Mössbauer Effect Study of ^{57}Fe in Transition Metal Semiborides
and Two-Dimensional Ferrous Chloride Complexes

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Mössbauer effect study of ^{57}Fe in transition metal semiborides
and two-dimensional ferrous chloride complexes

by

James Lamont Schurter

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Mössbauer effect study of ^{57}Fe in transition metal semiborides
and two-dimensional ferrous chloride complexes

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The nuclear hyperfine properties of $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$ and $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{FeCl}_4$ were studied by Mössbauer effect spectroscopy. The effective hyperfine fields as a function of temperature were determined by transmission experiments using powdered samples. Isomer shifts and quadrupole splittings were also determined. Methylammonium ferrous chloride and benzylammonium ferrous chloride appear to exhibit two-dimensional magnetic structure, and the hyperfine parameters were interpreted in terms of the two-dimensional Ising model.

The nuclear hyperfine properties of $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ where $x=0.2$ and 0.5 were also studied by Mössbauer effect spectroscopy. An unsuccessful attempt was made to produce $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ for x equal to 0.8 , 1 , 1.2 , 1.5 and 1.8 . In every case, X-ray spectroscopy revealed Mo_2FeB_2 and free iron. The effective fields of powder samples of $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$ and $\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$ as a function of temperature were determined by transmission

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experiments. The lack of dependence of the isomer shift, transition temperature, and hyperfine field of iron in $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ on iron concentration indicates that the iron in the Mo_2B matrix is well screened. Isomer shift data may be interpreted as suggesting an electron transfer from boron to the metal 3d band.

I. INTRODUCTION

A. General Discussion

The discovery of recoil free emission and resonant absorption of nuclear gamma rays in solids by Rudolf L. Mössbauer (1) in 1958 made available to the experimentalist a tool of amazing sensitivity. Using the Mössbauer Effect (M.E.) it is now possible to detect changes in gamma ray energies to one part in 10^{13} (2). This means that the experimentalist can easily resolve the hyperfine splitting of nuclear energy levels caused by the magnetic dipole and electric quadrupole interactions. The hyperfine splitting thus observed directly reflects the nuclear environment. Since the M.E. has become widely used, and is the subject of a great number of books and articles, only a short discussion of it will be given here. The M.E. is treated in detail by Frauenfelder among others (3).

When one considers the emission of a gamma ray by a nucleus bound in a lattice, three different situations should be recognized. If the recoil energy of the nucleus is larger than the binding energy of the atom, the atom will recoil right out of its lattice site. If the recoil energy is less than the binding energy of the atom, but greater than the phonon energy, the atom will heat the lattice, but will not be removed from its site. The case of particular interest here, however, is when the recoil energy is less than the phonon energy. In this situation, since the lattice is a quantum mechanical system, no mode of energy dissipation is available to the nucleus undergoing decay, and

the gamma ray is emitted without the recoil of the individual atom. In the zero-phonon emission process the line width is completely determined by the widths of the nuclear levels involved. This means that for ^{57}Fe , the source used in these experiments, which has a half-life of 10^{-7} seconds, the line width is $\sim 10^{-8}$ eV. A decay scheme of ^{57}Fe is shown in Figure 1.

The maximum cross section σ_0 , for resonance absorption is given by

$$\sigma_0 = \frac{\lambda^2}{2\pi} \frac{1 + 2I_e}{(1 + 2I_g)(1 + \alpha)} \quad (1)$$

where I_e is the nuclear spin of the excited state, I_g is the nuclear spin of the ground state, and α is the internal conversion coefficient. This cross section is $2.2 \times 10^{-18} \text{ cm}^2$ for ^{57}Fe , or about 200 times greater than the cross section for photoelectric absorption, the next most important process.

The Breit-Wigner formula

$$\sigma(E) = \sigma_0 \left[1 + A \left(\frac{E - E_0}{\Gamma} \right)^2 \right]^{-1} \quad (2)$$

where E_0 is the nuclear transition energy and Γ is the full line width at half maximum absorption (FWHM), gives the energy dependence of the absorption cross section. The experimentally observed line shape, for thin absorbers is just the sum of the source and absorber lines. The Lorentzian lines of the M.E., therefore, have a linewidth just equal to twice the linewidth of the emitted gamma ray, if both the source and absorber exhibit this natural linewidth.

Figure 1. Decay scheme of ^{57}Fe

The two topics considered here are well suited to study using the M.E. Both systems contain enough iron so that enrichment is not necessary, and since iron can be used as the source, no cooling of the source is necessary.

The case of interest is that in which the energy levels of iron in the absorber are split by the presence of a magnetic dipole and an electric quadrupole interaction. If we consider the case for ^{57}Fe (i.e. a $3/2 \rightarrow 1/2$ magnetic dipole transition), the Hamiltonian can be written as the sum of the two expressions:

$$H_Q = [e^2 Q V_{zz} / \{4I(2I-1)\}] [3I_z^2 - I(I+1) + \eta (I_x^2 - I_y^2)] \quad (3)$$

$$H_M = -g\mu_N H(0) [I_z \cos \theta + (I_x \cos \phi + I_y \sin \phi) \sin \theta] \quad (4)$$

where e is the charge of a proton; Q is the electric quadrupole moment; V_{zz} is $\partial^2 V / \partial z^2$, where V is the electrostatic potential; I is the spin of the nucleus; I_x, I_y, I_z are the matrices of the angular momentum operator; η is the asymmetry parameter of the electric field gradient defined as $\eta = (V_{xx} - V_{yy}) / V_{zz}$ where the components are chosen such that $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$; g is the nuclear g -factor; μ_N is the nuclear magneton; θ and ϕ specify the orientation of $H(0)$ with respect to the electric field gradient as shown in Figure 2.

If $H(0)$ is perpendicular to V_{zz} , then one can show (4) that the energies of the substates of the excited state are

$$E_{1,3} = (1/2)g\mu_N H(0) \pm (1/4)e^2 V_{zz} Q [\{(1/2)(1+\eta) - 4g\mu_N H(0)/e^2 V_{zz} Q\}^2 + (1/12)(3-\eta)^2]^{1/2} \quad (5)$$

Figure 2. Orientation of $H(0)$ with respect to the electric field gradient, where $H(0)$ is the hyperfine field at the nucleus

$$E_{2,4} = -(1/2)g_e\mu_N H(0) \pm (1/4)e^2V_{zz}Q \left[\{1/2\}(1+\eta) + 4g_e\mu_N H(0)/e^2V_{zz}Q \right]^2 + (1/12)(3-\eta)^2 \right]^{1/2} \quad (6)$$

where g_e is the nuclear g-factor of the excited state, and all other quantities are as previously defined. A level diagram is shown in Figure 3 for $6g_e\mu_N H(0) > e^2V_{zz}Q$.

For the general case, there is no closed form solution. A computer program has been written (5) which solves numerically the complete interaction Hamiltonian. Utilizing this program, one can determine: $H(0)$; the ratio of the quadrupole interaction to the magnetic interaction; θ ; ϕ ; and η ; for the systems being studied here.

B. Two-dimensional Magnetism

Magnetism has, since its discovery, been a topic which has generated considerable interest. Its many facets are not only of themselves intriguing, but its practical applications have been of great importance to the modern world. The study of magnetism, however, becomes rapidly difficult. If, following the lead of Heisenberg and Dirac, one writes the magnetic interaction (exchange interaction) as

$$H = 2 \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j \quad (7)$$

where $\vec{S}_i$ is the total spin operator for the atom on the i^{th} lattice site; and J_{ij} , the exchange integral, is a function of the relative sites i and j ; one is faced with an expression which cannot be solved exactly in three dimensions. Two alternatives to this problem readily

HYPERFINE SPLITTINGS OF THE GROUND
AND 14.4 Kev STATE OF ^{57}Fe WITH
 $6g_e\mu_N H(0) > e^2 V_{zz} Q$ WHERE $H(0) \perp V_{zz}$

Figure 3. Hyperfine splittings of the ground and 14.4 Kev state of ^{57}Fe with $6g_e\mu_N H(0) > e^2 V_{zz} Q$ where $H(0) \perp V_{zz}$

appear. One can make theoretical approximations of a simplifying nature, or one can simplify the situation experimentally by searching for physical systems which exhibit one or two-dimensional magnetism. Unfortunately, linear chains of interacting spins do not exhibit long range ordering (6). Therefore, two-dimensional systems provide the simplest examples of phase transitions. Systems which very closely approximate two-dimensional quadratic layer antiferromagnets have recently been studied (7), resulting in a renewed interest in two-dimensional magnetism.

