists for many decades. The first experimental studies were done by introducing magnetic impurities into superconducting materials [1,2]. These studies provided very valuable information about the superconducting state and the various pair-breaking mechanisms. However, the magnetic ions interacted so strongly with the superconducting electrons that superconductivity was destroyed before enough ions had been introduced to allow for the possibility of an ordered magnetic structure.

Then, in the 1970's, two classes of superconducting ternary compounds were discovered, namely $REMo_6(S, Se)_8$, and $RERh_4B_4$ (where RE stands for a rare-earth element) [2], and provided model systems for the study of the interaction between superconductivity and magnetic order. The general conclusion from these studies is that superconductivity can coexist with long range antiferromagnetic order, but that ferromagnetism usually leads to the ultimate destruction of superconductivity [2-12]. In other words superconductivity can coexist with magnetic order if no magnetic $\mathbf{B}$ field is produced which is uniform on the scale of the penetration length.

Most of the above mentioned superconducting compounds, however, exhibit magnetic transitions below the liquid helium temperature range ($\leq 1\text{ K}$), a fact that

makes experimental work on these materials very difficult. The recent discovery of the rare-earth nickel boride carbide family $RENi_2B_2C$ [13-16], has thus in a sense reopened the field providing a new model system for the study of the interplay between superconductivity and magnetism, since in these compounds the magnetic transitions occur at much higher temperatures ($T_N \approx 1.5 - 20$ K). A variety of low temperature ground states has been found in these materials, including superconductivity (for the *Lu* and *Y* compounds), superconductivity coexisting with magnetic order (*Tm*, *Er*, *Ho*, *Dy*), and magnetic order without superconductivity (*Gd*, *Tb*) [13-25]. The highest superconducting transition temperatures occur for the *Lu* and *Y* compounds (16.6 K, and 15.5 K respectively). From the magnetic rare-earths, *Tm*, *Ho*, *Er*, and *Dy* form superconducting compounds with transition temperatures of 10.8, 8.1, 10.5, and 6.2 K respectively,¹ while the *Gd* and *Tb* compounds are not superconducting down to approximately 2 K.

Since neutron scattering is the best technique for obtaining direct microscopic information about the magnetic structure of solids, we were motivated to start a systematic study of the $RENi_2B_2C$ compounds formed with magnetic rare-earths, using neutron diffraction techniques, in order to determine their magnetic structures. The availability of relatively large, high quality, single crystals greatly facilitates such studies.

A number of theoretical investigations, which we will discuss soon, suggest that electron-phonon interactions are very important in the rare-earth nickel boride carbide family. So, we also studied the lattice dynamical properties of these materials, by

¹The superconducting transition temperatures reported by different authors vary somewhat.

measuring the low lying phonon dispersion curves for $LuNi_2B_2C$ and $HoNi_2B_2C$, using inelastic neutron scattering.

Crystal Structure

The members of the $RENi_2B_2C$ family crystalize in a body centered tetragonal layered crystal structure (space group $I4/mmm$), which consists of $RE - C$ layers separated by Ni_2B_2 sheets [15]. This is the $ThCr_2Si_2$ structure with additional carbon atoms in each RE layer, and is reminiscent of the structures that occur in the high- T_c superconductors. The $RENi_2B_2C$ crystal structure is shown in Figure 1.1. For the heavy rare-earth compounds that we studied, the lattice constants for the tetragonal structure are $a \approx 3.5 \text{ \AA}$ and $c \approx 10.5 \text{ \AA}$.

Macroscopic Measurements

A large number of macroscopic measurements on the $RENi_2B_2C$ has been reported in the literature [13-25]. These include transport, magnetic, and thermal measurements. These measurements provided the motivation for us to begin neutron scattering studies, and they also provide information that facilitates the physical interpretation of the results. Of great importance for our work were the magnetic measurements performed in these compounds.

As an example, the low temperature electrical resistivity of $HoNi_2B_2C$ which becomes superconducting at about 8.1 K is shown in Figure 1.2, while in Figure 1.3 we show the specific heat $C(T)$ for the same material. We see that $C(T)$ exhibits two peaks at 5.7 K and 5.2 K which are due to two distinct magnetic transitions.

$HoNi_2B_2C$ is the most interesting of the compounds because, after becoming

Figure 1.1: The crystal structure of the $RENi_2B_2C$ family. Ho can be replaced by any rare-earth element. (After Reference 53)

Figure 1.2: The low-temperature resistivity of $\text{HoNi}_2\text{B}_2\text{C}$. (After Reference 24)

Figure 1.3: Temperature dependence of the specific heat for $\text{HoNi}_2\text{B}_2\text{C}$. (After Reference 24)

superconducting at 8.1 K , at around 5 K it becomes normal (or almost normal) again, then recovers superconductivity as the temperature is lowered [17,20,24]. More macroscopic results are described in the main part of the thesis, where appropriate.

Theoretical Studies

A number of authors have addressed various aspects of the $RENi_2B_2C$ compounds from a theoretical point of view. Electronic band-structure calculations have been performed [26-28] and suggest that these compounds are conventional superconductors with a relatively high density of states at the Fermi level. According to these calculations, there is a complex set of bands crossing E_F which are strongly coupled to the phonons and may be responsible for the superconducting properties of these materials. More recently, Mattheis, Siegrist, and Cava suggested [29] that a conventional electron-phonon mechanism is responsible for the superconductivity in these compounds. A high frequency boron A_{1g} mode is coupled to the sp -like conduction electrons and dynamically modulates the NiB_4 tetrahedral bond angles according to these authors. However, Pickett and Singh [26] incorporating resistivity data deduce a very strong electron-phonon coupling and suggest that the superconductivity of the $RENi_2B_2C$ may involve soft phonon modes or strong contributions from the heavier atoms.

Another relevant calculation is that of the generalized electronic susceptibility $\chi(q)$ performed by Rhee, Wang, and Harmon [30] for the $LuNi_2B_2C$ compound. The calculated (without matrix elements, and based on the normal state electronic band structure) $\chi(q)$ shows a pronounced peak along the a^* direction at a wavevector of about 0.6 (see Figure 1.4), and a broad peak along the c^* direction at a wavevector

of about 0.9. The strong peak along a^* is due to strong Fermi surface nesting, and that suggests that there may be Kohn anomalies in the phonon dispersion curves of this compound. The above theoretical predictions made it almost a necessity to study the phonon spectrum of these compounds using inelastic neutron scattering techniques.

Dissertation Organization

In the first two chapters we discuss the fundamentals of the neutron scattering technique. In Chapter 2 we give a short introduction to the theory of neutron scattering, and in Chapter 3 we present some experimental details. In both these chapters the emphasis is on topics that are closely related to the problems studied in this dissertation.

The main part of the dissertation consists of papers that are already published or submitted to scientific journals. In Chapters 4-7 we present the papers that describe the magnetic structure studies for the *Dy*, *Er*, *Tb*, and *Ho* compounds respectively. The order is not the historical one. We chose to describe first the simplest structures and then proceed to the more involved ones. In Chapter 8 we present some of our measurements on the phonon dispersion curves of $LuNi_2B_2C$, in particular the low lying dispersion curves where very interesting soft phonon behavior was discovered. Each of these papers includes its own list of references. The author's name was first in the papers describing the magnetic structure of $DyNi_2B_2C$ and $TbNi_2B_2C$, and in the paper describing the phonon dispersion curves of $LuNi_2B_2C$. In the other two papers the author's name was fifth. However, the author played a significant role in these papers and since their inclusion makes the dissertation a much more complete

Figure 1.4: The calculated generalized susceptibility along the a^* direction for $LuNi_2B_2C$. (After reference 30)

document, he felt justified to do so.

In Chapter 9 we summarize our conclusions, and in the Bibliography we list the references for Chapters 1-3, Chapter 9, and the two Appendices. The two Appendices that follow the Bibliography discuss two topics related to our experiments, namely magnetic structure factors for oscillatory magnetic structures and the extinction problem.

CHAPTER 2. ELEMENTS OF NEUTRON SCATTERING THEORY

There are four properties that make *thermal* neutrons a very useful probe for the study of matter. By thermal, we refer to neutrons which have kinetic energy of the same order of magnitude as a classical gas molecule has at room temperature ($\approx 25 \text{ meV}$).

First, neutrons have *no charge*, so they can penetrate deeply into matter and come close to the atomic nuclei. Thus, they can be scattered by nuclear forces, and for most elements the scattering is strong. This is in contrast with x-rays where the scattering is proportional to the square of the atomic number. So, neutrons can be used to investigate bulk properties of matter, and can also provide information for systems for which x-rays fail.

The wavelength of thermal neutrons is of the order of the interatomic distances in solids and liquids. So, one can have *interference* effects which provide valuable information about the scattering system.

The energy of thermal neutrons is of the same order as that of various excitations in solids (phonons, magnons, etc). Thus, *inelastic* scattering of neutrons can be used to study the spectrum of these excitations.

Finally, the neutron has a *magnetic moment*, which can interact with the magnetic moments in magnetic atoms. It is fair to say that our knowledge of the magnetic

architecture in solids comes mostly from neutron scattering experiments.

In this chapter we give a short outline of the way one proceeds to calculate the scattering cross sections, which are in effect what an experimentalist measures. After some basic definitions, we examine both nuclear and magnetic scattering from crystalline solids. For detailed treatments we refer to the standard monographs and textbooks [31-35]. The discussion presented here is based, in the main lines, on the presentation given by Squires [31].

Neutron Scattering Cross Sections

We give first some basic definitions. Consider the scattering experiment shown in Figure 2.1. A monochromatic beam of neutrons is incident upon a target. A counter can be used to detect the neutrons scattered in a given direction. The distance of the counter from the target is assumed large, so that the small solid angle $d\Omega$ subtended by the counter is well defined. The direction of the incident neutrons is taken as the polar axis in a system of spherical coordinates, and the direction of the scattered neutrons is specified by θ, ϕ . If we measure the number of neutrons scattered in a given direction as a function of their final energy E' , we can define the *partial differential cross section* by,

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{I(\theta, \phi, E')}{I_0 d\Omega dE'} \quad (2.1)$$

where $I(\theta, \phi, E')$ is the number of neutrons scattered into a small solid angle $d\Omega$ in the given direction, per unit time, with energy between E' and $E' + dE'$, and I_0 is the incident neutron flux, i.e. the number of incident neutrons per unit area and unit time, the area being normal to the incident direction. The dimensions of the cross section are [area] as the name indicates. If we do not analyze the energy of the

Figure 2.1: Typical scattering experiment.

scattered neutrons, but measure all the neutrons that scatter into $d\Omega$, we can define the *differential cross section* by,

$$\frac{d\sigma}{d\Omega} = \frac{I(\theta, \phi)}{I_0 d\Omega} \quad (2.2)$$

Obviously,

$$\frac{d\sigma}{d\Omega} = \int_0^\infty \left(\frac{d^2\sigma}{d\Omega dE'} \right) dE' \quad (2.3)$$

We can also define a *total scattering cross section* by,

$$\sigma_t = \int \left(\frac{d\sigma}{d\Omega} \right) d\Omega \quad (2.4)$$

the integration being over all directions.

The above definitions apply to any kind of scattering. At this point we do not

consider the fact that the neutron has a spin. The consequences of this will be discussed later.

Nuclear Scattering

We begin with the simplest case, i.e. scattering by a single nucleus fixed in position. The wavelength of a thermal neutron is of the order of $10^{-8}cm$ while nuclear forces have a range of about $10^{-13}cm$. So only the S waves will contribute, and the scattering is isotropic. Since the nucleus is fixed, and the energy of the neutron is assumed too small to change the internal state of the nucleus, the scattering is elastic and we can write the wavefunctions of the incident and scattered neutrons as,

$$\psi_i = \exp(ikz) \quad , \quad \psi_s = -\frac{b}{r}\exp(ikr) \quad (2.5)$$

where k is the magnitude of the neutron wavevector both before and after the scattering, and the geometry is that of Figure 2.1.

The quantity b is called the *scattering length*. In the present state of knowledge, nuclear scattering lengths can not be calculated from first principles, but they have to be determined by experiment. They are complex quantities and their imaginary part is related to *absorption*. Considering the scattering in the frame of the compound nucleus theory, we find that the imaginary part of the scattering length is large when the compound nucleus (original nucleus plus neutron) is formed near an excited state. This leads to the large absorption cross sections of nuclei like ^{113}Cd and ^{176}Lu . For most nuclei, however, the compound nucleus is not close to an excited state and the scattering length is practically real. In the following we will assume such nuclei.

Using the wavefunctions (2.5) we can immediately calculate the cross sections,

$$\frac{d\sigma}{d\Omega} = b^2 \quad (2.6)$$

and

$$\sigma_t = 4\pi b^2 \quad (2.7)$$

for this simple case.

Let us now consider the nuclear scattering of neutrons by a general assembly of nuclei which we shall call the *scattering system*. Let the incident neutron be characterized by a wavevector $\mathbf{k}$ and wavefunction $\psi_{\mathbf{k}}$ and the scattering system be initially in a state $|\alpha\rangle$ where by α we denote all the appropriate quantum numbers. The spin of the neutron is still not taken into account. We first calculate the cross section for a specific transition of the scattering system to a state α' . The scattering is assumed to take place through a potential V the form of which we determine later. The geometry is that of Figure 2.2, and the number of nuclei in the assembly is N .

The cross section $(d\sigma/d\Omega)_{\alpha \rightarrow \alpha'}$ for all processes for which the state of the scattering system changes from α to α' and the state of the neutron changes from $\mathbf{k}$ to $\mathbf{k}'$ is,

$$\left(\frac{d\sigma}{d\Omega}\right)_{\alpha \rightarrow \alpha'} = \frac{1}{I_0 d\Omega} \sum_{\mathbf{k}'} \mathbf{W}_{\mathbf{k}, \alpha \rightarrow \mathbf{k}', \alpha'} \quad (2.8)$$

where $\mathbf{W}_{\mathbf{k}, \alpha \rightarrow \mathbf{k}', \alpha'}$ is the number of transitions per unit time from state $\mathbf{k}, \alpha$ to $\mathbf{k}', \alpha'$, and the sum is over all values of $\mathbf{k}'$ in the small solid angle $d\Omega$.

