000-1700-11

NUCLEAR MAGNETIC RESONANCE STUDY
OF THE CRYSTALLINE PHASES OF NbN_x AND $NbBe_x$
AND SUPPLEMENT ON ACOUSTIC NUCLEAR MAGNETIC RESONANCE

by

Robert A. Bennett

MASTER

A DISSERTATION

Submitted to the Office for Graduate Studies,
Graduate Division of Wayne State University, Detroit, Michigan,
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

1969

MAJOR: PHYSICS (SOLID STATE)

LEGAL NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Advisor _____ Date _____

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY 941/Calvin Lamb
DATE 11/9/70

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

P7313

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ACKNOWLEDGMENTS

I wish to express my sincere thanks to my advisor, Professor H. O. Hooper, for his guidance and support during the course of this work.

The work was carried out under the partial support of the Atomic Energy Commission and the United States Air Force.

I would like to express my deep appreciation to my mother for the guidance, help and encouragement I have always received.

To my wife, Marilyn, whose patience, understanding and typing ability helped make this thesis possible, I am deeply thankful.

TABLE OF CONTENTS

Acknowledgements	Page ii
List of Tables	v
List of Figures	vi
Chapter	
I. Introduction	1
II. Basic Theory of NMR	4
Nuclear Magnetic Dipole Interaction	4
Nuclear Dipole-Dipole Interaction	6
Electric Quadrupole Interaction	7
Knight Shift	11
III. NMR Spectrometer	15
IV. Experimental Observations on NbN _x	21
Introduction	21
Identification of the Phases by NMR	24
Other NMR Measurements	33
Field Gradients in Related Interstitial Compounds	34
Conclusion	36
V. Experimental Observations on NbBe _x	39
Introduction	39
Beryllium Resonances	39
NbBe ₂	42
NbBe ₃	45

	Page
Nb ₂ Be ₁₇	51
NbBe ₁₂	64
Conclusion	67
VI. Supplement - Acoustic Nuclear Magnetic Resonance	69
Introduction	69
Theory	69
Experimental Equipment	73
Tuning the Matching Network	74
Locking-in the Pound Box	75
Sample Preparation and Acoustic Bonding	77
Experimental Results	79
Conclusion	83
List of References	87
Autobiographical Statement	90

LIST OF TABLES

Table		Page
1	Composition of NbN_x Samples	25
2	Crystal Structure of NbBe_x Samples	40
3	Quadrupole Coupling Constants and Knight Shifts of NbBe_3	49
4	Quadrupole Coupling Constants of NbBe_3	49
5	NMR Line Width of ^{93}Nb in $\text{Nb}_2\text{Be}_{17}$ at Various Frequencies	55

LIST OF FIGURES

Figure		Page
1	Powder patterns for symmetric field gradient. (a) First order pattern for $I = 3/2$, $\nu_0 = e^2 qQ/2h$. Dashed curve is without broadening. With dipolar broadening superimposed, the solid curve results. (b) Second order pattern, central component, $A = [I(I+1) - 3/4] \nu_0^2 / 16\nu$. Dashed curve is without broadening. Solid curve includes dipolar broadening.	12
2	Block diagram of the NMR wide-line spectrometer.	16
3	Diagram of the NMR probe.	17
4	(a) Modulation of the external magnetic field. (b) Derivative of the power absorption with respect to the magnetic field.	19
5a & b	First derivative of the NMR of ^{93}Nb in poly-phase samples of NbN_x , at 6MHz. Points A and A' denote the derivative peaks of the second order quadrupole split ($1/2 \rightarrow -1/2$) transition of the ϵ phase. B and B' are the ($\pm 3/2 \leftrightarrow \pm 1/2$) first order satellites of the ϵ phase. C is the signal due to the δ phase and D is the signal due to the γ phase. The bromine (^{79}Br) resonance from KBr was used as a field marker.	26 & 27
6	Separation of the peaks for the ($1/2 \rightarrow -1/2$) transition (ϵ phase) versus $1/\nu$. The points at $1/6\text{MHz}^{-1}$, $1/8\text{MHz}^{-1}$, $1/12\text{MHz}^{-1}$ represent an average of all six samples.	29
7	First derivative of the ^{93}Nb NMR obtained from sample No. 1 at two values of magnetic field.	31
8	First derivative of the ^{93}Nb resonance in NbBe_2 at 14MHz and 6MHz.	43
9	Separation of the peaks of the derivative curve of the ^{93}Nb resonance in NbBe_2 versus ν .	44

Figure		Page
10	First derivative of the ^{93}Nb resonance in NbBe_3 at 14MHz. Lines marked A, B and C are the central ($1/2 \rightarrow -1/2$) transitions. Lines marked B' and C' are first order split ($\pm 3/2 \leftrightarrow \pm 1/2$) transitions.	46
11	Separation of the peaks of the derivative curve for the ($1/2 \rightarrow -1/2$) transition of lines A, B and C from ^{93}Nb in NbBe_3 versus $1/\nu$.	48
12	First derivative of the ^{93}Nb resonance in $\text{Nb}_2\text{Be}_{17}$ at 14MHz. Line A is the ($1/2 \rightarrow -1/2$) transition. Lines B and B', C and C', D and D' are the ($\pm 3/2 \leftrightarrow \pm 1/2$), ($\pm 5/2 \leftrightarrow \pm 3/2$), ($\pm 7/2 \leftrightarrow \pm 5/2$) transitions, respectively.	53
13	Separation of the peaks of the derivative curve for the ($1/2 \rightarrow -1/2$) transition of ^{93}Nb in $\text{Nb}_2\text{Be}_{17}$ versus $1/\nu$. Solid curve is a plot of Eq. 43.	54
14	K_H versus $1/\nu^2$.	60
15	First derivative of the central ($1/2 \rightarrow -1/2$) transition of the ^{93}Nb resonance in $\text{Nb}_2\text{Be}_{17}$ at 15MHz.	62
16	First derivative of the ^{93}Nb resonance in NbBe_{12} at 14MHz.	65
17	Separation of the peaks of the derivative curve for the ($1/2 \rightarrow -1/2$) transition of ^{93}Nb in NbBe_{12} versus $1/\nu$.	66
18	Total primary impedance; reflected secondary impedance included. (A) Drawing (B) Photographed from oscilloscope.	76
19	Aluminum lapping ring for holding sample during lapping operation, to insure parallelness.	78
20	ANMR sample holder, with sample.	80

Figure		Page
21	ANMR recorded signal of ^{127}I in KI. The derivative of the power absorption curve is shown. Frequency is 10.1MHz, at a magnetic field of 5.9 kilogauss for $\Delta m = \pm 2$ transition.	82
22	Acoustically detected de Haas-van Alphen oscillations, in a single crystal of aluminum, at an oscillator frequency of 9.5MHz.	86

CHAPTER I

Introduction

Nuclear magnetic resonance (NMR) is that process in which nuclei possessing a magnetic dipole moment may change their energy by quantized amounts when placed in a magnetic field. This change in energy causes a reorientation of the dipole moment with respect to the magnetic field. The term resonance implies that in order to drive the transitions, energy pulses are needed of a proper frequency, that is, the natural frequency of the magnetic system. Electromagnetic radiation is used as the driving force which causes the transitions between energy levels in the magnetic system. The frequency of this radiation must obey the Bohr quantization rule

$$\nu = \Delta E/h \quad , \quad (1)$$

where ΔE is the spacing between energy levels.

The first work in this field was carried out by the Purcell, Torrey and Pound¹ group at Harvard and the Bloch, Hansen and Packard² group at Stanford in 1946. The field has grown to such an extent that NMR has become a basic tool in the investigation of liquids and solids. In solids, the resonant nuclei can be thought of as probes. Energy transitions of these nuclei yield information concerning the electrical and magnetic environment of the solid. The magnetic field at the site of the nucleus which determines the magnetic energy levels is composed of an externally

applied magnetic field and internal magnetic fields due to neighboring magnetic nuclei and paramagnetic electrons or ions present in the material.

In addition to a nuclear magnetic moment, nuclei with spin greater than $1/2$ possess an electric quadrupole moment. This quadrupole moment will interact with the internal electric field gradient at the site of the nucleus. This interaction will alter the magnetic energy levels and thus provide information on internal electrical charge distributions in the solid.

The systems under investigation, NbN_x and NbBe_x , both contain niobium nuclei which have a large nuclear quadrupole moment. These nuclei will serve as the probes in the investigation of these refractory materials. X-ray work has been carried out with these samples and their crystal structures have been determined³⁻⁶.

The crystal structure and atomic bonding will determine the magnitude and direction of internal electric field gradients. These field gradients interacting with the quadrupole moment of the ^{93}Nb nuclei will cause a modification of the NMR. It is then possible to identify individual crystalline phases of a system by analyzing the NMR spectrum. Imperfections in the crystal structure such as strains or vacancies, if in abundance, can also be detected. This detection of imperfections aids in the investigation of the NbN_x system which has a wide range of composition within the same phase, thought to be caused by defects

in the nitrogen sublattice. Also, the stoichiometry of the NbN_x system is non-integral and continuous up to $\text{NbN}_{1.0}$.

The crystalline phases of the intermetallic system NbBe_x can also be correlated with the NMR of the niobium nuclei. In these metallic samples there are paramagnetic electrons whose interaction with the nuclear moments are detectable by NMR yielding information concerning the electrical properties of the compounds.

If the nuclei are capable of interacting with the lattice via an electric quadrupole coupling, then it is possible to modulate this interaction energy by the introduction of acoustic power into the lattice. When the frequency of the acoustic wave satisfies a resonance condition, it is then possible to drive NMR transitions. The use of acoustic power, rather than electromagnetic power in driving NMR transitions, is termed "acoustic nuclear magnetic resonance (ANMR)". This technique has application in the investigation of bulk, single crystal, metallic samples in which electromagnetic radiation can penetrate only to the skin depth, whereas acoustic waves can penetrate through the sample. This technique is discussed in the supplement to this thesis.

CHAPTER II

Basic Theory of NMR

The technique of NMR is widely used, and literature concerning it has grown to enormous proportions. There are several good review articles⁷⁻⁹ and books¹⁰⁻¹² that are frequently useful. A brief description of some of the fundamental interactions employed in the analysis of the experimental data is provided here.

Nuclear Magnetic Dipole Interaction

All nuclei whose spin (I) is nonzero possess a magnetic dipole moment. It can be shown by quantum mechanics that the magnetic dipole moment ($\vec{\mu}$) can be written

$$\vec{\mu} = \gamma(\hbar\vec{I}) \quad (2)$$

where $\vec{I}$ is the total nuclear angular momentum in units of $\hbar = h/2\pi$ (Planck's constant divided by 2π). The proportionality constant γ is termed the "gyromagnetic ratio".

The application of a magnetic field H produces an interaction energy of

$$E = -\vec{\mu} \cdot \vec{H} \quad (3)$$

Therefore, the Hamiltonian is of the form

$$\mathcal{H} = -\vec{\mu} \cdot \vec{H} \quad (4)$$

Taking the field H_0 to be along the Z direction then

$$\mathcal{H} = -\gamma\hbar H_0 I_Z \quad (5)$$

Quantizing $\vec{I}$ along the Z direction, the eigenvalues of I_z are the magnetic quantum number m where $m = I, I-1 \dots -I$. The allowed energies are

$$E = -\gamma \hbar H_0 m \quad . \quad (6)$$

Thus one obtains a set of $2I + 1$ energy levels which are equally spaced. The difference in energy in terms of frequency, using the Bohr quantization Eq. 1 and Eq. 5, is given by

$$\nu_L = \gamma H_0 / 2\pi \quad . \quad (7)$$

Transitions from one energy level to another are driven by the application of electromagnetic energy of frequency ν_L (Larmor frequency) as given by Eq. 7. The oscillating magnetic component of the applied electromagnetic radiation must be positioned perpendicular to the applied field H_0 . This requires the axis of the rf coil to be perpendicular to H_0 . The requirement then allows the decomposition of the oscillating magnetic field into two oppositely rotating components, both of which are perpendicular to H_0 . Since the magnetic dipole will precess about the external magnetic field at a Larmor frequency ν_L , it will be rotating in phase with one of the components of the oscillating magnetic field and will constantly be going in and out of phase with the other component. The component of the oscillating magnetic field, which is in phase with the nuclear dipole moment, will exert a constant torque. This torque will cause the nuclear dipole to now precess around the oscillating

magnetic field, thus a reorientation of the nuclear dipole is achieved.