Compounds of the form $(\text{RNH}_3)_2\text{FeCl}_4$ where $\text{R}=\text{CH}_3$ (methyl) or $\text{C}_6\text{H}_5\text{CH}_2$ (benzyl) are two-dimensional quadratic layer antiferromagnets. Single crystal structure analysis was not carried out because of the poor quality of the crystals. However, powder pattern studies (8) of $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$ indicate a structure similar to that shown in Figure 4. Of particular interest are the metal-halogen sheets, the separation of which depends on the length of the substituted ammonium cation. Thus, these layers are effectively isolated from one another, and a two-dimensional structure is very closely approximated.

A more detailed discussion of two-dimensional magnetic structures is found in Section II.

C. Semiborides

The study of binary systems between various metals and boron has revealed many interesting and useful results. In general, these borides

Figure 4. Tetragonal structure of $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$

exhibit many metallic characteristics, have a high melting temperature, and are hard and inert. Transition metal borides have received considerable attention (9), and many technical uses are being found for these systems.

Metal borides of the form $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ present an interesting system for study by Mössbauer transmission spectroscopy. The Mössbauer effect is particularly useful in studying dilute iron impurities, since it is possible to obtain a resolved spectrum with as little as 10 ppb ^{57}Fe present in the sample. This sensitivity is useful in studying the semiborides since impurities containing iron, which are too dilute to be seen in X-ray patterns, will still be detectable using the standard Mössbauer techniques.

In general, boron atoms form chains, nets, or 3-dimensional frameworks (10) as the atomic percent of boron increases in metal-boron systems. However, a few systems, primarily semiborides, contain only isolated boron atoms. $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ is a member of this group, and is of the CuAl_2 (C-16) type. Figure 5 depicts the CuAl_2 structure. It will be noted that the metal atoms form successive layers which are translated by half their base diagonal. The triangular holes thus formed are vacant, while the square antiprismatic locations are occupied by the boron atoms.

Using Mössbauer spectroscopy the magnetic hyperfine parameters of Fe_2B , $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$, and $\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$ have been determined.

- BORON ATOMS IN $Z = 1/4, 3/4$
- METAL ATOMS IN $Z = 0, 1/2, 1$
- SOLID LINES IN $Z = 0, 1$
- DOTTED LINES IN $Z = 1/2$

Figure 5. C-axis projection of the CuAl_2 structure of the semiborides

II. THEORETICAL DISCUSSION

A. Introduction

In this section the existing theory which is directly applicable to the work presented will be considered. This will be divided into two parts: a discussion of the Ising model in two dimensions as it pertains to the measurements made on the $(\text{RNH}_3)_2\text{FeCl}_4$ compounds, and an examination of the magnetic interaction between localized moments as it pertains to the measurements made on the $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ system.

B. Two-dimensional Ising Model

The two-dimensional Ising model is discussed in detail in several texts on magnetism and solid state physics (11,12); also, there are many papers which consider the Ising model. The following discussion is based, in large part, on an article written by M. E. Fisher entitled, "The Theory of Equilibrium of Critical Phenomena," and published in 1967 in the Report on the Progress in Physics.

If it can be assumed that the electronic spins are sufficiently localized on lattice sites, then the Ising-Heisenberg magnetic Hamiltonian can be written as:

$$H = -2 \sum_{\vec{r}, \vec{r}'} \{ J_{11}(\vec{r}-\vec{r}') S_{\vec{r}}^z S_{\vec{r}'}^z + J_{\perp}(\vec{r}-\vec{r}') (S_{\vec{r}}^x S_{\vec{r}'}^x + S_{\vec{r}}^y S_{\vec{r}'}^y) \} - g\beta_B \sum_{\vec{r}} \vec{S}_{\vec{r}} \cdot \vec{H}_{\vec{r}} \quad (8)$$

where $\vec{S}_{\vec{r}}$ is the spin on the lattice site denoted by $\vec{r}$, $J_{11}(\vec{r})$ and $J_{\perp}(\vec{r})$ are the exchange integrals along and perpendicular to the easy

axis, respectively, g is the nuclear g -factor, β_B is the Bohr magneton, and $\vec{H}_{\vec{r}}$ is the external field on the site $\vec{r}$. $J_{11}(\vec{r}) = J_{\perp}(\vec{r}) = J(\vec{r})$ corresponds to the pure isotropic Heisenberg Hamiltonian, and the anisotropic limit, $J_{\perp}(\vec{r}) = 0$, corresponds to the Ising model Hamiltonian. If no externally applied magnetic field is present, and the scalar variables $S_{\vec{r}} = 2S_i^z = \pm 1$ (since $S = 1/2$) are introduced, then the Ising model Hamiltonian can be written

$$H = - \sum_{\vec{r}, \vec{r}'} 1/2 J_{11}(\vec{r}-\vec{r}') S_{\vec{r}} S_{\vec{r}'}, \quad (9)$$

and the partition function becomes

$$Z = \sum_{S_{\vec{r}} = \pm 1} \exp \left\{ \sum_{\vec{r}, \vec{r}'} 1/2 \beta J_{11}(\vec{r}-\vec{r}') S_{\vec{r}} S_{\vec{r}'} \right\} \text{ where} \quad (10)$$

$$\beta = 1/k_B T.$$

The simplest Ising antiferromagnet would have $J_{11}(\vec{r}) = -|J_{11}|$ for nearest neighbors, and $J_{11}(\vec{r}) = 0$ for all other pairs. If the lattice being considered is an alternating structure, that is, it can be decomposed into two interlacing sublattices, then the mathematical problem involved is exactly the same as that for the corresponding ($J_{11}(\vec{r}) = |J_{11}|$) ferromagnetic case. This can be seen by noting that in the expression for the partition function, one can change the sign of all the spin variables, $S_{\vec{r}}$, on one sublattice without altering the partition function itself. That is, the spins are all dummy variables. Therefore, the specific heat of two-dimensional antiferromagnets and ferromagnets exhibit the same behavior. Similarly, the spontaneous

sublattice magnetization, $M_O^I(T)$, behaves the same as the ferromagnetic spontaneous magnetization, $M_O(T)$. In fact, all measurable parameters, including the critical exponents, should be the same for the anti-ferromagnetic and ferromagnetic case.

In 1925, the Ising model in one dimension (13) was first solved exactly. The first important contribution toward solving the two-dimensional Ising model was made in 1944 by Lars Onsager (14) when he completed an exact calculation of the partition function of a plane square lattice with two interaction parameters: J_x for horizontal bonds, and J_y for vertical bonds. There are at least fifteen mathematical techniques (15) used in deriving the pertinent expressions from the Ising model assumptions. These methods tend to be quite involved, and they, in themselves, reveal practically nothing of the origin of the critical point phenomena which are described.

For the limiting free energy spin cases, Onsager calculated the explicit expression for the free energy:

$$-\frac{F(T)}{k_B T} = 1/2 \int_{-\pi}^{\pi} \frac{d\theta_1}{2\pi} \int_{-\pi}^{\pi} \frac{d\theta_2}{2\pi} \ln (\cosh 2K_x \cosh 2K_y - \sinh 2K_x \cos \theta_1 - \sinh 2K_y \cos \theta_2) \quad (11)$$

where $K_x = \frac{J_x}{k_B T}$ and $K_y = \frac{J_y}{k_B T}$. It can be shown that there is a critical temperature determined by

$$\sinh\left(\frac{2J_x}{k_B T_c}\right) \sinh\left(\frac{2J_y}{k_B T_c}\right) = 1. \quad (12)$$

That is, the argument of the logarithm vanishes quadratically with T .