We may now use *Fermi's Golden Rule* (see for example [36]) to evaluate the right-hand side of the last equation,

$$\sum_{\mathbf{k}'} \mathbf{W}_{\mathbf{k}, \alpha \rightarrow \mathbf{k}', \alpha'} = \frac{2\pi}{\hbar} \rho_{\mathbf{k}'} |\langle \mathbf{k}', \alpha' | V | \mathbf{k}, \alpha \rangle|^2 \quad (2.9)$$

Figure 2.2: Coordinates of neutron and nuclei. (Adapted from reference 31)

where $\rho_{k'}$ is the density of final states (number of final states per unit energy interval) for neutrons in $d\Omega$. Notice that the matrix element in the right-hand side is evaluated at the particular k' value which satisfies energy conservation. To calculate $\rho_{k'}$ we use the familiar procedure of normalization in a box of volume V . We easily obtain,

$$\rho_{k'} = \frac{V}{(2\pi)^2} k' \frac{m}{\hbar^2} d\Omega \quad (2.10)$$

The wavefunction of the incident neutron in the matrix element can be taken as $\exp(ik \cdot r)$ if we divide the matrix element by V , and the flux of incident neutrons is (we assume one neutron in the box of volume V),

$$I_0 = \frac{1}{V} \frac{\hbar}{m} k \quad (2.11)$$

Combining Equations (2.8)-(2.11) and keeping in mind the convention for the neutron

wavefunction in the matrix element we have,

$$\left(\frac{d\sigma}{d\Omega}\right)_{\alpha \rightarrow \alpha'} = \frac{k'}{k} \left(\frac{m}{2\pi\hbar}\right)^2 |\langle \mathbf{k}' \alpha' | V | \mathbf{k} \alpha \rangle|^2 \quad (2.12)$$

and as expected there is no dependence on the arbitrary volume used for normalization. Since $\mathbf{k}, \alpha$ and α' are fixed, energy conservation requires the scattered neutrons to have a fixed energy. So from (2.12) we can write the partial differential cross section as,

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\alpha \rightarrow \alpha'} = \frac{k'}{k} \left(\frac{m}{2\pi\hbar}\right)^2 |\langle \mathbf{k}' \alpha' | V | \mathbf{k} \alpha \rangle|^2 \delta(E_\alpha - E_{\alpha'} + E - E') \quad (2.13)$$

where E, E' initial and final energies for the neutron and similar for the scattering system. *This is our basic result.* Up to this point the only assumption is that we can use the Golden Rule. The potential for the scattering system following Figure 2.2 has the form,

$$V = \sum_j V_j(\mathbf{r} - \mathbf{R}_j) \quad (2.14)$$

and the matrix element becomes (after some steps),

$$\langle \mathbf{k}', \alpha' | V | \mathbf{k}, \alpha \rangle = \sum_j V_j(\mathbf{K}) \langle \alpha' | \exp(i\mathbf{K} \cdot \mathbf{R}_j) | \alpha \rangle \quad (2.15)$$

where,

$$\mathbf{K} = \mathbf{k} - \mathbf{k}' \quad (2.16)$$

the *scattering vector* and

$$V_j(\mathbf{K}) = \int V_j(\mathbf{x}_j) \exp(i\mathbf{K} \cdot \mathbf{x}_j) d\mathbf{x}_j \quad (2.17)$$

the Fourier transform of the potential for the j_{th} nucleus.

The form of the potential can be specified if we require that by calculating the cross section for a single fixed nucleus, using the present formalism, we get back the result of (2.6). We find that,

$$V(\mathbf{r}) = \frac{2\pi\hbar^2}{m} b\delta(\mathbf{r}) \quad (2.18)$$

which is called the *Fermi pseudopotential*, can be used. It is in fact the choice of this potential that justifies the use of the Golden Rule, which is based on first-order perturbation theory and it would seem at first thought that it can not be used for nuclear scattering [37,38].

The scattering length which we defined in (2.5) for a fixed nucleus, is called the *bound* scattering length. If the nucleus is free then the problem can be treated the same way in the center of mass system, if we replace the neutron mass with the reduced mass of the system. From the form of (2.18) we easily find that the *free* scattering length is related to the bound one by,

$$b_f = \frac{M}{m+M} b \quad (2.19)$$

where M the mass of the nucleus. For most nuclei the correction is small, but for the very light ones it can be important. For hydrogen,

$$b_f = \frac{1}{2} b \quad (2.20)$$

Returning to our problem, the potential of the j_{th} nucleus is,

$$V_j(\mathbf{x}_j) = \frac{2\pi\hbar^2}{m} b_j\delta(\mathbf{x}_j) \quad (2.21)$$

and from (2.17),

$$V_j(\mathbf{K}) = \frac{2\pi\hbar^2}{m} b_j \quad (2.22)$$

(2.13) and (2.15) now give,

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\alpha \rightarrow \alpha'} = \frac{k'}{k} \left| \sum_i b_j \langle \alpha' | \exp(i\mathbf{K} \cdot \mathbf{R}_j) | \alpha \rangle \right|^2 \delta(E_\alpha - E_{\alpha'} + E - E') \quad (2.23)$$

To proceed we use the expression,

$$\delta(E_\alpha - E_{\alpha'} + E - E') = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \exp\{i(E_{\alpha'} - E_\alpha)t/\hbar\} \exp(-i\omega t) dt \quad (2.24)$$

where,

$$\hbar\omega = E - E' \quad (2.25)$$

We also have to take into account that in an actual experiment we do not measure the cross section for a specific transition of the scattering system. What we measure is the partial differential cross section defined in (2.1). To get this we have to sum over all final states α' for a fixed initial state α and then average over the initial states.

The sum over the final states is easily done using the familiar *closure relations* of Quantum Mechanics, while to do the the average over the initial states we use the Boltzmann distribution,

$$P_\alpha = \frac{1}{Z} \exp(-E_\alpha \beta) \quad (2.26)$$

where Z the partition function and P_α is the probability for the system in equilibrium at temperature T to be in state α . Using the above and the definition of the *thermal average* of an operator A ,

$$\langle A \rangle = \sum_{\alpha} P_\alpha \langle \alpha | A | \alpha \rangle \quad (2.27)$$

we finally get,

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k} \frac{1}{2\pi\hbar} \sum_{jj'} b_j b_{j'} \int_{-\infty}^{\infty} \langle \exp\{-i\mathbf{K} \cdot \mathbf{R}_{j'}(0)\} \exp\{i\mathbf{K} \cdot \mathbf{R}_j(t)\} \rangle \exp(-i\omega t) dt \quad (2.28)$$

where $\mathbf{R}_{j'}(0)$, $\mathbf{R}_j(t)$ are *Heisenberg operators*.

This is our *final expression* for the partial differential cross section for nuclear scattering.

Coherent Scattering

Assume that our scattering system consists of one element only. If this element has more than one isotope then each one will have a different scattering length. Also, for isotopes that have a non zero nuclear spin I , the nucleus-neutron system may have spin $I+1/2$ or $I-1/2$. Each of these spin states has each own scattering length. Assuming that the value b_i occurs with probability f_i , we can define the average values of b and b^2 for the scattering system,

$$\bar{b} = \sum_i f_i b_i \quad (2.29)$$

$$\bar{b}^2 = \sum_i f_i b_i^2 \quad (2.30)$$

where, of course,

$$\sum_i f_i = 1 \quad (2.31)$$

We assume that the distribution of the nuclei with the various values of b in the system is completely random, which is a reasonable assumption for the macroscopic systems that we usually study. Then, the cross section that we measure from such a system is very close to the average cross section over all possible distributions of the scattering lengths. The term $b_j b_{j'}$ in (2.28) then has to be replaced with its average. Since the b distribution is random we have,

$$\overline{b_j b_{j'}} = (\bar{b})^2, \quad j \neq j' \quad (2.32)$$

$$\overline{b_j b_{j'}} = \overline{b^2}, \quad j = j' \quad (2.33)$$

Using the above we can write the cross section of (2.28) as,

$$\frac{d^2\sigma}{d\Omega dE'} = \left(\frac{d^2\sigma}{d\Omega dE'} \right)_{coh} + \left(\frac{d^2\sigma}{d\Omega dE'} \right)_{inc} \quad (2.34)$$

where the *coherent* and *incoherent* cross sections are given by,

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{coh} = \frac{\sigma_{coh}}{4\pi} \frac{k'}{k} \frac{1}{2\pi\hbar} \sum_{jj'} \int_{-\infty}^{\infty} \langle \exp\{-i\mathbf{K} \cdot \mathbf{R}_{j'}(0)\} \exp\{i\mathbf{K} \cdot \mathbf{R}_j(t)\} \rangle e^{-i\omega t} dt \quad (2.35)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{inc} = \frac{\sigma_{inc}}{4\pi} \frac{k'}{k} \frac{1}{2\pi\hbar} \sum_j \int_{-\infty}^{\infty} \langle \exp\{-i\mathbf{K} \cdot \mathbf{R}_j(0)\} \exp\{i\mathbf{K} \cdot \mathbf{R}_j(t)\} \rangle e^{-i\omega t} dt \quad (2.36)$$

with,

$$\sigma_{coh} = 4\pi(\bar{b})^2, \quad \sigma_{inc} = 4\pi\{\overline{b^2} - (\bar{b})^2\} \quad (2.37)$$

The coherent scattering can produce *interference* effects, since it depends on the correlation between the positions of different nuclei at different times. The incoherent scattering can not produce such effects, since it depends only on the correlations of the positions of the same nucleus at different times.

The experimental work in this dissertation is based only on coherent scattering, so in the following we restrict the discussion to this type. It is, of course, possible to gain valuable information from the study of incoherent scattering in various problems.

We give now some formulae for $\bar{b}$ and $\overline{b^2}$ for an element which consists of various isotopes. Let b_i^+ and b_i^- be the scattering lengths for the spin states $I + 1/2$ and $I - 1/2$ for the isotope i . The neutrons are assumed *unpolarized* and the nuclear spins randomly oriented. It is very easy to see that,

$$\bar{b} = \sum_i \frac{c_i}{2I_i + 1} \{(I_i + 1)b_i^+ + I_i b_i^-\} \quad (2.38)$$

and

$$\overline{b^2} = \sum_i \frac{c_i}{2I_i + 1} \{(I_i + 1)(b_i^+)^2 + I_i(b_i^-)^2\} \quad (2.39)$$

where c_i is the relative abundance of the isotope i . The quantity $\overline{b}$ is known as the *coherent* scattering length. Most nuclei have values around 10^{-12} cm .

The generalization of the above to scattering systems which contain more than one elements is straightforward. So far, we have not made any specific assumption about the scattering system. We now proceed to apply our results to crystalline solids.

Nuclear Scattering by Crystalline Solids

For a single crystal with N_c unit cells and one atom per unit cell, defined by three vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, a *lattice vector* is given by,

$$\mathbf{l} = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3 \quad (2.40)$$

and a *reciprocal* lattice vector by,

$$\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 \quad (2.41)$$

with,

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij} \quad (2.42)$$

The theory of lattices is assumed well known (see for example [39]). The position of the nucleus l , if the equilibrium position is at lattice site $\mathbf{l}$, is

$$\mathbf{R}_l = \mathbf{l} + \mathbf{u}_l \quad (2.43)$$

where $\mathbf{u}_l$ is the displacement from the equilibrium due to *thermal motion*.

In first approximation the interatomic forces in a crystal are *harmonic*, so the motion can be expanded into *normal modes* [41],

$$\mathbf{u}_I(t) = \sqrt{\frac{\hbar}{2MN_c}} \sum_{\mathbf{s}} \frac{\mathbf{e}_{\mathbf{s}}}{\sqrt{\omega_{\mathbf{s}}}} [a_{\mathbf{s}} \exp\{i(\mathbf{q} \cdot \mathbf{l} - \omega_{\mathbf{s}} t)\} + a_{\mathbf{s}}^{\dagger} \exp\{-i(\mathbf{q} \cdot \mathbf{l} - \omega_{\mathbf{s}} t)\}] \quad (2.44)$$

where $\mathbf{s}$ is a double index which includes the wavevector of the mode $\mathbf{q}$ and the *polarization index* j . With ω we denote the *angular frequency* of a mode. $a_{\mathbf{s}}$ and $a_{\mathbf{s}}^{\dagger}$ are the *destruction* and *creation* operators for the mode and $\mathbf{e}$ is the *polarization vector*. M is the mass of an atom. The sum is over the N_c allowed $\mathbf{q}$ values in the first *Brillouin zone*, and over the three polarization states.

Using the above and the following result for the thermal averages of a harmonic oscillator with position variable q (see [40]),

$$\langle \exp q \rangle = \exp\left\{\frac{1}{2}\langle q^2 \rangle\right\} \quad (2.45)$$

we get from (2.35) for a single crystal,

$$\left(\frac{d^2}{d\Omega dE'}\right)_{coh} = \frac{\sigma_{coh}}{4\pi} \frac{k'}{k} \frac{N}{2\pi\hbar} \exp\langle U^2 \rangle \sum_{\mathbf{l}} \exp(i\mathbf{K} \cdot \mathbf{l}) \int_{-\infty}^{\infty} \exp\langle UV \rangle \exp(-i\omega t) dt \quad (2.46)$$

where U and V are defined by,

$$U = -i \sum_{\mathbf{s}} g_{\mathbf{s}} a_{\mathbf{s}} + g_{\mathbf{s}} a_{\mathbf{s}}^{\dagger} \quad (2.47)$$

$$V = i \sum_{\mathbf{s}} h_{\mathbf{s}} a_{\mathbf{s}} + h_{\mathbf{s}}^* a_{\mathbf{s}}^{\dagger} \quad (2.48)$$

$$g_{\mathbf{s}} = \sqrt{\frac{\hbar}{2MN_c}} \frac{\mathbf{K} \cdot \mathbf{e}_{\mathbf{s}}}{\sqrt{\omega_{\mathbf{s}}}} \quad (2.49)$$

$$h_{\mathbf{s}} = g_{\mathbf{s}} \exp\{i(\mathbf{q} \cdot \mathbf{l} - \omega_{\mathbf{s}} t)\} \quad (2.50)$$

The energy of each of the $3N$ normal modes of the crystal is quantized in *phonons*. The state of the crystal can be described by giving the occupation numbers $n_1, \dots, n_{3N}$ of the modes. If we expand the $\exp\langle UV \rangle$ term of (2.46) as,

$$\exp\langle UV \rangle = 1 + \langle UV \rangle + \frac{1}{2!} \langle UV \rangle^2 + \dots \quad (2.51)$$

we can show that the n_{th} order term corresponds to the cross section for all n -phonon processes. So the zero order term, 1, gives the elastic cross section. The first order term gives the sum of the cross sections for all processes for which one of the occupation numbers changes by unity from the initial to the final state. And similarly for the higher order terms.