Whenever a magnetic dipole changes its orientation in a magnetic field, this consequently changes its energy level. The energy needed to change levels is extracted from the applied rf field. The transition probability is, however, the same for transitions to a higher energy level as for a transition to a lower energy level. There is a net absorption of energy due to the fact that nuclear dipoles obey a Boltzmann distribution

$$\frac{N_2}{N_1} = e^{-\frac{\Delta E}{kT}}, \quad (8)$$

where N_1 and N_2 are the number of spins in the lower and upper levels respectively, and ΔE is the energy separation between levels. This causes more spins to be in a lower energy level. This loss of energy from the rf field can be detected by appropriately monitoring the rf generator. Thus the resonance can be detected.

Nuclear Dipole-Dipole Interaction

In a solid, the nuclear dipoles are not only affected by the external magnetic field, but also the internal magnetic fields. One source of an internal magnetic field is the field produced by neighboring nuclei that possess magnetic dipole moments. Nuclei at a distance r apart and having a magnetic moment μ will produce an internal magnetic field H_{int} of the order

$$H_{\text{int}} = \mu/r^3 \quad (9)$$

which will be of the order of a few gauss. This field may either aid or oppose the external field H_0 , resulting in a variation of the net magnetic field at the nuclei, thereby causing a spread of the resonance condition.

Classically the dipole-dipole interaction between two magnetic moments is

$$E = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} - \frac{3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^5}, \quad (10)$$

where r is the radius vector from $\vec{\mu}_1$ to $\vec{\mu}_2$. The quantum mechanical dipole-dipole Hamiltonian is obtained by using Eq. 2 and Eq. 10

$$\mathcal{H}_d = \gamma_1 \gamma_2 \hbar^2 \left[\frac{\vec{I}_1 \cdot \vec{I}_2}{r^3} - \frac{3(\vec{I}_1 \cdot \vec{r})(\vec{I}_2 \cdot \vec{r})}{r^5} \right]. \quad (11)$$

Using typical external magnetic fields of about 10^4 gauss will cause $\mathcal{H}_d$ to be about 10^4 smaller than the energies given by Eq. 6. Thus perturbation theory may be used to calculate $\mathcal{H}_d$. Generally, this problem is not solvable exactly, but the so called method of moments technique due to Van Vleck¹³ enables many of the properties of the resonance line to be computed.

Electric Quadrupole Interaction

Nuclei which possess electric quadrupole moments will

interact with the internal electric field gradient that may be present at the site of the nucleus. Consider the interaction energy E of the charge distribution of a nucleus $\rho(\vec{r})$ and the potential of the internal electric field $V(\vec{r})$.

$$E = \int \rho(\vec{r})V(\vec{r})d\tau \quad . \quad (12)$$

Expanding $V(\vec{r})$ in a Taylor series about the origin yields

$$E = V_0 \int \rho d\tau + \left. \frac{\partial V}{\partial x_i} \right|_{r=0} \int x_i \rho d\tau + \frac{1}{2} \left. \frac{\partial^2 V}{\partial x_i \partial x_j} \right|_{r=0} \int x_i x_j \rho d\tau + \dots , \quad (13)$$

where the summation is taken on repeated indices and i and j are summed over 1, 2 and 3.

Analyzing the terms in Eq. 13, the first term is a constant and represents the interaction of the internal electric field with the charge of the nucleus taken as a point charge. This term need not be considered because it will not change the spacing between energy levels. The second term represents the nuclear electric dipole interaction, but this goes to zero because the symmetry of the nucleus causes the integral to be zero. The third term is the nuclear electric quadrupole interaction with the internal electric field gradient. Defining the tensors,

$$V_{ij} = \left. \frac{\partial^2 V}{\partial x_i \partial x_j} \right|_{r=0} , \quad (14)$$

$$Q_{ij} = \int (3x_i x_j - \delta_{ij} r^2) \rho d\tau ,$$

and using the fact that V must satisfy Laplace's equation,

$$\nabla^2 V = 0 \quad , \quad (15)$$

the quadrupole interaction energy can be written

$$E_Q = \frac{1}{6} V_{ij} Q_{ij} \quad . \quad (16)$$

The quantum mechanical quadrupole Hamiltonian may be written by invoking the Wigner-Eckart¹² theorem resulting in

$$H_Q = \frac{eQ}{6I(2I-1)} V_{ij} \left[\frac{3}{2} (I_i I_j + I_j I_i) - \delta_{ij} I^2 \right] \quad , \quad (17)$$

where Q , the quadrupole moment of the nucleus, can be represented by

$$Q = \langle I, I | Q_{33} | I, I \rangle \quad ; \quad (18)$$

that is, the expectation value of the 3,3 component of the Q_{ij} tensor evaluated at $m = I$.

The field gradient tensor V_{ij} may be written in terms of its principle axes such that

$$V_{ij} = 0 \quad \text{if } i \neq j \quad . \quad (19)$$

Requiring that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$, the asymmetry parameter (η) can be defined

$$\eta = \left| \frac{V_{xx} - V_{yy}}{V_{zz}} \right| \quad , \quad (20)$$

and the field gradient (q) by

$$eq = V_{zz} \quad . \quad (21)$$

At this point, it is noted that if cubic symmetry exists then

$$V_{xx} = V_{yy} = V_{zz} \quad , \quad (22)$$

but Laplace's equation implies

$$V_{xx} + V_{yy} + V_{zz} = 0 \quad (23)$$

Thus all components of the electric field gradient are zero.

If the quadrupole interaction energy is small compared to the nuclear magnetic energy levels, perturbation theory may be employed. Pound¹⁴ and Bersohn¹⁵ have calculated the energy correction using perturbation theory, to third order. For the case of large quadrupole interactions, additional calculations have been made by Volkoff and his co-workers¹⁶. The effects of the quadrupole interaction upon the magnetic Zeeman levels and the modifications of these results due to random distributions of orientations as found in a powdered specimen are summarized by Cohen and Reif⁷.

The first order perturbation in a powdered sample for an axially symmetric field gradient ($\eta = 0$) is given by

$$v_m^{(1)} = \frac{\gamma}{2\pi} H_0 m - \frac{1}{2} \left(m - \frac{1}{2}\right) v_Q \quad (24)$$

where

$$v_Q = 3e^2 qQ / 2I(2I - 1)h$$

Second order perturbation causes the central $(\frac{1}{2} \leftrightarrow -\frac{1}{2})$ transition to split such that the width, the separation between the peaks of the derivative curve, Δv is

$$\Delta v^{(2)} = (25/9)A \quad (25)$$

where

$$A = \left[I(I+1) - \frac{3}{4} \right] v_Q^2 / 16v_L$$

Note the central transition is not affected by odd orders of perturbation, thus the errors in Eq. 25 are in the fourth order. The separation between pairs of satellites obtained from Eq. 24 is

$$\Delta\nu^{(1)} = (m - \frac{1}{2})\nu_Q \quad . \quad (26)$$

Since only even orders of perturbation shift the center of gravity, the errors in Eq. 26 are in third order. The intensity of the transition $m \rightarrow m-1$ is very nearly proportional to $I(I+1)-m(m-1)$.¹⁷ In Fig. 1 the resulting theoretical absorption curves are presented with the effects of dipolar broadening being added.

An effect which modifies the electric field gradient at the site of the nucleus, is the Sternheimer¹⁸ antishielding factor γ_∞ . This parameter takes into account the distortion of the ion core electrons surrounding the nucleus due to internal electric fields of the crystal. This distortion produces an additional field gradient at the nucleus, thus the field gradient experienced by the nucleus is

$$q = q^0(1 - \gamma_\infty) \quad (27)$$

where q^0 is the field gradient in the absence of the distortion. This factor has the effect usually of amplifying q^0 by one or two orders of magnitude. Nuclei with large Z usually have a large antishielding factor due to more electrons in the ion.

Knight Shift

In metals, the conduction electrons which have magnetic moments may couple with the nuclear magnetic moments. This

Fig. 1 Powder patterns for symmetric field gradient. (a) First order pattern for $I = 3/2$, $\nu_0 = e^2 qQ/2h$. Dashed curve is without broadening. With dipolar broadening superimposed, the solid curve results. (b) Second order pattern, central component, $A = [I(I+1) - 3/4] \nu_0 / (16\nu_L)$. Dashed curve is without broadening. Solid curve includes dipolar broadening.

interaction is observed when performing NMR in metals. It was found that in a metal that the resonance frequency was higher for a given applied external magnetic field than for the same nucleus when it is in a salt. This shift of frequency (Knight shift) was explained by Knight¹⁹. He observed that the resonance of ⁶³Cu nuclei in metals occurs at a higher frequency than in the diamagnetic salt (CuCl) when observed at the same external magnetic field. This shift to frequencies approximately .1% to 1% higher than for diamagnetic samples is much greater than can be explained in terms of the bulk susceptibility of the metal. Knight proposed that the shift is caused by the orientation of the spin moments of the conduction electrons on the Fermi surface by the applied magnetic field. Since the conduction electrons often have a high probability density near the nucleus (s-wave), the shift may be understood in terms of a "lumping up" or concentrating of the local susceptibility in the vicinity of the nucleus.

The coupling of the spin of the electron to the spin of the nucleus in tensor form is given by²⁰

$$-\gamma \hbar \vec{I} \cdot \vec{T} \cdot \vec{S} \quad (28)$$

where $\vec{T}$ is the coupling tensor and $\vec{S}$ is the total electronic spin of the metallic sample. Since the total electronic spin is related to the applied field H_0 by the Pauli susceptibility χ_p we can write

$$-\gamma \hbar \vec{I} \cdot \vec{T} \cdot \vec{S} = -\gamma \hbar \vec{I} \cdot \vec{K} \cdot \vec{H}_0 \quad (29)$$

The tensor $\vec{K}$ can be decomposed in its diagonal form to an isotropic tensor plus an anisotropic tensor,

$$\vec{K} = \begin{pmatrix} K & & \\ & K & \\ & & K \end{pmatrix} + \begin{pmatrix} K_x & & \\ & K_y & \\ & & K_z \end{pmatrix} \quad (30)$$

where $K_x + K_y + K_z = 0$. The isotropic part of Eq. 29 can now be written as

$$-\gamma \hbar \vec{H}_0 \cdot \vec{I} K \quad (31)$$

yielding the new resonance frequency between Zeeman levels to be

$$\nu = \nu_L (1 + K) \quad (32)$$

K has the value²¹

$$K = \frac{\Delta \nu}{\nu_L} = \frac{\Delta H}{H_0} = \frac{8\pi}{3} X_p \langle |\psi_K(0)|^2 \rangle_F \quad (33)$$

where $|\psi_K(0)|^2$ is the probability density of the k^{th} electron evaluated at the site of the nucleus and $\langle \rangle_F$ is the average taken over the Fermi surface. Since only the type of electronic wave function that is spherically symmetric about the nucleus is the s-state, then only s-state wave functions contribute to the isotropic Knight shift. If, however, p-state or d-state electronic wave functions are present, which are directional, then the Knight shift will be anisotropic.