From this, it follows Fisher (15) that as $T \rightarrow T_c$,

$$F(T) = F_c + a(T - T_c) + b(T - T_c)^2 \ln |T - T_c| + \dots \quad (13)$$

where a and b are constants.

Now, by differentiation, one can calculate the internal energy and, then, the specific heat. The specific heat

$$\frac{C(T)}{k_B} = A \left| \ln \left| 1 - \frac{T}{T_c} \right| \right| - A_1 + \theta \{(T - T_c) \ln |T - T_c|\} \quad (14)$$

is seen to exhibit a symmetric, infinite singularity (see Figure 6).

The next important step was again made by Onsager when, in 1948, at a conference on phase transitions at Cornell University (16) he revealed the fact that the expression for the spontaneous magnetization of an Ising model ferromagnet was

$$M_0(T) = \{1 - (\sinh 2K_x \sinh 2K_y)^{-2}\}^{\beta}, \quad \beta = 1/8; \text{ but} \quad (15)$$

he chose not to reveal his method of derivation. It was not until 1952 that a derivation was arrived at and published by C. N. Yang (17). The Ising model expression for spontaneous magnetization of a ferromagnet (Eq. 15) predicts a value of $1/8$ for β , whereas classical

Figure 6. Two-dimensional Ising model specific heat

theory (12) predicts beta equal to 1/2. Near the critical temperature the spontaneous magnetization can be approximated (17) by

$$M_0(T) \simeq B \left(1 - \frac{T}{T_c}\right)^\beta \quad (16)$$

where $\beta = 1/8$, and $B = 1.222410$ for a quadratic lattice. It is these parameters, β and B , which can be determined by Mössbauer effect techniques.

C. The Magnetic Interaction as it Pertains to $\text{Mo}_{2-x}\text{Fe}_x\text{B}$

The origin of the magnetic field at the nuclear site (usually called the "effective field") is not completely understood. At present, no theory is capable of predicting accurately the magnitude and direction of the many known effective fields, and consequently, the results of the investigation of these fields is often of considerable interest.

Following the discussion of Goldanskii and Heber (18), when the nuclear magnetic dipole moment, $\vec{\mu}$, of iron experiences a magnetic field, $\vec{H}$, the interaction Hamiltonian can be written

$$H_m = -\vec{\mu} \cdot \vec{H} = -g\mu_N \vec{I} \cdot \vec{H}, \quad (17)$$

and the energy levels of the nuclear state will be shifted by

$$U_m = -g\mu_N H m_I \quad (18)$$

where g is the nuclear g -factor, μ_N is the nuclear magneton, $\vec{I}$ is the spin of the nucleus, and $m_I = I, I-1, \dots, -I$.

At the nuclear site the effective field, H_{eff} , is, for the most part, due to the spin and spatial distribution of the electron density in the atom. If $\hat{U}$ is designated as the magnetic interaction energy operator for one Dirac electron in a Coulomb field, then

$$\hat{U} = 2 \mu_B \vec{\mu} \cdot \left(\frac{8\pi}{3} \delta(\vec{r}) \hat{S} + \frac{\hat{l}}{r^3} + \frac{3(\vec{r} \cdot \hat{S}) \vec{r} - r^2 \hat{S}}{r^5} \right) \quad (19)$$

where $\hat{S}$ and $\hat{l}$ are operators for the spin and angular momenta of the electron, and $\vec{\mu}$ is the magnetic moment of the nucleus.

For ^{57}Fe the contribution of the last two terms in the energy expression is small. The first term, which describes the contact of an s-electron with the nucleus, is called the Fermi contact term, and is dominant.

Considering only the first term, the magnetic interaction energy of one Dirac electron can be written

$$U = \int \psi^* \hat{U} \psi d\tau = - \vec{\mu} \cdot \vec{H}_{\text{eff}} \quad (20)$$

which immediately yields the result:

$$\vec{H}_{\text{eff}} \simeq - \frac{8\pi}{3} \mu_B |\psi_{\uparrow}(0)|^2 \vec{S}. \quad (21)$$

$|\psi_{\uparrow}(0)|^2$ is the density at the nuclear site of s-electrons with spin + 1/2 projections. Generalizing to a multi-electron atom results in the expression for the effective field:

$$H_{\text{eff}} = - \frac{8\pi}{3} \mu_B \sum_S \{ |\psi_{\uparrow}^S(0)|^2 - |\psi_{\downarrow}^S(0)|^2 \} \quad (22)$$

where the sum is over all s-electrons and $|\psi_l^s(0)|$ is the density at the nuclear site of s-electrons with spin - 1/2 projections.

In a solid, the magnetic field at the nuclear site will depend on the filling of the relevant electronic shells, and on the interactions between atoms. In an atom which contains a partially filled magnetic shell such as the 3d-shell of iron, the interaction between the spin up polarized 3d shell and a spin up s-electron is attractive, while the same interaction with a spin down s-electron is repulsive. Therefore, even in filled s-shells, differences in spin up and spin down electron densities can exist. The existence of this difference in electron density between the spin up and spin down case means that even for paired s-electrons H_{eff} is not necessarily zero. Since the Fermi contact field from one 1s electron in iron is hundreds of megaoersteds (18), even a very small shift in the s-electron densities can produce the observed fields of about 100 to 600 kOe.

It can be assumed that for the iron borides the effective field is proportional to the magnetization $\bar{M}$. Considerable work has been done in examining this relationship (19), and it is found to hold very well for alloys of iron. Therefore, since the atoms of boron are isolated in the semiborides, it appears likely that the proportionality of the magnetization with the effective field will follow.

Since the neutron absorption cross section of boron makes the measurement of local moments difficult by neutron scattering, it is desirable to determine the local moment of iron in the borides by some other method. It is tempting to assume that the magnetic moment

of iron in the borides being examined is proportional to the effective field (20). But Wertheim, among others (2), points out that, in general, the hyperfine field is not uniquely determined by the local moment. None the less, a calculation of local moments by comparison with metallic iron has been made in the hope that the result may be of interest.

III. EXPERIMENTAL METHODS

A. Spectrometer

A constant acceleration spectrometer was used for these experiments. A block diagram of the spectrometer is shown in Figure 7. The source was mounted on a shaker assembly of Kankaleit (21) design, which was a minor modification (22) of the design reported in the literature. To facilitate alignment, the magnet gap was increased by a factor of two, and the overall size of the unit was reduced to about one half of the size reported. An assembly drawing is shown in Figure 8. A constant acceleration feedback amplifier adapted from the Cohen, et al. (23) design was used to drive the shaker. The triangle wave generator is driven at about 20Hz. and the sync pulse was used to start the time base generator. A frequency of 20 Hz. was chosen because this was the resonant frequency of the transducer, and, therefore, a minimum power output was required. The principal deviation from the Cohen, et al. design was in the use of an Opamp Labs 440KR operational power amplifier, rather than the power amplifier described in the literature.

Emitted radiation from the source passed through the absorber which was mounted in a heat leak cryostat. Photons which were not absorbed were then counted by a Reuter-Stokes gas proportional counter filled with a combination of krypton and carbon dioxide gas. Pulses emitted from the gas proportional counter were then shaped by a CSP-200

Figure 7. Block diagram of the Mössbauer spectrometer

Figure 8. Mössbauer spectrometer transducer

fast preamplifier and then amplified and shaped by a Canberra Instruments, model 1410, linear amplifier. The prompt output of the amplifier was routed to a Canberra Instruments, model 1430, single channel analyzer. For every incoming signal which falls within the window setting, the single channel analyzer emits a 10 volt pulse. The single channel analyzer output pulses were then routed to the time base input of a RIDL, model 30-128, 400 channel analyzer which stored these pulses. The delayed output of the amplifier was fed to the multichannel analyzer direct conversion input to be used in setting the single channel analyzer window.

