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MÖSSBAUER EFFECT STUDY OF ^{57}Fe IN
TRANSITION METAL BORIDES

Ph. D. Thesis Submitted to Iowa State University,
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Mössbauer effect study of ^{57}Fe
in transition metal borides

by

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TABLE OF CONTENTS

	Page
ABSTRACT	x
I. INTRODUCTION	1
A. Description of Metal Borides	1
B. Related Mössbauer Effect Experiments	2
II. THEORY	5
A. Present Understanding of Metal Borides	5
1. Three band model	5
2. Electron transfer theory	6
3. Atomic bonding	7
B. The Mössbauer Effect	8
C. Hyperfine Interactions in Metal Borides	10
1. Introduction	10
2. Isomer shift	11
3. Quadrupole coupling	14
4. Magnetic dipole coupling	16
a. Introduction	16
b. Effective field	17
c. Applied field	20
5. Generalized Hamiltonian	22
III. EXPERIMENTAL DETAILS	24
A. Formation of Metal Borides	24
1. Arc melts	24
2. Sintered and annealed borides	25
3. Commercial borides	28
B. Identification of Metal Borides	28
1. Introduction	28
2. X-ray diffraction	30
3. Chemical determinations	31
4. Mössbauer effect analysis	32

C. Mössbauer Effect Techniques	33
1. Source and absorber characteristics	33
2. Electronics	34
3. Low temperature experiments	36
4. High temperature experiments	38
5. Scattering experiments	39
6. Applied field experiments	40
7. Velocity calibration and data analysis	42
IV. X-RAY AND MOSSBAUER EFFECT RESULTS	46
A. Diborides	46
1. Introduction	46
2. TiB_2	46
3. CrB_2	48
4. MnB_2	48
5. FeB_2 and Fe_3B	50
B. Monoborides	51
1. Introduction	51
2. FeB phase	53
a. TiB	53
b. FeB	53
c. MnB	55
d. CoB	60
3. CrB phase	63
a. VB and CrB	63
b. NbB and MoB	63
c. NiB	64
C. U_3Si_2 Type Borides	66
D. Semiborides	73
1. Cr_2B , Mn_2B , and Co_2B	73
2. Fe_2B	75
V. INTERPRETATION OF HYPERFINE PARAMETERS	77
A. Isomer Shift	77
B. Quadrupole Coupling in Monoborides	79
1. Goldanskii-Karyagin effect	79
2. Coupling constants	80

C. Magnetic Effects	81
1. Effective field	81
2. Applied field	85
VI. SUMMARY AND FUTURE WORK	89
VII. REFERENCES	92
VIII. ACKNOWLEDGMENTS	97

LIST OF FIGURES

	Page
Figure 1. Spectra of iron foil with changing temperature	13
Figure 2. Orientation of effective field $\bar{H}_{\text{eff}}$ relative to the electric field gradient	22
Figure 3. Spectrum of commercial FeB at 4.2 K	29
Figure 4. Schematic diagram of the Mössbauer spectrometer	35
Figure 5. Monoboride $\text{Cr}_{0.7}\text{Fe}_{0.3}\text{B}$ spectrum at 77 K	37
Figure 6. Spectrum of FeB melt using scattering techniques	41
Figure 7. Monoboride $\text{Mn}_{0.1}\text{Fe}_{0.9}\text{B}$ spectrum at 4.2 K	45
Figure 8. Diboride AlB_2 structure: a) Atomic arrangement; b) Projection along [001]	47
Figure 9. Projection along the c axis of the orthorhombic monoboride structure: a) FeB; b) CrB	52
Figure 10. Atomic arrangement of βFeB	54
Figure 11. Spectrum of αFeB at 300 K	56
Figure 12. Spectrum of $\text{Mn}_{0.7}\text{Fe}_{0.3}\text{B}$ at 300 K	58
Figure 13. Temperature dependence of $\bar{H}_{\text{eff}}$ and magnetic moment for βFeB	61
Figure 14. Spectrum of $\text{Co}_{0.8}\text{Fe}_{0.2}\text{B}$ at 300 K with an $\text{Fe}_{2-\epsilon}\text{Co}_\epsilon\text{B}$ impurity, where $\epsilon < 0.1$	62
Figure 15. Temperature dependence of $\text{Ni}_{0.1}\text{Fe}_{0.9}\text{B}$ spectrum	65
Figure 16. Orthorhombic $\text{M}_2\text{M}'\text{B}_2$ structure: a) Atomic arrangement; b) Projection along the c axis	68

Figure 17.	Spectrum of Mo_2FeB_2 at 300 K; Γ is the full width at half maximum	70
Figure 18.	Reduced $\bar{H}_{\text{eff}}(T)$ data for Mo_2FeB_2	71
Figure 19.	Projection along the c axis of the CuAl_2 semiboride structure	74
Figure 20.	Spectra of Fe, Fe_2B , and βFeB at 300 K	76
Figure 21.	Variation of isomer shift with atomic percent boron content in metal borides	78
Figure 22.	Variation of electric quadrupole coupling constant with unit cell volume in CrB and FeB type monoborides	82
Figure 23.	Saturation magnetization and effective fields of FeB type monoborides	83

LIST OF TABLES

	Page
Table 1. Prepared transition metal borides	26
Table 2. Experimental isomer shifts (δ) and quadrupole coupling constants $(\Delta = \frac{e^2 q Q}{2})$ in borides	49
Table 3. Parameters derived from Mössbauer spectra of spontaneously magnetic borides	86

Mössbauer effect study of ^{57}Fe
in transition metal borides

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The phase characteristics and nuclear hyperfine properties of sixty different transition metal borides were studied by Mössbauer effect spectroscopy. The prepared mixed iron-transition metal boride phases include MB_2 , M_3B_4 , MB , M_3B_2 , and M_2B types. Transmission experiments with powders were completed in the range 4.2-1000 K; additional scattering and 18kOe applied field data was collected at 300 K. Measured nuclear hyperfine parameters are discussed in terms of atomic bonding, charge transfer, and spontaneous magnetism in the borides. Isomer shift data for all phases indicate an electron transfer from boron to the metal 3d band. The effective magnetic field of ferromagnetic monoborides is proportional to the magnetization, and also reveals a possible charge transfer from B to M. Quadrupole coupling results show a strong ionic contribution to the electric field gradient at the ^{57}Fe nucleus in monoborides. A region of ferromagnetism

below 173 K was found in ternary $M_2M'B_2$ borides, where M is Mo or W and M' is a 3d transition metal. Mössbauer effect studies of FeB reveal two distinct modifications, including a defect α phase.

I. INTRODUCTION

A. Description of Metal Borides

Boron belongs to the family of semimetals whose electronegativities lie in the range 1.8 to 2.2, between the distinct metal and nonmetal values. Each of these borderline elements forms an extensive variety of compounds. Borides are generally defined as the class of boron compounds with either metals or nonmetals which have typical hard, inert, intermetallic character. These and additional useful properties have led to a recent acceleration of interest in borides. New applications continue to appear; intermetallic borides offer an exciting and contributive field of study.

Metal borides are chemically ordered structures with specific atomic compositions. Thus far 150 distinct chemical phases have been indexed. A majority of them form with the transition metals, also true of the other semimetal compounds. The transition metal borides are complex solids combining ionic crystal structure with metallic electrical and magnetic properties. The brittleness and short B-B distances have historically been taken as evidence for covalent bonding interactions. Although the crystal structure of most borides is simple, the basic bonding mechanisms and charge distribution between atoms remains obscure. Available experimental and theoretical knowledge of borides

is summarized in several reviews (1-4).

A major goal of metal boride research is to explain their high temperature stability, brittleness, and hardness in terms of the electron properties. Nuclear magnetic resonance (NMR) experiments have been helpful in describing the environment surrounding boron and transition metal atoms in borides (5, 6). The purpose of this study is to measure additional nuclear hyperfine interactions in a variety of transition metal borides by Mössbauer effect resonance. The results are interpreted in terms of possible electron distributions and bonding mechanisms.

B. Related Mössbauer Effect Experiments

Most of the present information about nuclear hyperfine fields in metallic compounds has resulted from Mössbauer effect (ME) studies using the ^{57}Fe nucleus as a probe. The ^{57}Fe isotope exhibits a large ME resonance, has a known nuclear magnetic moment, and has a long lived parent ^{57}Co . Nuclear resonance techniques have several advantages for the analysis of alloys in general and metal borides in particular. The spontaneous magnetization present in many materials including metal borides is dramatically detected by ME spectroscopy. Variable temperature ME experiments of such magnetic materials give magnetization curves and ordering temperatures. In addition to this magnetic interaction,

nuclear resonance is sensitive to other hyperfine fields. Isomer shift measurements give atomic bonding and valence information. The quadrupole interaction detects charge distribution asymmetry around the site of the resonant nucleus.

As a dilute nuclear probe, the ^{57}Fe content in samples can be reduced to a small amount with little need to know the precise iron concentration. This is true because the ME is a microscopic measurement, sensitive to individual nuclei. The microscopic nature of nuclear resonance is valuable for the brittle borides, often available only in powder form. ME spectroscopy treats the crystallites individually, avoiding the porosity complications of conductivity experiments (7). To complement powder data, surface studies of cast boride melts are possible by Mössbauer scattering techniques.

The range of investigation of transition metal borides by the ME using ^{57}Fe is wide. Solid solution series exist between the FeB , Fe_2B iron borides and isomorphous phases of other transition metals. Unusual ternary borides containing iron also exist although little is known about them. Small iron concentrations dissolve into a variety of other metal boride phases as possible probes of the nuclear environment. Borides offer special opportunities for metal atom studies: the environment of an iron atom can be modified by ordered

boron neighbors without the statistical complications of alloys. Although transition metal borides display several crystal structures, metal and boron atoms normally occupy unique crystal sites. Hence the ^{57}Fe nuclei give simple ME spectra, unlike the complex patterns of iron carbides (8), nitrides (9), silicides (10), and phosphides (11). Nevertheless these other semimetal compounds have been studied more thoroughly by the ME than the borides.

Several ME studies of metal borides have been reported. Systematic variations in effective magnetic field and isomer shift have been studied in Fe, Fe_2B , and FeB (12, 13). The phase Fe_2B has been analyzed by both ME and NMR (14-16). Other related Mössbauer studies deal with FeNiBC alloys (17), mixed boride-phosphides (11), and dilute Fe impurities in boron (18). Finally, the ferromagnetic hexaboride EuB_6 was analyzed using the Mössbauer isotope ^{151}Eu (19).

II. THEORY

A. Present Understanding of Metal Borides

1. Three band model

The transition metals are complex systems and metal borides, complicate the situation further. Nevertheless many efforts have been made to understand the electronic characteristics and resulting physical properties of borides. The work has been largely experimental; energy band calculations have not been attempted for borides as they have for other semimetal compounds (20).

A three band model is often assumed for borides, consisting of conduction electrons, a hybridized $2s2p$ band, and localized $3d$ orbitals (21). Nonlocalized electrons from both the boron and metal atoms are thought to occupy a broad shallow conduction band. Giving rise to a metallic bonding contribution, these electrons move through the lattice of positive ion cores. Such free charges explain the high electrical and thermal conductivity of borides. Secondly, the proposed $2sp$ hybrid band provides a covalent bonding mechanism between boron atoms. The $2s^2$ and $2p^1$ electrons are considered to participate equally in the bonds. Thirdly, the metallic $3d$ electrons are interpreted in the rigid band model. One assumes the density of states curve is fixed as the electron concentration varies, with a sharing of outer

electrons between metal atoms. Thus mixed metal borides are discussed on the basis of the average electron-atom ratio of the constituent metals.