CHAPTER III

NMR Spectrometer

The NMR spectrometer used in this work was manufactured by Varian Associates, Palo Alto, California. The Varian model V-4200B wide line NMR spectrometer was used.²² A Varian model V-3400 9-inch electromagnet system with "Feldial" control for regulation was employed to supply the external magnetic field. The output of the spectrometer was recorded on a Varian model G-14 chart recorder. A block diagram of the equipment is presented in Fig. 2.

The heart of the spectrometer is the NMR probe²², Fig. 3. It consists of a pair of crossed coils, one for inducing the resonance and the other for detection of the resonance. Located inside the probe is a pair of modulation coils which when driven at audio frequency, modulates the external magnetic field thereby causing a modulation in the resonance signal. A.C. amplifiers can now be used to amplify the signal rather than D.C. amplifiers with their undesirable characteristics.

The crossed coils can be decoupled by use of two paddles which control the magnetic flux lines. The reactance of the two paddles are 90° out of phase with each other, one being inductive and the other resistive. Once the paddles are adjusted such that there is no leakage of flux into the receiver

Fig. 2 Block diagram of the NMR wide-line spectrometer.

Fig. 3 Diagram of the NMR probe.

coil a small amount of leakage is introduced which is either in phase or 90° out of phase, depending on whether the absorption or the dispersion mode, respectively, is to be observed.

It is the leakage voltage which has superimposed on it the resonance signal that is rf amplified, then detected, after which the audio component is audio amplified. The audio signal is then phase detected to convert it to a D.C. voltage in order to drive a recorder. The D.C. signal prior to entering the recorder goes through an R-C filter network, which will average out some of the random noise that has passed through the phase detector.

When recording a signal on this spectrometer, it is actually the first derivative of the absorption curve that is recorded. This is due to the type of magnetic field modulation employed, see Fig. 4. The smaller the amplitude of the modulation the more closely the recorded curve represents the derivative curve. If too little modulation is used, however, the signal is so weak that it is unobservable. A rule of thumb is that the amplitude of the modulation should be kept approximately one-tenth of the half-power width of the absorption curve, to keep distortion to a minimum. Another factor that must be considered is the amount of rf power that is supplied to the sample. If too much power is used, then the energy levels will become equally populated since the spins

Fig. 4 (A) Modulation of the external magnetic field.
 (B) Derivative of the power absorption with respect to the magnetic field.

cannot relax back to their lower energy level fast enough through the spin-lattice interaction. This condition is known as "saturation". When saturation occurs, the intensity of the absorption decreases to the extent that it is sometimes possible to miss the resonance entirely. Next, in order to maximize the output signal and to avoid distortion, the phase of the chopper in the phase sensitive detector must be adjusted.

Finally the R-C filter network must be set so that as much noise as possible is averaged out without distorting the resonance line. The type of R-C filter to be employed depends upon the sweep time of the magnetic field H_0 . When examining the NMR resonances, the R-C time constant, rf level and modulation amplitude were all varied and adjusted to obtain maximum resonance signal without distortion.

CHAPTER IV

Experimental Observations on NbN_x

Introduction

Nuclear magnetic resonance has been employed to study the structure of several samples of the system NbN_x where the mole fraction of nitrogen varied from 0.884 to 0.95.

The samples of NbN_x were in the form of powders obtained from J. W. Savage³. The chemical and x-ray analysis of these samples has been recently published³. In the preparation of the various phases of NbN_x , niobium or niobium hydride powder was heated in flowing nitrogen to the temperature (above 1200°) at which the solid phases of NbN_x are formed. The samples were rapidly cooled in a water-cooled chamber³. In such a manner crystalline phases of NbN_x which are formed and which are stable at high temperatures are quenched to room temperature where the crystalline phases are essentially stable. It should be noted that the superconducting properties of high temperature phases such as δ NbN have been examined^{3,23}. The powder samples used in these NMR investigations were examined at room temperature unless otherwise stated.

The work reported here illustrates the usefulness of the nuclear magnetic resonance technique as a tool for the investigation of bonding configuration and crystalline structure in

intermetallic compounds. The Nb nucleus is highly appropriate as a probe in such a study for it has a large nuclear electric quadrupole moment which will interact with an electric field gradient at the Nb sites. The quadrupole interaction manifests itself as a perturbation on the nuclear magnetic energy levels resulting in characteristic splitting and broadenings to the NMR spectrum of Nb nuclei. As previously shown, the presence of an electric field gradient at the site of a nucleus of spin I of half integer will produce pairs of satellite lines about ν_L , the Larmor frequency, for the nucleus in an external magnetic field H_0 . The separation between the pairs of $(\pm m \leftrightarrow \pm m-1)$ satellite transitions for a powder sample (to third order perturbation) are given by Eq. 26. Upon substituting $I = 9/2$ in the case of the ^{93}Nb nucleus, this yields,

$$\Delta\nu = e^2qQ/h(1/24) \quad . \quad (34)$$

In the case of ^{93}Nb with a spin $I = 9/2$, four sets of satellites would be expected corresponding to the transitions $9/2 \leftrightarrow 7/2$, $-9/2 \leftrightarrow -7/2$; $7/2 \leftrightarrow 5/2$, $-7/2 \leftrightarrow -5/2$; $5/2 \leftrightarrow 3/2$, $-5/2 \leftrightarrow -3/2$; and $3/2 \leftrightarrow 1/2$, $-3/2 \leftrightarrow -1/2$. If the quadrupole interaction is sufficiently large, the central $1/2 \leftrightarrow -1/2$ transitions will be altered producing a unsymmetrical NMR line close to ν_L which can be characterized by a separation of the positive and

negative peaks of the first derivative of the resonance line. If the separation is plotted against the inverse of the resonance frequency, a straight line relationship will result, see Eq. 25, and the slope of this straight line will yield the coupling constant,

$$\frac{e^2 q Q}{h} = \sqrt{(138.24)(\text{Slope})}, \quad (35)$$

using $I = 9/2$ for the ^{93}Nb nucleus. The above expression is correct to fourth order in a perturbation calculation. In Eqs. 34 and 35 the asymmetry parameter (η) for the field gradient has been taken as zero. From either expression (Eq. 34 or 35), it is possible to determine the quadrupole coupling constants for the Nb atoms which exist in various sites in the several crystalline phases of NbN_x .

The γ , δ , and ϵ phases of NbN_x have been identified by their NMR spectra by an examination of six NbN_x powdered samples containing various amounts of the phases mixed together. A Varian wide-line NMR spectrometer (V4210A) with a Varian 9 electromagnet (V-3400) was employed for the measurements. Some measurements were also made using a conventional Pound-Watkins spectrometer and a Varian superconducting solenoid capable of producing magnetic field up to 60 k gauss.

Identification of the Phases by NMR

The samples investigated are listed in Table 1. The composition of these samples was determined previously by x-ray work by Guard, Savage and Swarthout³. In all samples, two distinct lattice sites were observed for the ^{93}Nb nuclei. However, the spectra from sample No. 1 which is primarily the δ phase is predominantly a single resonance line. The spectra for the NbN_x samples are shown in Fig. 5. To obtain the resonance traces shown in Fig. 5, the magnetic field had to be scanned over a region of 1,000 gauss. In order to accurately calibrate the scan, the ^{79}Br and ^{81}Br resonances from a sample of KBr were simultaneously recorded. Also the ^{27}Al from the NMR probe was observed within the region of scan, at some resonant frequencies. By comparing the spectra of sample No. 1 containing primarily the δ phase with sample No. 2 containing δ phase and some ϵ phase, it is apparent that the ϵ phase of NbN_x exhibits a second order quadrupole split central ($1/2 \leftrightarrow -1/2$) resonance line and clearly visible first order satellite transitions. The presence of the ϵ phase is also apparent in the spectra for all the remaining samples with even a slight trace of the ϵ phase appearing in spectra for sample No. 1. These transitions identified with the ϵ phase were examined at various magnetic fields, and it was found that the transitions do have the proper frequency dependences, that is, the separation of the

TABLE 1

Composition* of NbN_x Samples

<u>Sample</u>	<u>Phase(s) Present</u>	<u>X, (N/Nb)</u>
No. 1	δ	.884
No. 2	δ , some ϵ	.90 - .91
No. 3	ϵ , some δ	.89
No. 4	ϵ , trace of γ	.95
No. 5	ϵ , some γ	.94
No. 6	$\epsilon + \delta$	.90

*Determined by x-ray analysis²⁴.

Fig. 5a

Fig. 5b

Fig. 5a and 5b First derivative of the NMR of ^{93}Nb in polyphase samples of NbN_x , at 6MHz. Points A and A' denote the derivative peaks of the 2nd order quadrupole split ($1/2 \rightarrow -1/2$) transition of the ϵ phase. B and B' are the $\pm 3/2 \leftrightarrow \pm 1/2$ first order satellites of the ϵ phase. C is the signal due to the δ phase and D is the signal due to the γ phase. The bromine (^{79}Br) resonance from KBr was used as a field marker.

$1/2 \leftrightarrow -1/2$ transition varies as $1/\nu_L$ while the separation of the $\pm 1/2 \leftrightarrow \pm 1/2$ satellites remains constant, (see Fig. 6). Upon applying a first order quadrupole perturbation to the $\pm 3/2 \leftrightarrow \pm 1/2$ transitions, one obtains the quadrupole coupling constant $(\frac{e^2 q Q}{h})$ of $10.77 \pm .1 \text{ MHz}$. Care must be taken in the measurement of the coupling constant because there occurs a shifting of the resonance derivative lines due to dipolar broadening²⁵. A second order perturbation calculation on the $(1/2 \leftrightarrow -1/2)$ transition, using the slope of the "least squares fit" of Fig. 6 gives $\frac{e^2 q Q}{h} = 10.63 \text{ MHz} \pm .1 \text{ MHz}$. It is interesting to note that a value for the magnitude of the dipolar contributions to the line width of the ^{93}Nb line $[(1/2 \leftrightarrow -1/2)$ transition] can be obtained from the intercept of the graph in Fig. 6 where the separation of the peaks of the derivative curve of the $1/2 \leftrightarrow -1/2$ transition have been plotted against $1/\nu_L$. The value of dipolar width (12.8 gauss) obtained in this way was in agreement with that predicted by the method of Adams, Williams and Hewitt²⁵ and agrees with the dipolar correction used to obtain the value of the quadrupole coupling constant from the separation of the satellite transitions. At higher frequencies (about 12 MHz) the pair of satellite lines due to the $\pm 5/2 \leftrightarrow \pm 3/2$ transitions is observed. These transitions, although weak, give a coupling constant in agreement with that value obtained from other transitions, verifying that they are indeed all part of the ^{93}Nb resonance in the ϵ phase. This fairly large

Fig. 6 Separation of the peaks of the derivative curve for the $1/2 \leftrightarrow -1/2$ transition (ϵ phase) versus $1/\nu$. The points at $1/6\text{MHz}^{-1}$, $1/8\text{MHz}^{-1}$, $1/12\text{MHz}^{-1}$ represent an average of all six samples.

coupling constant for the ϵ phase of NbN_x is easily understandable since one would expect a large electric field gradient from the hexagonal structure³ of the niobium ions.

A search was made for $\pm 7/2 \leftrightarrow \pm 5/2$ and $\pm 9/2 \leftrightarrow \pm 7/2$ transitions, in order to have the complete spectra of the Nb (spin 9/2) in the ϵ phase, but presumably because of the lower intensities of these lines and the broadening due to random strains and possibly crystalline imperfections and hence random quadrupole interactions, the resonances could not be detected.