A crystal controlled time base generator accepted a start pulse from the triangle wave generator and sent a start pulse to the multichannel analyzer operating in time mode. By setting the time base generator at 100 microsecond intervals between output pulses, the multichannel analyzer was advanced through 200 channels in a time corresponding to one period of the generated triangle wave. Therefore, two complete spectra were collected in the total 400 channel scan of the multichannel analyzer. Since the spectrum in the first 200 channels was collected while the source was undergoing positive acceleration, and the spectrum in the last 200 channels was collected while the source was undergoing negative acceleration, the parabolic effect caused by the change in distance between the source and the detector could be cancelled by the addition of the two spectra during the analysis of the data. Utilization of the above method of data collection simplified analysis of the data and still provided sufficient resolution.

B. Calibration of Velocity

The spectrometer velocity calibration was accomplished using the known spectrum of Armco iron. Since the velocities required ranged from about $1/4$ to $5/4$ of the velocity required for Armco iron, an Armco iron spectrum provided an accurate means of calibration. A determination of absolute zero velocity was not required, as all measurements were made relative to the Armco iron spectrum. Since the drive unit utilized a triangle wave, two spectra which were mirror images of each other were collected simultaneously. These spectra were, therefore, folded about their center of gravity during the analysis of the data. A calibration of the spectrometer was made at every velocity change, and at least every four days of continuous running. This was found to be satisfactory, as the spectrometer, once set, proved to be very stable.

C. The Absorber Cryostat

The absorber was placed in a cryostat (Figure 9) so that its temperature could be systematically controlled. The dewar insert shown in the figure allowed for the sample temperature to be varied from 4.5 to 300K. The copper sample holder is coupled to the helium can be means of an exchange gas chamber. A manganin heater wire wrapped around the sample holder enabled the temperature of the sample to be raised above that of the bath.

A copper constantan thermocouple was used to measure the temperature above 20K and a gold (iron) in copper thermocouple was used

Figure 9. Absorber cryostat

for temperatures below 20K. The appropriate thermocouple in conjunction with a servo system was used to control the temperature. The thermocouple was connected to a Leeds and Northrup type K-3 Universal Potentiometer and a Keithley Electrometer, model 153, was used as a galvanometer. When the electrometer indicator swung to the right of center, a potential difference was established across the electrometer output, and this potential difference was sensed by a current controller which varied the current in the heater wire. Therefore, by setting the potentiometer reading at the voltage corresponding to the desired temperature, the electrometer, current controller combination automatically established and maintained the indicated temperature. The temperature could be controlled to within $\pm .5K$ for a period of 24 hours by this method.

D. Source Preparation

The source used in these experiments was a commercially prepared 50 millicurie ^{57}Co source in a copper matrix. It had 1/4 square inch active area and was mounted on a plastic disk which was fastened directly to the shaker. With the source kept at 300K the full width at half maximum (FWHM) of resonance lines of Fe foil was .22 mm/sec. The natural linewidth (FWHM) for folded source and absorber is .19 mm/sec.

E. Absorber Preparation

1. Two-dimensional ferrous chloride complexes

Professor Roger D. Willett of Washington State University prepared several two-dimensional quadratic layer antiferromagnetic compounds which have the general formula $(\text{RNH}_3)_2\text{FeCl}_4$; RNH_3^+ being a substituted ammonium ion. Two compounds, $\text{R}=\text{CH}_3$ (methyl) and $\text{R}=\text{C}_6\text{H}_5\text{CH}_2$ (benzyl), were made available for study. These compounds were prepared by mixing in alcohol, in the absence of oxygen, the substituted ammonium chloride and FeCl_2 . A precipitate of flat yellow crystals of the compound then forms.

$(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$ was found to be isomorphous to the corresponding manganese compound (24). Lattice constants (8) of $a=5.1\text{\AA}$ and $c=19.2\text{\AA}$ for the tetragonal unit cell were indicated. Figure 4 shows an idealized version (8) of this structure. While no direct lattice measurements of the benzyl compound were made, it is believed that it quite closely resembles the methyl structure (25).

Since, due to the oxidation of Fe^{+2} to Fe^{+3} , these crystals turn brown if exposed to the air, the compounds were handled only under a dry inert atmosphere. An absorber was prepared by sealing approximately 30 mg. of the compound in a plexiglass holder (Figure 10) using General Electric #7031 low temperature varnish as an adhesive.

2. Semiborides

Semiborides Fe_2B , $\text{Mo}_{1.8}\text{Fe}_{.2}\text{B}$, and $\text{Mo}_{1.5}\text{Fe}_{.5}\text{B}$ were prepared by arc melting stoichiometrically determined amounts of high purity (Table 1)

Figure 10. $(\text{RNH}_3)_2\text{FeCl}_4$ sample holder

Table 1. Purity of elements used in $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ synthesis

Element	Description	Purity
Boron	Grade AA	99.3%
Iron	2.17% isotopic abundance of ^{57}Fe	99.9%
Molybdenum		-- ^a

^a It was necessary to electron beam melt the Mo before use, as it was available only as stock.

iron, molybdenum, and boron in an argon atmosphere. The resulting buttons were turned and remelted three times. Then the buttons were crushed until the resulting powder would pass through a NBS No. 325 mesh screen. Tape was used to bind a uniform layer of powder to a plexiglass disc which could be easily handled. The methods of phase determination which were used in evaluating the samples are discussed in Section IV.

Preparation of $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ with $x = .8, 1, 1.2, \text{ and } 1.8$ was attempted in the same manner as described above. The results of these attempts are also discussed in Section IV.

F. Least Mean Squares Fitting Program (VMMIN)

Analysis of the data was aided by the use of a least mean squares fitting program (VMMIN) adapted for Mössbauer data by Genin (26) and modified by Pinter (27). The program superimposes the two spectra from the 400 channel multichannel analyzer before fitting begins. As many as 13 Lorentzian lines can be fit simultaneously. The output consists of line positions, linewidths, line intensity, and a graph of intensity vs. velocity. This program has proven to be extremely useful in analyzing Mössbauer data.

IV. ANALYSIS AND DISCUSSION OF DATA

A. Two-dimensional Magnetic Systems

1. Previous measurements on two-dimensional magnetic systems

Interest in two-dimensional magnetic systems has resulted in the examination of several systems which seem to closely approximate two-dimensional antiferromagnetic behavior. These systems can be divided into two basic groups: (a) those systems in which there is some cancellation of interlayer forces so that the principal magnetic interaction is intralayer, (b) those systems where the layers are physically separated to such an extent that the intralayer interaction is dominant.

The antiferromagnetic divalent transition metal fluorides such as K_2NiF_4 (28), Rb_2MnF_4 (29), Rb_2FeF_4 (30), K_2MnF_4 (7), K_2CoF_4 (31) and Ca_2MnO_4 (32) are good examples of the first group. Examples of the second group which have been investigated, such as the copper (II) chloride complexes of the type $(RNH_3)_2CuCl_4$ (32), rely on the length of the substituted ammonium cation for the magnetic layer separation. The compounds $(CH_3NH_3)_2FeCl_4$ and $(C_6H_5CH_2NH_3)_2FeCl_4$ are believed to be examples of this second group.

Mostafa et al. (8), working with single crystals of the methyl and benzyl compounds, found by analysis of M.E. spectra that the principal axis of the electric field gradient is perpendicular to the metal-halogen sheet (8). The magnetic susceptibilities of powder samples were also measured (see Figure 11), indicating susceptibility maxima at 96K and 72K for the methyl and benzyl compounds respectively. The compounds

Figure 11. Magnetic susceptibility of $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$

appear to be antiferromagnetic since no field dependence was observed below the ordering temperature.

2. Analysis of M.E. spectra of $(\text{RNH}_3)_2\text{FeCl}_4$

a. Hyperfine splitting It has been shown (General discussion section) that the Hamiltonian for the $3/2 \rightarrow 1/2$ magnetic dipole transition of ^{57}Fe can be written as the sum of the two expressions:

$$H_Q = [e^2 Q V_{zz} / \{4I(2I-1)\}] [3I_z^2 - I(I+1) + \eta (I_x^2 - I_y^2)] \quad (23)$$

$$H_M = g\mu_N H(0) [I_z \cos \theta + (I_x \cos \phi + I_y \sin \phi) \sin \theta], \quad (24)$$

where all symbols have been defined previously.