Elastic Scattering

If we replace $\exp\langle UV \rangle$ by 1 in (2.46) and employ the sum rule,

$$\sum_l \exp(i\mathbf{K} \cdot \mathbf{l}) = \frac{(2\pi)^3}{v_o} \sum_{\mathbf{G}} \delta(\mathbf{K} - \mathbf{G}) \quad (2.52)$$

where $\mathbf{G}$ a reciprocal lattice vector and v_o the volume of the unit cell of the crystal, we get for the coherent elastic differential scattering cross section from a single crystal,

$$\left(\frac{d\sigma}{d\Omega} \right)_{coh, el} = \frac{\sigma_{coh}}{4\pi} N \frac{(2\pi)^3}{v_o} \exp(-2W) \sum_{\mathbf{G}} \delta(\mathbf{K} - \mathbf{G}) \quad (2.53)$$

where,

$$2W = -\langle U^2 \rangle = \langle \{\mathbf{K} \cdot \mathbf{u}(0)\}^2 \rangle \quad (2.54)$$

We see from (2.53) that scattering occurs only when $\mathbf{K} = \mathbf{G}$. This is the *Laue condition* and it is completely equivalent with the familiar *Bragg's Law*,

$$2d \sin\theta_b = n\lambda \quad n = 1, 2, \dots \quad (2.55)$$

Figure 2.3: Bragg scattering.

where d is the spacing between the lattice planes with *Miller indices* (h, k, l) , θ_b is the *Bragg's angle* (equal to half the scattering angle), and λ the neutron wavelength. The geometry for Bragg's interpretation of elastic scattering is shown in Figure 2.3. The $\exp(-2W)$ term in (2.53) is called the *Debye-Waller factor*. It corrects the cross section for the thermal motion of the nuclei, and its effect is to decrease the intensity of a diffraction line, the more so the larger the scattering angle and the higher the temperature. It does not effect though the *width* of the line (see last section of this chapter for some discussion about widths).

For a crystal with more than one atom in the unit cell (2.43) is modified as follows,

$$R_{ld} = 1 + d + u(l, d) \quad (2.56)$$

where $\mathbf{R}_{ld}$ the position of the d atom in cell l , and (2.53) becomes,

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh,el} = N_c \frac{(2\pi)^3}{v_o} \sum_{\mathbf{G}} \delta(\mathbf{K} - \mathbf{G}) |F_n(\mathbf{K})|^2 \quad (2.57)$$

where,

$$F_n(\mathbf{K}) = \sum_d \bar{b}_d \exp(i\mathbf{K} \cdot \mathbf{d}) \exp(-W_d) \quad (2.58)$$

the nuclear geometric *structure factor*. For a specific Bragg reflection which corresponds to the reciprocal lattice vector $\mathbf{G}_{hkl}$ we have,

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh,el}(\mathbf{G}_{hkl}) = N_c \frac{(2\pi)^3}{v_o} |F_n(\mathbf{G}_{hkl})|^2 \quad (2.59)$$

One-Phonon Scattering

The next term in the expansion (2.51) gives the cross section for the one-phonon processes. We find that the cross section is the sum of two terms corresponding to *phonon emission* and *phonon absorption*.

For *phonon emission* the coherent cross section is,

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{emission} = \frac{k'}{k} \frac{(2\pi)^2}{2v_o} \sum_{\mathbf{s}} \sum_{\mathbf{G}} \frac{1}{\omega_{\mathbf{s}}} \left| \sum_d \frac{\bar{b}_d}{\sqrt{M_d}} \exp(-W_d) \exp(i\mathbf{K} \cdot \mathbf{d}) (\mathbf{K} \cdot \mathbf{e}_{d\mathbf{s}}) \right|^2 \times \langle n_{\mathbf{s}} + 1 \rangle \delta(\omega - \omega_{\mathbf{s}}) \delta(\mathbf{K} - \mathbf{q} - \mathbf{G}) \quad (2.60)$$

We see that scattering in this case occurs when,

$$E - E' = \hbar\omega_{\mathbf{s}} \quad (2.61)$$

and

$$\mathbf{K} = \mathbf{G} + \mathbf{q} \quad (2.62)$$

These two conditions represent energy and momentum conservation.

For *phonon absorption* the cross section can be obtained from (2.60) if we replace $\langle n_s + 1 \rangle$ by $\langle n_s \rangle$, and modify the δ -functions so that the new conditions become,

$$\omega = -\omega_s \ , \ \mathbf{K} = \mathbf{G} - \mathbf{q} \quad (2.63)$$

One can proceed to higher order terms, but the most usefull information in the study of solids with is obtained from elastic and one-phonon neutron scattering, so we will not examine these terms here.

Magnetic Scattering

We discuss now magnetic scattering, assuming again unpolarized neutrons. The magnetic dipole moment of a neutron is,

$$\bar{\mu}_n = -\gamma\mu_N\bar{\sigma} \quad (2.64)$$

where $\bar{\sigma}$ is the Pauli operator (with eigenvalues of its components ± 1) and $\gamma = 1.913$. The magnetic field of a electron with momentum $\mathbf{p}$ at a point $\mathbf{R}$ from the electron,

$$\mathbf{B} = \mathbf{B}_S + \mathbf{B}_L = \frac{\mu_o}{4\pi} \left\{ \nabla \times \left(\frac{\bar{\mu}_e \times \hat{\mathbf{R}}}{R^2} \right) - \frac{2\mu_B}{\hbar} \frac{\mathbf{p} \times \hat{\mathbf{R}}}{R^2} \right\} \quad (2.65)$$

where $\hat{\mathbf{R}}$ is the unit vector along $\mathbf{R}$, interacts with the neutron magnetic moment with a potential,

$$V_m = -\bar{\mu}_n \cdot \mathbf{B} \quad (2.66)$$

To calculate the cross sections we can start again from (2.13), but now we have to consider the spin state σ of the neutron also. The result is,

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\sigma\alpha \rightarrow \sigma'\alpha'} = (\gamma r_o)^2 \frac{k'}{k} |\langle \sigma'\alpha' | \bar{\sigma} \cdot \mathbf{Q}_\perp | \sigma\alpha \rangle|^2 \delta(E_\alpha - E_{\alpha'} + \hbar\omega) \quad (2.67)$$

where $r_o = 2.818 \cdot 10^{-12}$ cm the *classical radius* of the electron, and $\mathbf{Q}_\perp$ is the component of $\mathbf{Q}$ in the plane perpendicular to the scattering vector, where the vector $\mathbf{Q}$ is related to the Fourier transform of the total *magnetization* $\mathbf{M}(\mathbf{r})$,

$$\mathbf{Q} = -\frac{1}{2\mu_B} \mathbf{M}(\mathbf{K}) \quad (2.68)$$

$$\mathbf{M}(\mathbf{K}) = \int \mathbf{M}(\mathbf{r}) \exp(i\mathbf{K} \cdot \mathbf{r}) d\mathbf{r} \quad (2.69)$$

So,

$$\mathbf{Q}_\perp = \mathbf{Q} - (\mathbf{Q} \cdot \hat{\mathbf{K}}) \hat{\mathbf{K}} \quad (2.70)$$

We now turn our attention to a *crystal*, and we assume that the unpaired electrons are *localized* close to the equilibrium positions of the ions in the lattice. We also assume that the *LS coupling* scheme is valid, and we use the *dipole approximation* which is valid when $|\mathbf{K}|^{-1}$ is large compared to the extend of the wavefunctions of the unpaired electrons. Finally, we use the fact that the orientation of the spins has a negligible effect on the motion of the nuclei.

For a crystal with one atom in the unit cell we get,

$$\begin{aligned} \frac{d^2\sigma}{d\Omega dE'} &= \frac{(\gamma r_o)^2}{2\pi\hbar} \frac{k'}{k} N_c \left\{ \frac{1}{2} g f(\mathbf{K}) \right\}^2 \sum_{ij} (\delta_{ij} - \hat{\mathbf{K}}_i \hat{\mathbf{K}}_j) \sum_l \exp(i\mathbf{K} \cdot \mathbf{l}) \\ &\times \int_{-\infty}^{\infty} \langle \exp\{-i\mathbf{K} \cdot \mathbf{u}_o(0)\} \exp\{i\mathbf{K} \cdot \mathbf{u}_l(t)\} \rangle \langle J_o^i(0) J_l^j(t) \rangle e^{-i\omega t} dt \end{aligned} \quad (2.71)$$

where i, j stand for the cartesian components x, y, z and J is the total angular momentum operator for the ion, or an effective angular momentum operator if the orbital angular momentum is partially *quenched*. g is the *Lande splitting factor* in the LS coupling scheme,

$$g = \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (2.72)$$

and $f(\mathbf{K})$ is the *magnetic form factor* which for an ion is defined by,

$$f(\mathbf{K}) = \int \rho_m(\mathbf{r}) \exp(i\mathbf{K} \cdot \mathbf{r}) d\mathbf{r} \quad (2.73)$$

where ρ_m is the normalized density of the unpaired (magnetic) electrons, that is the density of the unpaired electrons divided by their number. At $\mathbf{K} = 0$, $F = 1$.

Elastic Scattering from Magnetically Ordered Crystals

This is the only type of magnetic scattering that we study in this dissertation, so we turn our attention to it. From (2.71) we get for the elastic cross section from a crystal with one atom per unit cell,

$$\left(\frac{d\sigma}{d\Omega} \right)_{el} = (\gamma r_o)^2 N_c \left\{ \frac{1}{2} g f(\mathbf{K}) \right\}^2 \exp(-2W) \sum_{ij} (\delta_{ij} - \hat{\mathbf{K}}_i \hat{\mathbf{K}}_j) \sum_l \exp(i\mathbf{K} \cdot \mathbf{l}) \langle J_o^i \rangle \langle J_o^j \rangle \quad (2.74)$$

In a *ferromagnetic material* the magnetic moments of the ions,

$$\bar{\mu}_J = -g\mu_B \mathbf{J} \quad (2.75)$$

tend to align in the same direction. We will assume here that the alignment is perfect throughout the crystal, i.e. we have one domain. In practice we either have to apply an external magnetic field to achieve one domain, or we have to take proper averages to correct for the fact that there are different domains. From (2.75) we then get,

$$\left(\frac{d\sigma}{d\Omega} \right)_{el} = (\gamma r_o)^2 N_c \frac{(2\pi)^3}{v_o} \left\{ \frac{1}{2} g f(\mathbf{K}) \right\}^2 \exp(-2W) (1 - (\hat{\mathbf{G}} \cdot \hat{\mathbf{n}})^2) \langle J^z \rangle^2 \sum_{\mathbf{G}} \delta(\mathbf{K} - \mathbf{G}) \quad (2.76)$$

where $\hat{\mathbf{n}}$ is a unit vector in the average direction of the magnetic moments, which is taken as the z -axis. The important fact is that *ferromagnetic scattering occurs at the same positions as nuclear scattering*.

Figure 2.4: Vectors used in describing magnetic scattering.

We can write the term $(1 - (\hat{\mathbf{G}} \cdot \hat{\mathbf{n}})^2)$ as q^2 where the *magnetic interaction vector* $\mathbf{q}$ is,

$$\mathbf{q} = \hat{\mathbf{G}}(\hat{\mathbf{G}} \cdot \hat{\mathbf{n}}) - \hat{\mathbf{n}} \quad (2.77)$$

and from Figure 2.4 we see that,

$$q = \sin(\alpha) \quad (2.78)$$

where α the angle between the scattering vector and the magnetic moments. We can now define a *magnetic scattering length* p by,

$$p = \frac{1}{2} \gamma r_0 g f(\mathbf{K}) = (.27 \cdot 10^{-12} \text{ cm}) g J f(\mathbf{K}) \quad (2.79)$$

with the aid of which we can write the cross section for a magnetic Bragg reflection in the general case of a crystal with many atoms in the unit cell,

$$\left(\frac{d\sigma}{d\Omega}\right)_{mag,el}(\mathbf{G}_{hkl}) = N_c \frac{(2\pi)^3}{v_o} |\mathbf{F}_m(\mathbf{G}_{hkl})|^2 \quad (2.80)$$

where the vector quantity,

$$\mathbf{F}_m(\mathbf{K}) = \sum_d \mathbf{q}_d p_d \exp(i\mathbf{K} \cdot \mathbf{d}) \exp(-W_d) \quad (2.81)$$

is the *magnetic structure factor*.

The similarity of (2.80) with the corresponding (2.59) for nuclear scattering is obvious. It is important to write the cross sections that way, since in most of the work we are interested in *relative* cross sections rather than the absolute values which are very hard to measure.

We emphasize the form factor dependence of the magnetic scattering length. This leads to a great reduction of the magnetic scattering cross sections as the scattering angle becomes larger. Also, we note that the values of the magnetic scattering lengths p can be calculated from first principles in contrast with the nuclear scattering lengths.

Antiferromagnetic, Spiral and Sinusoidal Magnetic Structures

For more complicated ordered arrays of magnetic moments, we can still use equation (2.80) and the magnetic structure factor of equation (2.81).

Consider for example the *antiferromagnetic* structure of Figure 2.5, which is based on a body centered cubic structure. For nuclear scattering only reflections with $h + k + l = 2n$ are present, as we can easily see from (2.59). But from (2.81) we see that for magnetic scattering only reflections with $h + k + l = 2n + 1$ exist. Thus, if we have a material which undergoes a transition from a paramagnetic to an

Figure 2.5: Example of antiferromagnetic structure. (After reference 32)

antiferromagnetic state at some temperature, then below this temperature additional diffraction peaks appear.

For *spiral*, *sinusoidal* or more complicated magnetic structures, additional peaks called *satellites* appear at scattering vectors which are non-integer multiples of a reciprocal lattice vector. Some examples are treated in the experimental part of this dissertation, while in Appendix A we describe in detail how one proceeds to calculate structure factors for these types of magnetic structures. For a review of the wealth of magnetic structures that occur in nature we refer for example to [32] [43] or [44].

In all the previous discussion we did not consider the direction of the neutron spins. This is justified for beams of unpolarized neutrons, which was the only type used for the work described in this dissertation. In general there is some coherence

between the nuclear and magnetic scattering, but for unpolarized neutrons it averages out to zero [32].

Connecting Theoretical Results with Experiment

Our results for the cross sections have assumed ideal situations, and have to be modified in order for a comparison with experiment to be possible.

Consider for example Bragg scattering, which we described by equations (2.57)-(2.59). In an experiment we measure the intensity of a Bragg peak as, by changing some parameter, we pass through the Bragg condition $\mathbf{K} = \mathbf{G}$. Due to *mosaic spread* in the crystal and instrumental *resolution*, the peak has a finite *width* (in contrast with the theoretical δ -function).

As an example, consider measuring a Bragg peak by *rotating the crystal*. In Figure 2.6 we show the geometry of this experiment. The crystal is rotated about an axis perpendicular to the scattering plane. As ψ is changing we pass through the Bragg reflection condition $\mathbf{K} = \mathbf{G}$. Such a curve is called a *rocking curve*, and an example from one of the experiments described in this dissertation is given in Figure 2.7. For this method we can show that the *integrated* number of scattered neutrons in the Bragg peak is,

$$P = \frac{V}{v_o^2} I_o \frac{\lambda^3}{\sin 2\theta_b} |F_n(\mathbf{K})|^2 \quad (2.82)$$

where λ the incident neutron wavelength. The last equation allows us to compare very easily the relative intensities of two Bragg peaks, since the only quantities that depend on a specific reflection are the structure factor and the scattering angle. As an example, we can use Equation (2.82) and the similar expression for magnetic scattering to determine the values of the atomic magnetic moments in magnetically

Figure 2.6: Rotating crystal method.

ordered crystals from a comparison of the intensities of nuclear and magnetic Bragg peaks.