The electronic and magnetic properties of metal borides and the pure transition metals are very similar. Hence 3d electrons belonging to the boride metal atoms are thought to behave as in the pure metal, with the boride properties being largely determined by the degree of filling of the 3d band. The parameters of electron transfer, exchange splitting of 3d subbands, and band energies are often adjusted to explain the correspondence between metal borides and transition metals. These techniques have been critically evaluated by Toth (22). The crystal structures of the transition metal borides are generally not cubic. Hence caution is necessary in assuming similarities between the band structure of borides and metals.

2. Electron transfer theory

Electron transfer theories exist for compounds of several semimetals. Charge transfer evidence has been reviewed for carbides (20), phosphides (23), and borides (5). In transition metal borides with more than 67% boron, indications are that the metal atoms (M) donate electrons to boron. For example the MB_6 octahedral structure requires twenty outer B electrons per formula unit; B atoms alone

provide only eighteen (4). The evidence for MB_2 diborides is inconclusive as to the direction of electron movement. A variety of evidence is available for electron migration in either direction between M and B (3, 5). Less extensively studied, borides with 50% or less boron content give indications that charges move from B to the unfilled metal 3d band. Magnetic properties especially support this view. Contrarily however, recent x-ray and neutron diffraction studies of Fe_2B demonstrate a delocalization of both boron and metal electrons with no noticeable electron exchange between atoms (24).

The electronegativities of B and the transition metals differ by only 10-20% so both atom types will compete for available electrons. Hence electron transfer may depend sensitively on the boride composition. In addition an interatomic electron donor theory is not essential. The presence of boron may stabilize the metal 3d band with respect to the 4s band and promote 4s $\rightarrow$ 3d transfer (25).

3. Atomic bonding

Since electron exchange between boron and metal atoms is uncertain the bonding character is not evident. An actual charge transfer between atoms should contribute ionically to bonding. NMR experiments do give evidence for a partial ionicity in monoborides (5); the ME should also be sensitive

to charged ions in the lattice through the electric quadrupole interaction.

The brittleness of borides suggests strongly directional covalent bonds. Diborides are especially good prospects, with B-B distances of 1.7 - 1.9 Å. However, NMR experiments show a lack of covalency between boron atoms (5). Low temperature specific heat studies extend this apparent lack of covalent bonding to the M_2B semiborides (26). Other covalent bonds of M-M and M-B types have also been suggested (20, 27). Metal atom bonding effects in mixed Fe borides should be measurable by the ME isomer shift interaction.

In addition to ionic and covalent bonding possibilities, the presence of the conduction band suggests a metallic bonding contribution. Hence borides may well be held together by a variety of interactions resembling all of the bonding types. Such a superposition of bonds may occur in general for intermetallic compounds (22).

B. The Mössbauer Effect

Mössbauer effect spectroscopy can be described by comparisons with NMR experiments. Both techniques give information on all interactions which influence the energy levels of resonant atomic nuclei. In NMR a nuclear energy level with nonzero spin I is split by an applied magnetic field $\bar{H}_{app}$. Resonant energy transitions of the order of 10^{-8} ev

between the nuclear levels are induced by a radio frequency generator. The resonance may be scanned by varying $\bar{H}_{app}$. Corresponding ME transitions occur between neighboring nuclear spin states with keV energy differences; no $\bar{H}_{app}$ is needed to lift level degeneracy. In ^{57}Fe the 14.4keV transition showing the resonance effect is between the ground and first excited spin states with respective I values of $1/2$ and $3/2$. ME resonance occurs when a photon emitted from a decaying nucleus is reabsorbed by an identical nucleus in the ground state. The absorption effect is scanned by moving the source or absorber and thereby Doppler shifting the gamma energy. Transmitted or scattered photon intensity is recorded as a function of the relative velocity between source and absorber. In a ME experiment all of the constituent resonant nuclei in the sample are detected with equal sensitivity. The NMR concerns of skin depth and domain wall enhancement in metallic solids are avoided by the ME due to the larger intrinsic resonance energy.

The range of ME studies is limited by a strong condition which governs the resonance process. Gamma emission and absorption by crystal bound nuclei without energy transfer to internal degrees of freedom of the lattice must be possible. This condition prevails when the nuclear recoil energy is comparable to the quantized phonon energies. If the photon does change in energy due to phonon creation or

annihilation during the nuclear transition, resonance is quenched. The portion of transitions where no lattice vibrations are excited is called the recoil-free fraction f .

Mössbauer effect resonance has been observed in forty-two elements; NMR is possible with twice this number. Only NMR applies to the light elements with Z less than 19, since the characteristic large nuclear recoil energies in this region give a vanishingly small f . NMR shows twenty times better resolution of hyperfine energies than ME experiments with ^{57}Fe , 100kHz versus 2MHz. However, the inherently wide ME resonance line is valuable when there is broadening due to anisotropic hyperfine interactions, since NMR resolution is quickly lost. The two methods of nuclear resonance complement each other. In the mixed iron-metal borides useful comparisons are possible between the NMR of boron and metal atoms and the ^{57}Fe ME resonance.

C. Hyperfine Interactions in Metal Borides

1. Introduction

Information about the ^{57}Fe environment in borides is obtained from the hyperfine structure of resonant 14.4keV photons. Hyperfine interactions result from energy coupling between the nucleus and electrons in the solid. This perturbation H_{per} on the free nuclear-electron Hamiltonian produces shifts and splittings of the nuclear energy levels

and therefore of the possible gamma transition energies. Treating the nuclei independently, $\mathcal{H}_{\text{per}}$ for the electronic interaction with an individual nucleus may be written as the sum

$$\mathcal{H}_{\text{per}} = \mathcal{H}_{\text{I}} + \mathcal{H}_{\text{Q}} + \mathcal{H}_{\text{M}} \quad (1)$$

The coupling terms are respectively the electric monopole, electric quadrupole, and magnetic dipole interactions. These $\mathcal{H}_{\text{per}}$ components will be discussed individually and in combination.

2. Isomer shift

The operator $\mathcal{H}_{\text{I}}$ representing the electric monopole interaction causes an isomer shift δ of the Mössbauer spectrum to a lower or higher relative energy. The isomer shift can be expressed as

$$\delta = |N \frac{\Delta R}{R}| \left[|\psi(0)|_s^2 - |\psi(0)|_a^2 \right] \quad (2)$$

where N involves nuclear parameters only, $\Delta R/R$ is the relative change in nuclear radius between the excited and ground states, and $|\psi(0)|_s^2$ and $|\psi(0)|_a^2$ are the total electron charge densities at the source and absorber nuclei.

The energy shift of the photon allows a measure of the absorber's electron density with respect to the source.

A negative isomer shift arises from a decrease in the ^{57}Fe

nuclear level splitting between the $3/2$ and $1/2$ spin I levels as charge density at the resonant absorber nucleus increases. Addition of 4s electrons to an iron atom increases the charge density at the origin; additional 3d electrons increase δ by screening the 3s and 4s electrons. Usually the direct and screening contributions cannot be separated experimentally.

Isomer shifts are much more sensitive to covalent bonding than to ionic surroundings, reflecting the relative effect on s electrons. Detailed studies of chemical bonding are hence often possible by δ measurements. Since the 3s and 4s electrons of ^{57}Fe are strongly shielded by 3d charges, the δ in borides may be partially determined by the number of 3d electrons on the atom. The increase in δ with B content in Fe, Fe_2B , and FeB has thus been interpreted as showing a transfer of boron electrons to the iron 3d band (12).

In comparing Mössbauer effect spectra at different temperatures, the second order Doppler shift due to lattice energy differences must be considered. As an iron boride absorber is heated the intrinsic ^{57}Fe nuclear resonance energy decreases in proportion to the increase in mean kinetic energy of the lattice atoms. The energy shift is thus a linear function of the heat capacity of the particular lattice. Between 300 - 1000 K the shift of the

Figure 1. Spectra of iron foil with changing temperature

^{57}Fe resonance line is 0.55 mm/sec. This effect can be seen in Figure 1, a series of ME spectra of an iron foil absorber. The centroid of the spectrum shifts to lower source velocity as the temperature increases.

3. Quadrupole coupling

Electric quadrupole coupling occurs between a nuclear quadrupole moment $\bar{Q}$ and an electric field gradient (EFG) $\bar{\nabla E}$ at the nuclear site. The interaction is quadratic in the nuclear spin I , splitting the upper $3/2$ level of ^{57}Fe . The EFG is a 3×3 tensor which can be reduced to a diagonal form specified by the three second derivative potential components V_{xx} , V_{yy} , and V_{zz} . The interaction Hamiltonian for a general spin I is written

$$\begin{aligned} \mathcal{H}_Q &= \bar{Q} \cdot \bar{\nabla E} \\ &= \frac{e^2 q Q}{4I(2I-1)} [3I_z^2 - I(I+1) + \eta(I_x^2 - I_y^2)] \end{aligned} \quad (3)$$

I_j is the projection of the nuclear spin I on the j axis, the principal V_{zz} axis is written as eq, and η is the asymmetry parameter,

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad (4)$$

The two eigenvalues $E_{\pm}$ of $\mathcal{H}_Q$ for ^{57}Fe represent possible photon resonance energies

$$\begin{aligned}
 E_{\pm} &= \pm \frac{1}{4} e^2 q Q (1 + \frac{1}{3} \eta^2)^{1/2} \\
 &= \pm \frac{\Delta}{2} (1 + \frac{1}{3} \eta^2)^{1/2}
 \end{aligned}
 \tag{5}$$

where Δ is the electric quadrupole coupling constant.

In unordered borides, Mössbauer doublet quadrupole spectra commonly occur. The metal site is generally one of noncubic symmetry and EFG's are present from the lattice charge distribution and from valence electrons of the atom itself. If ionic bonding is predominant in the solid, quadrupole coupling is sensitive to the lattice constants with the EFG varying inversely with the unit cell volume. If covalent bonds are important, shared electrons often result in a large EFG which masks ionic effects. Hence the change in quadrupole coupling in borides with different metal atoms and lattice parameters is of interest for bonding considerations.

A feature of electric quadrupole spectra receiving increased attention is the intensity asymmetry of the resonance doublet. This Goldanskii-Karyagin effect occurring for both powder and single crystal absorbers arises when there is a crystalline anisotropy of the recoil-free fraction f (28). A crystal direction with a large f implies a strong bonding direction with a small atomic vibrational amplitude. Hence the atom is held tightly along

this axis and a zero phonon nuclear event is more probable than for a small f . Since the boride ME absorbers are polycrystalline, the angle between the incident resonance photon and a crystal axis is random. For this case the quadrupole doublet asymmetry ratios have been calculated as a function of the recoil free fraction ratio A (29),

$$A = f_{11}/f_{\perp} \quad (6)$$

The f_{11} and $f_{\perp}$ represent Mössbauer fractions for incident gamma rays parallel and perpendicular to the crystal axis of highest symmetry, with $A = 1$ for perfect isotropy of f . Hence the relative line intensities of boride quadrupole resonances give information on the directional anisotropy of bonding.

4. Magnetic dipole coupling

a. Introduction When iron nuclei in a ME experiment experience a large magnetic field $\bar{H}$, the familiar six line magnetic dipole radiation spectrum occurs (Figure 1). The nuclear magnetic field may be applied externally as $\bar{H}_{app}$ or may arise as an effective field $\bar{H}_{eff}$ from surrounding magnetic electrons. The interaction $\mathcal{H}_M$ between the nuclear magnetic moment $\bar{\mu}$ and $\bar{H}$ is written

$$\begin{aligned} \mathcal{H}_M &= - \bar{\mu} \cdot \bar{H} \\ &= - g_N \mu_N \bar{I} \cdot \bar{H} \end{aligned} \quad (7)$$

where g_N and μ_N are the nuclear g factor and magneton.

