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A nuclear magnetic resonance study of Sc45 hyperfine interactions in scandium-rich Sc-Y, Sc-Zr, and Sc-Gd alloys

Bruce Ronald McCart

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A NUCLEAR MAGNETIC RESONANCE STUDY OF $^{45}$Sc HYPERFINE INTERACTIONS IN
SCANDIUM-RICH Sc-Y, Sc-Zr, AND Sc-Gd ALLOYS

by

Bruce Ronald McCart

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1965
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I. INTRODUCTION

Nuclear magnetic resonance (nmr) techniques have proven to be very useful in the study of alloy systems. Information about changes in the electronic structure across the alloy system may be gained from the study of Knight shifts and electric quadrupole interactions in the alloy. The isotropic and anisotropic Knight shifts are directly related to the character of the electrons at the Fermi surface. Conduction electrons play an important role in electric quadrupole interactions.

Previously, virtually no nmr studies have been made on alloy systems in which the isotropic Knight shift, anisotropic Knight shift, and quadrupole interactions are all observable and measurable. An exception to this was the work of Segel (52) on Sc-Y alloys. Segel’s work and the study of scandium metal by Barnes, et al. (4), indicated that several scandium alloy systems would be interesting to study and that the Sc$^{45}$ nucleus would make a very useful and unique nmr probe.

Scandium is the first element in the first transition series, with a $3d^{1}4s^{2}$ electron configuration. Its valence electron configuration of $4s^{2}$ gives it physical and chemical properties which are very similar to those of the rare earth elements. Scandium metal has the "hcp" structure with the major component of the electric field gradient tensor along the "c" axis. Since Sc$^{45}$ has a spin of $7/2$, there is an interaction between the quadrupole moment of the scandium nucleus and the electric
field gradient.

Conveniently, while the quadrupole interaction is strong enough to cause both first and second order perturbation effects, it is not large enough to completely dominate the anisotropic Knight shift effects which are also present. The central transition of the $^{45}$Sc nmr spectrum studied as a function of frequency demonstrates this fact. Barnes, et al. (4), show that the resonance line shape with an almost pure quadrupole appearance at 2 Mc/sec changes continuously, until at 24 Mc/sec, its appearance is that of an anisotropic Knight shift broadened line. This means that it is possible to derive good values for the anisotropic Knight shift and electric field gradient as well as the isotropic Knight shift from a study of the $^{45}$Sc nmr line.

Scandium forms alloy systems of the "hcp" structure with a number of other elements. As required for a meaningful nmr study, these alloy systems are solid solutions allowing for a continuous change in the parameters of interest. Segel's study (52) of the Sc-Y system indicated that a study of scandium alloy systems would be of considerable interest. Segel found that the electric quadrupole coupling appeared to increase monotonically more than two-fold as the yttrium content increased from zero atom percent to an extrapolated 100 percent. This result was quite unexpected since the lattice contribution to the electric field gradient remains essentially constant across the system, and the identical valence
electron configurations of the two elements would seem to preclude such drastic alterations in the electronic structure of the alloys.

Segel's study did not include alloys with yttrium content less than 33 atom percent. This study is in part an expansion of the work on the Sc-Y system to the alloys with 10 atom percent yttrium content and less. In this region of the alloy system, the $^{45}$Sc$^{17}$ nmr line still has an intensity which allows rather precise measurements of line width and position. Hence, the Knight shifts and quadrupole interaction parameters can be determined with good certainty. The low yttrium content allows the yttrium nuclei to be treated as impurities which somewhat simplifies the interpretation of experimental results.

This study also includes a study of the Sc-Gd and Sc-Zr alloy systems in the region of dilute gadolinium and zirconium concentrations. These two systems are similar to the Sc-Y system in that they are solid solutions in the region of study and have the "hcp" structure. However, there are important differences which make these two systems of interest.