In attempting to analyze the spectra of the δ and γ phases, difficulty is encountered in distinguishing between the spectra from both phases. Both of these phases have structures that are similar; δ -fcc, γ -slightly distorted fcc³. Similar crystal structures would give rise to comparable quadrupole coupling constants (expected to be small since perfect cubic symmetry would give zero electric field gradient, eq), thus both phases should have resonances of almost the same shape exhibiting little or no quadrupolar perturbation. Only the δ phase was available in relatively pure form with slight contamination of the ϵ phase (sample No. 1). The spectra of sample No. 1 at high frequencies (Fig. 7) exhibits a large central transition and a pair of small "bumps". Analysis of the central transition, by plotting the separation of the derivative maxima against $1/\nu$, yields a quadrupole coupling constant of $4.3 \pm .4 \text{ MHz}$ and a dipolar line width

Fig. 7 First derivative of the ^{93}Nb NMR obtained from sample No. 1 at two values of magnetic field.

of 5.5 gauss for the ^{93}Nb sites in the δ phase.

The dipolar line width which is due to a nuclear dipole-dipole interaction depends upon the lattice spacing (a) as $1/a^3$. Note that the ratio of dipolar broadening of the ϵ phase to that of the δ phase is in agreement with this inverse ratio of the cube of the lattice spacing. Upon a detailed examination of the bumps (Fig. 7) at several frequencies, it was found that they correspond to the central transition of the ϵ phase since they yield the appropriate coupling constant and their separation depends linearly upon $1/\nu$. These bumps do not correspond to a pair of satellites for the Nb atoms in the δ phase for the separation of such satellites would remain constant with field. From the relative intensities of the two lines found in sample No. 1, it is estimated that less than a few percent of this sample is ϵ phase. It is of interest to note that the satellite lines for the δ phase were not detected presumably due to extreme broadening of the line because of distribution of coupling constants which may have been produced by random strains in the powdered sample.

The γ phase was available only when mixed with easily detectable amounts of ϵ phase. The signal from the ϵ phase distorts the signal of the γ phase so that the difference between γ and δ phase is not discernable (see Fig. 5b samples No. 5 and No. 6). It is assumed, however, that the γ phase would have a slightly

larger electric field gradient than the δ phase on the basis that its structure is further from cubic symmetry. This might be easily verified if pure γ and δ phases NbN_x were available.

Other NMR Measurements

A measurement of the Knight¹⁹ shift of the niobium NMR in sample No. 3 was attempted using Nb metal and its known Knight shift as a reference. The amount of shift, if any, was masked by the difficulty in determining the center of the broad resonances. Hence, the Knight shift estimated to be zero or extremely small. This finding is consistent with the results of Jaccarino and Davies²⁶.

Sample No. 3 was cooled to 4.2°K to determine if any electronic effects would alter the NMR, since NbN is a known superconductor. The resonance could not be found, due to the fact that the increased conductivity "loaded down" the tank circuit of the Pound-Watkins oscillator which was used for these measurements.

Sample No. 3 was again run at 77°K, at a frequency of 8 MHz to see if the lower temperature would affect the NMR spectrum. No effect other than a slight increase in the quadrupole coupling constant was observed.

Since the quadrupole coupling constant had been determined from NMR measurements for the ϵ phase of NbN_x , an attempt was made to detect the pure quadrupole resonance of Nb in the absence

of an external magnetic field. A frequency modulated Pound-Watkins oscillator was used. The four expected resonances were calculated to appear at $1.78 \pm 0.2\text{MHz}$, $1.34 \pm 0.2\text{MHz}$, $0.892 \pm 0.2\text{MHz}$ and $0.446 \pm 0.2\text{MHz}$ for the $\pm 9/2 \leftrightarrow \pm 7/2$, $\pm 7/2 \leftrightarrow \pm 5/2$, $\pm 5/2 \leftrightarrow \pm 3/2$, $\pm 3/2 \leftrightarrow \pm 1/2$ transitions respectively. The search was carried out at room temperature from 1.72MHz to 0.97MHz . This frequency range should have produced the $\pm 7/2 \leftrightarrow \pm 5/2$ transition. At these relatively low frequencies since the sensitivity of the oscillator is poor only large resonances, which are not very wide, are detectable. In this case, no resonance was seen.

Field Gradients in Related Interstitial Compounds

The ^{93}Nb resonance observed by Froideraux and Rossier²⁷ in NbC_x is a second-order perturbed NMR line showing no satellite structure²⁸ as seen in the VC_x . It is not surprising that the NMR spectra of ^{93}Nb in these compounds differ from the ^{51}V NMR spectra in similar materials because both the nuclear quadrupole moment and Sternheimer^{7,29} antishielding factor for ^{93}Nb are much larger than that for the ^{51}V nucleus. This fact results in a much larger quadrupole coupling constant for ^{93}Nb than that observed in ^{51}V when both nuclei are in equivalent electric field gradients. This larger quadrupole perturbation of the NMR line removes the satellites further from ν_L and causes a larger splitting of a second-order perturbed central ($1/2 \leftrightarrow -1/2$)

transition. In addition and perhaps a much more important effect to consider is that the presence of random strains in powdered samples produces increased broadening of all NMR transitions and hence makes the transitions more difficult to observe. The random broadening is produced because the sites of nuclei will vary slightly due to mechanical strains or the presence of defects even if the defects occur several atomic sites away from the nuclei under investigation. The increased broadening does not allow a determination of any discrete defect structure in the niobium compounds. However, the presence of large changes in the sites of large numbers of ^{93}Nb nuclei due to major changes in the crystalline structure, i.e., phases are readily observed in the NbN_x system. It should also be noted that in the δ phase of NbN_x no satellite lines were observed whereas in the ϵ phase a much larger quadrupole coupling constant was found for the Nb atoms yet the satellite lines were observed. This would indicate that in the more nearly cubic δ phase a distribution of strains is present to such a degree that the satellite lines are smeared out and are unobservable. A reasonable source for these strains would be defects in this high temperature δ phase. A similar situation appears in NbC_x as reported by Froidevaux and Rossier. It would appear that in the nearly cubic, high temperature δ phase of NbN many imperfections exist while in the ϵ phase most of the Nb sites are identical with the absence of large numbers of defects.

Conclusion

The technique of NMR is very useful in analyzing the polyphase samples of NbN_x . The NMR spectra of the ϵ phase with its large quadrupole coupling constant is extremely different from the spectra of the δ or γ phases. Also, if one wishes to perform a double integration of the derivative curve, this will yield the area under the absorption curve, which is proportional to the number of nuclei in that phase. The relative amounts of the phases present in a sample could then be calculated. This was done for sample No. 3 and approximately 7% of δ phase was present which compares with the approximately 5% which was obtained by x-ray.²⁴ If there is some uncombined niobium metal present, this resonance is also observable and will appear at a lower magnetic field due to its large Knight shift¹⁹. Such a spectrum was obtained for an impure sample of NbN. This sample was manufactured by Gallard-Schlesinger Chemical Manufacturing Corporation, Carle Place, New York.

The use of NMR in the identification of phases should prove to be a valuable analytical tool. Once the quadrupole coupling constants are known for the various phases of a system, it is only a matter of obtaining the NMR of an unknown sample and then measuring the separation between the lines to quickly determine the phases present and the amounts of such phases by comparing intensities.

It is interesting to note the conspicuous absence of an

applicable isotropic Knight shift in this well-known superconducting material which indicates an absence of s-state conduction electrons. Thus it is presumed that the superconducting electrons must be of a p-state or d-state rather than s-state. Because of the large width of the NMR lines, an anisotropic Knight shift, if present, was not resolved. The anisotropic Knight shift would have yielded information concerning the presence of p-state or d-state electrons. Since there is an increase in directional type of bonding, covalent bonding, in the niobium nitrides as compared with niobium metal, this in general causes a more brittle material and thus a higher Debye temperature (θ_D). $\text{NbN}_{0.91}$ can be considered as a sort of "stifflead".³⁰ BCS theory predicts that the superconducting transition temperature varies as θ_D , if other quantities remain constant.

Finally it should be noted that these NbN_x samples were discovered to give an absorption at room temperature when the external magnetic field was turned down in preparation to be turned off. The samples were then investigated utilizing the Varian probe placed in a set of Helmholtz coils to supply a weak external field. One set of coils supplied a variable magnetic field from 0 to 40 gauss while the other set was used to cancel out the earth's magnetic field. A large absorption of power was noted at zero field. This decreased as the magnetic field was increased until at around 5 gauss the absorption had

vanished. The sample of NbN_{.884} was observed at 8MHz and at 16MHz and the width of the signal did not change appreciably.

It is assumed at this stage of investigation that this absorption is caused by the phenomena of magnetoresistance and possibly some low field electron spin resonance. In order to investigate the phenomena, the temperature dependence of the line width as well as its frequency dependence should be examined.

CHAPTER V

Experimental Observations on NbBe_x

Introduction

The intermetallic compounds of the system, NbBe_x , are of interest because these materials are observed to have high strength, strength retention at elevated temperatures and thermal-shock resistance³¹. These refractory compounds also possess high melting points, low specific gravity and show good oxidation resistance³². The limiting use temperature of beryllides appears to be about 3000°F. The beryllides of niobium are considered to have potential in structural applications at elevated temperatures. The compounds investigated were NbBe_2 , NbBe_3 , $\text{Nb}_2\text{Be}_{17}$ and NbBe_{12} . X-ray analysis has been performed and the results are given in Table 2.⁴⁻⁶ Because of the similarity in the NMR of the ^9Be nucleus in the above mentioned compounds, these results will be examined jointly in the following discussion. The ^{93}Nb nucleus, however, exhibits a vastly different NMR for each compound and thus each compound will be considered separately.

Beryllium Resonances

The NMR of the beryllium nuclei in each of the compounds was investigated at room temperature on the Varian spectrometer described previously. The signals were all quite weak and appeared to consist of one unsplit line. These resonances were easily power saturated, indicating that there existed very little

TABLE 2
Crystal Structure* of NbBe_x Samples

Beryllide	Structure	a _o (Å)	c _o (Å)	c _o /a _o
NbBe ₂	fcc	6.535		
NbBe ₃	rhombohedral	7.495		
Nb ₂ Be ₁₇	rhombohedral	5.599		
NbBe ₁₂	tetragonal	7.376	4.258	.577

*Determined by x-ray analysis⁴⁻⁶.

interaction between the Be nuclear quadrupole moment, which is relatively small, and the electric field gradient. Very little interaction of the Be nucleus and the conduction electrons was apparent also, since this interaction could help relax the nucleus to its lowest NMR energy level and thus avoid power saturation.

The signal-to-noise ratio in the resulting spectra was poor, thereby causing uncertainty in the line width measurements. The line widths of NbBe_3 , $\text{Nb}_2\text{Be}_{17}$ and NbBe_{12} are all within $7.5\text{G} \pm 1.0\text{G}$. NbBe_2 exhibited a line width of $9.3\text{G} \pm 2.0\text{G}$ and was extremely weak. The NbBe_2 and NbBe_3 were examined only at 8MHz which corresponds to the most sensitive region in the 4MHz to 8MHz NMR probe. An external magnetic field of 13.4kG is then needed to achieve the resonance condition. The resonances could not be observed at any lower frequencies due to loss of sensitivity and possibly some random broadening. The NMR of $\text{Nb}_2\text{Be}_{17}$ and NbBe_{12} were examined at both 8MHz and 6MHz. The line width stayed constant to within the uncertainty in the measurements.

In order to measure any Knight shift that may be present, the position of the resonance was measured relative to the NMR of ^9Be in $\text{Be}(\text{NO}_2)_2$, and the shift, if any, is estimated to zero. Thus very little information was obtained from the ^9Be NMR, other than that of the absences of large quadrupole coupling and electron-nuclear interactions.