Figure 2.7: Example of a rocking curve.

CHAPTER 3. EXPERIMENTAL TECHNIQUES

In this chapter we give some details about practical aspects of neutron scattering. We focus on matters that are directly related to this dissertation.

Neutron Sources

Nuclear reactors and *spallation sources* are the two kinds of sources presently used for the production of neutrons. In a reactor neutrons are produced in the *fission* processes. The fissionable material is usually uranium enriched in the ^{235}U isotope. The high energy neutrons that are produced in fission are brought to thermal energies after passing through a material which acts as a *moderator*, like water or graphite.

At thermal energies the velocity distribution of neutrons is close to that of Maxwell's for the temperature T of the moderator [32],

$$\phi(v) = Av^3 \exp(-\frac{1}{2}mv^2/k_B T) \quad (3.1)$$

where $\phi(v)dv$ is the neutron flux with velocities between v and $v + dv$, and A a constant. The distribution is continuous with a maximum at,

$$v = \sqrt{\frac{3k_B T}{m}} \quad (3.2)$$

Using the following relation for the kinetic energy of the neutron,

$$\frac{1}{2}mv^2 = \frac{\hbar^2 k^2}{2m} \quad (3.3)$$

Figure 3.1: Thermal neutron distribution at 300 K .

where $k = 2\pi/\lambda$, we get the wavelength distribution,

$$\phi(\lambda) = \frac{C}{\lambda^5} \exp(-h^2/2mk_B T \lambda^2) \quad (3.4)$$

In Figure 3.1 we plot the distribution (3.4) for $T = 300\text{ K}$. We note that the spectrum is *white*, i.e. there are no sharp characteristic lines as in the case of x-rays. A neutron at 300 K has kinetic energy of about 25 meV and a wavelength of about 1.8 $\text{\AA}$. It is possible to obtain neutrons with higher (*hot*) or lower (*cold*) energies, by using a amount of moderating material at high or low temperatures. For more information about neutron sources we refer to the article by Carpenter and Yelon [46].

Figure 3.2: Production of a monochromatic neutron beam.

Monochromatic Neutron Beams

A monochromatic neutron beam can be produced by scattering a collimated neutron beam of white radiation from a single crystal, as in Figure 3.2. A collimated beam can be produced by using a collimator that consists of long steel sheets coated with Boron which has a very large absorption cross section for thermal neutrons [32]. Only neutrons that travel within a small angle range about the direction parallel to the slits will pass through the collimator and a well defined (in direction) beam will emerge.

Then we can place a single crystal so that the condition for a Bragg reflection is satisfied for a particular wavelength. The emerging scattered beam contains the specific wavelength λ which satisfies (2.55) for $n = 1$ as well as $\lambda/2$, $\lambda/3$ etc., which

also satisfy this equation for $n = 2, n = 3 \dots$

These additional wavelengths, which are usually called *higher order contaminations*, will complicate the interpretation of scattering data, and one would like to minimize their presence. For instance, instead of selecting the primary wavelength at the peak of the distribution (3.4) to get the maximum intensity, a shorter wavelength is selected because then the percentage of the $\lambda/2$ contamination (which is the most important) becomes smaller, as an inspection of Figure 3.1 verifies.

Since the available neutron fluxes are not very large, in order to obtain sufficiently intense beams the horizontal collimation of the incident beam is relaxed and a crystal with relatively large mosaic is used to select a band of wavelengths. Typically the horizontal divergence of the beam is $\pm \frac{1}{2}^\circ$ and the width of the wavelength band is 0.05 Å.

Neutron Counters

A *proportional* [42] counter filled with BF_3 or 3He gas is most frequently used to count the scattered neutrons. The Boron is enriched in the neutron absorbing isotope ^{10}B . Neutrons, having no charge, do not produce ionization by their own, but once the reaction

takes place, the lithium and helium nuclei do so, and the counter operates in the usual way [42]. The pulses produced by γ -radiation are much smaller than the ones for neutrons and can be discriminated easily. A typical counter is cylindrical with a diameter of a few centimeters and a length of the order of 30 cm. The counting efficiencies are around 80%.

In the ${}^3\text{He}$ counter the reaction is,

The ${}^3\text{He}$ counter requires lower operating voltage than the BF_3 type and is more efficient, so it has become the most frequently used today.

Neutron Spectrometers

All the experimental work in this dissertation was done using a *triple axis spectrometer*, which is the most versatile instrument used in neutron scattering. A schematic diagram of a triple axis spectrometer is shown in Figure 3.3. A large single crystal (usually pyrolytic graphite or beryllium) is used as a *monochromator* to select neutrons of particular wavelength, by a Bragg reflection. Of course, one can easily change the value of the selected wavelength.

The beam is then incident on the sample, which can be rotated about the axis perpendicular to the scattering plane. At the scattering angle ϕ we have an *analyzer* crystal, with which we can select scattered neutrons with a certain wavelength (energy). A counter is then used to count the neutrons.

Collimators are placed along the path of the neutrons to improve the resolution of the instrument. This decreases the intensity, and, in general, we have to make some compromise in order to perform the measurements in a realistic time scale.

As we mention before, we also get higher order Bragg reflections from the monochromator. Fortunately, some materials are very transparent at certain wavelengths but almost opaque at the corresponding $\lambda/2$. This is either a *transmission effect* or is due to a *nuclear resonance*. These materials can be used to make *filters* which greatly reduce the presence of the contamination. These filters are placed in

Figure 3.3: Diagram of the HB3 triple axis spectrometer at the HFIR reactor.

frond or after the sample, depending on the type of experiment.

Massive shielding is placed around the monochromator to minimize the radiation levels in the working area, as well around the counter to avoid counting particles other than the neutrons scattered from the sample. The counter is placed quite far from the sample (one meter or so) to improve angular resolution. As a result of the above, neutron spectrometers are very massive and require very strong construction.

A triple axis spectrometer can be used as a *diffractometer* for the study of elastic scattering. We just have to set the analyzer to select neutrons with the same energy as the ones that are incident on the sample.

But the great power of the instrument is in the study of inelastic scattering. We illustrate below how we can measure phonon dispersion relations using the triple axis spectrometer. For a detailed description of the triple axis spectrometer and its advantages see the articles by Iyengar [47], Dolling [48], and the original paper by Brockhouse [49].

Measuring Phonon Dispersion Relations

The phonon *dispersion relations* $\omega = \omega(\mathbf{q})$ contain valuable information about the electronic and physical properties of crystals (see [39] or any textbook in Solid State Physics).

The determination of a point $(\omega, \mathbf{q})$ on the dispersion curve by neutron scattering is based on Equation (2.60), or the equivalent for phonon absorption. We need to satisfy,

$$\frac{\hbar^2(k^2 - k'^2)}{2m} = \hbar\omega \quad (3.5)$$

$$\mathbf{Q} = \mathbf{G} + \mathbf{q} \quad (3.6)$$

and the dispersion relation,

$$\omega = \omega(\mathbf{q}) \tag{3.7}$$

where we denote now the scattering vector with $\mathbf{Q}$, as is the custom in the literature.

We have a system of five equations with four unknowns ω, q_x, q_y, q_z , which has a limited number of solutions. The most frequently used experimental method is the *constant- $\mathbf{Q}$ method*. In this method the scattering vector $\mathbf{Q}$ is kept fixed, while the energy transfer is varied. Usually, either the final or the incident neutron energy is also kept fixed so we only vary k or k' . A reciprocal space diagram illustrating the method for fixed final energy is given in Figure 3.4.

Provided that a phonon with energy in the range of the scan exists, we get a Gaussian-like *neutron group* which gives the frequency ω of the phonon. This, together with the wavevector $\mathbf{q}$ which we have chosen gives us a point on the dispersion curve. An example of a neutron group from the work presented in this dissertation is given in Figure 3.5.

Of course, to use the method successfully we have to select a reciprocal lattice vector $\mathbf{G}$ so that the cross section (2.60) is large, and take into consideration *resolution* conditions while selecting the instrumental parameters. For a review of neutron scattering applications in Lattice Dynamics see for example [41] or the article by Stassis [50].

Figure 3.4: Diagram in reciprocal space showing three different positions along a constant- Q scan, for fixed final energy.

Figure 3.5: Example of a constant-Q scan.

CHAPTER 4. MAGNETIC STRUCTURE OF $\text{DyNi}_2\text{B}_2\text{C}$

A paper published in *Physica B*¹

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Abstract

Neutron diffraction techniques have been used to study the magnetic structure of $\text{DyNi}_2\text{B}_2\text{C}$. The measurements, performed on *single* crystals of this compound depleted in the neutron absorbing ^{10}B nuclei, show that below approximately 10K the compound is a simple collinear antiferromagnet. The moments are aligned ferromagnetically in each rare-earth carbon layer perpendicular to the c-axis with the magnetic moments of two consecutive layers aligned in opposite directions. In contrast to the case of both $\text{HoNi}_2\text{B}_2\text{C}$ and $\text{ErNi}_2\text{B}_2\text{C}$ no modulation along the a^* direction was observed in this compound.

Introduction

The physical properties of the rare-earth nickel boride carbides, $\text{RENi}_2\text{B}_2\text{C}$, wher RE stands for a rare-earth element, have been the subject of many recent stud-

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ies [1-10].² The structure [3,7] of these compounds is body centered tetragonal (space group $I4/mmm$) and consists of $RE-C$ layers separated by Ni_2B_2 sheets. This layered structure is similar to that of $ThCr_2Si_2$ and is reminiscent of the high- T_c oxide superconductors. Several members of this family of quaternary intermetallic compounds are superconducting with T_c as high as 16.6 K for $LuNi_2B_2C$ and 15.6 K for YNi_2B_2C . It is interesting that superconductivity is also observed for the compounds containing magnetic rare-earth elements, such as Ho , Er and Tm . In these latter compounds, strong resistive and upper critical field anomalies were observed both in powder [5] and single crystal measurements [6]. Actually $HoNi_2B_2C$ exhibits reentrant behavior in a small temperature range around 5 K in zero or very small magnetic field [5,6]. Therefore, this family of intermetallic compounds is ideal for a systematic study of the interplay between magnetism and superconductivity, previously examined [11-14] in the $RERh_4B_4$ and REM_6S_8 magnetic superconductors. Electronic band structure calculations [8-10] for the $RENi_2B_2C$ compounds suggest that these materials are conventional superconductors with a relatively high electronic density of states at the Fermi level.

Recently, single crystals of these compounds were grown at the Ames Laboratory and this made it possible for us to undertake a systematic study of the magnetic structure of these compounds by neutron diffraction techniques. The diffraction experiments [15] on single crystals of $HoNi_2B_2C$ show that below approximately 4.7 K the Ho moments are ordered in a simple, collinear, antiferromagnetic structure: the moments are aligned ferromagnetically in each rare-earth carbon layer, with the magnetic moments on two consecutive layers aligned in opposite directions. The most

²In Chapters 4-8 references refer to the list at the end of each chapter.

interesting result of that study [15] is that in the vicinity of 5 K , where the resistive and H_{c2} anomalies occur, an intermediate modulated structure characterized by two incommensurate wave vectors $k_1 = 0.585 \text{ a}^*$ and $k_2 = 0.915 \text{ c}^*$ is observed [16]. In $ErNi_2B_2C$, on the other hand, only a transverse spin wave with incommensurate wave vector of 0.553 a^* was observed below approximately 7 K in our single crystal measurement [17] as well as in measurements on powder samples [18]. In view of these observations, it is tempting to attribute the almost reentrant behavior [5,6] of H_o in the vicinity of 5 K to the pair breaking associated with the intermediate modulated structure with wave vector along c^* observed in this compound. The observation, on the other hand, of a modulation along a in both the Ho and the Er compounds suggests that there may be common Fermi surface nesting features in these compounds along a which lead to the modulated ordering of the rare-earth ions via the RKKY interaction with the conduction electrons. Recent band theoretical calculations [19] of the generalized susceptibility $\chi(q)$ of $LuNi_2B_2C$ also suggest such an interpretation.

To obtain more information about the magnetic ordering in these compounds, we performed a systematic study of $DyNi_2B_2C$ by magnetization and neutron diffraction measurements. Magnetization measurements performed in this laboratory on single crystals of $DyNi_2B_2C$, show that this compound is superconducting at 6.2 K ; (see *Note added in Proof*). The neutron diffraction study was also performed on single crystals of $DyNi_2B_2C$ and in this paper we report the results of these experiments.

Experiment

Single crystals of $DyNi_2B_2C$ were grown at the Ames Laboratory by the high-temperature flux technique as described elsewhere [20]. The boron used for the

preparation of the samples was depleted in the heavily neutron absorbing ^{10}B nuclei. Neutron diffraction measurements showed that in all cases examined the as grown platelets were single crystals of high quality (measured mosaic spread of less than 0.1°) with the c -axis perpendicular to their flat surface. The crystal used for the neutron diffraction experiments was approximately $5 \times 5 \times 0.5 \text{ mm}^3$.

Magnetization measurements as a function of temperature were performed on single crystals of $DyNi_2B_2C$ using a Quantum Design SQUID magnetometer. The experimental results obtained with the field applied both parallel and perpendicular to the c -axis are summarized in Figure 4.1. It is seen that the susceptibility is highly anisotropic. The susceptibility for $H \perp c$ follows a Curie-Weiss behavior at high temperatures and clearly shows that the compound orders antiferromagnetically at low temperatures. In comparison, the susceptibility for $H \parallel c$ is practically independent of temperature. These observations strongly suggest that the moment is in the basal plane. An effective magnetic moment of $9.8 \mu_B$ was obtained by fitting the high temperature susceptibility data to a Curie-Weiss temperature dependence; the value obtained is only slightly smaller than that expected from a Dy^{3+} ion.

The neutron diffraction experiments were performed using the HB1A triple-axis spectrometer of the Oak Ridge National Laboratory. This is a constant incident neutron energy (14.7 meV) spectrometer utilizing a double pyrolytic graphite monochromator (reflecting from the (002) planes) and a pyrolytic graphite filter to minimize the $\lambda/2$ contamination of the incident beam. Measurements over the 2.3 K to 300 K temperature range were performed with the crystal oriented so that the a - c plane is coincident with the scattering plane.

Figure 4.1: Susceptibility measurements for $H \parallel c$ (circles) and $H \perp c$ (squares). The insert shows the temperature variation of the susceptibilities.

Results and Discussion

At temperatures above approximately 10 K only nuclear scattering is observed. A typical scan along c^* , taken in this temperature range ($T = 19\ K$) is given in Figure 4.2. Only nuclear reflections (hkl) with $h+k+l = 2n$ are observed as expected from the crystal structure of the compound. Similar results were obtained in scans parallel to a^* and other directions in the a - c plane. Therefore, at temperatures above approximately 10 K $DyNi_2B_2C$ is paramagnetic.