Yttrium with its $4d^{1}5s^{2}$ electron configuration, like scandium, has physical and chemical properties which are similar to those of the rare earth elements. In particular, yttrium and gadolinium have almost identical chemical and metallurgical characteristics since they have the same metallic radius (26). Of course, there is one major difference between these two elements. Gadolinium with its $4f$ electrons has
magnetic properties not possessed by yttrium. Hence, alloying gadolinium with scandium shows the effect of a large magnetic moment on the electronic structure.

Zirconium is adjacent to yttrium in the periodic table, possessing an additional 4d electron. Therefore, the alloying of zirconium with scandium demonstrates the effects of adding an additional electron to the conduction band of scandium. Also, a study of this system should indicate whether the additional electron has essentially s-character or d-character.

In this study, the isotropic Knight shift, anisotropic Knight shift, and electric quadrupole parameters are measured for a series of dilute Sc-Y, Sc-Gd, and Sc-Zr alloys. Several conclusions as to the effects of alloying on the electronic structure of scandium are drawn from these results.
II. LINE SHAPE THEORY (PHENOMENOLOGICAL)

A. Isotropic and Anisotropic Knight Shifts

The shape of the nuclear magnetic resonance line associated with a polycrystalline (powder) sample is a complicated function of the resonance frequency, the anisotropic Knight shift, the nuclear quadrupole interaction, and the nuclear dipole-dipole interaction. The theory of this study will be principally concerned with the extraction of the interaction parameters from data associated with the resonance line shape. However, first some discussion of each of the parameters of interest will be made.

The isotropic Knight shift determines the position of the resonance line in a metal, but does not affect the shape. Since this section is primarily concerned with the shape of the nmr line, the isotropic Knight shift will only be briefly commented upon now. A more detailed discussion of the theory of the isotropic Knight shift will be made in Section V with the discussion of the experimental results.

A definition of the isotropic Knight shift will be sufficient for the purpose of the present discussion. The resonance frequency of a nuclear magnetic resonance line in a metal compared with the resonance frequency in a diamagnetic reference salt or solution in the same external magnetic field is

\[ \nu_o = \nu_R (1 + K_{iso}) \]  \hspace{1cm} (1)
where
\[ \nu_o = \text{resonance frequency in the metal,} \]
\[ \nu_R = \text{resonance frequency in the reference sample,} \]
\[ K_{\text{iso}} = \text{isotropic Knight shift.} \]
Actually, \( K_{\text{iso}} \) as defined in Equation 1 is the relative Knight shift rather than the absolute Knight shift. The relative Knight shift is the more convenient parameter to work with since it is constant as a function of frequency. Throughout this study, the relative isotropic Knight shift will be the parameter of interest.

The anisotropic Knight shift has a pronounced effect upon the resonance line shape. The anisotropic Knight shift and the related line shape effects arise in the following way. An interaction occurs between the nuclear moment and the unpaired electron spins which are outside the nucleus. Consider a single crystal: If the electron charge distribution about the nucleus is symmetric, the net magnetic coupling between the nucleus and the non s-state electron spins will be zero, even for the case of an applied magnetic field. However, anisotropy of the electron charge distribution results in a non-zero magnetic coupling in the presence of a magnetic field which polarizes the electron spins. The magnitude of the magnetic coupling for a given magnetic field is dependent upon the orientation of the crystal axes with respect to the direction of the applied field. The orientation dependent magnetic coupling corresponds
to an orientation dependent effective magnetic field at the nucleus. Consequently, if the crystal is rotated in the magnetic field, the resonance frequency will move back and forth within a small frequency range. The "hcp" structure of scandium metal and the scandium alloys indicates an anisotropy of the electron charge distribution which makes this interaction important in this study.

An expression for the change in magnetic field at the nucleus due to the charge distribution anisotropy is given by Bloembergen and Rowland (9).

\[
\Delta H_{\text{anis}} = \beta^2 \nu_{\text{o}} N(E_F) q_F (3 \cos^2 \theta - 1) H_o ,
\]

where

\[
q_F = \langle \psi^*(3 z^2 - r^2) r^{-5} \psi \rangle
\]

\(H_o = \) applied magnetic field,

\(\theta = \) angle between the crystal symmetry axis and the magnetic field direction,

\(\beta = \) Bohr magneton,

\(V_o = \) atomic volume,

\(N(E_F) = \) density of electron states at the Fermi surface per unit volume and energy.