The observed M.E. spectra of the $(\text{RNH}_3)_2\text{FeCl}_4$ compounds can be interpreted in terms of the above Hamiltonian such that the magnetic field, $H(0)$; the electric field gradient at the nuclear site; the ratio of the electric quadrupole interaction to the magnetic dipole interaction; θ ; ϕ ; and η can be determined.

For only a few cases of high symmetry can the energy levels be calculated exactly. There is, in general, no closed form. However, a computer program has been prepared (5) by Professor W. Kündig of the University of California at Los Angeles which solves numerically the complete interaction Hamiltonian for any combination of magnetic field, and electric field gradient tensor.

This program calculates the differences between the eigenvalues of the ground and excited states, and the intensities assuming a powder source and any combination of $H(0)$, $e^2 Q V_{ZZ}$, θ , η and ϕ ¹.

The M.E. spectrum line positions and intensities are calculated as functions of the ratio $R = |e^2 Q V_{ZZ} / \{2q_{3/2} \mu_N H(0)\}|$, θ , η and ϕ . This data is presented in the form of a graph. By matching a particular spectrum against the corresponding graph one can obtain the parameters which have already been enumerated.

b. Isomer shift The iron nucleus is surrounded and penetrated by an electronic charge distribution with which it interacts electrostatically. Therefore, a change in valence could result in a change in the s-electron charge density, consequently modifying the electric monopole interaction. Until the discovery of the Mössbauer Effect there was no way of measuring the resulting change in the nuclear transition energies of an element in two chemically different environments. The energy modification is called the isomer shift, and causes a shift of the center of gravity of a Mössbauer spectrum to either a higher or lower energy. Typically, isomer shifts are of the order of 10^{-8} electron volts, which makes them easily measurable.

The isomer shift can be written as:

$$\text{isomer shift} = \frac{4\pi}{5} Z e^2 R^2 \left(\frac{\delta R}{R} \right) \{ |\Psi(0)|_{\text{abs}}^2 - |\Psi(0)|_{\text{source}}^2 \} \quad (25)$$

¹The following values for the nuclear g-factor were used:

$$g_{1/2} = .18048,$$

$$g_{1/2} / g_{3/2} = -1.7493.$$

where δR is the difference between the excited and ground state nuclear radius, Z is the number of protons, e is the charge on a proton, R is the ground state radius, and $|\psi(0)|_{\text{abs}}^2$ and $|\psi(0)|_{\text{source}}^2$ are the total electronic charge densities at the nucleus of the absorber and source, respectively. Thus, we see that the isomer shift is a measure of the s electron charge density of the absorber relative to the source.

A positive isomer shift would indicate an increase in the energy difference between the $3/2$ and $1/2$ spin nuclear levels due to a decrease in the charge density at the absorber nucleus. (This is because the nuclear radius of the excited state of ^{57}Fe is less than the ground state radius.) The charge density can be decreased by adding $3d$ electrons which screen the $3s$ and $4s$ electrons, or by the removal of $4s$ electrons. The Mössbauer effect does not differentiate between the direct and the screening effect on the charge density.

c. IFIT computer program A computer program was developed which fits in a least squares sense, the data to the two-dimensional Ising Model expression:

$$\frac{M(T)}{M(0)} = B(1 - T/T_N)^\beta \quad (26)$$

where the predicted values of B are 1.2 to 1.7 and β is equal to $1/8$.

The iterative method used was first developed by Davidson (33) and makes possible the treatment of B , T_N and β as variables. Different initial parameters yield slightly different "fits". Therefore, a series of initial parameters was used and the best fit in the least squares sense was selected.

3. $(\text{CN}_3\text{NH}_3)_2\text{FeCl}_4$

This compound closely approximates the tetragonal unit cell illustrated in Figure 3. Magnetic iron atoms are located in two-dimensional metal-halogen sheets, the separation of which is determined by the length of the ammonium cation.

Mössbauer spectra were obtained for the methylnammonium compound starting at 8.8K, and at regular intervals to 95.0K. A Mössbauer spectrum was also obtained at room temperature. Typical spectra are shown in Figures 12 and 13.

At room temperature the Mössbauer spectrum exhibits the two lines often seen when examining ferrous compounds and which are due to the interaction of the electric quadrupole moment with the crystal electric field gradient. The electric quadrupole splitting was determined to be $2.21 \pm .03$ mm/sec. A positive isomer shift at room temperature of $1.11 \pm .03$ mm/sec. relative to magnetic iron was also measured.

The third Mössbauer line to be seen in the room temperature spectrum is an unordered iron impurity. This line was present in all spectra and remained unsplit for all temperatures down to 8.8K, the lowest temperature at which a spectrum was taken.

Below 95.5K the spectrum of the methylnammonium compound exhibited additional splitting due to the magnetic dipole hyperfine interaction. Also present in this temperature range were the six lines of a quite dilute ordered impurity, the saturated hyperfine field of which was determined to be 474 kOe at 8.8K. It is suspected that this impurity is

Figure 2. Mössbauer effect spectrum of (CH₃NH₃)₂FeCl₄ at 8.8K

Figure 13. Mössbauer effect spectrum of (CH₃NH₃)₂FeCl₄ at 294K

Fe_3O_4 , since the internal magnetic field of Fe_3O_4 is reported variously as 473 kOe or 507 kOe and 450 kOe at two nonidentical sites (34).

A computer fit of the experimental spectra to the predicted theoretical spectra when both magnetic dipole and electric quadrupole hyperfine interactions are present (5) was made utilizing the VMMIN program previously described. After the two impurity spectra were subtracted, only the $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$ spectrum remained. Table 2 lists the initial results of this analysis. A plot of the reduced data is shown in Figure 14. The solid line is included for clarity, and is not fitted. The plotted point at $T/T_N = 0$ is not a measured value, but, rather, the result of extrapolation. This yielded a saturation hyperfine field of 280 kOe. Similarly, the point plotted at $T/T_N = 1$ is not a measured, but a fitted value.

The critical temperature was determined by fitting the data points near the critical temperature to the two-dimensional Ising Model expression:

$$H(T)/H(0) = B(1 - T/T_N)^\beta, \quad (27)$$

using the computer program IFIT, previously described. Only those points near the critical temperature were used, since the power law is a good approximation only near T_N . This resulted in a fitted value of $T_N = 95.5 \pm .6\text{K}$. The calculated value for B was 1.1 as compared to the Ising Model value of 1.2 for a quadratic lattice. Beta was determined to be 0.23 which is between the Ising model prediction of 0.125, and the three-dimension predicted value of 0.5. A plot of this data is shown in Figure 15. The solid line is fitted to the data in a least squares

Table 2. Results of analysis of the Mössbauer effect spectrum of $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$ using the VM MIN program

T(K)	H(T) (kOe)	H(T)/H(0)
0.0 ^a	280 ^a	1
8.8	279	.995
16.5	277	.991
26.5	276	.988
46.5	265	.946
66.5	239	.855
76.5	220	.784
81.5	204	.727
84.0	197	.703
86.5	178	.636
89.0	169	.605
90.5	155	.552
91.5	149	.531
95.5 ^a	0 ^a	.000

^aThese are calculated values and are not the direct result of the VM MIN fitting routine.

Figure 14. Reduced $H_{\text{eff}}(T)$ data for $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$

Figure 15. Reduced $H_{\text{eff}}(T)$ data for $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$ fitted to $H/H(0) = B (1 - T/T_N)^\beta$

sense. As an additional check of the critical parameter β , a log-log plot of $H(T)/H(0)$ vs. $(1 - T/T_N)$ was made (see Figure 16). Using this approach the calculated value of β was again found to be 0.23, agreeing with the results of the IFIT fitting routine.

Applying Kündig's methods (5) to the reduced 8.8K spectrum reveals the following:

1. The field gradient is axially symmetric (The electric field gradient tensor asymmetry parameter is $< .2$), and θ (as defined in Figure 7) is 90 degrees.
2. R , the ratio of the electric quadrupole interaction to the magnetic dipole interaction is 1.2.
3. The sign of the quadrupole interaction is positive.
4. The sublattice hyperfine field is 280 kOe.
5. V_{zz} is $-7.52 \times 10^{17} \text{ V/cm}^2$.