At temperatures below approximately 10 K , scattering develops at the positions of the forbidden nuclear reflections (hkl) with $h+k+l = 2n+1$, as it can be seen in the scan along c^* taken at 5 K (Figure 4.2). The intensity of these magnetic reflections increases as the temperature decreases below 10 K (Figure 4.3) and start to saturate by approximately 8 K . Therefore, at temperatures below 10 K , $DyNi_2B_2C$ is a commensurate antiferromagnet. Since no magnetic reflections with half-integer indices were observed, the magnetic cell has the same dimensions as the chemical cell of the compound. In this temperature range, the moments are aligned ferromagnetically in each layer perpendicular to the c -axis with the magnetic moments of two consecutive layers aligned in opposite directions. The magnetic structure is, therefore, the same as that observed [15] in $HoNi_2B_2C$ at low temperatures ($\leq 4.7\ K$).

It should be emphasized that no modulated incommensurate structure was observed in $DyNi_2B_2C$ down to the lowest temperature (2.3 K) reached in the present experiments. In particular, in contrast to both [15,17] $HoNi_2B_2C$ and $ErNi_2B_2C$, no modulation along a^* was observed. As we mentioned earlier, (see Introduction) the observation of a modulation along a^* in both $HoNi_2B_2C$ and $ErNi_2B_2C$, with

Figure 4.2: Typical neutron diffraction scans, along c^* , at 19 K and 5 K . Four monitors correspond to a counting interval of approximately 3.6 sec.

Figure 4.3: Temperature dependence of the intensity of the (001) magnetic reflection.

comparable wave vectors, can be attributed to common nesting features in these compounds along $\mathbf{a}^*$. Actually recent band theoretical calculation [19] of the generalized electronic susceptibility of $\text{LuNi}_2\text{B}_2\text{C}$ (without matrix elements) suggest that such a nesting feature along $\mathbf{a}^*$ may be common to the normal state of all compounds in this family, since $\chi(q)$ exhibits a pronounced peak at a wave vector of approximately 0.6 along $\mathbf{a}^*$. Such a simple interpretation seems to be in conflict with the results of the present experiment. The modulation along $\mathbf{a}^*$ appears in both $\text{HoNi}_2\text{B}_2\text{C}$ ($T_c \simeq 8 \text{ K}$) and $\text{ErNi}_2\text{B}_2\text{C}$ ($T_c \simeq 11 \text{ K}$) at temperatures below their superconducting transition temperature, at 6 K for the *Ho* and 7 K for the *Er* compound. The *Dy* compound, on the other hand, orders magnetically at 10 K and becomes superconducting well below this temperature (see Introduction). The absence of modulation along $\mathbf{a}^*$ in the *Dy* compound is therefore surprising, since one would expect that any normal state Fermi surface nesting strong enough to persist through the onset of superconductivity in the *Ho* and *Er* compounds would be present in $\text{DyNi}_2\text{B}_2\text{C}$. Detailed band theoretical calculations for the *Ho*, *Er*, and *Dy* compounds that take into account the onset of superconductivity may provide an explanation for the absence of modulation along $\mathbf{a}^*$ in the *Dy* compound.

Note added in proof. Recent measurements of electrical resistivity and low applied magnetic field ($H = 10 \text{ G}$) magnetization on single crystal samples of $\text{DyNi}_2\text{B}_2\text{C}$ show that there is superconductivity below $T_c = (6.2 \pm 0.1) \text{ K}$.

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CHAPTER 5. MAGNETIC STRUCTURE OF $\text{ErNi}_2\text{B}_2\text{C}$

A paper published in Physical Review B¹

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and D. C. Johnston

Abstract

Neutron-diffraction techniques have been used to study the magnetic structure of the superconductor $\text{ErNi}_2\text{B}_2\text{C}$ ($T_c = 11\text{ K}$). The experimental results, obtained on single crystals, show that below approximately 7 K this compound is in an incommensurate modulated antiferromagnetic state, with wave vector $0.553\mathbf{a}^*$, that coexists with superconductivity. The field dependence of the magnetic structure of this compound was studied at 5.5 K as a function of an externally applied magnetic field both along the b and c axes of the tetragonal structure.

Introduction

The study of the physical properties of the recently discovered [1-4] superconducting rare-earth nickel boride carbides, $\text{RNi}_2\text{B}_2\text{C}$ (where R stands for a rare-earth

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element), may provide a better understanding of the competition between superconductivity and magnetism. The layered structure of these compounds is reminiscent of that of the high- T_c oxide superconductors and consists of $R - C$ layers separated by Ni_2B_2 sheets. Superconductivity is observed [2-5] in these compounds not only for the nonmagnetic rare-earth elements but also for the magnetic rare-earth elements (Tm , Ho , Er , Dy). Electronic band-structure calculations [6-8] for these compounds suggest that these materials are conventional superconductors.

Of particular interest for the heavy rare-earth nickel boride carbides are the resistive and upper critical field anomalies observed in measurements on powder samples by Eisaki *et al.* [5], and single-crystal measurements by Canfield *et al.* [9]. In a small temperature interval around 5 K the Ho compound was found to be reentrant under zero [5] or a finite but very small (20 G) [9-10] applied magnetic field. Similar, but less pronounced, resistance anomalies are observed below 2.5 K and around 5.5 K for the Tm and Er compounds, respectively, but only under a modest magnetic field.

In a previous study [11] we reported the results of neutron-diffraction experiments on single crystals of $HoNi_2B_2C$. The experimental results [11] show that below approximately 4.7 K the Ho atoms are ordered in a simple antiferromagnetic structure: the moments are aligned ferromagnetically in each layer, with the magnetic moments of two consecutive layers aligned in opposite directions. The most interesting result of that study was that in the 4.7-6 K temperature range a transient modulated structure, characterized by two incommensurate wave vectors $k = 0.585a^*$ and $k' = 0.915c^*$, was observed. This suggests [11] that the pair breaking associated with the transient magnetic structure may be responsible for the deep minimum in H_{c2} and the almost reentrant behavior in this compound at approximately 5 K .

To obtain more information about the possible relationship between the magnetic structure and the H_{c2} and resistive anomalies in these compounds we performed a systematic neutron-diffraction study of the magnetic structure of $ErNi_2B_2C$. In this paper we report the results of these experiments.

Experimental Details

Single crystals of $ErNi_2B_2C$ were grown at the Ames Laboratory by the high-temperature flux technique [9], using boron depleted in the heavily neutron absorbing ^{10}B nuclei. Single-crystal platelets extracted from the flux were examined by x-rays and neutrons and were found to be single crystals of high quality with the c axis perpendicular to their flat surface. Magnetization measurements as a function of temperature and magnetic field were performed in a Quantum Design superconducting quantum interference device magnetometer on single crystals from the same batch as those used in the neutron-diffraction experiments.

The neutron-diffraction experiments were performed using the triple-axis spectrometer HB1A at the HFIR reactor of the Oak Ridge National laboratory. Paralytic graphite reflecting from the (002) planes was used as monochromator and analyzer, and a paralytic graphite filter was used to minimize the $\lambda/2$ contamination of the incident beam. All measurements were performed with a constant incident neutron energy of 14.7 meV. The crystal used in the present experiment was of high quality with a mosaic spread characterized by a full width at half maximum ($FWHM$) of 0.09° measured by making use of a perfect germanium crystal as analyzer. The mosaic spread was found to increase by almost a factor of 2 between 7 and 1.7 K because of magnetostriction. Measurements over the 1.7-300 K temperature range

were taken for two different crystal orientations, namely, with the scattering plane coincident with the a - b or a - c planes. The field dependence of the magnetic structure at 5.5 K was studied up to a field of 14 kG applied either along the tetragonal c axis or the basal plane b axis.

Results and Discussion

In the absence of an applied field, between 300 K and approximately 7 K only nuclear reflections (hkl) with $h + k + l = 2n$ are observed. As the temperature is decreased below approximately 7 K additional diffraction peaks start to develop in rows parallel to the reciprocal a axis (or the equivalent b axis of the tetragonal structure). The observed additional diffraction peaks are pairs of first- and higher-order satellites to each allowed nuclear reflection (hkl) with $h + k + l = 2n$, with a fundamental incommensurate wave vector of (0.553, 0, 0). Figure 5.1 shows the first- and third-order satellites observed in the ($h0l$) scattering plane. Fifth-, seventh-, and ninth-order satellites were also observed. The intensity of the observed satellites increases with decreasing temperature and approaches saturation below 3 K (Figure 5.2). No other magnetic phase transition was observed down to approximately 1.7 K , the lowest temperature reached in the present experiment. The above experimental observations imply that between 300 K and approximately 7 K the Er moments are not ordered, since in this temperature range, only nuclear and critical magnetic scattering is observed. Between approximately 7 K and 1.7 K , the lowest temperature reached in the present experiments, ordering of the moments is observed. In this temperature range the Er^{3+} moments are modulated along the a axis (or the equivalent b axis) with a wave vector $k = 0.553a^*$, nearly doubling

Figure 5.1: Reciprocal space plane showing the points associated with nuclear scattering (filled circles), and the first- and third-order satellites (shaded circles) associated with the modulation wave vector $k = 0.553a^*$.

Figure 5.2: Temperature dependence of the (1.447, 0, 0) satellite for increasing (filled triangles) and decreasing (open triangles) temperature.

the chemical unit cell in the basal plane. The observations of satellites to all nuclear reflections, including (000), in both the a^* and b^* directions shows that the structure is a *transverse* spin wave with a propagation vector along a^* (or b^*). Furthermore, the observation of higher-order harmonics shows that the modulation is not purely sinusoidal, but squared. The nuclear and magnetic structure factors obtained from the observed intensities are subject to large uncertainties due to secondary extinction effects. The extinction problem is particularly severe in the present experiments because of the high perfection of the crystals ($FWHM \simeq 0.1^\circ$) and the fact that as a result of magnetostriction, the mosaic of the crystals changes substantially as the temperature is reduced below the magnetic ordering temperature. Nevertheless, given these large uncertainties, the moment obtained ($\simeq 8 \mu_B$) by assuming that no moment is induced on the nickel atoms is in reasonable agreement with the results obtained by Sinha *et al.* [12], on powder samples.

The magnetic ordering in $ErNi_2B_2C$ is similar to one of the transient modulated structures observed in $HoNi_2B_2C$ in the temperature region between 4.7 and 6 K. The magnetic wave vector along the a^* (b^*) in the *Er* compound (0.553) is only slightly smaller than that observed (0.585) for the *Ho* compound. In $HoNi_2B_2C$, however, additional satellites are observed corresponding to a squared modulation of the magnetic moments along the c axis, and no squaring of the magnetic structure along the a axis was observed in zero applied field. Since this modulated structure characterized by $k = 0.553a^*$ coexists with superconductivity in $ErNi_2B_2C$, it is tempting to attribute the almost reentrant behavior of $HoNi_2B_2C$ at 5K to the magnetic modulated structure characterizes by $k' = 0.915c^*$ observed in this compound.

The magnetic structure of $ErNi_2B_2C$ has been also studied at 5.5 K as a function of a field applied either along the b or c axis. The results obtained with the crystal oriented in the $(h0l)$ plane and the field applied parallel to the b axis are summarized in Figure 5.3(a). It is seen that the intensity of the satellites decreases with increasing magnetic field and becomes negligible at approximately 10 kG . In addition, an increase of the intensity of the nuclear Bragg peaks was observed. With the crystal oriented so that the $(hk0)$ plane is in the scattering plane and the field along the c axis, on the other hand, no change in the magnetic structure is seen for fields up to 14 kG [Figure 5.3(b)]. These observations are consistent with bulk measurements on single crystals of $ErNi_2B_2C$ which show that T_N is strongly field dependent for a field applied in the basal plane, but rather insensitive to a field applied along the tetragonal c axis; actually, these measurements show that for a field of 10 kG applied parallel to the b axis, the ordering temperature T_N for the Er moments is below 5.5 K . Thus, for fields exceeding approximately 5 kG applied along the b axis the magnetic moments are not completely ordered, as shown (Figure 5.3) by the decrease in the intensity of the magnetic satellite, and as a result, a moment is induced by the applied field causing an increase in the nuclear intensities. In summary, the magnetic structure of $ErNi_2B_2C$ is found to be different from that observed in the corresponding Ho compound. In particular, in Er , the moments below 6 K order in an incommensurate modulated structure with the wave vector parallel to $\mathbf{a}^*$, whereas in Ho an incommensurate modulated structure, characterized by two wave vectors, one along $\mathbf{a}^*$ (with magnitude only slightly larger than that observed in the Er compound) and one along $\mathbf{c}^*$, is observed only between 4.7 and 6 K . This may be the origin of the observed differences in the magnetotransport properties of

Figure 5.3: (a) Field dependence at 5.5 K of the (0.553,0,0) satellite and (200) nuclear reflection for increasing (filled triangles) and decreasing (open triangles) fields along the b axis. (b) Field dependence of the (0.553,0,0) satellite at 5.5 K for increasing field along the c axis.

these two compounds. In particular, it is tempting to attribute the almost reentrant behavior of *Ho* in the vicinity of 5 K to the pair breaking associated with the transient modulated structure along c^* . This conclusion is also suggested by band theoretical calculations [13] of the generalized susceptibility $\chi(q)$ of $\text{LuNi}_2\text{B}_2\text{C}$ (without matrix elements). In these calculations, the generalized susceptibility for wave vectors along a^* has a pronounced peak for a wave vector of approximately 0.6, a value close to the values observed for *Ho* (0.585) and *Er* (0.553). Since the calculations were performed for $\text{LuNi}_2\text{B}_2\text{C}$ it is natural to assume that the modulated structure with the wave vector along a^* and magnitude close to 0.6 is a common feature of these compounds and can be attributed to a nesting of their Fermi surfaces. Clearly, calculations with matrix elements may provide a better understanding of the magnetic ordering in these compounds.

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CHAPTER 6. MAGNETIC STRUCTURE OF $\text{TbNi}_2\text{B}_2\text{C}$

A paper submitted to Physical Review B¹

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Abstract

Neutron diffraction techniques have been used to study the magnetic structure of $\text{TbNi}_2\text{B}_2\text{C}$. The measurements, performed on single crystals of this compound, show that below approximately 15 K the moments order in an almost longitudinal spin wave with wave vector along $\mathbf{a}^*$. The magnitude of the wave vector is close to that obtained in the Ho , Er , and Gd compounds. This observation provides additional evidence that there are common Fermi surface nesting features along $\mathbf{a}^*$ in the rare-earth nickel boride carbides which cause the magnetic ordering of the rare-earth moments via the RKKY mechanism. Below approximately 8 K , the experimental results indicate the development of a small ferromagnetic component.