NbBe_2

The NMR of NbBe_2 was obtained at room temperature on the Varian spectrometer described previously. Resonances of the niobium nuclei were obtained at frequencies ranging from 6MHz to 14MHz. Typical resonances are shown in Fig. 8. Analysis of the resonance shows that the peak to peak separation is independent of the resonance frequency. This indicates the absence of any nuclear quadrupole interaction. An intensity measurement was next performed, comparing this signal with the spectrum from $\text{Nb}_2\text{Be}_{17}$ in which the individual satellite lines are readily identified (this $\text{Nb}_2\text{Be}_{17}$ spectrum will be discussed later). This comparison of integrated intensity of the resonance lines took into account the known number of nuclei present in both samples and indicated that all of the satellite transitions were present in an unsplit central transition from NbBe_2 . If the satellites were not present, the signal intensity would have been reduced by a factor of about four (actually 95/25), see Chapter II. The absence of a nuclear quadrupole coupling interaction is consistent with x-ray analysis of NbBe_2 , which indicates that it has a fcc structure⁴ resulting in a vanishing electric field gradient, see Chapter II.

The width of the derivative curve is plotted against the resonance frequency and is shown in Fig. 9. The separation is

Fig. 8. First derivative of the ^{93}Nb resonance in NbBe_2 at 14MHz and 6MHz.

Fig. 9 Separation of the peaks of the derivative curve of the ^{93}Nb resonance in NbBe_2 versus ν .

found to be $7.5G \pm 0.5G$. The uncertainty in the line width measurement is due to the difficulty in determining the exact positions of the peaks. The line width is presumably due to the magnetic dipole-dipole interaction between the niobium nuclei and their neighbors; 12 Be atoms at $2.71 \text{ \AA}$ and 4 Nb atoms at $2.83 \text{ \AA}$.⁴ The center of this resonance does exhibit a Knight shift. The shift was measured using ^{79}Br NMR in KBr as a reference marker. A value of $0.70\% \pm 0.03\%$ was obtained at room temperature. This relatively large Knight shift is comparable to that of pure niobium metal, 0.82% .³³ These similar shifts suggest that the bonding in NbBe_2 is highly metallic.

NbBe_3

The NMR of the niobium nuclei in NbBe_3 was next investigated under similar experimental conditions. The spectrum obtained is much more complex than that of NbBe_2 . The many resonances that appeared, Fig. 10, had to be studied as a function of resonance frequency in order to properly categorize and identify them. As a result of this frequency analysis, it appears that there are three different niobium crystalline positions present yielding three separate families of lines. This result is supported in the following discussion. Line A in Fig. 10 appears to be an unsplit central ($1/2 \rightarrow -1/2$) transition, whereas lines B and C are central transitions that are highly split by an electric quadrupole interaction. Since NbBe_3 should have only

Fig. 10 First derivative of the ^{93}Nb resonance in NbBe_3 at 14MHz. Lines marked A, B and C are the central ($1/2 \rightarrow -1/2$) transitions. Lines marked B' and C' are first order split ($\pm 3/2 \leftrightarrow \pm 1/2$) transitions.

two distinct crystalline sites⁴, one of the resonances is most likely due to an impurity. The analysis of these resonances was carried out by plotting the peak to peak separation of the derivative of each line versus $1/\nu$. The results are shown in Fig. 11. The spectra used in the plot were only those taken at fairly high frequencies, 12MHz to 15MHz. This procedure is employed because the extremely large splittings and presumably some random broadening present in the lines resulted in a decrease of the resolution of the spectrum at the lower frequencies. From Fig. 11 it is evident that a straight line relationship can be drawn through the data points. The slope of such a line will then yield the quadrupole coupling constant, e^2qQ/h . Because of the limited frequency range in which the NMR could be detected, a least square fit to the data resulted in a negative intercept. In order to obtain an average value for the slope, a line was first drawn without going beyond the error bars, having the minimum slope. Then a second line was drawn that would have maximum slope but with the condition that the line width at infinite frequency could be no less than zero. The minimum coupling constant and the maximum coupling constant obtained in this manner were then averaged to give the quoted value. The resulting coupling constants are given in Table 3.

Fig. 11 Separation of the peaks of the derivative curve for the $(1/2 \rightarrow -1/2)$ transition of lines A, B, and C from ^{93}Nb in NbBe_3 versus $1/\nu$.

Table 3 Quadrupole Coupling Constants and Knight Shifts of NbBe₃

Line	e^2qQ/h	Knight Shift
A	0MHz	0.693% $\pm$ 0.03%
B	24.31MHz $\pm$ 0.45MHz	0.724% $\pm$ 0.03%
C	30.57MHz $\pm$ 0.74MHz	0.532% $\pm$ 0.03%

Analysis of line A reveals that the width is independent of the resonance frequency, to within the uncertainty in the measurements. Thus, the niobium nuclei which are contributing to this line must be in a highly symmetric environment. In Fig. 10, the sets of lines denoted by B' and C' are identified as the first order split ($\pm 3/2 \rightleftharpoons \pm 1/2$) transitions of the lines B and C, respectively. The separations of the lines are a constant, within the uncertainty of measurement. The coupling constants derived from first order perturbation theory yield the values given in Table 4.

Table 4 Quadrupole Coupling Constants of NbBe₃

Line	e^2qQ/h
B'	24.19MHz $\pm$ 0.2MHz
C'	30.10MHz $\pm$ 0.3MHz

By comparing the coupling constants in Table 3 with those in Table 4, it appears that the satellite lines give very nearly the same coupling constants as the split central lines even though the coupling constants in the case of the satellites were

derived using first order perturbation, while for the split central line second order perturbation was employed. Thus as in the case of the niobium nitrides, both methods give the same results, indicating that third order effects are still too small to be observed at these resonance frequencies.

The centers of lines A, B, and C were found to exhibit Knight shifts. Measurements of the Knight shifts taken from the center of gravity of the satellite transitions are incorrect and must not be used, unless the proper correction is made, due to the shifting of these lines by second order quadrupole effects. It must be noted that the center of the split ($1/2 \rightarrow -1/2$) transition is not midway between the peaks but rather the distance $9/25$ of the separation between the peaks as measured from the low field peak, see Fig. 1. The measured values of the Knight shifts, utilizing the positions of the central transitions, are found in Table 3. The shifts were measured using ^{79}Br NMR in KBr as a reference marker.

It is proposed that line A is the result of a contamination of NbBe_3 by a small amount of NbBe_2 . This is substantiated by comparing the Knight shift of line A, which is given in Table 3, with that of NbBe_2 . Both shifts are the same within the limits of error. In comparing the line widths, line A is found to have a width of 16G, which is of course, larger than that of niobium in NbBe_2 . However, this is due to overmodulation by a field modu-

lation of 12G which was required to observe the entire spectrum. A large filtering time constant was also employed. Both of these parameters would tend to broaden a narrow line. Further investigation of this line when examined at a slower scanning rate and slightly less modulation reveals a much narrower line width similar to that seen in NbBe_2 . When NbBe_2 was examined under the same condition, both line A and the NbBe_2 resonances exhibited the same, slightly distorted, line width of about 10.5G. Upon performing a double integration of the spectrum, which yields a number that is proportional to the number of nuclei participating in the resonance, it was found, assuming all of the satellites were present in this resonance, that only about 1.5% of the niobium nuclei were in the NbBe_2 phase. It was further discovered that approximately 61.5% of the nuclei were present in line B while about 37% were in line C. This ratio of Nb nuclei in lines B and C agrees quite favorably, when considering the inherent errors in integrating a highly split resonance line, with the two-to-one ratio predicted for the two different sites from x-ray analysis⁴.

$\text{Nb}_2\text{Be}_{17}$

The NMR of the niobium nuclei in $\text{Nb}_2\text{Be}_{17}$ was examined under the same conditions as were used for NbBe_2 and NbBe_3 . The ^{93}Nb spectrum exhibits a split central line ($+1/2 \rightarrow -1/2$) and four

pairs of satellites, corresponding to the $(\pm 3/2 \rightleftharpoons \pm 1/2)$, $(\pm 5/2 \rightleftharpoons \pm 3/2)$, $(\pm 7/2 \rightleftharpoons \pm 5/2)$ and $(\pm 9/2 \rightleftharpoons \pm 7/2)$ transitions. In Fig. 12 the split central line and the first two pairs of satellites are displayed. The central line is enlarged beyond the chart paper in order to show the satellites. The last two pairs, $(\pm 7/2 \rightleftharpoons \pm 5/2)$ and $(\pm 9/2 \rightleftharpoons \pm 7/2)$, of transitions which are very weak, are not shown but have been observed. In order to resolve the satellites, high modulation amplitude, approximately equal to the line width, was required. This results in a distortion of the derivative signal.

The peak to peak separation of the split central transition, taken from the derivative curve, was plotted against the inverse of the resonance frequency (Fig. 13). Table 5 is also presented to clearly indicate the values of the line widths and their associated uncertainties in measurement. A straight line cannot be fitted within the error bars, to include both the low frequency data and the high frequency data. If only the low frequency data points are considered, that is, from 6MHz to 2.5MHz, a straight line can be fitted. The slope of such a line yields a quadrupole coupling constant of 5.92MHz with a residual line width of approximately zero gauss. If the higher frequency data, from 8MHz to 14MHz are fitted with a straight line, its slope is greater than that of the lower frequency data and the intercept of the line when extrapolated to infinite

Fig. 12 First derivative of the ^{93}Nb resonance in $\text{Nb}_2\text{Be}_{17}$ at 14 MHz. Line A is the $(1/2 \rightarrow -1/2)$ transition. Lines B and B', C and C', D and D' are the $(\pm 3/2 \leftrightarrow \pm 1/2)$, $(\pm 5/2 \leftrightarrow \pm 3/2)$, $(\pm 7/2 \leftrightarrow \pm 5/2)$ transitions, respectively.

Fig. 13 Separation of the peaks of the derivative curve for the $(1/2 \rightarrow -1/2)$ transition of ^{93}Nb in $\text{Nb}_2\text{Be}_{17}$ versus $1/\nu$. Solid curve is a plot of Eq. 43.

TABLE 5

NMR Line Width of ^{93}Nb in $\text{Nb}_2\text{Be}_{17}$ at Various Frequencies

Frequency (MHz)	Line Width (gauss)
14MHz	$14.23\text{G} \pm 0.5\text{G}$
12MHz	$17.75\text{G} \pm 0.3\text{G}$
10MHz	$22.07\text{G} \pm 0.45\text{G}$
8MHz	$28.64\text{G} \pm 0.5\text{G}$
6MHz	$39.56\text{G} \pm 0.5\text{G}$
4MHz	$59.8\text{G} \pm 1.0\text{G}$
3MHz	$81.9\text{G} \pm 2.0\text{G}$
2.5MHz	$96.6\text{G} \pm 2.0\text{G}$

frequency is -4.3 gauss. This negative line width that is predicted when the electric quadrupole interaction has vanished is of course non physical. Thus some other interaction must be distorting the signal, and this distortion becomes more prominent at higher frequencies. This interaction has the effect of narrowing the resonance.

This narrowing of the resonance, beyond that which can be accounted for by the vanishing of the electric quadrupole interaction at higher frequencies, has been found to be due to a slight anisotropy in the Knight shift. Bloembergen has discussed in detail the first order effects of an anisotropic shift tensor on the line shape of the resonance of a conductor in the absence of electric quadrupole effects³⁴. In the case of an axially symmetric shift tensor, all of the $2I + 1$ pure Zeeman levels are shifted by an equal amount in first order, with the result that only a single resonance line appears for the case of a single crystal³⁴. The frequency of this single line is given by

$$\nu = \nu_0 (1 + K_{iso}) [1 + K_{ax} (3\cos^2\theta - 1) / (1 + K_{iso})] , \quad (36)$$

where θ is the angle between the Z axis of the principle axes system of the shift tensor and the direction of the applied external magnetic field.