The energy of the nuclear state will change by E_m ,

$$\begin{aligned} E_m &= - g_N \mu_N H m_I \\ &= - \frac{\mu}{I} m_I H \end{aligned} \quad (8)$$

where m_I is the magnetic quantum number with $2I+1$ values.

b. Effective field Details of the origin of the effective field $\bar{H}_{\text{eff}}$ at the nuclear site in a magnetic solid are not well understood. For ^{57}Fe the $\bar{H}_{\text{eff}}$ contributions from unquenched orbital angular momentum and dipole-dipole interactions are small. The major remaining term, the Fermi-contact interaction between the nucleus and unpaired s electron spin densities, is usually considered alone. This contact interaction appears when core and conduction s electrons are spin-polarized by unpaired 3d electrons of the iron atom. The polarization process is complex; a calculation of core polarization by d charges requires unrestricted Hartree-Fock methods (30).

In a ferromagnetic solid a spontaneous magnetic moment arises from the strong exchange coupling between atomic electron spins $\bar{S}$. $\bar{S}$ is written instead of the total angular momentum $\bar{J}$ since the orbital moment is quenched in the transition metals; the crystal field interaction is much stronger than spin-orbit coupling. Hyperfine structure

(hfs) arises from the nuclear-electron interaction

$$\mathcal{K}_{\text{hfs}} = A' \bar{\mathbf{I}} \cdot \bar{\mathbf{S}} \quad (9)$$

where A' is the hfs constant. Considering the $\mathcal{K}_{\text{hfs}}$ interaction as the origin of $\bar{\mathbf{H}}_{\text{eff}}$,

$$\begin{aligned} \mathcal{K}_{\text{hfs}} &= - \bar{\boldsymbol{\mu}} \cdot \bar{\mathbf{H}}_{\text{eff}} \\ &= - g_N \mu_N \bar{I}_z \cdot \bar{\mathbf{H}}_{\text{eff}} \end{aligned} \quad (10)$$

where

$$\bar{\mathbf{H}}_{\text{eff}} = \frac{-A' \bar{S}_z}{g_N \mu_N} \quad (11)$$

Here $\bar{\mathbf{H}}_{\text{eff}}$ is taken in the z direction. Equation 11 is valid for most magnetic iron compounds since s electron polarization is proportional to the number of unpaired 3d electrons. $\bar{S}_z$ is the time average electron spin of the ^{57}Fe atom because the 10^{-8} second nuclear spin precession period is long compared to the fluctuation time of the ordered electron moments. Equation 11 implies that $\bar{\mathbf{H}}_{\text{eff}}$ is proportional to the sample magnetization $\bar{\mathbf{M}}$ for simple ferromagnets. Much experimental work has involved temperature dependent comparisons of $\bar{\mathbf{H}}_{\text{eff}}$ and $\bar{\mathbf{M}}$. The proportionality is found to hold very well for chemically ordered iron alloys (31), so agreement should also be good for the iron borides. $\bar{\mathbf{H}}_{\text{eff}}$ disappears at the magnetic ordering temperature T_c since

the measured time average $\bar{S}_z$ of a paramagnetic sample is zero. T_c determinations by the ME require no extrapolation because the magnetic hyperfine spectrum sensitively collapses to a single resonance line at T_c (Figure 1).

The dominant Fermi-contact interaction involving core electrons contributes negatively to $\bar{H}_{\text{eff}}$. The negative sign means that $\bar{H}_{\text{eff}}$ is antiparallel to the bulk magnetization $\bar{M}$. The polarization of 4s electrons contributes positively to $\bar{H}_{\text{eff}}$ and is small (32). Additional complications of 4s admixture into the 3d band may arise, though the effect on $\bar{H}_{\text{eff}}$ is unknown. In magnetic alloys $\bar{H}_{\text{eff}}$ is often interpreted as the sum

$$\bar{H}_{\text{eff}} = a\bar{\mu}(\text{Fe}) + b\bar{\mu} \quad . \quad (12)$$

The first part is the contribution from the localized 3d spin-magnetization on the iron atom. This is the core polarization term, proportional to the magnetic moment $\bar{\mu}(\text{Fe})$ at the iron site. The second term represents polarization of the conduction electrons; $\bar{\mu}$ is the bulk saturation moment. Many attempts have been made to establish the exact dependency of $\bar{H}_{\text{eff}}$ on localized moments in alloys by evaluation of constants a and b in Equation 12. Unfortunately, in borides local moments have not been measured. The usual thermal neutron scattering methods are difficult due to the large neutron absorption cross section

of boron nuclei. If one assumes that $\bar{H}_{\text{eff}}$ varies linearly with $\bar{\mu}(\text{Fe})$ in boride samples, then $\bar{\mu}(\text{Fe})$ can be determined by ME comparisons with pure iron,

$$\left| \frac{\bar{\mu}(\text{Fe})}{\bar{H}_{\text{eff}}(0)} \right| = \frac{2.22\mu_B}{340\text{kOe}} \quad (13)$$

$\bar{H}_{\text{eff}}(0)$ is the saturation value of the effective field in the sample at 4.2 K; $|\bar{H}_{\text{eff}}(0)|$ in pure iron metal is 340kOe.

c. Applied field A variety of Mössbauer effect polarization experiments are possible using an applied field $\bar{H}_{\text{app}}$. The technique is especially valuable for paramagnetic absorbers, including many transition metal borides. Consider the localized magnetic moment model applied to an array of paramagnetic atoms, each with angular momentum $\bar{S}$ and atomic moment $\bar{\mu}_a$. Depending on the electron relaxation time and temperature T , the $\bar{H}_{\text{app}}$ may induce a net magnetization $\bar{M}(T)$ of the electron moments. This magnetization will have a Brillouin function T dependence due to the interaction between magnetic moments and the lattice. An induced hyperfine magnetic field $\bar{H}_{\text{in}}(T)$ will arise at the nuclear site,

$$\begin{aligned} \bar{H}_{\text{in}}(T) &= C'\bar{M}(T) \\ &= C'\bar{S}B_S(x) \end{aligned} \quad (14)$$

where

$$x = \frac{\mu_a \bar{H}_{app}}{kT} .$$

For small x ,

$$\begin{aligned} \bar{H}_{in}(T) &= \frac{C'S(S+1)\bar{H}_{app}}{3kT} \\ &= C(T)\bar{H}_{app} . \end{aligned} \quad (15)$$

In addition to any induced effects the nuclei will interact directly with the applied field $\bar{H}_{app}$. Therefore the measured field $\bar{H}_{mea}$ responsible for the paramagnetic spectral splitting is

$$\begin{aligned} \bar{H}_{mea} &= \bar{H}_{app} + C(T)\bar{H}_{app} \\ &= \bar{H}_{app}[1 + C(T)] . \end{aligned} \quad (16)$$

Experimentally the sign of $\bar{H}_{in}$ is established from the change in $\bar{H}_{mea}$ with $\bar{H}_{app}$. In the case of ordered solids the signs of both $\bar{H}_{in}$ and $\bar{H}_{eff}$ are determined by $\bar{H}_{app}$.

In applied field experiments the $\bar{H}_{app}$ also polarizes the conduction electrons to produce the Knight shift. The contribution to the nuclear magnetic field from the ordinary Knight shift is 0-2% of $\bar{H}_{app}$. Such a field can only be detected by ME experiments when $\bar{H}_{app}$ increases beyond 50kOe (33).

5. Generalized Hamiltonian

Mössbauer spectra of several magnetic monoborides show a combination of strong electric quadrupole and magnetic dipole hyperfine interactions. The generalized Hamiltonian $\mathcal{H}$ in this case has no closed form solution,

$$\mathcal{H} = -g_N \mu_N H_{\text{eff}} [I_z \cos \theta + (I_x \cos \phi + I_y \sin \phi) \sin \theta] + \frac{e^2 Q q}{4I(2I-1)} [3I_z^2 - I(I+1) + \eta(I_x^2 - I_y^2)] \quad (17)$$

The z direction is chosen along the principal V_{zz} EFG axis. I_i is the i th component of the nuclear angular momentum and the Euler angles θ and ϕ specify the relative orientation of $\vec{H}_{\text{eff}}$ and the EFG tensor (Figure 2). Various special

Figure 2. Orientation of effective field $\vec{H}_{\text{eff}}$ relative to the electric field gradient

cases of $\mathcal{H}$ have been solved by Wertheim (34) and Williams and Bancroft (35). For borides no information is available on the orientation of the magnetic and EFG axes with respect to each other or to the crystal axes, so the most general available solution must be used. This is the case of an asymmetric EFG tensor with any one axis parallel to $\bar{H}_{\text{eff}}$. Eigenvalues of the diagonalized Hamiltonian $\mathcal{H}$ are presented in graphical form for comparison with experimental resonance line positions (36). The hyperfine parameters $\bar{H}_{\text{eff}}$, Δ , η , and the angles θ and ϕ can then be determined.

In the $\mathcal{H}$ solutions, both Δ and η are very sensitive to the positions of the inner ME resonance lines. Hence for the borides these parameter values were compared with least squares calculations (37) and with pure quadrupole Mössbauer spectra above T_c to reduce uncertainties.

When ME data shows combined structure from $\mathcal{H}_Q$ and $\mathcal{H}_M$, the isomer shift is still easily obtained. The centroid of the pattern is the average of the four outer iron resonance lines, without any weighting factors. This is true regardless of the asymmetry of the EFG tensor or the orientation of $\bar{H}_{\text{eff}}$ relative to the EFG principal axes (38).

III. EXPERIMENTAL DETAILS

A. Formation of Metal Borides

1. Arc melts

The Metallurgy Division of the Ames Laboratory prepared polycrystalline boride buttons by melting stoichiometric amounts of the elements together in a vacuum arc furnace. A water cooled copper crucible held the borides at the typical 2500°C melting temperature. Diborides were the most difficult to form, requiring temperatures above 3000°C. On two occasions part of the tungsten electrode was dissolved into the diboride button. Constituent transition metals were of 99.9% purity, except for the Mo which was available only as stock. Therefore the Mo was initially electron beam melted to reduce oxide contamination. The grade AA boron was certified as 99.3% pure. Iron used in samples had a natural 2.17% isotopic abundance of ^{57}Fe and was electrolytically prepared.

Vaporization of the boron during metal boride production due to its high volatility is a common problem, especially for samples with more than 50% boron (39). In this study the only resultant B deficiencies were detected in the diborides. Manganese also has a high vapor pressure at the necessary melting temperatures, but no Mn losses occurred in mixed Mn borides. An additional constituent

loss problem was the spraying of powder from the furnace crucible due to evolution of absorbed gases as the temperature was raised. In such cases where the sample showed a weight loss greater than 4%, it was replaced by a new melt. The produced metal boride samples, generally weighing 0.2 mole, are listed in Table 1.