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Introduction

The compounds of the $RENi_2B_2C$ family (where RE stands for a rare-earth element) [1-4] exhibit very interesting physical properties at low temperatures. The structure [3] of these compounds is body-centered tetragonal (space group $I4/mmm$) and consists of $RE - C$ layers separated by Ni_2B_2 sheets. The compounds formed with the non-magnetic rare-earth elements Lu and Y are superconductors [2-5] with relatively high superconductivity transition temperatures (16.6 K and 15.6 K for the Lu and the Y compound, respectively). It is particularly interesting that the compounds formed with magnetic rare-earth elements such as Tm , Er , Ho , and Dy are also superconductors [2-7] and that superconductivity coexists with magnetic order in these compounds. The compounds formed with Gd and Tb , on the other hand, order magnetically at low temperatures but they are not superconducting, at least down to approximately 2 K .

The magnetic structure of the superconducting Ho , Er , and Dy compounds have been studied by neutron diffraction techniques [7,10-13] using samples depleted in the heavily absorbing ^{10}B nuclei. The non-superconducting, down to 2 K , Gd compound has been recently studied with magnetic x-ray scattering [14]. One of the most interesting results of these experiments is that in the magnetic state of Ho , Er , and Gd compounds an incommensurate modulation of the moments along a^* is observed with wave vectors of 0.585, 0.553, and 0.553, respectively. This result suggests that there are common Fermi surface nesting features along a^* in these compounds which cause the magnetic ordering of the rare-earth moments via the RKKY mechanism.

Electronic band structure calculations [15-18] indicate that these compounds

are three dimensional metals with relatively high density of states at the Fermi level. These calculations as well as the recent observation [19] of soft phonons in $LuNi_2B_2C$, provided convincing evidence that the superconducting compounds of this family are strongly coupled conventional superconductors. More pertinent to an understanding of the magnetic ordering in these compounds is a recent calculation [20] (without matrix elements), of the generalized electronic susceptibility $\chi(q)$ of $LuNi_2B_2C$ based on the normal state electronic band structure of this compound. It is encouraging that the calculated [20] $\chi(q)$ exhibits a peak along a^* with a wave vector close to those observed in the Ho , Er , and Gd compounds.

In this paper we present the results obtained in a neutron diffraction study of the magnetic ordering in the Tb compound which, like Gd , is not superconducting at least down to 2 K . Of particular interest, of course, is whether the magnetic structure of this compound at low temperatures includes an incommensurate modulation with wave vector along a^* and the determination of the magnitude of this wave vector.

Experimental Details

Single crystal specimens, depleted in the strongly neutron absorbing ^{10}B nuclei, were grown at the Ames Laboratory by the high temperature flux technique as described elsewhere [21]. Neutron diffraction measurements showed that the as-grown platelets of the $RENi_2B_2C$ compounds prepared at the Ames Laboratory were indeed single crystals of high quality (measured mosaic spread of less than 0.1 degrees) with the c -axis perpendicular to their flat surface. The $TbNi_2B_2C$ crystal used in the present experiment was a $3 \times 2 \text{ mm}^2$ platelet of 0.5 mm thickness.

Magnetization measurements were performed on single crystals of $TbNi_2B_2C$

using a Quantum Design SQUID magnetometer [9]. The data pertinent to the present study are summarized in Figure 6.1. It is seen in Figure 6.1(a) that the susceptibility is anisotropic suggesting that the rare-earth moments are confined to the basal plane. Both the high field and low field data clearly show that there is an antiferromagnetic transition at approximately 15 K . In addition, the low field data (Figure 6.1(b)) indicate that below approximately 8 K a weak ferromagnetic component may be developing.

The neutron diffraction experiments were performed using the HB1A triple-axis spectrometer at the High Flux Isotope Reactor (HFIR) of the Oak Ridge National Laboratory. This is a constant incident neutron energy (14.7 meV) spectrometer utilizing a double paralytic graphite monochromator and a paralytic graphite analyzer. A paralytic graphite filter was used to attenuate higher-order contaminations. Measurements, over the 2.3 – 300 K temperature range, were performed with the crystal oriented so that the a - c crystal plane coincides with the horizontal scattering plane.

The nuclear and magnetic structure factors evaluated from the single crystal measured intensities are subject to large uncertainties because the latter quantities must be corrected for the effects of secondary extinction and absorption. The extinction problem is particularly severe in the present experiments because of the high perfection of the crystals ($FWHM \simeq 0.1^\circ$) and the fact that as a result of magnetostriiction, the mosaic of the crystals changes as the temperature is reduced below the transition temperature. The absorption correction is also subject to large uncertainties because of the irregular shape of the platelets and its extreme sensitivity to the exact amount of ^{10}B contained in the depleted samples.

Figure 6.1: Temperature dependence of the measured magnetization of a $TbNi_2B_2C$ single crystal.

Results and Discussion

At temperatures above approximately 15 K only nuclear reflections with $h + k + l = 2n$ are observed as expected from the crystal structure of the compound. Therefore, at temperatures above approximately 15 K the magnetic moments in $TbNi_2B_2C$ are not ordered.

As the temperature is lowered below approximately 15 K additional diffraction peaks (see Figure 6.2) start to develop in rows parallel to the reciprocal a -axis (or the equivalent b -axis of this tetragonal structure). These additional diffraction peaks can be indexed as first-and higher-order satellites of the allowed nuclear reflections ($h + k + l = 2n$). These observations imply that below approximately 15 K the magnetic moments are ordered in a modulated structure with wave vector parallel to the reciprocal a -axis. The magnitude of the wave vector changes (see insert of Figure 6.3) from 0.551 ± 0.001 at 15 K to 0.545 ± 0.001 at 2.3 K , the lowest temperature reached in the present experiment.

It can be seen (Figure 6.2) that the intensities of the ($h00$) satellites are considerably lower than those of the corresponding ($h0l$) satellites. This implies that the direction of the moments is close to that of the a^* axis. From the observed intensities the magnitude of the transverse component of the moment was estimated (see previous section) to be approximately forty times smaller than the longitudinal component. Thus below approximately 15 K the magnetic structure of $TbNi_2B_2C$ can be described approximately as an almost longitudinal spin wave with propagation vector parallel to the reciprocal a -axis. This almost longitudinal spin wave is not purely sinusoidal but considerably squared as shown by the observation of relatively intense higher-order harmonics. Actually the estimated ratios of the moments of the

Figure 6.2: Typical scans along the $[h01]$ and $[h00]$ symmetry directions. The satellites of the $(h0l)$ reflection are denoted $(h0l)_n^\pm$ where the superscript $+$ (or $-$) means that the magnetic wave vector is added (or subtracted) from the reciprocal point of the reflection, and the subscript n is the order of the satellite.

third and fifth harmonics to that of the first harmonic are close to those expected ($1/3$ and $1/5$, respectively) for a completely squared wave. Below 15 K the intensity of the observed satellites increases with decreasing temperature and approaches saturation below approximately 6 K (Figure 6.3). No significant hysteresis effect on the observed intensities (Figure 6.3) was found within the precision of the present experiment.

To examine whether a ferromagnetic component develops below 8 K as indicated by the low-field magnetization measurements (Figure 6.1b) we recorded the temperature dependence of the intensities of the (006) and (105) reflections, which have the smallest intensities among all reflections that could be reached with the present experimental arrangement. The intensities of these nuclear reflections (Figure 6.4) exhibit a small anomaly at the antiferromagnetic transition (a feature common to all nuclear reflections), remain constant down to approximately 8 K and then increase with decreasing temperature. This result suggests the presence of a small ferromagnetic component below approximately 8 K in agreement with the low-field magnetization results (Figure 6.1b). It is clear, however, that only polarized neutron experiments, presently in preparation, can provide a definitive proof of the existence of a ferromagnetic component below 8 K .

The magnitude of the wave vector of the modulated magnetic structure of $TbNi_2B_2C$ is very close to the values obtained for Ho , Er , and Gd (0.585 , 0.553 , 0.553 , respectively); actually, the magnitude of the wave vector close to the transition (0.551) is almost identical to the magnitudes observed in Er and Gd . Thus, the present results provide additional evidence that there are common Fermi surface nesting features along a^* in the $RENi_2B_2C$ family that are responsible for the magnetic

Figure 6.3: Temperature dependence of the first, $(101)^+$, and third, $(\bar{1}01)_3^+$, order satellites. The data with open (filled) symbols were taken with increasing (decreasing) temperature.

Figure 6.4: Temperature dependence of the relative change, $\Delta I = I - I_0$, of the (006) nuclear reflection, I_0 stands for the intensity at 16 K.

ordering of the rare-earth moments via the RKKY mechanism. It is important to notice that the generalized susceptibility $\chi(q)$ of $\text{LuNi}_2\text{B}_2\text{C}$ calculated by Rhee, Wang, and Harmon [20] using the normal-state electronic band structure of this compound, exhibits a pronounced peak along a^* at a wave vector (0.6) close to the observed values of *Ho*, *Er*, *Gd*, and *Tb* compounds. Presumably, this nesting of the Fermi surface is not substantially altered by the opening of antiferromagnetic and, in the case of *Ho* and *Er* compounds, superconducting gaps at the Fermi level. Finally, it should be pointed out that the same Fermi surface nesting feature may be responsible for the strong phonon anomalies observed [19] in the low lying $[\xi 00]$ dispersion curves of $\text{LuNi}_2\text{B}_2\text{C}$. If this is the case, phonon softening and magnetic ordering are competing to decrease the energy of the system in the magnetic compounds of this family as a result of this nesting of the Fermi surface.

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CHAPTER 7. MAGNETIC PAIR BREAKING IN $\text{HoNi}_2\text{B}_2\text{C}$

A paper published in Physical Review B¹

A. I. Goldman, C. Stassis, P. C. Canfield, J. Zarestky, P. Dervenagas, B. K. Cho, D. C. Johnston and B. Sternlieb.

Abstract

Neutron-diffraction techniques have been used to study the interplay between superconductivity and magnetism in $\text{HoNi}_2\text{B}_2\text{C}$ ($T_c = 8\text{ K}$). The experimental results, obtained in single crystals, show that below approximately 4.7 K , this compound is in a simple antiferromagnetic state that coexists with superconductivity. Between approximately 4.7 and 6 K , an incommensurate magnetic structure has been found. This observation strongly suggests that pair breaking associated with this incommensurate magnetic structure is responsible for the deep minimum in H_{c2} and the near-reentrant behavior observed in this compound at approximately 5 K .

Introduction

Since the discovery of high- T_c superconductivity considerable effort has been directed towards an understanding of various layered structures containing transi-

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tion elements. The purpose of such studies is a better understanding of the interplay between magnetism and superconductivity. Among these layered structures, of particular interest is the recently discovered [1-4] family of rare-earth nickel boride carbides, RNi_2B_2C , where R stands for a rare-earth element. The structure [3] of these compounds is tetragonal (space group $I4/mmm$) and consists of $R-C$ layers separated by Ni_2B_2 sheets, a layered structure similar to the $ThCr_2Si_2$ structure and reminiscent of the high- T_c oxide superconductors. Perhaps the most interesting feature of these compounds is that superconductivity is observed [2,5] not only non-magnetic rare-earth elements but also for the magnetic rare-earth elements (Tm , Er , Ho , Dy). In this respect, the properties of the magnetic rare-earth nickel boride carbides are reminiscent of the magnetic superconductors RRh_4B_4 and RMo_6S_6 .

Among the heavy rare-earth nickel boride carbides, $HoNi_2B_2C$ ($T_c = 8\text{ K}$) is of particular interest. Resistivity and upper critical field measurements by Eisaki *et al.*, [5], performed on powder samples, demonstrated that this compound exhibits reentrant behavior even under zero field in a small temperature range around 5 K [10]. Their susceptibility measurements [5] and those by Canfield *et al.* [11] however, show that at temperatures below 5 K the compound is in a simple antiferromagnetic state that coexists with superconductivity. Therefore, it is natural to assume that, in the reentrant (or near-reentrant [10-11]) temperature range, the magnetic structure of $HoNi_2B_2C$ is different from the antiferromagnetic state at low temperatures. This observation motivated us to initiate a systematic study of the magnetic structure of this compound by neutron diffraction techniques. The measurements were performed on single crystals of $HoNi_2B_2C$ grown and characterized as described below.

Experimental Details

Single crystals of $HoNi_2B_2C$ of sufficient size for neutron-scattering experiments were grown at the Ames Laboratory by the high-temperature flux growth technique [12] and characterized by x-ray diffraction and magnetization measurements [11]. The boron used in the sample was isotopically depleted in the heavily absorbing ^{10}B nuclei. Single crystal platelets of $HoNi_2B_2C$ with dimensions as large as $2 \times 4 \times 0.1 \text{ mm}^3$ were removed from the flux. X-ray and neutron-diffraction measurements showed that in all cases examined, the platelets were single crystals of high quality (mosaic spread less than 0.2°) with the c axis perpendicular to the flat surface.

Magnetization measurements as a function of temperature and magnetic field were performed [11] on single crystals from the same batch as those used in the present experiments. The low-temperature normal-state magnetic susceptibility is highly anisotropic with a Curie-Weiss temperature dependence for $\mathbf{H} \perp c$ and with practically temperature independent paramagnetic behavior for $\mathbf{H} \parallel c$. The moment obtained by fitting the data for $\mathbf{H} \perp c$ to a Curie-Weiss law was found [11] to be $10.4 \mu_B$ in good agreement with the value obtained by measurements [13] on polycrystalline samples. These observations suggest that the moment is in, or very close to, the basal plane and its magnitude is consistent with that expected for Ho^{3+} ions. A detailed account of these experiments will be published elsewhere [11].

The neutron-diffraction experiments were performed using the triple-axis spectrometers HB2 and HB1A at the HFIR reactor of the Oak Ridge National Laboratory and H7 at the HFBR reactor of Brookhaven National Laboratory. For all three measurements, pyrolytic graphite (002) was used as monochromator and analyzer and parolytic graphite filters were used to minimize the $\lambda/2$ contamination of the inci-

dent beam. The measurements were performed with incident neutron energies of 14.7 and 41 *meV*. Measurements over the 1.7-300 *K* temperature range were taken for two different crystal orientations, namely, with the scattering plane coincident with the *a-b* or *a-c* planes.

Results and Discussion

At temperatures above approximately 7 *K*, only nuclear reflections (*hkl*) with $h + k + l = 2n$ are observed as expected from the crystal structure of the compound. As the temperature is decreased below approximately 6 *K* three additional types of diffraction peaks start to develop, as shown in the reciprocal space map of Figure 7.1. Scattering develops at the positions of the forbidden nuclear reflections (*hkl*) with $h + k + l = 2n + 1$. Pairs of satellites to each allowed nuclear reflection appear with incommensurate wave vectors of approximately (0,0,0.915) and (0.585,0,0). In addition, third-order satellites of the (0,0,0.915) reflection are observed.