If the resonance frequency of the $(1/2 \leftrightarrow -1/2)$ transition in a single crystal is considered when second order quadrupole

effects are present (assuming an axially symmetric field gradient), then⁷ the resonance frequency becomes

$$\nu(1/2 \leftrightarrow -1/2) = \nu_L \{ 1 + (\nu_Q^2 / 16\nu_L^2) [I(I+1) - 3/4] \times (1 - \cos^2\theta)(1 - 9\cos^2\theta) \} \quad (37)$$

where θ is the angle between the Z axis of the principle axes system of the electric field gradient tensor and the applied external magnetic field. If the effect of an isotropic Knight shift were to be added, all that would be necessary would be to replace ν_L with ν_o where

$$\nu_o = \nu_L (1 + K_{iso}) \quad (38)$$

When second order electric quadrupole effects and a first order anisotropic Knight shift are both present, then the frequency of the central transition in a single crystal is given by combining equations 36, 37, and 38³⁵.

$$\nu(1/2 \leftrightarrow -1/2) = \nu_o \{ 1 + (\nu_Q^2 / 16\nu_o^2) [I(I+1) - 3/4] \times (1 - \cos^2\theta)(1 - 9\cos^2\theta) + K_{ax}/(1+K_{iso})(3\cos^2\theta-1) \}. \quad (39)$$

It is assumed in this case that the axially symmetric magnetic shift tensor has its principle axes coincident with that of the axially symmetric electric field gradient tensor. The line shape that will result from a polycrystalline sample, following Cohen and Reif⁷, yields peaks in the derivative curve at³⁵,

$$\nu_{Hi} = \nu_o + b/\nu_o - a\nu_o \quad (40a)$$

$$\nu_{Lo} = \nu_o - 16b/9\nu_o + (2/3)a\nu_o - a^2\nu_o^3/4b \quad (40b)$$

where ν_{Hi} and ν_{Lo} are the positions of the singularities in the probability distribution which locates the high frequency and low frequency peaks where the definitions, $b = \nu_Q^2[I(I+1) - 3/4]/16$ and $a = K_{ax}/(1 + K_{iso})$ are introduced. The separation between the peaks ($\Delta\nu$) can be written,

$$\Delta\nu = \nu_{Hi} - \nu_{Lo} = 25b/9\nu_o - 5a\nu_o/3 + a^2\nu_o^3/4b \quad (41)$$

Analyzing the above equation, the first term is the splitting due to the second order quadrupole interaction, see Eq. 25. The second term is the contribution due to the anisotropic Knight shift. Note, if $K_{ax} > 0$ then $a > 0$, this will then cause the separation between the peaks to be less than if only the electric quadrupole interaction were present and hence explain the data obtained from the Nb_2Be_{17} powdered sample. The third term depends upon a^2 and can be neglected because of the smallness of a . If there is a finite dipolar line width present, then the separation can be written as³⁵,

$$\Delta\nu = 25b/9\nu_o - 5a\nu_o/3 + 1/2 \sigma \quad (42)$$

A least squares calculation was performed fitting Eq. 42 without the dipolar contribution, since the low frequency data if extrapolated indicated an extremely small amount of dipolar broadening. The resulting equation is,

$$\Delta\nu = 0.255\nu_o^{-1} - 0.000238\nu_o \quad (43)$$

In Fig. 13, a curve is drawn to show the fit to the data.

The splitting is given in gauss. Utilizing the values obtained in Eq. 43, the quadrupole coupling constant and the axial component of the shift tensor may be computed, yielding $e^2qQ/h = 5.93 \pm 0.15\text{MHz}$ and $K_{ax} = 0.014\%$. If a more accurate value of K_{iso} were desired other than that value obtained by neglecting the small shift of the center of the split central transition due to K_{ax} , one can plot the relative shift of the low field peak, given by³⁵,

$$K_H = (\nu_{H1} - \nu_L)/\nu_L = (H_L - H_{Lo})/H_L = K_{iso} - a + b/\nu_L^2 \quad (44)$$

against the inverse of the resonance frequency squared. Note, that the difference between ν_L and the actual resonance frequency is insignificant in this particular calculation. The magnetic field was measured using ^{79}Br in KBr. The plot is shown in Fig. 14. A least squares fit yields the following equation,

$$K_H = 0.0032 + 0.1064/\nu^2 \quad (45)$$

The infinite frequency intercept determines $K_{iso} = 0.334 \pm 0.02\%$, once the value of "a" is known from Eq. 42. Note the value of K_{iso} obtained by neglecting any shift due to the effects of K_{ax} and defining the center of the resonance as in Fig. 1 is, $K_{iso} = 0.34 \pm 0.02\%$, which coincides with the previous value within the uncertainties of the measurement. This fairly small Knight shift as compared with the previously examined beryllides

Fig. 14 K_H versus $1/\nu^2$.

indicates that there are relatively fewer s-state electrons in the conduction band. The slope of the line resulting from a plot of Knight shift versus $1/\nu^2$ shown in Fig. 14 can also be used to determine the quadrupole coupling constant, but this method is basically less accurate than the previous method. The reason for this is that the value obtained for the slope in Fig. 14 depends upon an absolute knowledge of the magnetic field and not upon the splitting of the signal as in Eq. 43.

When applying Eq. 42 to the data for $\text{Nb}_2\text{Be}_{17}$, the contribution to the line width due to dipolar broadening was omitted. This is due to the fact that if only the low frequency (6MHz or less) data were utilized, where the effect of K_{ax} is diminished, the straight line relationship between the separation of the peaks of the derivative curve and the inverse of the resonance frequency could be applied. When this line is extrapolated to infinite frequency, the intercept indicates a residual line width of approximately zero gauss. The resonance of $\text{Nb}_2\text{Be}_{17}$ at 15MHz still exhibits a sharply split line, that is, the two peaks are not smeared into one another due to a large dipole-dipole interaction, see Fig. 15. An estimate of the dipole-dipole width may be obtained by comparing the interatomic spacing between niobium atoms in NbBe_2 , which is $2.830\text{\AA}^4$, with the spacing between niobium atoms in NbBe_{17} which is $3.463\text{\AA}^5$. Since the dipole-dipole interaction varies as $1/a^3$, where "a"

Fig. 15 First derivative of the central ($1/2 \rightarrow -1/2$) transition of the ^{93}Nb resonance in $\text{Nb}_2\text{Be}_{17}$ at 15MHz.

is the spacing, a ratio of the cubes will yield the inverse ratio of their dipole broadening. In this approximation, the effect of the beryllium atoms is considered to be essentially the same in both phases. This results from spacings between the niobium and beryllium being very closely the same. The niobium nucleus also possesses a magnetic moment that is of the order of six times larger than that of beryllium, thus the dipole-dipole interaction due to Nb atoms is presumed to overshadow any of the differences that occur because of the packing of Be atoms about the Nb atoms in the two different structures. Thus by using the value of the line width due to dipolar broadening in NbBe_2 determined earlier in this chapter and the ratio of the cubes of the Nb-Nb spacing, a line width due to dipolar broadening of approximately 4G is predicted.

The separation between the $(\pm 3/2 \rightleftharpoons \pm 1/2)$ satellite transitions is measured to be $254 \pm 3\text{G}$ and is constant within the frequency range it is observed, 4 to 14MHz. This width being a constant again indicates that first order perturbation due to the quadrupole interaction would still be valid. The individual satellite lines possess a width which is due to over modulation. This extra width can be subtracted off using the method give by Hewitt et al²⁵. Once this is done, a coupling constant of $5.8 \pm 0.2\text{MHz}$ is obtained. This value is in agreement with the corrected value obtained from the central transition.

NbBe_{12}

The last beryllide to be investigated was NbBe_{12} , which has the highest atomic ratio of beryllium to niobium. The NMR of the niobium nuclei was observed at room temperature. The resonance was extremely weak due to the low abundance of ^{93}Nb nuclei present, consequently, high gain and high modulation amplitude were necessary to resolve the signal. The resonance frequencies at which the sample was investigated ranged from 10MHz to 15MHz. The spectra contained an extremely split central transition, Fig. 16. The $(\pm 3/2 \rightleftharpoons \pm 1/2)$ transitions could also be seen but they were extremely weak. A graph was made of the peak to peak separation of the central transition against the inverse of the resonance frequency, Fig. 17. The resulting straight line relationship indicated that the resonance line is split by the second order quadrupole perturbation. An electric quadrupole coupling constant of $21.73 \pm 0.3\text{MHz}$ was determined by a least squares fit. This large interaction caused by strong electric field gradients is the consequence of non cubic symmetry. This is in complete agreement with the non cubic tetragonal crystal structure determined by x-ray, Table 2.

A Knight shift was observed and measured at room temperature using ^{79}Br in KBr and ^{93}Nb metal powder resonances as references. A value of $0.552\% \pm 0.02\%$ was determined using the center of the resonance as determined in Fig. 1.

Fig. 16 First derivative of the ^{93}Nb resonance in NbBe_{12} at 14MHz.

Fig. 17 Separation of the peaks of the derivative curve for the $(1/2 \rightarrow -1/2)$ transition of ^{93}Nb in NbBe_{12} versus $1/\nu$.

Conclusion

The different phases of the niobium beryllides are easily identifiable and can be categorized through their NMR spectrum. The quadrupole splitting and Knight shifts are strikingly different for each phase. Thus the analytic tool of NMR lends itself to the investigation of phase impurities in these multistochiometric compounds. The relative amounts of niobium in the various phases as well as any uncombined niobium nuclei may be calculated by the process of a double integration of the resonance curve as outlined previously.

In the case of NbBe_3 , x-ray analysis⁴ stated that the niobium nuclei were in the form of a linear chain of three. The two niobium nuclei at each end of the chain have the beryllium atoms packed around them in the same configuration as in NbBe_2 . The NMR signal caused by these nuclei are identified as line B since this was the most intense line. The comparable Knight shift of line B with that of the niobium nuclei in NbBe_2 indicates that the Knight shift depends heavily upon the beryllium configuration about the niobium nucleus. The quadrupole coupling, however, is greatly different in these two resonances indicating that the configuration of the large niobium nucleus greatly disturbs the electric field gradients.

Finally, it should be noted that these compounds also exhibited a low field absorption as discussed at the end of Chapter IV.

These signals are in general much weaker and tend to be broader in width than those of the niobium nitrides.

SUPPLEMENT

Acoustic Nuclear Magnetic Resonance

Introduction

Nuclear magnetic resonance transitions can be driven by the application of ultrasonic energy to the nuclear spin system rather than electromagnetic power as previously described. This effect was first observed indirectly in the acoustic saturation experiments of Proctor and Tantilla^{37,38} on ³⁵Cl nuclei in NaClO₃. Acoustic energy of the proper frequency was introduced into the sample, and the saturation effect of the conventional NMR was observed. The first direct observation of acoustic nuclear magnetic resonance (ANMR) was performed by Bolef and Menes on indium antimonide and in a series of alkali halides³⁹⁻⁴². The primary advantage of this technique would be in its use in large metallic single crystals where the acoustic waves could propagate very easily. In conventional NMR the electromagnetic power cannot penetrate very deeply because of the high conductivity of the samples. The electromagnetic power cannot penetrate appreciably beyond the skin depth which is approximately 10^{-2} mm at normal NMR frequencies.

Theory

In ANMR, transitions are induced by the interaction of the nuclear electric quadrupole moment with the electric field gradient produced by the lattice vibrations. The electric quadrupole

interaction in tensor form can be written

$$\mathcal{H}_Q = Q : \nabla E \quad , \quad (46)$$

where Q is the nuclear electric quadrupole moment tensor, and ∇E is the crystalline electric field gradient tensor. The effect of an acoustic wave is to cause a time varying strain in the locality of the nucleus, thus of interest is only that part of the electric field gradient which is a function of strain. Upon expanding the electric field gradient tensor in a Taylor series of the strain components to second order the results are⁴³:

- a) constant terms
- b) terms linear in the strain components
- c) terms quadratic in the strain components.