2. Sintered and annealed borides

During the arc melting process the boride ingots were turned and remelted 6-8 times to ensure homogeneity. Twelve of the samples were additionally annealed in evacuated quartz tubes for 48 hours at 1200°C. It was thought that boride annealing might relieve internal stress and reduce electric field gradients due to crystal imperfections. Since the EFG is directly measured by Mössbauer quadrupole data, sample spectra were recorded before and after annealing. The only variations observed were slight changes in relative intensity of resonance lines; quadrupole coupling did not change. With the exception of the monoboride αFeB which undergoes a phase change at high temperature, sample heat treatments caused no changes in phase composition, lattice parameters, or magnetic properties. Thus the arc melting process alone provides adequate annealing. Several arc melted samples were duplicated by sintering fine powders in the range

Table 1. Prepared transition metal borides

Phase (%B)	Sample	x values		
		Single Phase	Impurity Phases Also Present	Could Not Make
MB ₂ (66%)	Ti _{1-x} Fe _x B ₂			0.1, 0.2
	Cr _{1-x} Fe _x B ₂		0.05	
	Mn _{1-x} Fe _x B ₂		0.05, 0.1	
M ₃ B ₄ (57%)	Mo ₂ FeB ₄	✓		
MB (50%)	Ti _{1-x} Fe _x B		0.1, 0.2, 0.3	0.6, 0.8, 0.9
	V _{1-x} Fe _x B		0.05, 0.1, 0.75	
	Cr _{1-x} Fe _x B	0.05, 0.1, 0.2, 0.3, 0.4, 0.5	0.7, 0.74	0.9
	Mn _{1-x} Fe _x B	0.06, 0.16, 0.27, 0.32, 0.5, 0.8, 0.85, 0.9, 0.95	0.4, 0.45	
	Mn _{1-2x} Cr _x Fe _x B	0.05		
	Mn _{1-2x} Co _x Fe _x B	0.05		
	Mn _{1-2x} Ti _x Fe _x B	0.05		
	αFeB	✓		
	βFeB	✓		

Table 1 (Continued)

Phase (%B)	Sample	x values		
		Single Phase	Impurity Phases Also Present	Could Not Make
M ₃ B ₂ (40%)	Co _{1-x} Fe _x B		0.05, 0.1, 0.2, 0.3, 0.6, 0.7, 0.8, 0.9	
	Ni _{1-x} Fe _x B	0.6, 0.9, 0.93		
	Nb _{1-x} Fe _x B	0.1	0.2	
	Mo _{1-x} Fe _x B		0.1	
	Mo ₂ FeB ₂		✓	
	Mo ₂ Co _{1-x} Fe _x B ₂		0.2, 0.7, 0.8	
	W ₂ FeB ₂		✓	
M ₂ B (33%)	Cr _{2-x} Fe _x B	0.2		
	Mn _{2-x} Fe _x B	0.1		
	Fe ₂ B	✓		
	Co _{2-x} Fe _x B			0.1
	Mo _{2-x} Fe _x B		0.2	

1000 - 1450 K. There are no resultant differences between the two preparation techniques.

3. Commercial borides

The borides FeB and Fe₂B were also obtained commercially from Cooper Metallurgical Associates. The commercial production technique involves co-reduction of Fe and B oxides (4). Arc melted and commercial Fe₂B samples give identical x-ray and Mössbauer effect spectra. Analysis of the commercial FeB shows a 10% Fe₂B impurity phase and a trace of free boron. Figure 3 shows a twelve line computer fit to both iron phases in the FeB Mössbauer spectrum; the weak outer peaks are due to Fe₂B.

B. Identification of Metal Borides

1. Introduction

Several methods were used to identify the phase content of metal boride samples. A thorough analysis is essential because of the variety of possible phases and the preparation difficulties. This is especially true in the formation of mixed Fe-transition metal borides since few systematic solid solution studies have been made. The labeled compositions of samples in this report are the best values, taking into account all of the analytical results. In the several cases where there was a resultant discrepancy

Figure 3. Spectrum of commercial FeB at 4.2 K

in the boride phase stoichiometry, the sample was replaced.

2. X-ray diffraction

All samples were x-rayed by powder diffraction methods and lattice constants were determined with a least squares IBM 360/65 computer program (40). The component diffraction lines of multiphase samples were sorted out before analysis. Comparisons were made with the ASTM interplanar d-spacing index which is presently incomplete in listing boride phases. Therefore x-ray results for many borides were compared either with the crystallographic literature (NbB, α FeB) or with patterns computed on the basis of atom positions in the crystal lattice (Cr_3B_4 , MnB, Mn_2B , NiB, W_2FeB_2). An additional problem is the confusion of kX and $\text{\AA}$ x-ray units in reported boride lattice parameters. The ASTM index and Post (2) list lattice constants for FeB and CoB in kX values but label them in $\text{\AA}$. Hanson *et al.* (41) list boride lattice parameters with a mixture of kX and $\text{\AA}$ values without identifying the units. Other references appear to be correct (3, 42).

Partial information is available on the variation of lattice parameter with composition in mixed metal borides (43). Deviations of 5% from Vegard's linearity rule are common for the solid solutions. In series such as $\text{Co}_{1-x}\text{Fe}_x\text{B}$ where the lattice constants change little between

the end points, compositions were determined from variations in the unit cell volume. Since the scattering factors of Fe, Co, and Ni are equivalent, x-ray patterns of such metal borides are very similar. The characteristic narrow homogeneity range of boride phases is indicated by the reproducibility to within 1% of the lattice parameters. Free boron or boron rich phases are not easily detected by x-rays because of boron's low scattering power. Also unreacted transition metal diffraction lines appear diffuse from the sample grinding process. Nevertheless x-rays remain the most valuable phase analysis technique.

3. Chemical determinations

Wet chemical techniques are standard in the analysis of semimetal refractory compounds (44). In addition to vaporization losses, the stoichiometric determinations are valuable for the detection of defect structures with missing semimetal atoms. A common property of intermetallics, certain carbide phases can have 25-50% of the C sites empty with no crystal phase change (20). Though defect studies are lacking for borides, the problem is probably minor since boride phase homogeneity ranges are very narrow when compared with other semimetal intermetallics. Eighteen of the boride samples including all phase types were examined by the Ames Laboratory Analytical Chemistry Group. Four independent

determinations of element concentrations were made for each sample, generally agreeing to within 0.2%. The chemical content of each of the representative borides was the same as the starting composition to within 0.5%.

4. Mössbauer effect analysis

The ME is a sensitive detector of impurity resonant nuclei in solids. As few as 10^{12} ^{57}Fe nuclei (10 ppb) in an absorber will give a resolved spectrum revealing the chemical environment of the iron. The boride ME measurements show that in mixed iron-transition metal borides, traces of Fe, FeB, and Fe_2B frequently occur. The relative concentration of these impurity phases in samples was determined by comparing areas of the impurity and dominant spectra. These magnetic impurities were often not detected in the x-ray analysis. Since the ME is sensitive only to phases containing iron, the combination of x-ray and nuclear resonance is useful for sample identification. The ordering temperature T_c of magnetic borides often varies rapidly with composition. Since T_c values are known for many metal borides, experimental T_c measurements by ME are also useful for phase analysis.

C. Mössbauer Effect Techniques

1. Source and absorber characteristics

Radioactive sources, kept at 300 K during experiments, were commercial Cu foils containing 10-20 mCi of ^{57}Co . When Co atoms diffuse into copper the nuclear-electron charge density overlap decreases. Hence photons emitted during the 14.4keV transition are increased in energy by 2.4 natural line widths. This energy shift is accounted for by expressing all isomer shifts relative to the midpoint of the absorption spectrum of metallic iron at 300 K. The full width at half maximum (FWHM) of resonance lines of borides and Fe foils was 0.20-0.35 mm/sec. The intrinsic FWHM based on the ^{57}Fe nuclear lifetime for folded source and absorber is 0.19 mm/sec.

For Mössbauer transmission experiments the arc melted boride buttons were crushed to powders of particle size less than 44μ (NBS Mesh No. 325). A uniform layer of the powder was bound to a plexiglass disk between layers of tape. The 2mm thick plastic backing is useful for attenuation of the 6.3keV internal conversion x-rays. The absorbers contain a natural isotopic abundance of ^{57}Fe in areal density of 0.3 mg/cm^2 .

2. Electronics

Decay photons from the ^{57}Co source are Doppler shifted by an Austin K-3 coil-and-magnet vibrator (Figure 4). The source is driven with constant acceleration by a servo amplifier to produce a velocity which is a linear function of time. For these ^{57}Fe experiments the typical sweep frequency was 24Hz with a maximum source velocity of 1.0 cm/sec and 0.02mm displacement amplitude. For driving two source shakers simultaneously a two channel power amplifier was built. The amplifier is available as Kit UT-S from Southwest Technical Products Corp., with gain control modifications necessary for low velocity Mössbauer experiments. Photons are detected with a Reuther-Stokes Kr-CO₂ Model RSG 61 M-2 proportional counter. Energy resolution for the 14.4keV photon is 13%. The discriminated detector pulses are shaped, amplified, and stored in successive channels of a multichannel analyzer (MCA) operated in a time sweep mode. The MCA moves sequentially through its storage channels once for each source vibration cycle. The equal storage time spent in each channel is controlled by a crystal oscillator to ensure that the source velocity scale is linear with channel number. Mössbauer spectra were stored both in 400 channel (RIDL 34-12B) and 4096 channel (NC 25603) analyzers. The NC analyzer was operated in a multiplex mode, with four 512 channel inputs available. Usually two quadrants were

Figure 4. Schematic diagram of the Mössbauer spectrometer

used for simultaneous experiments while the remaining memory monitored the source velocity calibrations.

3. Low temperature experiments

For low temperature experiments the boride absorber disk was clamped unto a copper rod connected to the helium reservoir in a stainless steel cryostat. Vacuum beryllium windows in the dewar tail allowed transmission of the 14.4keV photons. A small resonant absorption intensity from ^{57}Fe impurity nuclei in the Be was also observed (45). Figure 5 shows a four line monoboride spectrum including a weak quadrupole doublet from the dewar windows. The impurity line on the left appears as a hump at -0.2 mm/sec.

The absorber temperature was varied by a manganin wire heater attached to the sample holder and an exchange gas cavity in the Cu rod. With liquid N_2 or He_2 in the dewar, proper control of the gas pressure and heater current permitted experiments anywhere between 4.2-300 K. Temperature was measured with a calibrated Cu/constantan thermocouple. Control to within ± 0.1 K was possible by applying the thermocouple potential difference to a microvolt potentiometer. The error signal due to the potentiometer unbalance was used in an electromechanical feedback arrangement to control the current supply to the sample heater.

Figure 5. Monoboride Cr_{0.7}Fe_{0.3}B spectrum at 77 K

4. High temperature experiments

During Mössbauer experiments between 300-1000 K the boride sample was placed in a Ricor MF-2 vacuum furnace. The 15 ohm Ta coiled heater element in the furnace dissipates a maximum power of 60 watts. The compact furnace allows gamma radiation transmission with a maximum 23° conical angle. External transmission windows are vacuum sealed mylar. There are four concentric thermal shields inside the furnace with aluminum foils mounted in the path of the gamma radiation. During experiments a vertical geometry was used with the source shaker mounted above the furnace. It was found that scaffold vibrations caused resonance line broadening unless the base was firmly anchored. The vertical alignment of the shaker slightly changed the velocity calibration for a given driving voltage as compared with the conventional horizontal arrangement.

Samples were conveniently handled by spreading a uniform layer of powder with 0.3 mg/cm^2 of ^{57}Fe in a boron nitride holder. A highly refractory and fragile material, BN is stable above 3000°C in an inert atmosphere. No reaction between BN holders and transition metal boride samples was evident during the experiments. The sample temperature was monitored with a chromel/alumel thermocouple whose junction was in contact with the BN holder. Temperature was servo-controlled as during cryogenic experiments. The

high thermal conductivity of the metal borides and the highly reflective furnace shields ensured that the sample temperature was uniform with no thermal epoxy required. Since the observed spectra of ferromagnetic materials near T_c showed no line broadening, the sample temperature variation must be less than 2 K over the whole range (46). The furnace thermocouple was calibrated by effective field measurements of Fe foils as a function of T. This ME calibration technique is widely used since $\bar{H}_{\text{eff}}(T)$ reference data is available (47). Calibration changes to a lower thermocouple voltage for a given T occurred over a period of months, perhaps due to absorption of impurities by the thermocouple junction.