The temperature dependence of the intensities of the observed satellites are shown in Figure 7.2. Below $T_c = 8$ *K*, but above approximately 6 *K*, the local moments are paramagnetic. The intensities of the satellites increase as the temperature of the sample decreases below 6 *K*, reach a maximum at approximately 5 *K*, and then sharply decrease in intensity, and practically disappear at approximately 4.7 *K*. The intensity of the magnetic peaks at the commensurate antiferromagnetic positions ($h + k + l = 2n + 1$), on the other hand, increase monotonically as the temperature decreases and start to saturate below approximately 4.7 *K*. These commensurate reflections are observed down to 1.7 *K*, the lowest temperature reached in these experiments. To within experimental uncertainty, the intensities of the nuclear

Figure 7.1: (a) One quadrant of the $h0l$ reciprocal space plane showing the points associated with nuclear scattering (filled circles) and the commensurate antiferromagnetic Bragg points (open circles); (b) the first- and third-order satellites associated with the modulation wave vector $K_1 = 0.915c^*$ (shaded circles); (c) the satellite positions associated with the modulation wave vector $K_2 = 0.585a^*$.

diffraction peaks remain constant over the entire temperature range investigated.

The above observations imply that there are three different magnetic regimes for the local moments in this compound in the $300 - 1.7\text{ K}$ temperature range. Between 300 K and approximately 6 K the local moments are paramagnetic. In this region, only nuclear scattering and critical magnetic scattering are observed. Below approximately 4.7 K down to 1.7 K , the lowest temperature reached in the present experiment, the compound is a commensurate antiferromagnet, since in addition to nuclear scattering, magnetic reflections (hkl) with $h + k + l = 2n + 1$ are observed. In this temperature range the Ho^{3+} moments are aligned ferromagnetically in each layer (basal plane of the tetragonal structure), with the magnetic moments of two consecutive layers (along the c axis) aligned in opposite directions. The magnetic cell has the same dimensions as the chemical cell, consistent with the absence of magnetic reflections with half-integer indices. Since the structure factors obtained from the intensities of the observed antiferromagnetic peaks are subject to relatively large uncertainties due to secondary extinction effects (especially those obtained from the measurements performed with an incident neutron energy of 14.7 meV) powder diffraction measurements were also performed at these temperatures. The powder diffraction intensities, and those obtained from the 41 meV single crystal data (although the latter, as mentioned above are subject to large uncertainties), are consistent with the moment being in the basal plane. The magnitude of the moment was found to be $(10.5 \pm 1)\mu_B$, a value consistent with that expected from Ho^{3+} .

The most interesting temperature range is between approximately 4.7 and 6 K . Here, in addition to the developing commensurate antiferromagnetic structure described above, a modulated magnetic structure, or structures, characterized by

Figure 7.2: Temperature dependence of (a) the (003) commensurate antiferromagnetic peak (filled ellipse) and the (101) nuclear Bragg peak (open rectangles); (b) the first- (open ellipse) and third-order (filled ellipse) satellites associated with the modulation wave vector $\mathbf{K}_1 = 0.915c^*$; (c) the $\mathbf{K}_2 = 0.585a^*$ magnetic satellite; and (d) the upper critical field H_{c2} (Ref. 11) determined via temperature-dependent magnetization measured parallel (open rectangles) and perpendicular (filled ellipse) to the tetragonal c axis. Lines are intended as guides to the eye.

wave vectors $\mathbf{K}_1 = 0.915\mathbf{c}^*$ and $\mathbf{K}_2 = 0.585\mathbf{a}^*$ occur. The Ho^{3+} moments, to first order, form a c -axis spiral with a turn angle of approximately 165° (0.915π); this spin arrangement is close to that of the low-temperature collinear antiferromagnetic structure described above. The presence of the third harmonic reflections indicates a "squaring" of the simple spiral. Along the a axis (or the equivalent b axis of the tetragonal structure) the magnetic ordering can be described in terms of a structure where neighboring moments are rotated by approximately 104° (0.585π). Alternatively, the structure can be viewed as a transverse spin wave with propagation wave vector along $\mathbf{a}^*$ (or $\mathbf{b}^*$). If this structure was commensurate, it would have a magnetic cell twice as large as the chemical cell in the basal plane. Therefore, the modulated structure(s) between 4.7 and 6 K may best be characterized as nearly antiferromagnetic. We point out here that it is not known, at this point, whether the modulations along the a and c axes described above are characteristic of a single domain or two, physically distinct magnetic structures. Indeed, the temperature dependence of the two modulations, shown in Figures 7.2(b) and 7.2(c) exhibit some differences.

The most important result of the present experiment is the observation of this modulated structure between approximately 4.7 and 6 K . This is the same temperature range where there is an anomalously deep minimum in the upper critical field. Further, in this temperature range, features in the temperature-dependent specific heat and magnetization [11], can be associated with the onsets of both the incommensurate and commensurate antiferromagnetic states. The coincidence of the incommensurate ordering with the deep minimum in H_{c2} is clearly illustrated in Figure 7.2 where [in figure 7.2(d)] the upper critical field is plotted as a function of temperature for fields parallel and perpendicular to the tetragonal c axis. Since simi-

lar anomalies have been observed in the antiferromagnetic superconductors RRh_2B_4 and RMo_6S_8 [14-21] it is natural to attribute their occurrence in $HoNi_2B_2C$ to the interaction between the local moment magnetism and superconductivity in this compound. What is unique, however, in $HoNi_2B_2C$ is that it exhibits reentrant, or in the case of bulk single crystals, nearly reentrant behavior in the vicinity of 5 K where the satellites characterizing the modulated structure reach their maximum intensity. It is, therefore, reasonable to assume that the deep minimum in the upper critical field is due to the pair-breaking interactions associated with the modulated structure. Compared with the previously known antiferromagnetic superconductors (RRh_4B_4 and RMo_6S_8) this interaction in $HoNi_2B_2C$ must be particularly strong to bring about the observed deep minimum in H_{c2} .

Although considerable progress has been achieved towards a theoretical understanding of antiferromagnetic superconductors [22] no detailed microscopic theory of the magnetic structures that occur is presently available to assess how the magnetic structure is influenced by superconductivity. $HoNi_2B_2C$ presents us with an important opportunity to reopen this issue since the strength of the magnetic interactions at low temperature which favor the commensurate antiferromagnetic structure seems close to the strength of those favoring the intermediate modulated phase. Since the difference in energies between these two magnetic ground states appears to be small, the energy associated with the stabilization of the superconducting ground state may be significant in determining the ultimate low-temperature ground state of the coupled electron-local moment system. Indeed, preliminary neutron-scattering work on the magnetic field-temperature phase diagram of $HoNi_2B_2C$ indicates a rich variety of magnetic phases in weak fields at low temperature. These results will be presented

elsewhere.

In summary, we have observed a modulated magnetic structure in $HoNi_2B_2C$ between 4.7 and 6 K that may account for the near-reentrant behavior of this compound. The particularly strong pair-breaking interaction between conduction electrons and the spin system in $HoNi_2B_2C$ makes this system a particularly promising candidate for the theoretical understanding of the interplay between magnetism and superconductivity.

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CHAPTER 8. SOFT PHONONS IN SUPERCONDUCTING $\text{LuNi}_2\text{B}_2\text{C}$

A paper published in Physical Review B¹

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Abstract

Inelastic neutron scattering techniques have been used to measure the low-lying phonon dispersion curves of superconducting $\text{LuNi}_2\text{B}_2\text{C}$ along the $[\xi 00]$ and $[00\xi]$ symmetry directions. The most important result of this experiment is that the phonon frequencies of the acoustic and first optical Δ_4 $[\xi 00]$ branches in the vicinity of the zone boundary point G_1 decrease with decreasing temperature. Actually these two branches exhibit pronounced dips at low temperatures, close to G_1 . This shows that the electron-phonon interaction is quite strong and causes an incipient lattice instability, a behavior typical of strongly coupled conventional superconductors. Furthermore, the phonon anomalies occur at wave vectors close to those of the incommensurate magnetically ordered structures observed in the magnetic compounds of this family, which suggests that both the magnetic ordering and the incipient lattice

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instabilities are influenced by common nesting features of the Fermi surfaces of the rare-earth nickel boride carbides.

Introduction

The quaternary intermetallic compounds of the recently discovered [1-4] family of rear-earth nickel boride carbides, $RENi_2B_2C$ (where RE stands for a rare-earth element), have very interesting physical properties. The structure [3] of these compounds is body-centered tetragonal (space group $I4/mmm$) and consists of $RE - C$ layers separated by Ni_2B_2 sheets. Many of these compounds are superconducting with the highest superconducting temperatures, 16.6 K and 15.6 K , observed for the Lu and Y compounds, respectively. Particularly interesting is that superconductivity is not only observed for non-magnetic rare-earth elements but also for magnetic rare-earth elements such as Tm , Er Ho [2-5] and most recently Dy [6,7]; the Tm , Ho , Er , and Dy compounds are superconducting with superconducting temperatures of 10.8 K , 8 K , 10.5 K , and 6.2 K , respectively, whereas the Gd and Tb compounds are not superconducting at least down to approximately 2 K . This family of intermetallic compounds is, therefore, particularly well suited for a detailed study of the interplay between superconductivity and magnetism, which has been previously examined [8-11] in the $RERhB_4$ and $REMo_6S_8$ magnetic superconductors.

The magnetic structure of Ho , Er , and Dy compounds have been studied [7, 12-15] by neutron diffraction techniques and that of $GdNi_2B_2C$ by resonant magnetic x-ray scattering [16]. In $DyNi_2B_2C$ and below 4.7 K in $HoNi_2B_2C$ a simple antiferromagnetic structure, consisting of ferromagnetically alligned basal-plan layers with the magnetic moments of two consecutive layers pointing in opposite directions,

has been observed. In the *Ho* compound, two incommensurate modulations of the moments were observed between 4.7 and 6 *K*, one with wave vector along $\mathbf{c}^*$, and the other with wave vector along $\mathbf{a}^*$. The latter modulation has also been observed in the *Er* and *Gd* compounds. The above experimental results suggest [7, 12-15] that there are common Fermi surface nesting features along $\mathbf{a}^*$ and/or $\mathbf{c}^*$ which cause the magnetic ordering of the rare-earth moments via the RKKY mechanism.

Electronic band structure calculations [17-19] suggest that these materials are conventional superconductors with a relatively high density of states at the Fermi level. These calculations show that there is a rather complex set of bands crossing E_f which are strongly coupled to the phonons and may be responsible for the superconducting properties of these materials. More recently, Mattheiss, Siegrist, and Cava suggested [20] that superconductivity in those systems can be attributed to a conventional electron-phonon mechanism that couples the s-p like conduction electrons to a high frequency boron A_{1g} phonon mode in which the boron atoms move along the c-axis relative to the other atoms. The energy of the Raman active boron A_{1g} mode was calculated [17] by Pickett and Singh to be 106 *meV* ($=850 \text{ cm}^{-1}$), a value in good agreement with Raman scattering measurements [21,22]. Furthermore, Pickett and Singh obtained an estimate of 20 *meV* for the average phonon frequency by using resistivity data to estimate the electron-phonon coupling parameter ($\lambda \simeq 2.6$). Since this estimate of an average phonon energy is considerably lower than the energy of the boron A_{1g} mode, they suggest that superconductivity in these compounds, may involve soft modes or strong contributions from the heavier atoms.

More recently, Rhee, Wang, and Harmon [23] performed a calculation (without matrix elements) of the generalized electronic susceptibility $\chi(q)$ of $\text{LuNi}_2\text{B}_2\text{C}$

based on the normal state electronic band structure of this compound. Peaks in the calculated $\chi(q)$ occur near wave vectors corresponding to those observed for the incommensurate magnetic structures observed in $HoNi_2B_2C$. Of particular interest is that the sharp peak in the calculated $\chi(q)$ along a^* is due to strong Fermi surface nesting and occurs at a wave vector of approximately 0.6, which is close to the values of the incommensurate magnetic modulations along a^* observed in the Ho , Er , and Gd compounds (0.585, 0.553, 0.553, respectively). If such a strong nesting feature is indeed present at the Fermi surface of $LuNi_2B_2C$, one also would expect strong Kohn anomalies in the phonon dispersion curves of this compound.

It is clear from the above discussion that experimental studies of the lattice dynamical properties of these compounds may lead to a better understanding of their properties. No detailed experimental study of the phonon dispersion curves of these compounds has been performed to date, since the presently available crystals are not of sufficient size for inelastic neutron scattering experiments. However, by mounting two crystals together, we were able to measure several low-lying phonon dispersion curves of the Lu compound. In this report we present the results of these experiments.

Experiment

Single crystals of $LuNi_2B_2C$ were grown at the Ames Laboratory by the high-temperature flux technique as described elsewhere [24]. The crystals obtained are platelets with the c -axis perpendicular to their flat surface. Since the size of the crystals (approximately $5 \times 5 \times 0.5 \text{ mm}^3$) is relatively small for inelastic neutron scattering, a composite crystal, consisting of two of those crystals, was used in the present experiments. The two crystals were mounted together and their align-

ment was adjusted until their Bragg reflections were found to coincide to within the instrumental resolution.

The experiments were performed using the HB1A, HB2, and HB3 triple axis spectrometers at the High Flux Isotope Reactor (HFIR) of the Oak Ridge National Laboratory. Pyrolytic graphite reflecting from the (002) planes was used as both monochromator and analyzer in the HB2 and HB3 spectrometers and the data were collected using fixed scattered neutron energies of 14.7 and 30.5 *meV*. The HB1A spectrometer is a constant incident energy (14.7 *meV*) instrument utilizing a double pyrolytic graphite monochromator (reflecting from the (002) planes). The collimation before the sample was either 20 or 40 minutes of arc and after the sample was 40 minutes of arc. Pyrolytic graphite filters were used in all spectrometers to attenuate higher-order contaminations.

All data were collected with the crystal oriented so that the scattering plane coincides with the a-c crystal plane. Measurements of the phonon dispersion curves were performed along the $[\xi 00]$ and $[00\xi]$ high symmetry directions. The measurements along the $[\xi 00]$ direction were extended beyond the zone boundary point G_1 (at $\frac{\pi}{a}(1 + \frac{a^2}{c^2})$) to $(2\pi/a, 0, 0)$ which is the same point as the zone boundary Z along the $[00\xi]$ direction. While most measurements were performed at room temperature, the temperature dependence of the phonon frequencies of the interesting Δ_4 branches along the $[\xi 00]$ direction was determined by measurements at 120, 60, 25, 10, and 2 *K*. A selected number of phonon frequencies of the other branches were also measured at 10 *K* to assess whether they exhibit anomalous behavior.