These results are summarized in Table 3.

4. $(C_6H_5CH_2NH_3)_2FeCl_4$

Benzylammonium ferrous chloride is similar in structure to the previously discussed methylammonium compound (illustrated in Figure 4). Mössbauer Effect spectra were obtained for this compound at temperatures ranging from 5.6 to 80.0K. A spectrum was also obtained at room temperature. Typical spectra are shown in Figures 17 and 18.

At room temperature the Mössbauer spectrum exhibits the expected quadrupole splitting due to the interaction of the electric quadrupole movement with the crystal electric field gradient. The electric

Figure 16. Log-log plot of reduced $H_{\text{eff}}(T)$ data for $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$ (14,35)

Table 3. Results of analysis of the 8.8K Mössbauer effect spectrum of $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$ and of the 5.6K Mössbauer spectrum of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{FeCl}_4$.

Parameter	$(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$	$(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{FeCl}_4$
Hyperfine field	280 kOe	263 kOe
R, the ratio of the electric quadrupole interaction to the magnetic dipole interaction	1.2	2.8
Sign of the quadrupole interaction	positive	positive
η , the asymmetry parameter of the electric field gradient tensor	<.2	<.2
$\ominus$	90°	90°
V_{zz}	$-7.52 \times 10^{17} \text{ V/cm}^2$	$-16.7 \times 10^{17} \text{ V/cm}^2$

Figure 17. Mössbauer effect spectrum of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{FeCl}_4$ at 5.6K

Figure 18. Mössbauer effect spectrum of $(C_6H_5CH_2NH_3)_2FeCl_4$ at 295K

quadrupole splitting was determined to be $2.34 \pm .07$ mm/sec. A positive isomer shift of $1.17 \pm .09$ mm/sec. relative to magnetic iron was also present in the room temperature spectrum.

As in the methylammonium compound a single unordered iron impurity of unknown composition and a dilute ordered impurity were present. The measurable parameters of the impurities were identical with those reported in the methylammonium ferrous chloride case.

Again, the VMMIN computer program was used to reduce the data. Table 4 lists the initial results of this analysis. A plot of the reduced data is shown in Figure 19. The solid line is included for clarity and is not fitted. The plotted point at $T/T_N = 0$ is not a measured value, but rather the result of extrapolation. A saturation sublattice hyperfine field of 265 kOe was determined by this method.

Using the same methods as described in the report of the methylammonium ferrous chloride results, benzylammonium ferrous chloride was found to have a Néel Temperature of 75.6K. The fitted value for B was found to be 1.04 as compared to 1.1 for the methylammonium compound and 1.2 for the Ising Model. Beta was determined by the same methods previously described and was found to be 0.28 for benzylammonium ferrous chloride as compared to 0.23 for methylammonium ferrous chloride and 0.125 for the Ising Model. Figure 20 is a plot of the IFIT results used to determine T_N , and Figure 21 is a log-log plot of $H(T)/H(0)$ vs. $(1 - T/T_N)$.

Applying the methods suggested by Kündig (5) to the reduced 5.6K spectrum of benzylammonium ferrous chloride, the following results obtain:

Table 4. Results of analysis of the Mössbauer effect spectrum of $(C_6H_5CH_2NH_3)FeCl_4$ using the VMMIN program

T(K)	H(T) (kOe)	H(T)/H(0)
0.0 ^a	265 ^a	1
5.6	263	.992
10.0	260	.981
25.0	238	.898
40.0	212	.800
55.0	175	.660
65.0	142	.536
67.5	119	.449
70.0	109	.411
71.5	93	.351
73.0	87	.328
75.6 ^a	0 ^a	0.00

^aThese are calculated values and are not the direct result of the VMMIN fitting routine.

Figure 19. Reduced $H_{\text{eff}}(T)$ data for $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{FeCl}_4$

Figure 20. Reduced $H_{\text{eff}}(T)$ data for $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{FeCl}_4$ fitted to $H/H(0) = B(1 - T/T_N)^\beta$

Figure 21. Log-log plot of reduced $H_{\text{eff}}(T)$ data for $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{FeCl}_4$ (14)

1. The field gradient is axially symmetric (asymmetry parameter $\eta < .2$) with θ (as defined in Figure 7) equal to 90 degrees.
2. R , the ratio of the electric quadrupole interaction to the magnetic dipole interaction is 2.8.
3. The sign of the electric quadrupole interaction is positive.
4. The sublattice hyperfine field is 263 kOe.
5. V_{zz} is $-16.7 \times 10^{17} \text{ V/cm}^2$.

These results and the corresponding results for methylammonium ferrous chloride are summarized in Table 3.

5. Remarks

a. Mössbauer effect line broadening No meaningful data could be obtained at temperatures closer to T_N than $.96 T_N$ for $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$ and $.97 T_N$ for $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{FeCl}_4$ at which points $H_{\text{eff}} = .531 H(0)$ and $.328 H(0)$, respectively. Line broadening made accurate measurements closer to T_N impossible. There are at least four possible explanations for this observed behavior. A distribution of Néel temperatures could cause the line broadening noted when T is near T_N . If slippage, or stacking faults were present, a distribution of Néel temperatures might result. Due to the difficulty encountered in obtaining good single crystals (8), and the somewhat inexact knowledge of the crystal structure of the ferrous chloride compounds (8), no definite conclusion can be reached as to whether or not a Néel temperature distribution is present in the samples.

Another possible explanation might be a distribution of temperatures within the sample. This would result in a distribution of hyperfine

fields. As $T \rightarrow T_N$ a small temperature gradient would give rise to a relatively large hyperfine field deviation. Near T_N the data were shown to fit:

$$H(T) = H(0)B(1 - T/T_N)^\beta.$$

From this it can be shown that

$$dH/H(T) = -\beta(1 - T/T_N)^{-1}dT/T_N.$$

As $T \rightarrow T_N$ any small change dT will result in a large change in the hyperfine field. However, since the sample was in good thermal contact with a cold finger, as explained in Section III. E., and the usual time required for data collection was 12 to 24 hours, it seems unlikely that a temperature distribution within the sample would exist for such a long period of time.

If the temperature of the entire sample were to fluctuate, line broadening would result. However, the feedback technique used to control temperature appears to quite stable (Section III. C.) and this explanation seems unlikely.

It is also possible that relaxation effects may become important near the Néel temperature. If, as $T \rightarrow T_N$, fluctuations of the internal hyperfine field direction due to relaxation effects become comparable to the Larmor precession rate of the nucleus, line broadening will result.

The reason for the observed line broadening as $T \rightarrow T_N$ can not be ascertained with certainty at this time, because Mössbauer spectroscopic techniques do not differentiate between the possible causes of line broadening just enumerated.

b. The critical exponent β The critical exponent β is of particular interest. The data were shown to fit the curve (See Figures 21 and 26.) $H(T)/H(0) = B(1 - T/T_N)^\beta$ from T_N to at least $.6 T_N$. The meaning of β , however, except in the immediate neighborhood of T_N is questionable. It is still interesting to note that this power law explains the temperature dependence of the hyperfine field over a wide range of temperatures. While β has been successfully determined by neutron scattering experiments (35,36) for two-dimensional magnetic structures where the interplane magnetic interaction cancels (Type I compounds), there are no reported values for β (8,32,37) in compounds where the two-dimensional character is due to large magnetic plane separation (Type II compounds). For Type I compounds the reported (15,35,36) β values vary from .14 to .23, in relatively good agreement with the two-dimensional Ising model prediction of .125. (These Type I materials were studied by neutron diffraction, and therefore, the two-dimensional character of the crystals is indicated not only by the β values, but also by the presence of two-dimensional correlations.) It is interesting to note that for several samples (35) the magnetization data was shown to fit $M/M(0) = B(1 - T/T_N)^\beta$ over a wide temperature range; a behavior not common when three-dimensional ordering is present.