5. Scattering experiments

Possible microscopic sample changes due to boride grinding were checked by ME scattering experiments. Alteration of properties by mechanical treatment has been reported for transition metals (48) and phosphides (49). Mössbauer scattering involves resonance of ^{57}Fe nuclei within $\sim 10^{-3}$ cm of the surface of unground boride buttons. One can record either the 6.3keV x-rays or 8keV electrons resulting from ^{57}Co internal conversion, or the 14.4keV transition photons. For unenriched thick absorbers the 14.4keV gamma gives optimum results (50). Although the signal to background improves

with scattering geometry, the counting rate is low. The constant acceleration source motion is useful during scattering experiments of ~36 hours since the spectrum is insensitive to drift in the counting electronics. Best results were obtained with the shielded source and detector at normal angles of 45° relative to the scattering plane.

Scattering spectra were recorded for a variety of boride phases with quadrupole and magnetic hyperfine patterns. Figure 6 shows the scattering spectrum from an FeB melt, plotted directly from the MCA memory. Some geometrical broadening is evident due to the large elliptical $\sim 16 \text{ cm}^2$ scattering area of the sample. In all cases the inverted scattering spectra are similar to corresponding powder transmission patterns. Hence the crushing process has no measurable effect on the EFG homogeneity or $\bar{H}_{\text{eff}}$ value. These negative results agree with ME scattering and transmission studies involving transition metal alloys (51).

6. Applied field experiments

During a series of boride ME experiments the absorber was placed in a 0-18 kOe applied magnetic field. This Harvey-Wells electromagnet field was directed perpendicular to the photon beam. The radioactive source and detector were positioned just inside the 1.75 in gap of the 7 in pole caps. The field at the central absorber position was

Figure 6. Spectrum of FeB melt using scattering techniques

uniform to within 1.0 Oe. An aluminum channel was used for support and as an alignment track. A horizontal 60 cm stainless steel tube with phosphor-bronze spring supports connected the source to the shaker. The copper source matrix is especially suitable for external magnet experiments since line broadening is minimized.

7. Velocity calibration and data analysis

The source velocity was generally calibrated by comparing α Fe foil spectra with reference ME measurements (52). Narrow velocity scans and small isomer shifts were calibrated with a single crystal absorber of Sodium Nitroprusside obtained from the National Bureau of Standards. The absolute zero velocity position was found by standard constant acceleration techniques (53). The ME sign conventions and parameter symbols in this report were chosen in accordance with National Research Council recommendations (52).

Mössbauer effect data was analyzed with a least mean squares computer program (54). A Lorentzian line shape was used to fit the boride resonances. The measure of fit is a minimization function proportional to χ^2 for a given set of velocity increments and corresponding photon counts. A data point typically represents 300K - 1 M counts so the statistical uncertainty is less than 0.2%.

When sample resonance lines were superimposed due to

combined $\mathcal{H}_Q$ and $\mathcal{H}_M$ interactions, intensity and width constraints were imposed on the fitting routine as determined by the remaining resolved lines in the spectrum. This situation appears in Figure 7 for the $\text{Mn}_{0.1}\text{Fe}_{0.9}\text{B}$ monoboride. In cases where outer peaks were unresolved in an ordered spectrum due to a small $\bar{H}_{\text{eff}}$ value, the field was estimated from the relative broadening (33). Each of the $\bar{H}_{\text{eff}}$ versus T experiments required a large number of ME spectra. In these cases the spectral data was reduced visually without computer fitting. In all cases the listed ME hyperfine parameters represent the average of several determinations.

The NC multiplex analyzer was useful for preliminary reduction of data. The analyzer processing section is capable of integration, differentiation, and statistical smoothing of memory content. The additional ability of subtracting one memory quadrant from another was often of value in simplifying multiphase boride data. For example, by storing a reference FeB spectrum in the memory, subsequent FeB impurity resonance lines appearing in other boride spectra could be stripped out by instantaneous analyzer operations. Conversely, compound spectra could be produced by combining resonance lines from separate absorbers. A paper tape library of Fe, Fe_2B , and FeB spectra was established, to be read into the memory whenever any of these phases appeared as a sample impurity. The procedure is efficient, though

it is essential to operate the spectrometer with velocity calibrations and absorber temperatures which are compatible with the library reference spectra.

Figure 7. Monoboride $\text{Mn}_{0.1}\text{Fe}_{0.9}\text{B}$ spectrum at 4.2 K

IV. X-RAY AND MOSSBAUER EFFECT RESULTS

A. Diborides

1. Introduction

Diborides are the hardest and best electrical conducting borides. They are all isomorphic compounds with a simple hexagonal structure. Figure 8 shows the [001] projection and an overall view of the diboride atomic arrangement consisting of alternate honeycomb layers of metal and boron atoms. Both M and B atoms are in axially symmetric sites. Diboride stoichiometry is broad compared with other borides (3). Hence the boron content of MB_2 phases may vary from the exact 67%.

Diborides have received considerable attention in mixed metal studies. Solid solutions readily form when the difference in radii of the metal atoms does not exceed 15% (2). Mixed transition metal diborides are especially compatible for metals in the same period (7). Since FeB_2 does not occur as a pure binary phase, only limited iron substitution into the prepared diborides of Ti, Cr, and Mn was expected.

2. TiB_2

In TiB_2 the attempts to replace 10-20% of the Ti atoms by iron failed. X-ray diffraction gives strong TiB_2 lines alone; ME data shows that all of the Fe is in the pure FeB

(a)

(b)

METAL ATOMS IN $z = 0, c$ BORON ATOMS IN $z = 1/2 c$

Figure 8. Diboride AlB₂ structure: a) Atomic arrangement; b) Projection along [001]

phase. This result is explained by Hägg's (43) empirical formation rule: In a multiphase boride system the metal atom with lower atomic number Z will concentrate in the phase richest in boron. Hence transition metal atoms are more strongly bound to B as Z decreases. This trend is especially true of TiB_2 since Group IV metals form the most stable diborides.

3. CrB_2

The sample $Cr_{0.95}Fe_{0.05}B_2$ was prepared with a 5% Cr_2B impurity also present. This result is different from previous CrB_2 formations where a Cr_3B_4 component usually appeared (6). Although pure CrB_2 is antiferromagnetic with a Néel temperature T_N of 88 K, ME spectra show no magnetic hyperfine structure. Instead an electric quadrupole doublet is present between 4.2-300 K. Independent of temperature, the quadrupole coupling constant is listed with others in Table 2. The lack of magnetic order in the mixed Cr-Fe diboride was expected; substitution of 1% V or Mn into CrB_2 causes a rapid decrease in T_N (17).

4. MnB_2

Two MnB_2 samples were made with 5% and 10% of the Mn atoms replaced by Fe. X-ray analysis in both cases detects the phase FeB and $Mn_{1-\epsilon}Fe_{\epsilon}B_2$ where ϵ is smaller than 0.1.

Table 2. Experimental isomer shifts (δ) and quadrupole coupling constants

$$(\Delta = \frac{e^2 q Q}{2})$$

in borides

Phase (%B)	Sample	Hyperfine Parameters ^a	
		δ^b (mm/sec)	$\Delta = \frac{e^2 q Q}{2}$ (mm/sec)
MB ₂ (66%)	Cr _{1-x} Fe _x B ₂	0.47	0.47
	Mn _{1-x} Fe _x B ₂	0.4-0.47	0.3-0.45
M ₃ B ₄ (57%)	Mo ₂ FeB ₄	0.45	0.75
MB (50%)	Ti _{1-x} Fe _x B	0.0-0.04	0.0
	V _{1-x} Fe _x B	0.33-0.35	0.24-0.3
	Cr _{1-x} Fe _x B	0.34-0.39	0.27-0.36
	Mn _{1-x} Fe _x B	0.34-0.43	0.2-0.32
	α FeB	0.35	0.4
	β FeB	0.39	0.24-0.3
	Co _{1-x} Fe _x B x < 0.5	0.38-0.42	0.57-0.63
	x $\geq$ 0.5	0.35-0.4	0.3-0.4
	Ni _{1-x} Fe _x B	0.39-0.43	0.42-0.44
	Nb _{1-x} Fe _x B	0.0	0.0
	Mo _{1-x} Fe _x B	0.4	0.0

^aFor a given sample, δ and Δ are reproducible to within ± 0.005 mm/sec.

^bIsomer shift values are at 4.2 K, relative to Fe at 300 K.

Table 2 (Continued)

Phase (%B)	Sample	Hyperfine Parameters ^a	
		δ^b (mm/sec)	$\Delta = \frac{e^2qQ}{2}$ (mm/sec)
M_3B_2 (40%)	$Mo_2(Co_{1-x}Fe_x)B_2$	0.22-0.26	0.0
	W_2FeB_2	0.25	0.0
M_2B (33%)	$Cr_{2-x}Fe_xB$	0.29	0.0
	$Mn_{2-x}Fe_xB$	0.20	0.3
	Fe_2B	0.24	0.01
	$Mo_{2-x}Fe_xB$	0.17	0.0

Likewise the ME spectra at 300 K include a $Mn_{1-\epsilon}Fe_\epsilon B_2$ quadrupole doublet plus the six FeB absorption lines. Post (2) mentions that a single phase MnB_2 sample is difficult to make. Low temperature ME spectra are broad unresolved resonance minima. The change must be due to the complex spontaneous magnetic order of MnB_2 below 157 K (55). Attempts to simplify the low temperature spectra by stripping out FeB lines have not yet been successful.

5. FeB_2 and Fe_3B

The possible existence of the phases FeB_2 (56) and Fe_3B (57, 58) was tested by ME analysis. Lattice parameters were originally reported for these iron borides but have not

been reproduced. Since ME spectroscopy should be sensitive to even small concentrations of such phases, attempts were made to prepare and detect them. Results show that neither of the iron borides occur at 300 K. The stoichiometric FeB_2 melt resulted in FeB and free boron; the Fe_3B analysis shows Fe_2B and pure ordered iron.

B. Monoborides

1. Introduction

The monoborides are divided into three structural classes, named for the first identified representatives as FeB, CrB, and MoB types. The FeB and CrB orthorhombic forms were studied by ME. Characterized by chains of boron atoms and a narrow homogeneity range, these two crystals are also common structures of rare earth intermetallics. Both monoborides have the metal atoms at corners of trigonal prisms with a similar atomic environment (Figure 9). Near neighbors to the metal atom M include 6 M's at 2.6-2.7Å, 4 M's at 2.9Å, and 6 B's at 2.15Å. The boron distances are ideal values; x-ray studies accurately yield only the metal atom positions. For comparison the eight near neighbors in pure bcc Fe are at 2.48Å. The prepared FeB type transition metal monoborides include Ti, Mn, Fe, and Co. The CrB types studied are V, Cr, Ni, Nb, and Mo.