The measured frequencies were assigned to the various branches by comparing the measured intensities of the corresponding neutron groups with calculations of

intensities based on Born-von-Karman force constant models, the parameters of the force-constant models were determined by fitting the neutron scattering data along with the frequencies of the measured [21,22] Raman active modes. The way we have chosen to satisfy the compatibility relations at the zone boundary point Z is only one of several alternatives, since the phonon frequencies belonging to different representations are so close to each other in the vicinity of Z that the corresponding neutron groups cannot be sufficiently resolved with the resolution of the present experiment.

The lowest lying acoustic and optical branches were both obtained by measurements from the (008) reciprocal point, i.e., with a configuration appropriate for transverse branches with polarization along the c -axis. By symmetry, the acoustic branch with this polarization belongs to the Δ_4 representation. Based on the analysis of the data using a Born-von-Karman force constant model (see previous paragraph), the optical branch was also assigned to the Δ_4 representation. For small wave vectors both Δ_4 branches are purely transverse with atomic displacements along the c -axis. For the acoustic branch all atoms move in phase, whereas in the optical branch the motion of the Ho atom is out of phase with that of the other atoms. For larger values of the wave vector the Ho and C displacements remain transverse, while the Ni and B atoms develop a longitudinal component.

Results and Discussion

At room temperature, the phonon frequencies of the acoustic and optical branches, with zone-center energies at approximately 14, 15, and 24 meV , were measured. The room temperature acoustic and lowest lying optical branches are plotted in Figure

8.1. The highest measured energy at the zone center ($\simeq 24 \text{ meV}$) is in good agreement with the experimentally determined [21,22] lowest lying Raman active $Ni-B_{1g}$ mode. A complete analysis of these measurements in terms of lattice dynamical models will be published elsewhere.

The most interesting result of these experiments is the temperature dependence of the observed phonon frequencies. The frequencies of selected phonons on all the measured branches, except the $\Delta_4 [\xi 00]$, show no significant change with temperature. The phonon frequencies of the acoustic and first optical Δ_4 branches in the vicinity of the zone boundary point G_1 on the other hand, decrease with decreasing temperature. Actually, these two branches exhibit pronounced dips at low temperature close to G_1 (Figure 8.2). This is quite a unique case of soft phonon behavior: the softening occurs over the same region of wave vectors for two Δ_4 branches that cannot cross by symmetry.

The observed phonon softening shows that the electron-phonon interaction is quite strong in this compound and causes an incipient lattice instability, a behavior which is typical of conventional superconductors with relatively high superconducting transition temperatures. This observation provides experimental support for the argument, based on band theoretical calculations, [17-19] that this compound is a conventional superconductor. The strong electron-phonon interaction is presumably responsible both for the relatively high T_c of this compound as well as the observed incipient lattice instability.

As mentioned in the Introduction, Pickett and Singh argued [17] that soft phonon modes, as those observed in this experiment, may be involved in determining the superconducting properties of this compound. However, the importance of the

Figure S.1: Room temperature acoustic and lowest lying optical phonon dispersion curves of $\text{LuNi}_2\text{B}_2\text{C}$ along the $[\xi 00]$ and $[00\xi]$ symmetry directions. The lines are intended as guides to the eye. The size of the symbols is a measure of the estimated uncertainties in the measured frequencies.

Figure 8.2: The Δ_4 $[\xi 00]$ branches at 295 K and 10 K. The lines through the 10 K points are intended as guides to the eye.

observed soft phonons in determining T_c relative to that of the boron A_{1g} mode in the model [19] of Mattheiss, Siegrist, and Cava cannot be presently ascertained without comparing the experimental results with detailed lattice dynamical calculations incorporating the electron-phonon interaction.

The calculated [23] (without matrix elements) generalized electronic susceptibility of $LuNi_2B_2C$ along $[\xi 00]$ exhibits a pronounced peak close to G_1 due to a strong nesting feature of the Fermi surface of this compound. This nesting feature may be responsible for the observed incommensurate magnetic ordering wave vectors in the magnetic rare-earth nickel boride carbides. The same Fermi surface nesting feature may be responsible for the strong anomalies observed in the present experiment for the Δ_4 $[\xi 00]$ phonon modes close to G_1 . Therefore, it appears that in the magnetic compounds of this family we may have the interesting situation where, due to the nesting of the Fermi surface, phonon softening and magnetic ordering are competing to decrease the energy of the system. Therefore, the electron-phonon and RKKY interactions in the magnetic superconducting systems are extremely interesting and further experimental and theoretical investigations will be required to establish a detailed understanding of the low temperature properties of these materials. An experimental study of the phonon dispersion curves of $HoNi_2B_2C$ is presently in progress in this laboratory.

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CHAPTER 9. CONCLUSIONS

In the present work neutron scattering techniques were used to investigate the magnetic structures and lattice dynamical properties of various members of the recently discovered rare-earth nickel boride carbide family $RENi_2B_2C$.

The magnetic structure of $DyNi_2B_2C$, $ErNi_2B_2C$, $TbNi_2B_2C$ and $HoNi_2B_2C$ was studied as a function of temperature (in the 2 K to 300 K range), using single crystal neutron diffraction. Some very interesting incommensurate magnetic structures were discovered. In particular, sinusoidally modulated magnetic structures with similar wavevectors along the a^* direction exist in all the above compounds (with the exception of $DyNi_2B_2C$), as well in $GdNi_2B_2C$ [51]. The peak of the calculated generalized susceptibility $\chi(q)$ at about $0.6 a^*$ [30], which is due to Fermi surface nesting features gives a promising insight into the physics of these materials, but more sophisticated calculations will be required to account for the differences between the various compounds. We mention again that in the Dy , Er and Ho compounds we have magnetic order coexisting with superconductivity.

From an experimental point of view, the study of the magnetic structure of other compounds and alloys could provide useful information. The author has performed a preliminary experiment on the magnetic structure of the $Ho_{0.5}Tm_{0.5}Ni_2B_2C$ alloy, but this work has not been completed yet. The use of polarized neutron scattering

is also crucial. In fact we have performed a first experiment on $TbNi_2B_2C$ with polarized neutrons, in order to confirm that the small ferromagnetic component that seems to develop in this compound below 8 K is indeed real, but the issue is not yet settled. More work will be done in order to study the magnetic form factor, and verify possibly the existence of an induced moment on the Ni sites which has been found in ^{57}Fe Mossbauer spectra [52].

The low energy phonon dispersion curves of the $LuNi_2B_2C$ compound have also been presented in this dissertation. The pronounced soft phonon behavior discovered in the acoustic and first optical Δ_4 branches, at wavevectors close to those of the incommensurate magnetically ordered structures indicates that the electron-phonon interactions are very strong in these materials, as expected for strongly coupled conventional superconductors. Both the phonon anomalies and the incommensurate magnetic structures seem to be influenced by the above mentioned Fermi surface nesting features. We have also measured higher energy phonon branches for the Lu compound and their analysis in terms of lattice dynamical models is now in progress. The low energy phonon branches for $HoNi_2B_2C$ have also been determined. Similar soft phonon behavior is present in this compound, but the existence of crystal field levels in the region of interest complicates the analysis of the results. The phonon branches of other compounds would be desirable but the small size of the available crystals will probably delay this work.

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APPENDIX A. STRUCTURE FACTORS FOR OSCILLATORY MAGNETIC STRUCTURES

We describe here the way one proceeds to calculate structure factors for oscillatory magnetic structures. We derive first a general result and then we apply it to the case of a sinusoidally modulated magnetic structure. Our starting point is Equation (2.81),

$$\mathbf{F}_m(\mathbf{K}) = \sum_d \mathbf{q}_d p_d \exp(i\mathbf{K} \cdot \mathbf{d}) \exp(-W_d) \quad (\text{A.1})$$

where the sum is over the atoms of the unit cell, p_d is the magnetic scattering length of atom d and $\mathbf{q}_d$ the magnetic interaction vector (Equation (2.77)).

Consider a general form of modulated magnetic moment distribution. Let $\bar{\mu}_d^l$ be the magnetic moment at the d^{th} atom site in the unit cell at $\mathbf{l} = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3$. In this case the magnetic moment can be written as a generalized Fourier series,

$$\bar{\mu}_d^l = \sum_{t=-\infty}^{\infty} \mathbf{A}_t^d e^{i(\phi_d + \delta_t)} e^{i\bar{\tau}_t \cdot (\mathbf{l} + \mathbf{d})} \quad (\text{A.2})$$

where ϕ_d is a phase for the sites d in the unit cell relative to the origin of the unit cell at $\mathbf{l}$, $\bar{\tau}_t$ is the t^{th} modulation vector and δ_t is the phase factor for the t^{th} Fourier component relative to the origin. Substituting the expression for the magnetic interaction vector and the above magnetic moment distribution into Equation (A.1)

we get,

$$\mathbf{F}_m(\mathbf{K}) = \frac{pof}{N_c} \left[\sum_d \sum_t \left[\mathbf{A}_t^d - \hat{\epsilon}(\hat{\epsilon} \cdot \mathbf{A}_t^d) \right] e^{i[(\mathbf{K} + \bar{\tau}_t) \cdot \mathbf{d} + \phi_d + \delta_t]} \right] \times \sum_l e^{i(\mathbf{K} + \bar{\tau}_t) \cdot \mathbf{l}} \quad (\text{A.3})$$

The last factor in the above equation is zero unless $\mathbf{K} + \bar{\tau}_t = \mathbf{G}$, where $\mathbf{G}$ a reciprocal lattice vector since,

$$\sum_l e^{i(\mathbf{K} + \bar{\tau}_t) \cdot \mathbf{l}} = \pm N_c \delta(\mathbf{G} - \mathbf{K} - \bar{\tau}_t) \quad (\text{A.4})$$

and since $(-\mathbf{G})$ is also a reciprocal lattice vector we have magnetic scattering when $\mathbf{K} = \mathbf{G} \pm \bar{\tau}_t$.

If the modulation is incommensurate with the lattice, then there is only one $\bar{\tau}_t$ in the sum over t for which $\mathbf{K} = \mathbf{G} - \bar{\tau}_t$, and we get,

$$\mathbf{F}_t(\mathbf{G} - \bar{\tau}_t) = \pm pof \sum_d \left[\mathbf{A}_t^d - \hat{\epsilon}(\hat{\epsilon} \cdot \mathbf{A}_t^d) \right] e^{i(\mathbf{G} \cdot \mathbf{d} + \phi_d)} e^{i\delta_t} \quad (\text{A.5})$$

and as we expected the intensity does not depend on δ_t . For a sinusoidally modulated magnetic moment distribution,

$$\bar{\mu}_d^l = \hat{\mu} \mu_o \sum_n A_n \cos n\bar{\tau} \cdot (1 + \mathbf{d}), \quad n = 0, 1, 2, \dots \quad (\text{A.6})$$

The Fourier components in this simple case are readily found,

$$\mathbf{A}_t^d = \mathbf{A}_{-t}^d = \hat{\mu} \mu_o \frac{A_t}{2} \quad (\text{A.7})$$

and the modulation vectors are multiples of the fundamental vector $\bar{\tau}$. In this case magnetic satellites appear at scattering vectors $\mathbf{K} = \mathbf{G} \pm t\bar{\tau}$.

Equation (A.5) becomes for this case,

$$\mathbf{F}_t = pof \mu_o \frac{A_t}{2} (\hat{\mu} - \hat{\epsilon}(\hat{\epsilon} \cdot \hat{\mu})) \sum_d e^{i(\mathbf{G} \cdot \mathbf{d})} \quad (\text{A.8})$$

and recalling Equation (2.78) for the magnitude of the magnetic interaction vector, we have for the square of the modulus of the structure factor (which is proportional to the intensity),

$$|\mathbf{F}|_{\mathbf{G} \pm n\bar{\tau}}^2 = \frac{1}{4} p_o^2 f^2 \mu_n^2 \sin^2 \alpha \left| \sum_d e^{i\mathbf{G} \cdot \mathbf{d}} \right|^2 \quad (\text{A.9})$$

where α is the angle between the scattering vector and the magnetic moments, and $\mu_n = \mu_o A_n$.

APPENDIX B. THE EXTINCTION PROBLEM

Our single crystal diffraction results for the determination of magnetic structures were affected by 'extinction', so we give here a short description of the problem. We must stress that extinction does not affect much our knowledge of the magnetic structure, but makes difficult an accurate calculation of the magnitudes of the magnetic moments.

The integrated intensity for a Bragg reflection (rotating crystal method) can be written,

$$R = Q\delta V \quad (\text{B.1})$$

for a crystal of volume δV and assuming unit flux. The quantity Q is defined as [32],

$$Q = \frac{\lambda^3 N_c^2}{\sin 2\theta} |F|^2 \quad (\text{B.2})$$

where λ is the neutron wavelength, N_c the number of unit cells, θ the Bragg angle, and F the structure factor. With this definition Equation (B.2) is equivalent with (2.82).

However, the above formula does not apply when the crystal is large (typically considerably thicker than 1000 Å). This is because the intensity of the incident beam diminishes as it penetrates through the crystal. This phenomenon is called 'extinction', and is extremely severe in 'perfect' crystals where effectively only a thin layer

of the order of $10^{-4}cm$ contributes to the Bragg reflection. In such cases one speaks about 'primary extinction'.

In general, crystals are far from being perfect. They are divided into small regions called 'mosaic blocks', which are themselves perfect but which are slightly misoriented with respect to each other. If the size of the mosaic blocks is small enough that 'primary extinction' is negligible then 'secondary extinction' can occur since there will be in general mosaic blocks that have the same orientation. The neutrons scattered from individual mosaic blocks are not coherent, so one has to sum intensities rather than amplitudes in calculating the integrated intensity from the crystal. In addition one has to consider the effect of absorption, which is usually not very important for neutrons.

The analysis of the effects of extinction in neutron diffraction was developed by Bacon and Lawde [45] who considered a parallel crystal slab of a material with very low absorption. They assumed that the mosaic structure of a crystal can be approximated by a Gaussian distribution function,

$$W(\Delta) = \frac{1}{\eta\sqrt{2\pi}} \exp(-\Delta^2/2\eta^2) \quad (\text{B.3})$$

so that $W(\Delta)d\Delta$ is the fraction of mosaic blocks which have their normals between the angles Δ and $\Delta + d\Delta$ from the crystal surface and η is the standard deviation of the mosaic blocks. With the above assumptions Bacon and Lawde calculated the integrated reflection from mosaic crystals. The general result is that extinction is more pronounced for strong reflections, for crystals with small mosaic spreads and for thick crystals. They also proposed a criterion for a '*thin crystal*', defined so that

the integrated reflection will be within 5 per cent of proportionality to Q . This is,

$$\frac{1}{\eta} \frac{Q t_o}{\sin \theta} < \frac{1}{4} \quad (\text{B.4})$$

where t_o is the thickness of the crystal slab. For more details we refer to Bacon [32]. It should be noted that in our experiments the 'thin crystal' criterion was satisfied only for the weakest reflections.