The constant terms are responsible for the zero-field quadrupole interaction, which shifts the NMR lines discussed previously.

In the alkali halides these terms are zero because of the cubic symmetry if no straining is present. The linear terms relate the time varying strain produced by the acoustic wave to the time varying electric field gradient. These terms also enter into the single phonon relaxation process. Finally, the quadrupole terms are responsible for the indirect or Raman type of relaxation process.

In high magnetic fields, where the quadrupole interaction is small compared to the magnetic energy levels, we can write the following matrix elements⁴⁴:

$$\langle m | \frac{eQ}{I(I+1)} | m \rangle = A[3m^2 - I(I+1)] (\nabla E)_0 \quad (47)$$

$$\langle m | \frac{eQ}{I(I+1)} | m \pm 1 \rangle = \mp (6^{1/2}/2) A (2m \pm 1) [(I \pm m + 1)(I \mp m)]^{1/2} (\nabla E)_{\pm 1} \quad (48)$$

$$\langle m | \frac{eQ}{I(I+1)} | m \pm 2 \rangle = (6^{1/2}/2) A [(I \mp m)(I \mp m - 1)(I \pm m + 1)(I \pm m + 2)]^{1/2} (\nabla E)_{\pm 2} \quad (49)$$

where $A = eQ/2I(2I-1)$ and Q is the electric quadrupole moment of the nucleus.

Considering only the case in which a longitudinal acoustic wave is propagated in the direction of a cubic axis, the field gradient caused by the strain will then have axial symmetry along the direction of propagation. Thus the field gradient elements can be written⁴⁵:

$$(\nabla E)_0 = 1/4eq(3\cos^2\theta - 1) \quad (50)$$

$$(\nabla E)_{\pm 1} = \pm (1/4)(6^{1/2})eq \sin\theta \cos\theta e^{\pm i\phi} \quad (51)$$

$$(\nabla E)_{\pm 2} = (1/8)(6^{1/2})eq \sin^2\theta e^{\pm i\phi} \quad (52)$$

where θ is the angle between the axis of symmetry and the direction of the applied magnetic field, ϕ is the angle between the projection of the symmetry axis on the XY plane and the X axis. The scalar q is a measure of the magnitude of the axially symmetric field gradient.

A Taylor expansion of the field gradient in terms of the strain can be written⁴⁶

$$q = q_0 + q_1 \left(\frac{r-a}{a}\right) + \frac{1}{2} q_2 \left(\frac{r-a}{a}\right)^2 + \dots \quad (53)$$

where $(r-a)/a = \delta$ is the strain caused by the longitudinal acoustic wave and q_1 and q_2 are the first and second derivatives, respectively, of q with respect to δ .

The field gradient elements $(\nabla E)_0$ causes the static splitting of the high field magnetic energy levels. $(\nabla E)_{\pm 1}$ and $(\nabla E)_{\pm 2}$ enter into the transition probabilities for $m=\pm 1$ and $m=\pm 2$ respectively. The transition probability (W_m) is given by,

$$W_{m,m}^1 = \frac{1}{4h} 2 |\langle m | H_1 | m^1 \rangle|^2 g(\nu) , \quad (54)$$

where $g(\nu)$ is the shape function of the absorption curve. Upon substituting the values obtained in Eqs. 47 through 52 into Eq. 54, the following transition probabilities are obtained:

$$W_{m,m\pm 1} = (9\pi^2/16h^2) e^2 A^2 q^2 (2m\pm 1)^2 (I_{\pm m+1})(I_{\pm m}) \sin^2 \theta \cos^2 \theta g(\nu) \quad (55)$$

$$W_{m,m\pm 2} = (9\pi^2/64h^2) e^2 A^2 q^2 (I_{\pm m})(I_{\pm m-1})(I_{\pm m+1})(I_{\pm m+2}) \sin^4 \theta g(\nu). \quad (56)$$

Substituting the results of Eq. 53 into the above, the transition probabilities due to terms linear in strain are obtained. It is interesting to note that the central transition $(+\frac{1}{2} \rightarrow -\frac{1}{2})$ is missing from the acoustic lines. Also, in order to drive $\Delta m=2$ transitions Eq. 56 is maximized when $\theta = 90^\circ$. Thus the externally applied magnetic field must be perpendicular to the acoustic axis in order to observe the largest signal.

Experimental Equipment

In order to observe the small absorption of acoustic power, it was necessary to couple a transducer to the conventional Pound-Watkins type oscillator (Pound box)⁴⁷. The coupling was accomplished by a matching network which matched the impedance of the transducer to a value that would allow the oscillator to oscillate and still remain sensitive⁴⁸. The sample which was a KI single crystal in the shape of a cylinder 1/2 inch in diameter and 5/8 inch long was obtained from the Harshaw Chemical Company. The sample was acoustically bonded to a 1/4 inch diameter X-cut quartz transducer obtained from the Valpey Company to form a composite acoustic cavity. It is in this acoustic cavity that standing waves will be established at specific resonance frequencies.

Since the transducer exhibits an impedance minimum at the cavity resonance, while the Pound box oscillates at an impedance maximum, the matching network must also be an inverting network. Thus the spectrometer will be forced to oscillate at a frequency corresponding to a cavity resonance. The level of oscillation will be controlled by any loss of acoustic power. The Pound box is then said to be locked-in to the acoustic system. The matching network is simply an air core transformer. The primary coil is connected to the Pound box and consists of a coil of #24 wire wound on a 5/8 inch phenolic rod such that

the Pound box will oscillate at approximately 10MHz. The number of turns will vary depending on how tightly the coil is wound. The secondary coil was wound with twentyfive turns of #24 wire alongside the primary so that it could be positioned at various distances to adjust the amount of coupling. The secondary was then connected to a shielded cable (RG-62) of 18 inches in length, which in turn was connected to the transducer. A shunt resistor of 10^4 ohms was placed across the secondary coil in order to "smooth" out the impedance curve, thus forcing the Pound box to oscillate at the desired cavity resonance.

Tuning the Matching Network

In order to couple power out of the primary coil, the secondary circuit must be precisely tuned so that its resonance frequency corresponds to the acoustic standing wave condition of the transducer-sample cavity. The primary circuit is easily tuned to this frequency by just varying the tuning capacitor on the Pound box. Both circuits can be tuned simultaneously by connecting a sweep generator (Heathkit T.V. Alignment Generator) across the primary coil and an oscilloscope in order to monitor the impedance curve. Since 10MHz transducers were used, the sweep generator was set so that its center frequency was approximately at 10MHz. The primary circuit was then tuned so that the center of its impedance curve was centered on the oscilloscope display. At this point the secondary coil was

moved close to the primary, approximately 1/2 inch apart, so that the two circuits would be overcoupled and power would be extracted by the secondary circuit. At this point, the two impedance curves should now be seen on the oscilloscope, if not, the number of turns on the secondary should be varied until this is achieved. Now the two curves must be made to overlap. This is accomplished by slightly varying the spacing, ie. the capacitance, of the secondary coil. Once this overlapping has been achieved, spikes will appear on the impedance curve at frequencies corresponding to the acoustic cavity resonance, Fig. 18. The coupling and the frequency are adjusted slightly in order to position one of these spikes on top of the impedance maxima that will determine where the Pound box will oscillate.

Locking-in the Pound Box

After the tuning of the matching network has been accomplished, the sweep generator and oscilloscope are then disconnected. The Pound box is now turned on and allowed sufficient time to warm up. If the Pound box does not break into oscillation, the coupling between the secondary and primary should be decreased. Once oscillation occurs, slowly vary the frequency of the Pound box and slight increases in the level of oscillation, as seen by monitoring the plate current, will occur at regular intervals corresponding to the spikes of the acoustic cavity resonance.

Fig.18 Total primary impedance; reflected secondary impedance included. (A) Drawing (B) Photographed from oscilloscope.

Set the Pound box oscillating on the largest spike and slowly increase the coupling of the matching network to the point when oscillation will cease if the frequency is shifted to either side of the spike. The frequency of the Pound box has now been locked into the resonant frequency of the acoustic system. The Pound box is now sensitive to any losses of acoustic power which will arise when nuclear magnetic resonance occurs.

Sample Preparation and Bonding

The KI sample must be ground so that its faces are parallel in order that acoustic standing waves can be set up. The acoustic waves at 10MHz have a wavelength in the order of 0.1mm. This imposes the restriction that the error in parallelness must be much less 0.1mm. This was accomplished by grinding an aluminum lapping ring on a surface grinder which was parallel to 10^{-4} inches, Fig. 19. The sample was then glued in the lapping ring with wax and the excess of the sample which protruded from the ends was lapped off on an optically flat glass plate. The lapping compound used was fine emery grit mixed with silicone oil. After the sample was lapped parallel, it was given a final polish by rubbing its surfaces on a piece of paper placed on the glass plate. The paper was moistened with acetone for lubrication. This extra polishing made the sample optically transparent.

The sample must now be acoustically bonded to the quartz

Fig. 19 Aluminum lapping ring for holding sample during lapping operation, to insure parallelness.

transducer. The best bonding agent found was paraffin (Standard Oil Parowax) which was applied while the sample and transducer were heated slightly above room temperature on an electric hot plate. The heating was necessary to melt the paraffin into a low viscosity fluid. A piece of aluminum foil had to be bonded between the face of the transducer and the sample to serve as an electrical contact, thus two acoustic bonds must be made. Bonding is accomplished by placing a very small drop of paraffin between each surface and with a slight pressure and circular motion, the liquid paraffin is caused to form a very thin layer between the surfaces. Once the excess paraffin has been squeezed out, the sample is allowed to cool to room temperature until the paraffin hardens. The completed sample and sample holder are shown in Fig. 20. It should be noted that a coaxially plated transducer could have been used which would have eliminated the need for the aluminum foil contact. However, these transducers do not have as large an acoustically active area and the longitudinal wave they generate is not as pure due to mixing in of traces of transverse modes.

Experimental Results

The KI sample was placed in the magnetic field so that the acoustic axis was perpendicular to the applied field for maximum signal of the $\Delta m = \pm 2$ transition, Eq. 56. It is only the $\Delta m = \pm 2$ transition that is of interest since this transition cannot be

Fig. 20 ANMR sample holder, with sample.

produced by stray electromagnetic fields. Only $\Delta m = \pm 1$ is allowed with electromagnetic radiation. The magnetic field was sinusoidally modulated at 280Hz. The output of the Pound box was fed into a lock-in amplifier (E.M.C. Model RJB) and phase detected. The output of the phase detector then went to a R-C filter network to average out random noise. The signal was then recorded on a Varian strip chart recorder (Model G-14).

In searching for the ANMR of ^{127}I in the KI single crystal, the magnetic field was swept at the rate of 1gauss/min. The Pound box frequency was locked-in to the 10.1MHz acoustic cavity resonance. During the search for the $\Delta m = \pm 2$ transitions, the magnetic field must be one half the value it would normally be for the NMR of $\Delta m = \pm 1$ transitions. Therefore, the magnetic field was set at 5.9kilogauss. After running various samples, all of which gave no resonance, the signal was finally observed, Fig. 21. The peak to peak width of the signal, the derivative of the absorption curve, was found to be $3.4 \pm .4$ gauss. The signal is presumably broadened due to straining which may be present. The large amplitude of the field modulation which was of the order of 1gauss would also broaden the resonance. The large modulation was necessary, however, to bring the signal out of the background noise.