- METAL ATOMS IN $x, 1/4, z$ AND $1/2+x, 1/4, 1/2-z$
 ● METAL ATOMS IN $\bar{x}, 3/4, \bar{z}$ AND $1/2-x, 3/4, 1/2+z$
 ○ BORON ATOMS IN $x, 1/4, z$ AND $1/2+x, 1/4, 1/2-z$
 ● BORON ATOMS IN $\bar{x}, 3/4, \bar{z}$ AND $1/2-x, 3/4, 1/2+z$

$$\left. \begin{array}{ll} x_M = 0.180 & z_M = 0.125 \\ x_B = 0.037 & z_B = 0.625 \end{array} \right\} \text{ FOR CoB}$$

- METAL ATOMS IN $0, y, 1/4$ AND $1/2, 1/2+y, 1/4$
 ● METAL ATOMS IN $0, \bar{y}, 3/4$ AND $1/2, 1/2-\bar{y}, 3/4$
 ○ BORON ATOMS IN $0, y, 1/4$ AND $1/2, 1/2+y, 1/4$
 ● BORON ATOMS IN $0, \bar{y}, 3/4$ AND $1/2, 1/2-\bar{y}, 3/4$
 $y_M = 0.146, y_B = 0.440$ FOR CrB

Figure 9. Projection along the c axis of the orthorhombic monoboride structure:
 a) FeB; b) CrB

2. FeB phase

a. TiB The existence of the atypical TiB phase continues to be questioned (4). The M/B radii ratio for TiB is 13% larger than the other monoborides; the unit cell volume is 30% larger. At low temperatures TiB is unstable and shows anomalous specific heat behavior (25). In six attempts no single phase $\text{Ti}_{1-x}\text{Fe}_x\text{B}$ samples were made. For $x < 0.4$ an impurity TiB_2 phase appeared along with $\text{Ti}_{1-x}\text{Fe}_x\text{B}$. The associated ME resonance pattern is a single temperature independent Lorentzian line. If Hägg's rule as discussed for TiB_2 is obeyed, then the iron atoms are dissolved in the TiB phase. For $x > 0.5$ three distinct pure phases were invariably formed: FeB, Fe_2B , and TiB_2 .

b. FeB Two orthorhombic modifications of FeB have been reported with the less familiar αFeB phase forming upon diffusion of B into Fe at 750°C (1, 59). At higher temperatures the αFeB transforms irreversibly to normal βFeB . Both FeB types have the same lattice constants and Curie temperature. X-ray evidence for αFeB is the lack of several diffraction lines present in βFeB . Fruchart (59) suggests a defect arrangement for αFeB with an exchange of atomic positions between an Fe atom and a pair of B atoms lying in adjacent trigonal prisms. Figure 10 shows a model of the βFeB structure with these neighboring Fe and B atoms identified by black rings. The ME ^{57}Fe resonance should be

Figure 10. Atomic arrangement of βFeB

sensitive to crystal changes and resulting magnetic effects in α FeB.

Both α and β forms of FeB were studied by the ME. A series of samples were formed by sintering powders between 750-1200°C. The phase transition from α to β was gradual, proceeding more rapidly as the temperature was raised above 1100°C. The β FeB samples prepared either by sintering or arc melting are identical. Respective FeB α and β ME spectra are shown in Figures 11 and 20. The $\bar{H}_{\text{eff}}(0)$ of the α phase is 14% smaller than that of β FeB. Figure 11 shows that ^{57}Fe nuclei in α FeB see a distribution of hyperfine fields. Hence the metal atoms may be at inequivalent sites as suggested by Fruchart (59). However the proposed exchange of B and Fe atoms would lead to M-M distances less than the separation in pure Fe metal and also a breakup of the boron atomic chains. Such alterations should strongly effect the Curie temperature, but there is no T_c change between α and β FeB.

c. MnB A series of twelve Mn-Fe monoborides were made for ME study. The change in orthorhombic lattice constants of the $\text{Mn}_{1-x}\text{Fe}_x\text{B}$ series has been investigated by Hägg and Kiessling (43); mutual solubility is complete. Manganese, while itself not magnetic, becomes strongly ferromagnetic if Mn atoms are further separated by solute

Figure 11. Spectrum of α FeB at 300 K

B atoms forming MnB. As x increases from zero in $\text{Mn}_{1-x}\text{Fe}_x\text{B}$, the saturation magnetic moment decreases linearly while T_c passes through a maximum at $x = 0.5$ (23). Hence the exchange interaction between magnetic moments is strongly dependent on the metal atom concentrations. Perhaps the situation is similar to Fe-Mn alloys, where the Fe-Mn interaction remains weak while the Mn-Mn and Fe-Fe interactions vary with relative concentration (60).

ME experiments with $\text{Mn}_{1-x}\text{Fe}_x\text{B}$ reveal a variety of features. Regular six line spectra are found for $x < 0.3$, with parameters listed in Table 3. For x values between 0.3-0.5 the usual six line pattern is complicated by a seventh strong resonance peak near zero source velocity (Figure 12). The unknown phase responsible for this central absorption line is not detected by x-ray analysis. In the x range between 0.5-0.9, combined electric quadrupole and magnetic dipole interactions are emphasized by the ME. The resulting shift of resonance peaks is shown in Figure 7 for $x = 0.9$. Hyperfine parameters for this type of spectrum were evaluated by the Kündig graphical technique (36) and tabulated in Tables 2 and 3. Experimental EFG asymmetry parameters and Euler angles for the magnetic monoborides are included in Table 3. The small η values agree with previous NMR experiments (5). The narrow resonance lines shown for $\text{Mn}_{0.1}\text{Fe}_{0.9}\text{B}$ in Figure 7 indicate a unique $\bar{H}_{\text{eff}}$ value for all

Figure 12. Spectrum of $\text{Mn}_{0.7}\text{Fe}_{0.3}\text{B}$ at 300 K

of the ^{57}Fe nuclei. This situation is different from the semiboride $\text{Mn}_{0.1}\text{Fe}_{1.9}\text{B}$ where two separate $\bar{H}_{\text{eff}}$ values arise due to the Mn neighbors (14).

As x increases from 0.0 to 0.7, the ^{57}Fe $\bar{H}_{\text{eff}}$ value decreases linearly (Figure 23). For $0.7 < x < 0.95$ however, the $\text{Mn}_{1-x}\text{Fe}_x\text{B}$ samples have $\bar{H}_{\text{eff}}$ values that deviate from the linear variation with composition. Table 3 shows that the similar magnetic hyperfine fields for the four samples in this range are 11% smaller than that of pure βFeB . The similarity of effective field values and spectral shape to that of αFeB may indicate that these Mn-Fe monoborides also have the α defect structure. Since the samples were arc melted and annealed at 1150°C , Mn must then stabilize the αFeB structure at high temperature. The presence of Ni in M_3B_2 borides has similarly been found to increase the range of phase stability (61). An attempt to make a low Fe content α phase sample of $\text{Mn}_{0.8}\text{Fe}_{0.2}\text{B}$ by sintering at 750°C failed. The normal β phase was obtained just as in the arc melting case. Thus although Fruchart (59) reports a pure αMnB phase, the α structure appears to be limited to the region near pure FeB.

High temperature ME experiments with Mn-Fe monoborides reveal ferromagnetic ordering temperatures and magnetization ($\bar{H}_{\text{eff}}$ versus T) curves. No variation was noted in the reduced $\bar{H}_{\text{eff}}(T)$ curves with Mn concentration, in contrast to

Mn-Fe alloy experiments (62). An example curve for FeB appears in Figure 13, compared with bulk magnetization $\bar{M}$ data and a spin 1/2 Brillouin function. The reduced $\bar{H}_{\text{eff}}$ values for Mn-Fe monoborides are slightly larger than $\bar{M}$. This difference probably arises because the external field in the $\bar{M}$ measurements incompletely aligns the sample electron moments. The magnetization is known to be strongly anisotropic in monoborides (39). Contrarily the microscopic ME is not sensitive to crystal magnetic anisotropy; $\bar{H}_{\text{eff}}$ represents the full atomic spin alignment.

d. CoB As Fe substitutes for Co in diamagnetic CoB, spontaneous ferromagnetism first occurs with 8% iron (62). Figure 14 shows the strong quadrupole spectrum that typically arises for Fe-Co monoborides above T_c . An impurity phase of $\text{Fe}_{2-\epsilon}\text{Co}_\epsilon\text{B}$ is also noticeable in the ME pattern. For samples of $\text{Co}_{1-x}\text{Fe}_x\text{B}$ with $x \geq 0.6$, an Fe_2B impurity phase occurred just as in the $\text{Ti}_{1-x}\text{Fe}_x\text{B}$ monoborides with high Fe content. Hence except for Mn, dilute amounts of transition metals cannot be easily substituted into FeB.

The narrowest resonance lines of all borides studied appeared for the $\text{Co}_{1-x}\text{Fe}_x\text{B}$ samples with $0.05 \leq x \leq 0.25$, indicating an identical environment for each of the iron atoms. The FWHM of the individual quadrupole lines were 0.20 mm/sec, within 6% of the natural width.

Figure 13. Temperature dependence of $\bar{H}_{eff}$ and magnetic moment for βFeB

Figure 14. Spectrum of Co_{0.8}Fe_{0.2}B at 300 K with an Fe_{2-ε}Co_εB impurity, where $\epsilon < 0.1$

3. CrB phase

a. VB and CrB Up to 50% Fe was found to substitute into the CrB type monoborides of V, Cr, and Ni. These mixed metal phases are characterized by quadrupole ME spectra (Table 2). The $\text{Cr}_{0.7}\text{Fe}_{0.3}\text{B}$ pattern is shown in Figure 5 together with a weak doublet from Fe impurities in the beryllium windows of the cryostat. None of the mixed CrB type borides of V, Cr, or Ni showed low temperature magnetic order. However, after the transition to the FeB structure, the spontaneous $\bar{H}_{\text{eff}}$ rises linearly as the iron content increases beyond 50% (Figure 23). Thus dilute amounts of the transition metals V, Cr, and Ni in FeB behave like non-magnetic impurities.

b. NbB and MoB Nb and Mo monoborides with the CrB structure were formed with 10% Fe. The $\text{Mo}_{0.9}\text{Fe}_{0.1}\text{B}$ absorber gives a temperature independent single line spectrum. The two prepared $\text{Nb}_{0.9}\text{Fe}_{0.1}\text{B}$ samples show a single resonance line with large broadening below 100 K. No resolution of individual hyperfine lines is observed, but the FWHM of the broadening has a Brillouin function temperature dependence characteristic of magnetic order. Since pure NbB is non-magnetic (25) and other CrB type structures do not order, this result for the Nb-Fe monoboride is unusual.

c. NiB Since neither Fe nor Ni nuclei are convenient NMR probes, Mössbauer spectroscopy is of special interest in the study of mixed Fe-Ni monoborides. Three $\text{Ni}_{1-x}\text{Fe}_x\text{B}$ samples were made with $x = 0.6, 0.9, \text{ and } 0.93$. The two latter samples have the FeB structure and display pure quadrupole spectra in the unordered state. Below T_c an unusual pattern appears, showing possible superparamagnetic or ferromagnetic relaxation effects (Figure 15). The main features of the $\text{Ni}_{0.1}\text{Fe}_{0.9}\text{B}$ spectra with increasing temperature are a broadening of the magnetic Zeeman lines and a growth of the inner doublet. Superparamagnetism arises in ultrafine (10^2 - $10^3\text{\AA}$) single domain crystallites which have thermally fluctuating moments. The magnetization of such particles averages to zero over the experimental nuclear Larmor period, and paramagnetic effects appear below the bulk ordering temperature. Resulting ME spectra show both a central line and broad magnetic structure from superparamagnetic and larger crystallites (63). To test this possibility six $\text{Ni}_{0.1}\text{Fe}_{0.9}\text{B}$ absorbers with varying minimum particle size between 100 - $10^6\text{\AA}$ were made. All resulting ME spectra are identical; therefore size effect superparamagnetism is not occurring.