Since crystal quality of the Type II compounds, generally, does not permit neutron diffraction, the M.E. becomes increasingly important as a tool with which some of these compounds can be examined. While the M.E. is less definitive than neutron diffraction, it does provide

sufficient information to suggest several conclusions. The fact that the H_{eff} data for both methylammonium ferrous chloride and benzylammonium ferrous chloride fit

$$H/H(0) = B(1 - T/T_N)^\beta$$

over a wide temperature range definitely suggests two-dimensional ordering. Also, the values reported for β (.23 and .28 for methylammonium ferrous chloride and benzylammonium ferrous chloride, respectively) indicate the two-dimensional character of the crystals. The effects of the inexact nature of the Type II crystal structure (8,32,37) on the critical exponent values are not well understood. It is expected (7), however, that crystal asymmetry will cause the β values to be increased (as is indicated by the present data).

It is concluded that two-dimensional magnetic ordering is definitely indicated for methylammonium and benzylammonium ferrous chloride.

B. Semiborides

1. MoFe

While no studies of iron impurities in Mo_2B have been reported, considerable work has been done with the MoFe alloy system. Kitchens, et al. (38) report that for MoFe samples with 50 ppm and 1500 ppm Fe, a saturation field of 114.5 kOe is found, independent of the Fe concentration. They found an added resonance strength at low temperatures located near the center of the hyperfine spectrum which could not be explained. Another anomaly noted by Kitchens, et al. was a threefold increase in the linewidth of Fe in Mo over the natural linewidth of

.19 mm/sec. A Mössbauer spectroscopy study of MoFe (4 atomic percent Fe) by Window, et al. (39) reported a saturation field of 116 ± 5 kOe. Again, the saturation field showed little or no dependence on the Fe concentration. Their published data indicates a linewidth (FWHM) of about 0.48 mm/sec. at 300K and an ordering temperature of 30K for MoFe (4 at. %). A positive isomer shift of $0.056 \pm .003$ mm/sec. relative to alpha-iron is also reported.

2. Mo_{2-x}Fe_xB

a. Chemical analysis The Mo_{2-x}Fe_xB semiborides were examined by the Ames Laboratory Analytical Chemistry Group using standard wet chemical techniques. Only the Mo and Fe content were determined. It was assumed that the remaining material was boron. Table 5 indicates the nominal and actual composition of the samples analyzed. A minimum of four separate content determinations was made for each sample. The agreement between the separate content determinations of a particular sample was generally within 0.5%. Quite good agreement was found between the concentrations predicted by the stoichiometrically determined quantities which were arc melted and the actual chemical analysis. This result, however, does not rule out the possibility of the presence of several phases, or of free iron or Mo.

b. X-ray analysis The most useful method of phase identification was found to be X-ray diffraction. All semiboride samples were examined by powder diffraction methods, and phase identification was made by comparing the resulting diffraction lines with the ASTM

Table 5. Nominal and actual composition of the $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ samples

Nominal composition	Actual composition
$\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$	$\text{Mo}_{1.80}\text{Fe}_{0.20}\text{B}_{1.00}$
$\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$	$\text{Mo}_{1.52}\text{Fe}_{0.49}\text{B}_{0.99}$
$\text{Mo}_{1.2}\text{Fe}_{0.8}\text{B}$	$\text{Mo}_{1.21}\text{Fe}_{0.81}\text{B}_{0.98}$
$\text{Mo}_{1.0}\text{Fe}_{1.0}\text{B}$	$\text{Mo}_{0.77}\text{Fe}_{1.09}\text{B}_{1.14}$
$\text{Mo}_{0.8}\text{Fe}_{1.2}\text{B}$	$\text{Mo}_{0.83}\text{Fe}_{1.26}\text{B}_{0.91}$
$\text{Mo}_{0.5}\text{Fe}_{1.5}\text{B}$	$\text{Mo}_{0.31}\text{Fe}_{1.55}\text{B}_{1.14}$
$\text{Mo}_{0.2}\text{Fe}_{1.8}\text{B}$	$\text{Mo}_{0.16}\text{Fe}_{1.73}\text{B}_{1.11}$

interplanar d-spacing index. The Fe_2B and $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$ samples were found to be single phase, and the measured d-spacings agreed with those listed in the ASTM index. Samples nominally labeled $\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$ were found to be primarily of the Mo_2B structure, but they did contain Mo_2FeB_2 as an impurity phase. All samples of higher iron concentration (nominally listed as $\text{Mo}_{2-x}\text{Fe}_x\text{B}$, where $x = .8, 1.0, 1.2, 1.5$ and 1.8) were found to be Mo_2FeB_2 and free iron. No single phase sample of the form $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ was successfully prepared for x greater than 0.5 . The free iron was identified by the presence of the characteristic Mössbauer lines of iron in the sample spectra, rather than by X-ray diffraction.

Havinga, et al. report (40) a similar problem. They attempted to prepare MoFeB , but X-ray diffraction revealed Mo_2FeB_2 and free iron. After repeated attempts, they also remained unsuccessful in obtaining MoFeB .

c. Mössbauer spectroscopy

1) Fe_2B Fe_2B has recently received considerable attention (20,41). Therefore, since the M.E. results are well known, Fe_2B was used as a check of sample preparation, absorber mounting, and data reduction techniques. The resulting spectra were in complete agreement with the previously published results (see Figure 22), and, consequently, the methods used with the $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ samples can be viewed with increased confidence.

2) $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$ Mössbauer spectra were obtained for $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$ beginning at 4.5K and at regular intervals to 78K . A Mössbauer spectrum was also obtained at room temperature. A typical

Figure 22. Mössbauer effect spectrum of Fe₂B at 78K

spectrum is shown in Figure 23. At room temperature the Mössbauer spectrum is a single asymmetric line with a width (FWHM) of 0.69 mm/sec. For $T = 4.5\text{K}$ the central Mössbauer lines were not well resolved, but the two outside lines make possible the calculation of the effective field and the measurement of a positive isomer shift of $0.170 \pm .005$ mm/sec. relative to α -iron.

At all intermediate temperatures, the effective field was determined by comparing the splitting of the two outside lines with the Armco iron spectrum. The results of these determinations are presented in Table 6, and this data, in reduced form, is plotted in Figure 24. In Figure 24 the Δ 's represent the experimental data for α -iron, the '+'s represent the Brillouin function for $S = 1/2$, the dashed line represents the Brillouin function for $S = \infty$, and the o's represent the $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$ measurements. (The solid line was added for clarity.) The saturation effective field was found to be 85.5 kOe, and the critical temperature was determined to be 66.0K.

3) $\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$ Mössbauer spectra were obtained for $\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$ beginning at 4.5K and at regular intervals to 90K. At room temperature a Mössbauer spectrum was also obtained. A typical spectrum is shown in Figure 25. The room temperature spectrum was a single asymmetric line quite similar in shape to the room temperature spectrum of $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$. The line width (FWHM) was found to be 0.73 mm/sec. for the $\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$ sample. At $T = 4.5\text{K}$ the Mössbauer spectrum of $\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$ closely resembles that of $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$. The isomer shift

Figure 23. Mössbauer effect spectrum of Mo_{1.8}Fe_{0.2}B at 296K

Table 6. Results of analysis of the Mössbauer effect spectrum of $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$

T (K)	H(T) (kOe)	H(T)/H(0)
0.0 ^a	85.5 ^a	1
4.5	85.5	1
15.0	85.5	1
25.0	85.0	0.99
35.0	82.5	0.96
45.0	76.3	0.89
50.0	67.6	0.79
55.0	57.7	0.67
60.0	44.4	0.52
65.0	9.9	0.12
66.0 ^a	0.0 ^a	0.0

^a These values are the result of extrapolation, not direct measurement.

Figure 24. Reduced $H_{\text{eff}}(T)$ data for $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$

Figure 25. Mössbauer effect spectrum of Mo_{1.5}Fe_{0.5}B at 300K

measured at 4.5K was $+ 0.17 \pm .005$ mm/sec., agreeing with the $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$ value to within the experimental error.