The crystals that did not exhibit ANMR were investigated using the conventional Varian NMR spectrometer, described elsewhere in the text. It was found that the normal NMR signals

Fig. 21 ANMR recorded signal of ^{127}I in KI. The derivative of the power absorption curve is shown. Frequency is 10.1MHz, at a magnetic field of 5.9 kilogauss for $\Delta m = \pm 2$ transition.

were less intense than usual. The decrease in intensity was due to random straining of the samples, presumably due to manufacturing. This straining causes the satellite transitions, the only ones observed in ANMR, to be smeared out and therefore not detectable. In order to relieve the straining, annealing had to be performed. After lapping and final polishing, the samples were placed in an oven (Blue M. Model M-15A-1A) and the temperature after five hours came to equilibrium at 460°C . The oven was then shut off and allowed to cool down to room temperature overnight, about 12 hours. When these samples were run again in the conventional NMR spectrometer, their intensity had increased. At this point it was noticed that if the samples were rotated about their cylindrical axes which were perpendicular to the applied external field, the intensity of the resonance would vary. This variation of intensity with angle, indicated that oriented dislocations⁴⁹ were present which had not been annealed out. The samples were then oriented and marked at the position which gave maximum intensity. These samples were run again using ANMR and in all cases, the resonances were observed.

Conclusion

The intensity of the ANMR line is extremely sensitive to slight straining and hence, the ability to observe the resonance depends greatly upon how strain free and perfect the crystal is. Perhaps this explains why certain researchers have

not been able to detect ANMR in alkali halides. The technique of ANMR applied to the study of single crystal metals has not been very successful. To date only tantalum has been observed⁵⁰ with a reasonable signal-to-noise ratio. ANMR has been detected in a single crystal of copper⁵¹ but the resolution of the signal leaves much to be desired. It is assumed that because very pure metallic single crystals are relatively soft they are very likely strained to the point that the ANMR signal is so broadened by nuclear quadrupole interaction that it is undetectable. The problem of broadening the resonance signal is compounded by requiring that the nucleus have a large electric quadrupole moment in order to couple the acoustic power to the nucleus. If these ANMR lines are broad, then a large amplitude of field modulation is required to resolve them. In an attempt to detect ANMR in single crystal metals, vacuum annealed samples of copper, aluminum and niobium were investigated but no resonance could be detected. It is presumed that residual straining and possibly impurities may have broadened these resonances to the point where they could not be detected.

A single crystal of gold is to be tried in the hope that the large electric quadrupole moment of this nucleus will couple acoustic power into the nuclear spin system sufficiently such that the ANMR may be observed.

Finally, since the Pound box is sensitive to small losses

of acoustic power, other phenomena may be observed, for example, acoustic absorption due to de Haas-van Alphen oscillations that occur in single metallic crystals at low temperature⁵². An aluminum single crystal was investigated at a temperature of approximately 1.2°K and at an oscillator frequency of 9.5MHz. The direction of propagation of a transverse acoustic wave and the magnetic field were along a [100] direction. The resulting spectrum given in Fig. 22 is then obtained by sweeping the magnetic field while using a high magnetic field modulation amplitude the order of 50gauss. Investigation of the spectrum reveals two oscillations, one fast due to electrons on the belly of the Fermi surface and one slow due to electrons on the neck of the Fermi surface. It can be seen in Fig. 22 that the signal-to-noise ratio is quite good even though the oscillations were detected at a relatively small applied magnetic field where these oscillations should be relatively weak. Thus this type of acoustic spectrometer is shown to be very sensitive.

Fig. 22 Acoustically detected de Haas-van Alphen oscillations, in a single crystal of aluminum, at an oscillator frequency of 9.5MHz.

REFERENCES

1. E.M. Purcell, H.C. Torrey, and R.V. Pound, Phys. Rev. 69, 37 (1946).
2. F. Bloch, W.W. Hansen, and M.E. Packard, Phys. Rev. 69, 127 (1946).
3. R.W. Guard, J.W. Savage, and D.G. Swarthout, Trans. Met. Soc. 239 643 (1967).
4. D.E. Sands, A. Zalkin, and O.H. Krikorian, Acta Cryst. 12, 461 (1959).
5. Ibid, p. 713.
6. F.W. von Batchelder and R.F. Raeuchle, Acta Cryst. 10, 648 (1957).
7. M.H. Cohen and F. Reif, Solid State Physics, (Academic Press, Inc., New York, 1957) Vol. 5.
8. G.E. Pake, Solid State Physics, (Academic Press, Inc., New York, 1956) Vol. 2.
9. N. Bloembergen, Defects in Crystalline Solids, Report of the 1954 Bristol Conference, p. 1, London (1955).
10. A. Abragam, The Principles of Nuclear Magnetism, (Oxford University Press, London, 1961).
11. E.R. Andrew, Nuclear Magnetic Resonance (Cambridge University Press, London, 1955).
12. C.P. Slichter, Principles of Magnetic Resonance (Harper and Row, New York, 1963).
13. J.H. Van Vleck, Phys. Rev. 74, 1168 (1948).
14. R.V. Pound, Phys. Rev. 79, 685 (1950).
15. R. Bersohn, J. Chem. Phys. 20, 1505 (1952).
16. G.M. Volkoff, H.E. Petch, and D.W.L. Smellie, Can. J. Phys. 30, 270 (1952).
17. A. Abragam, loc. cit., p. 234.
18. R.M. Sternheimer, Phys. Rev. 84, 244 (1951).
19. W.D. Knight, Solid State Physics, (Academic Press, Inc., New York, 1956) Vol. 2.

20. A. Abragam, loc. cit., p. 200.
21. Ibid, p. 202.
22. Varian Manual for the Model V-4200B Wide Line Spectrometer, (Varian Associates, Palo Alto Calif.), Publication No. 87-100-001.
23. G. Aschermann, E. Friederich, E. Justi, and J. Kramer, Z. Physik 42, 349 (1941).
24. Private communication with J. W. Savage.
25. J.E. Adams, B.F. Williams and R.R. Hewitt, Phys. Rev. 151, 238 (1966).
26. Cited by T.H. Geballe et al as a private communication (Reference 17), Physics 2, 293 (1966).
27. C. Froidevaux and D. Rossier, J. Phys. Chem. Solids, 28, 1197 (1967).
28. J.D. Venables, D. Kahn and R.G. Lye, Phil. Mag. 18, 177 (1968).
29. R.M. Sternheimer and H.M. Foley, Phys. Rev. 102, 731 (1956).
30. T.H. Geballe, B.T. Matthias, J.P. Remfika, A.M. Clogston, V.B. Compton, J.P. Maita and H.J. Williams, Physics 2, No. 6, 293 (1966).
31. Engineering Properties of Selected Ceramic Materials (The American Ceramic Society, Columbus, Ohio, 1966).
32. G.V. Samsonov, Russian Chem. Rev., Uspekhi Khimie, 35, 339 (1966).
33. P.O. Van Ostenburg, D.J. Lam, M. Shimizu, and A. Katsuki, J. Phys. Soc., Japan 18, 1744 (1963).
34. N. Bloembergen and T.J. Rowland, Acta Met. 1, 731 (1953).
35. W.H. Jones, Jr., T.P. Graham, and R.G. Barnes, Phys. Rev. 132, 1898 (1963).
36. C. P. Slichter, loc. cit., p.154.
37. W.G. Proctor and W.H. Tantilla, Phys. Rev. 98, 1854 (1955).
38. W.G. Proctor and W.H. Tantilla, Phys. Rev. 101, 1757 (1956).

39. M. Menes and D.I. Bolef, Phys. Rev. 109, 218 (1958).
40. D.I. Bolef and M. Menes, Bull. Am. Phys. Soc. 3, 144 (1958).
41. D.I. Bolef and M. Menes, Phys. Rev. 114, 1441 (1959).
42. M. Menes and D.I. Bolef, J. Phys. Chem. Solids 19, 79 (1961).
43. D.I. Bolef and M. Menes, NMR Acoustic Absorption in KI and KBr, Westinghouse Research Laboratories Scientific Paper 6-40301-1-P1, p. 3, (1959).
44. Ibid, p. 4.
45. Ibid, p. 5.
46. H.J. Zieger and D.I. Bolef, Phys. Rev. 85, 788 (1952).
47. G.D. Watkins, Ph.D. Thesis, Harvard University (1952).
48. D.I. Bolef and M. Menes, NMR Acoustic Absorption in KI and KBr, Westinghouse Research Laboratories Scientific Paper 6-4-301-1-P1, p.11, (1959)
49. H.O. Hooper and P.J. Bray, J. Appl. Phys. 37, 1633 (1966).
50. E.H. Gregory and H.E. Bommel, Phys. Rev. Letters 15, 404 (1965).
51. D.J. Barnes, Nature, 200, 253 (1963).
52. C. Kittel, Introduction to Solid State Physics (John Wiley & Sons, Inc., New York, 1967) p. 290.

AUTOBIOGRAPHICAL STATEMENT

Name: Robert Alexander Bennett

Birth: September 29, 1941, Detroit, Michigan

Family: Married Marilyn Rutkowski on
June 22, 1965

Education: High School Diploma, Mackenzie High
School, Detroit, Michigan, 1959;
Bachelor of Science in Physics, Wayne
State University, 1963; Master of
Science, Wayne State University, 1965.

Professional Membership: The Society of Sigma Xi

Publications: ³⁵Cl Nuclear Quadrupole Resonance
from some Charge-Transfer Complexes,"
Robert A. Bennett and H. O. Hooper, J.
Chem. Phys. 47, 4855 (1967).

"Stroboscopic Pictures of Collisions
on a Linear Air Track," H. Hooper and
R. Bennett, Am. J. Phys. 35, 1172
(1967).

"Strobe Photography of Events on a
Linear Air Track, A Lecture Demonstra-
tion," Robert A. Bennett and H. O.
Hooper, Am. J. Phys. 36, 59 (1968).

"Nuclear Magnetic Resonance Study of
the Niobium-Nitrogen System NbN_x,"
Robert A. Bennett, H. O. Hooper and
U. Roy, J. App. Phys., April, 1969.

"NMR Study of the Crystalline Phases
of NbN_x and NbBe_x," Robert A. Bennett
and H. O. Hooper, Bull. Am. Phys. Soc.
14, 332, March, 1969.

Publications:

"Nuclear Magnetic Resonance Study of the Intermetallic System NbBe^x," Robert A. Bennett, H. O. Hooper, and U. Roy, to be submitted to J. App. Phys..

"Some Techniques in Acoustic Nuclear Magnetic Resonance," Robert A. Bennett and H. O. Hooper, to be submitted.

Name : Robert A. Bennett Approved by:
Major : Physics (Solid State) Date of Approval:
Degree : Doctor of Philosophy
Date of Graduation: June, 1969

Dissertation Abstract

Nuclear Magnetic Resonance Study of the Crystalline Phases of NbN_x and NbBe_x and Supplement on Acoustic Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) has been employed to study the environment of niobium in the systems, NbN_x and NbBe_x . The beryllium resonance was also detected. The γ , δ and ϵ phases of the NbN_x systems were identified by ^{93}Nb NMR spectra through an examination of six NbN_x powdered samples containing varying amounts of the phases mixed together. The crystalline environment of niobium atoms has been identified by the quadrupolar broadening and splittings of the NMR lines obtained for niobium at different sites in the phases present. No appreciable Knight shifts were observed in the NbN_x samples. The quadrupole coupling constants and Knight shifts in several NbBe_x compounds have been obtained and employed to describe the local electronic environment at the Nb and Be sites. Multiple Nb sites in some of the NbBe_x compounds are clearly identified by different quadrupole coupling constants and Knight shifts.

In the supplemental pages, a description of an acoustic nuclear magnetic resonance (ANMR) spectrometer is given. The ANMR of ^{127}I in KI was observed. Preparation of the single crystal KI sample is described.