Instead, the data may represent ferromagnetic relaxation effects. The $\bar{H}_{\text{eff}}$ at the ^{57}Fe nucleus is proportional to the net atomic spin alignment $\bar{S}$ around the iron atom.

Figure 15. Temperature dependence of $\text{Ni}_{0.1}\text{Fe}_{0.9}\text{B}$ spectrum

If τ is the relaxation time of $\bar{S}$ between hyperfine states and ω_L is the nuclear Larmor frequency, then relaxation phenomena are noticed when

$$\tau \simeq (\omega_L)^{-1} . \quad (18)$$

Long relaxation times are generally unlikely in metallic materials such as $\text{Ni}_{1-x}\text{Fe}_x\text{B}$ borides. However similar spectra which have been accounted for by increasing spin-lattice relaxation times include Ni-Zn ferrites (64) and Fe-Ni alloys (65).

Attempts were made to decrease the electron relaxation rate in $\text{Ni}_{0.1}\text{Fe}_{0.9}\text{B}$ by applying an external magnetic field $\bar{H}_{\text{app}}$. One might expect resulting changes in relative line widths and intensities if ferromagnetic relaxation is present. Unfortunately the application of just 0-5kOe caused a broad minimum to appear, with a loss of resolution of the hyperfine lines.

C. U_3Si_2 Type Borides

Several metal borides of the form $\text{M}_2\text{M}'\text{B}_2$ where M represents a molybdenum or tungsten atom and M' is a 3d transition metal atom were investigated by ME spectroscopy (66). Two crystal systems of these ternary borides occur. Mo_2FeB_2 has a tetragonal structure. Additional tetragonal borides

with Al or Ti for the M atoms and 3d transition metal atoms for M' have also been predicted (67). Orthorhombic phase compounds include:

In general the $\text{M}_2\text{M}'\text{B}_2$ borides have the cementite lattice structure with M atoms forming tetrahedral mosaic layers, the edges of the tetrahedra forming interstitial spaces of triangular prisms and square antiprisms (Figure 16). The boron atoms occupy the triangular prisms between coincident M layers, forming isolated pairs. M' atoms are thought to enter preferentially the closely cubic (5% tetragonal distortion) interstices (68).

The prepared samples $\text{Mo}_2(\text{Co}_{1-x}\text{Fe}_x)\text{B}_2$ with $x = 0.2, 0.7, 0.8, 1.0$, and W_2FeB_2 have the typical hard, brittle character of borides. The x-ray lattice parameters for Mo_2FeB_2 were determined as $a = 6.115\text{\AA}$ and $c = 3.433\text{\AA}$, somewhat larger than previous results (69). A trace of the monoboride phase MoB was detected in the powder pattern. The x-ray of the orthorhombic W_2FeB_2 revealed very weak lines from WB and W_2B impurity phases.

The 300 K Mössbauer spectrum of Mo_2FeB_2 is a single

(a)

(b)

- ⊙ M METAL ATOMS IN $z = 1/2 c$
- M' METAL ATOMS IN $z = 0, c$
- BORON ATOMS IN $z = 0, c$

Figure 16. Orthorhombic $M_2M'B_2$ structure: a) Atomic arrangement; b) Projection along the c axis

Lorentzian line (Figure 17). Weak absorption lines from ordered iron ($|\bar{H}_{\text{eff}}| = 330\text{kOe}$) are noticeable in the background of the spectrum, with absorption intensities 0.03 that of the Mo_2FeB_2 . The pure Fe was not detected in the x-ray analysis; iron diffraction lines may be diffuse due to the crushing process. The Mo_2FeB_2 line width of 0.32 mm/sec indicates that all of the iron atoms are at equivalent sites. Hence the preferential ordering of the iron in the cubic interstices is apparent. The low temperature Mössbauer data displays magnetic hyperfine structure with a 173 K ordering temperature and a small effective saturation field at 4.2 K of 86kOe. In spite of the small magnetic field, the six resonance lines are well resolved below 100 K. If the hyperfine field is proportional to the magnetic moment of the Fe atom, then $\bar{\mu}(\text{Fe}) = 0.59 \mu_B$. The reduced effective field $\bar{H}_{\text{eff}}(\text{T})$ data is shown in Figure 18 together with Brillouin curves.

The additional mixed $\text{Mo}_2(\text{Co}_{1-x}\text{Fe}_x)\text{B}_2$ boride absorbers were prepared to test the extent of magnetic order. Replacing 20% of the iron by Co lowers the ordering temperature significantly to 100 K with no change in $\bar{H}_{\text{eff}}$. The ordering point for 30% Co falls linearly to 79 K with $|\bar{H}_{\text{eff}}(0)| = 75\text{kOe}$. The insensitivity of $\bar{H}_{\text{eff}}(0)$ to iron concentration implies that the Fe atoms are well screened by the Mo matrix. The sample $\text{Mo}_2(\text{Co}_{0.8}\text{Fe}_{0.2})\text{B}_2$ has

Figure 17. Spectrum of Mo₂FeB₂ at 300 K; Γ is the full width at half maximum

Figure 18. Reduced $\bar{H}_{\text{eff}}(T)$ data for Mo_2FeB_2

orthorhombic structure. Absorbers of both this phase and W_2FeB_2 give single asymmetric lines at 300 K. The two compounds do not show resolved hyperfine structure, but between 300 - 4.2 K the respective resonance lines broaden: $Mo_2(Co_{0.8}Fe_{0.2})B_2$ (0.37 $\rightarrow$ 0.5 mm/sec) and W_2FeB_2 (0.6 $\rightarrow$ 1.2 mm/sec). This broadening may arise from several sources:

1. Occurrence of spontaneous magnetic order with a small effective field (18-25kOe in the case of W_2FeB_2).
2. Superimposed spectra from the impurity phases if they contain iron.
3. Fe atoms may be positioned on both M and M' sites.

The chemically ordered Fe atoms in $M_2M'B_2$ borides have eight near M neighbors, just as Fe impurities have when substituted into the bcc Mo and W metals. Mössbauer studies of such dilute alloys with 300 ppm Fe give effective fields of 115kOe for FeMo (70) and 76kOe for FeW (33). Ordering in the ternary borides is presumably ferromagnetic as in these alloys. The alloy-boride structure correspondence indicates that the W_2FeB_2 broadening is probably due to spontaneous magnetic order, though one would expect to find a larger hyperfine field for W_2FeB_2 .

D. Semiborides

1. Cr₂B, Mn₂B, and Co₂B

The CuAl₂ tetragonal crystal system is similar to the U₃Si₂ structure, except that successive metal atom layers are translated by half their base diagonal (Figure 19). Boron atoms occupy the square antiprismatic sites; triangular holes are vacant. Kuentzler (26) reported the preparation of several M_{2-x}Fe_xB semiborides for low temperature specific heat experiments. In this ME study mixed Cr-Fe and Mn-Fe semiboride samples were arc melted. Additional attempts to substitute ⁵⁷Fe as a nuclear probe into Co₂B resulted in Fe_{2-ε}Co_εB and free cobalt.

The Cr₂B half boride has an uncertain chemical composition and two possible structures (3). In previous experiments Cr_{2-x}Fe_xB was found to form in equilibrium with the alloy Fe-Cr (71), but a single phase Cr_{1.8}Fe_{0.2}B sample was successfully made for ME study. Paramagnetic in physical behavior, the ME analysis gives a single narrow resonance line at all temperatures. The semiboride sample Mn_{1.9}Fe_{0.1}B on the contrary has a characteristic quadrupole spectrum (Table 2). These two samples have similar x-ray patterns, but the metal atoms in Mn₂B evidently occupy sites of lower symmetry than in Cr₂B. Such crystal differences between Cr and Mn semiborides have

○ METAL ATOMS IN $Z = 0, 1/2c, c$

● BORON ATOMS IN $Z = 1/2c$

SOLID LINES IN $Z = 0, c$

DOTTED LINES IN $Z = 1/2c$

Figure 19. Projection along the c axis of the CuAl_2 semiboride structure

been suggested by Anderson and Kiessling (72).

2. Fe₂B

It is believed that iron atoms in Fe₂B occupy two inequivalent magnetic sites with unequal magnetic hyperfine interactions (15). This is not evident from the 300 K ME spectrum, which can be fit to just six Lorentzian lines (Figure 20). However, a noticeable line intensity asymmetry does appear at 4.2 K, due to two $\bar{H}_{\text{eff}}$ values differing by 3%.

An unexpected crystal phase transition was noticed during furnace ME experiments with pure Fe₂B. At 700 K the Fe₂B resonance peaks began to weaken and pure Fe resonance lines appeared. As the temperature was raised in 25 K steps with 3 hour intervals between, the Fe₂B pattern grew progressively weaker relative to the iron spectrum. Above 900 K only an impurity Fe₂B spectrum remained with an intensity 10% that of the iron pattern. This spectral ratio remained constant as the sample was cooled back to 300 K, showing the transformation to be irreversible. A final x-ray analysis detected only the diffraction lines of iron metal and a trace of Fe₂B. Although the measured T_c for the Fe₂B component was 1015 K in agreement with others (23), the semiboride phase must be unstable at high temperature when under vacuum.

Figure 20. Spectra of Fe, Fe₂B, and β -FeB at 300 K

V. INTERPRETATION OF HYPERFINE PARAMETERS

A. Isomer Shift

In borides and other metallic systems the isomer shift δ is found to be unexpectedly small and unaffected by alloying. The theoretical δ change occurring with the addition of one 4s electron to a ^{57}Fe (3d)⁷ configuration is 1.4 mm/sec (73). However, the typical δ for borides is only 20% of this value and differs little for dissimilar phases. Apparently each Fe atom polarizes the surrounding electrons to cause a constant net charge density at its nucleus for different compositions of the solid. Since the δ values are small, comparison between individual borides are difficult. Differences in lattice spacing, M/B radii ratio, and metal atom electronegativity will all affect the isomer shift. One interesting correlation appears when δ is plotted against atomic percent boron content for all of the samples studied (Figure 21). A progressive δ increase with atomic % boron is evident, with the exception of Ti and Nb monoborides. Previous ME studies of dilute Fe atoms in boron also show a large positive isomer shift (11). The uncertainty in δ for a given sample is ± 0.005 mm/sec. The larger variation shown in Figure 21 for a given mixed Fe metal boride series reflects δ differences between samples. All of the plotted isomer shifts are 4.2 K values measured

Figure 21. Variation of isomer shift with atomic percent boron content in metal borides

relative to Fe metal. Hence the second order Doppler contribution due to lattice motion is not included; only zero-point motion remains.

A similar variation in isomer shift has been found for the whole range of iron silicide phases, where δ increases with the atomic percent Si content (73). Because of the complex origin of the isomer shift, conclusions are difficult. One appealing interpretation of the δ variation in borides and silicides is a general transfer of semimetal electrons to the transition metal 3d band for all phases. This transfer would reduce the s electron density at the ^{57}Fe nucleus by additional 3d shielding, increasing the δ in proportion to the number of available boron or silicon electrons.