The effective field at all temperatures was determined by comparing the splitting of the two outside lines with the Armco iron spectrum. The results of these determinations are presented in Table 7, and this data, in reduced form, is plotted in Figure 26. In Figure 26, as in Figure 24, the Δ 's represent the experimental data for α -iron, the '+'s represent the Brillouin function for $S = 1/2$, the dashed line represents the Brillouin function for $S = \infty$, the o's represent the $\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$ measurements, and the solid line is added for clarity. For $\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$ the saturation hyperfine field was found to be 89 kOe, and the critical temperature was 91K.

4) $\text{Mo}_{1.2}\text{Fe}_{0.8}\text{B}$, MoFeB , $\text{Mo}_{0.8}\text{Fe}_{1.2}\text{B}$, $\text{Mo}_{0.5}\text{Fe}_{1.5}\text{B}$,

$\text{Mo}_{0.2}\text{Fe}_{1.8}\text{B}$ In every case the Mössbauer spectrum of the samples of stoichiometrically determined mixtures of Mo, Fe, and B which were arc melted and nominally labeled $\text{Mo}_{1.2}\text{Fe}_{0.8}\text{B}$, MoFeB , $\text{Mo}_{0.8}\text{Fe}_{1.2}\text{B}$, $\text{Mo}_{0.5}\text{Fe}_{1.5}\text{B}$, and $\text{Mo}_{0.2}\text{Fe}_{1.8}\text{B}$ revealed Mo_2FeB_2 and free iron. No single phase semiboride of the form $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ was successfully made for $x > 0.5$.

3. Remarks

a. M.E. line broadening The observed linewidths (FWHM) of .69 mm/sec. and .73 mm/sec. for $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$ and $\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$, respectively, are approximately 2 to 3 times the linewidth expected for ^{57}Fe

Table 7. Results of analysis of the Mössbauer effect spectrum of $\text{Mo}_{1.5}\text{Fe}_{.05}\text{B}$

T(K)	H(T) (kOe)	H(T)/H(0)
0.0 ^a	89.0 ^a	1
4.5	88.0	0.99
15.0	87.4	0.98
25.0	85.4	0.96
35.0	80.9	0.91
45.0	78.0	0.88
55.0	73.0	0.82
65.0	69.0	0.78
78.0	54.4	0.61
85.0	45.8	0.51
90.0	5.2	0.06
91.0 ^a	0.0 ^a	0.00

^aThese values are the result of extrapolation, not direct measurement.

Figure 26. Reduced $H_{\text{eff}}(T)$ data for $\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$

in equivalent lattice sites. This line broadening may be due to the iron being in inequivalent magnetic sites, or spin coupling between iron atoms may exist, or the addition of iron to the Mo_2B lattice may cause strains which result in quadrupole splitting. Kitchens, et al. (38) report similar line broadening of M.E. lines for iron impurities in $\text{Mo}_2\text{Fe}_2\text{B}$, which has the same CuAl_2 (C-16) crystal structure as Mo_2B was found by Weisman, et al. (41) to have magnetically inequivalent Fe sites. The M.E. does not provide a method for differentiating between these possible causes of line broadening; it does, however, show that there is some variation of the ^{57}Fe nuclear environment in the $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ compounds.

b. Critical temperature and hyperfine field It is interesting to note that as the iron concentration is increased from 10 atomic percent ($\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$) to 25 atomic percent ($\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$) and then to 100 atomic percent (Fe_2B), the Curie point increases from 66.0K to 91.0K, and then to 1015K, respectively. Over this same iron concentration range the hyperfine field increases from 85.5 kOe to 89.0 kOe and then to ~ 248 kOe for $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$, $\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$, and Fe_2B , respectively. That is, a 15% increase in Fe concentration results in a 2.5% increase in the Curie temperature, and a 1.5% increase in the hyperfine field. (All percentages are relative to the appropriate Fe_2B values.) This relative independence of the hyperfine field on Fe concentration in this range of composition reflects a similar situation found for Fe impurities in Mo (39). This independence suggests that the iron

electronic wave functions undergo little change with increased iron concentration. The isomer shift data provides another check on this conclusion.

c. Local moment The determination of the local moment of iron in the borides by neutron scattering is difficult due to the large neutron absorption cross section of boron. In general, it cannot be assumed that the hyperfine field is uniquely determined by the local moment (2). For the magnetic monoborides MnB, FeB, CoB, the effective fields are nearly proportional to the magnetic moments (9). The proportionality constant is 105 kOe: $1 \mu_B$ (where μ_B is the Bohr magneton). For Fe metal the same ratio is 153 kOe: $1 \mu_B$, and for Fe_2B (9) the ratio is 130 kOe: $1 \mu_B$. Since Fe_2B and $Mo_{2-x}Fe_xB$ have the same crystal structure the middle value of 130 kOe: $1 \mu_B$ was chosen as being most likely to be applicable to the Mo compounds. This results in calculated magnetic moment values for $Mo_{1.8}Fe_{0.2}B$ and $Mo_{1.5}Fe_{0.5}B$ of $.66 \mu_B$ and $.69 \mu_B$ respectively.

d. Isomer shift The measured isomer shifts of $Mo_{1.8}Fe_{0.2}B$ and $Mo_{1.5}Fe_{0.5}B$ were both positive $0.170 \pm .005$ mm/sec. relative to α -iron. This lack of dependence of the isomer shift on iron concentration, coupled with the hyperfine field independence of iron concentration supports the conclusion that the electronic wave functions of the iron are little changed by the increased iron concentration.

As noted in Section IV. A. 2. b., for ^{57}Fe , a positive isomer shift represents a decrease in the electron charge density at the nuclear

site. An increase in the number of 3d-electrons would result in increased shielding of the 4s electrons, resulting in a decrease in the electronic charge density at the nucleus. Therefore, it appears that the number of 3d electrons associated with the iron atom in $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ is greater than the number present in Fe metal. Many factors, such as the metal to boron radius ratio and differences in lattice spacing, are known to affect the isomer shift. Therefore, the increased screening of s-electrons may be explained by a transfer of electrons from boron to the iron 3d band, however, the small magnitude of the isomer shift and the relatively unknown electronic structure of iron in Mo_2B suggest that other interpretations of the isomer shift may be possible.

e. Summary Because of the limited solubility of Fe in Mo_2B it is important to establish that the compounds studied are indeed $\text{Mo}_{2-x}\text{Fe}_x\text{B}$, and not $\text{Mo}(\text{Fe})$ or Mo_2FeB_2 . It is particularly important to compare the present data to the results obtained for Mo_2FeB_2 , since, as reported in Section IV. B. 2., all attempts to synthesize $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ for x greater than 0.5 yielded Mo_2FeB_2 and free iron. However, since Mo_2B has the CuAl_2 (C-16) structure, whereas Mo_2FeB_2 has a cementite structure (20), the X-ray powder patterns of these two compounds are very different, and little chance for confusion exists in X-ray pattern interpretation (see Section IV. B. 2. b.). The ordering temperature of Fe in Mo is reported (39) as 30K, and the ordering temperature of Mo_2FeB_2 (20) is 173K. However, T_c values for $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$ and $\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$ are 66.0K and 91.0K, respectively. This information all suggests that a new compound, $\text{Mo}_{2-x}\text{Fe}_x\text{B}$, and not the Mo_2FeB_2 or $\text{Mo}(\text{Fe})$ was synthesized. Thus, the

X-ray and T_c data both support the conclusion that the compound $\text{Mo}_{2-x}\text{Fe}_x\text{B}$ ($x \leq 0.50$) orders ferromagnetically and is indeed distinct from the compound Mo_2FeB_2 and the alloy $\text{Mo}(\text{Fe})$.

The magnitudes of the saturated hyperfine field are however rather similar, with $H_{\text{sat}} = 85.5 \text{ kOe}$, 89.0 kOe , 116 kOe and 86 kOe for $\text{Mo}_{1.8}\text{Fe}_{0.2}\text{B}$, $\text{Mo}_{1.5}\text{Fe}_{0.5}\text{B}$, $\text{Mo}(\text{Fe})$ and Mo_2FeB_2 , respectively. In view of the relative isolation of the boron in the metal rich compounds, it is not unreasonable that the Mo band structure will dominate the hyperfine interaction of the iron, so that a rather narrow range of H_{sat} values arises.

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