B. Quadrupole Coupling in Monoborides

1. Goldanskii-Karyagin effect

Temperature independent differences in intensity of the powder ME absorption lines are observed for the monoboride quadrupole spectra. The FeB type monoborides including Mn, Fe, and Co have Mössbauer spectra with the higher energy resonance line relatively 4-10% more intense (Figure 14). The only exception is the FeB type $\text{Ni}_{1-x}\text{Fe}_x\text{B}$ with $x > 0.8$ (Figure 15). CrB phase samples including V, Cr, and Ni show an opposite variation with a more intense

low source velocity resonance line (Figure 5). These Goldanskii-Karyagin asymmetry effects in the monoborides determine the recoil free fraction ratio A which appears in Equation 6. The measured relative line intensities indicate that A is 2.0 for CrB type and 0.5 for FeB type monoborides. Since f is small in a direction of weak crystal binding, the results show that the axis of the maximum EFG tensor is a direction of weak binding in FeB and strong binding in CrB. Hence for the two orthorhombic modifications the metal atoms must have dissimilar bonding directions relative to the EFG. However the only metal atom environment differences between the crystal types are small changes in the nearest neighbor distances. The relative bonding strengths must be very sensitive to these interatomic differences. The lack of magnetic order in CrB type crystals as opposed to the ferromagnetic FeB type also shows the importance of these relative spacings.

2. Coupling constants

The ME spectra of CrB type monoborides and FeB phases at paramagnetic temperatures are often characterized by electric quadrupole doublets. The splitting is insensitive to temperature and small. The largest monoboride splittings were observed in $\text{Co}_{1-x}\text{Fe}_x\text{B}$ samples with $\Delta \approx 0.6$ mm/sec; many iron compounds have a splitting 3-4 times this amount. For solid solution series such as the Cr-Fe monoborides the

coupling constant Δ changes little with x . This indicates small distortions from the site symmetry with metal atom substitution, just as found in iron silicides (10).

A variety of quadrupole correlations are possible for the monoborides. One interesting trend is the variation of coupling constant with unit cell volume (Figure 22). This interpretation of Δ tests the possibility that positively charged boron ions in monoboride crystals produce ionic bonding effects (5). Such a lattice contribution to the EFG at a ^{57}Fe site should be inversely proportional to the cell volume. Indeed the quadrupole splitting does get larger with decreasing nearest neighbor distances; linearity is uncertain from the available data. The similarity of the variations for both the nonmagnetic CrB and ferromagnetic FeB type monoborides is unexpected. Quadrupole coupling constants for the FeB type crystals should be strongly affected by the unpaired 3d electrons responsible for the magnetism.

C. Magnetic Effects

1. Effective field

Figure 23 shows a summary of saturation magnetization (24) and $ME \bar{H}_{\text{eff}}(0)$ data for the magnetic monoborides. The proportionality $105\text{kOe}:1.0\mu_B$ appears to hold for all of the magnetic monoborides except those $\text{Mn}_{1-x}\text{Fe}_x\text{B}$ samples with

Figure 22. Variation of electric quadrupole coupling constant with unit cell volume in CrB and FeB type monoborides

Figure 23. Saturation magnetization and effective fields of FeB type monoborides

$0.7 < x < 0.95$. Only the defect α phase occurred in this range of Mn-Fe monoborides; all data points in Figure 23 represent the normal βFeB type structure. The linear relation for the bulk moment and $\bar{H}_{\text{eff}}(0)$ indicates an averaging effect between the moments of the constituent metal atoms as in the rigid band model. Between the CrB and NiB limits where ferromagnetism disappears, the monoboride magnetization curve is similar to the Slater-Pauling curve of the pure 3d transition metals. The boride curve reaches an abrupt maximum at MnB. Attempts to make samples such as $\text{Mn}_{.95}\text{Cr}_{.05}\text{B}$ with a larger saturation moment than MnB have failed thus far, since the FeB structure quickly transforms to the nonmagnetic CrB type. The extrapolated ^{57}Fe $\bar{H}_{\text{eff}}$ value in $\text{Mn}_{1-x}\text{Fe}_x\text{B}$ for $x \rightarrow 0$ is 226kOe, also the ^{55}Mn nuclear field in pure MnB as determined by NMR (74).

From Figure 23, MnB and FeB appear magnetically equivalent to Co and Ni metals, respectively. The correspondence may arise because of a transfer of ~ 2 boron electrons to the metal 3d band. The possibility also exists for a partial $4s \rightarrow 3d$ electron transfer on the iron atom itself. The magnetization curve for semiborides (23) also shows the Slater-Pauling type behavior. Mössbauer effect measurements on ordered series of semiborides would be of interest in further testing the relation between saturation moment $\bar{\mu}$ and hyperfine field $\bar{H}_{\text{eff}}$.

Two systematic variations in the $\bar{\mu}$ and $\bar{H}_{\text{eff}}$ values for boride phases are apparent from Table 3 (32):

1. With increasing boron content, both $|\bar{H}_{\text{eff}}|$ and $|\bar{H}_{\text{eff}}/\bar{\mu}|$ linearly decrease:

2. For a given crystal structure, $|\bar{H}_{\text{eff}}/\bar{\mu}|$ and $|\bar{H}_{\text{eff}}|$ decrease with metal atomic number:

Thus the general effect of boron atoms is to decrease the $|\bar{H}_{\text{eff}}/\bar{\mu}|$ ratio for a transition metal. Equation 12 shows that this ratio decreases as the positive conduction electron polarization contribution to $\bar{H}_{\text{eff}}$ increases relative to the negative core polarization. Boron electrons may be entering either 3d or 4s iron levels. A filling of the d band will decrease core polarization; direct contributions to the 4s shell will have the same resultant effect on $\bar{H}_{\text{eff}}$.

2. Applied field

The $\bar{H}_{\text{eff}}$ of all magnetic transition metal borides decreases when an external field $\bar{H}_{\text{app}}$ is applied. Hence $\bar{H}_{\text{eff}}$ has the usual opposite direction relative to the magnetization. The decrease of $\bar{H}_{\text{eff}}$ in FeB and Fe_2B corresponds exactly to $\bar{H}_{\text{app}}$, showing a demagnetization factor of unity. The presence of $\bar{H}_{\text{app}}$ does not induce a net magnetization in any of the unordered borides. In all cases the resonance

Table 3. Parameters derived from Mössbauer spectra of spontaneously magnetic borides

Phase (%B)	Sample	x	$ H_{\text{eff}}(0) $ (kOe)	T_c (K)	$\eta(\pm 0.1)$	$\theta(\pm 10^\circ)$	$\phi(\pm 10^\circ)$
	Fe Metal		340	1043			
M_3B_4 (57%)	Mo_2FeB_4		75	90			
MB (50%)	$V_{1-x}Fe_xB$	0.75	71	325			
	$Cr_{1-x}Fe_xB$	0.7	100	560			
		0.74	112	570			
	$Mn_{1-x}Fe_xB$	0.06	208	620			
		0.16	201	740	0.0	85	90
		0.27	189	775			
		0.32	182	783	0.0	90	90
		0.5	170	791	0.1	85	90
		0.6	142	780	0.15	90	90
		0.7	122	755			
		0.8	112	720			
		0.85	104	696	0.1	90	90
		0.9	104	655	0.0	80	
		0.95	106	620			
	$Mn_{1-x}Cr_xFe_xB$	0.05	200	590			
	$Mn_{1-x}Co_xFe_xB$	0.1	189	625			
	βFeB		124	590	0.15	90	90
	αFeB		102-116	590			

85

Table 3 (Continued)

Phase (%B)	Sample	x	$ H_{\text{eff}}(0) $ (kOe)	T_c (K)	$\eta(\pm 0.1)$	$\theta(\pm 10^\circ)$	$\phi(\pm 10^\circ)$
M_3B_2 (40%)	$Co_{1-x}Fe_xB$	0.6	46	360	0.15	85	90
		0.7	80	440			
		0.8	93	480			
		0.9	124	516			
	$Ni_{1-x}Fe_xB$	0.9	116	345	0.0	90	90
		0.93	119	380			
	$Nb_{1-x}Fe_xB$	0.1	73	100			
	Mo_2FeB_2		86	173			
	$Mo_2(Co_{1-x}Fe_x)B_2$	0.7	75	79			
		0.8	86	110			
M_2B (33%)	Fe_2B		247	1015	0.0	50	90

line broadening corresponds closely to $\bar{H}_{app}$, showing a direct interaction between the nuclear magnetic moment and the applied field. Hence although a strong local moment character is predicted for several borides (39), the $C(T)$ parameter in Equation 16 is found to be zero. Perhaps a larger $\bar{H}_{app}$ would show an induced contribution to $\bar{H}_{eff}$. Applied superconducting fields of 50kOe are commonly used in such experiments (33).

VI. SUMMARY AND FUTURE WORK

The phase characteristics and hyperfine properties of sixty different transition metal boride samples were studied by ME transmission and scattering spectroscopy. Phases were identified by several methods including determinations of lattice constants, magnetic ordering temperatures, and chemical stoichiometry. No differences were found between sintered and arc melted samples. The nuclear hyperfine parameters of polycrystalline powders and uncrushed button melts are also similar.

Major experimental attention was given to the monoborides, both because of successful single phase preparation and because of the interesting region of ferromagnetism in FeB type crystals. The magnetic hyperfine data for several of these monoborides was sufficiently precise to determine the EFG asymmetry parameter and the EFG orientation relative to $\bar{H}_{\text{eff}}$. Monoboride $\bar{H}_{\text{eff}}$ values reveal a rigid band model variation with composition, similar to transition metal alloys. $\bar{H}_{\text{eff}}$ is closely proportional to the bulk magnetization of monoborides. Comparison of magnetization curves of monoborides and transition metals indicates the addition of ~ 2 electrons to the 3d band of each boride metal atom. Such electrons may be transferred from boron atoms and from the metal 4s band. Narrow magnetic hyperfine resonance lines

in borides show a closely uniform effective field at Fe atomic sites. The occurrence of both α and β phases of FeB was verified by differences in the respective ME spectra. This is the first proof of two FeB modifications since Fruchart's initial x-ray work (59) in 1959. The α defect structure was also found in mixed Mn-Fe monoborides with 30% or less Mn.

Ferromagnetism and preferential atomic ordering was detected in certain ternary borides of the form $M_2M'B_2$, where M is Mo or W and M' is a transition metal. Curie temperatures and saturation hyperfine fields were determined for the spontaneously magnetic samples. The ease of substitution of Fe into $M_2M'B_2$, MB_2 , and M_2B phases may indicate a similarity of bonding of the metal atom in the different boride phases.

The isomer shift δ trend for all of the boride samples can be interpreted in terms of a general transfer of electrons from boron to metal atoms for phases with 33-66% boron. This conclusion is not unique; the δ variation may also be due to a rearrangement of the electrons belonging to the iron atom. The magnitude of δ and its insensitivity to different boride compositions implies an ionic bonding environment for ^{57}Fe . Quadrupole coupling constants of CrB and FeB type monoborides also show a variation with unit cell volume that is characteristic of significant ionic

bonding effects.

Several areas touched upon in this report of ME experiments require further study, including the following:

1. The extent of ferromagnetic relaxation in the Fe-Ni monoboride series is not known. The relaxation phenomenon might be further clarified by use of the difficult ME isotope ^{61}Ni .
2. The spontaneous magnetism found in $\text{Nb}_{0.9}\text{Fe}_{0.1}\text{B}$ is unexplained.
3. Stability studies of Fe_2B are of interest following the decomposition of the Fe_2B phase during high temperature ME experiments.
4. The ^{57}Fe $\bar{H}_{\text{eff}}$ field variation in the $\text{Co}_{2-x}\text{Fe}_x\text{B}$ semiboride series is dissimilar to other metal borides (16).
5. ME determinations of the recoil free fraction f in single crystal monoboride crystals would be valuable for further study of lattice dynamics as a function of the crystal axes.
6. The boride phases αFeB , Mo_2FeB_2 , and Mo_2FeB_4 have received little experimental attention. Similar compounds with a variety of other metal atoms may exist.

Transition metal borides indeed display an intriguing variety of properties.

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