The quantity \(q_F\) represents the electric field gradient of the electrons at the Fermi surface, assuming that the crystal has a symmetry axis in the \(z\)-direction.
The anisotropic Knight shift is defined as $K_{ax}$ where

$$K_{ax} = \beta^2 \frac{V}{N(E_F)} q_{F}(1 + K_{iso})$$  \quad (3)

If both the isotropic and anisotropic Knight shifts are considered, the resonance frequency in a single crystal is given by

$$\nu = \nu_o \left[1 + \frac{K_{ax}}{1 + K_{iso}} (3 \cos^2 \theta - 1)\right]$$  \quad (4)

where

$$\nu_o = (1 + K_{iso}) \nu_R = \text{resonance frequency in the metal.}$$

Equation 4 may be rewritten as

$$\nu = \nu_o \left(1 + a (3 \cos^2 \theta - 1)\right)$$  \quad (5)

where

$$a = \frac{K_{ax}}{1 + K_{iso}}.$$

Since $K_{iso}$ is small compared to 1, $a \approx K_{ax}$ and in following discussions, a will often be referred to as the anisotropic Knight shift.

A polycrystalline sample is necessary for an NMR study of metals because of skin depth effects. Since all crystal orientations are represented in such a sample, an average must be taken over all possible orientations. When the contributions from all orientations are averaged together it is found that the resonance line remains unshifted in frequency, but the line is broadened and assumes a characteristic shape. Bloembergen and Rowland (9) show how the average over crystal orientations is made and what the characteristics of an anisotropic Knight shift
The shape of the anisotropic shift broadened nmr line is found to be asymmetric. An important aspect of this asymmetry is that the maximum of the line appears at a frequency which is higher or lower than the isotropic resonance frequency depending upon whether $a$ is positive or negative. Thus, the line shape indicates the sign of $q^e$, the conduction electron electric field gradient, since all other terms in Equation 3 are positive.

B. Nuclear Quadrupole Interaction

A quadrupole moment may be identified with a non-spherical nucleus. The quadrupole moment is essentially a measure of the deviation of the nucleus from spherical symmetry. If an electric field gradient is present at the nuclear site, an interaction will occur between the quadrupole moment and the electric field gradient. Since $^{45}\text{Sc}$ has a spin of $7/2$ and scandium metal and alloys have the "hcp" structure which has a characteristic electric field gradient, it is necessary to discuss the nuclear quadrupole interaction.

Only the case for which the quadrupole interaction energy is small compared to the Zeeman energy will be considered. This restriction allows the use of perturbation theory. Pound (48) and Cohen and Reif (20) have determined the perturbation effects of the quadrupole interaction upon
the Zeeman energy levels and transition frequencies.

Consider a single crystal for which an axially symmetric field gradient exists at the nuclear site. For this case, a second order perturbation calculation yields the following expression for the transition frequencies of a nucleus with spin \( I \).

\[
\nu(m \leftrightarrow m-1) = \nu_o + \frac{1}{2} \nu_Q (3\mu^2 - 1)(m - \frac{1}{2}) + \\
\frac{\nu_Q^2}{32\nu_o} (1 - \mu^2) \left[ 102m(m-1) - 18I(I+1) + 39 \right] \mu^2 \\
- [6m(m-1) - 2I(I+1) + 3],
\]

(6)

where

\( \nu_o = \) quadrupole frequency,

\( \mu = \cos \theta \) (\( \theta \) = angle between the crystal symmetry axis and the magnetic field direction),

\( m = z \) - component of the nuclear spin.

The terms linear in \( \nu_Q \) are from first order perturbation theory and the terms quadratic in \( \nu_Q \) are from second order theory.

The quadrupole frequency \( \nu_Q \) is a convenient definition which reflects the strength of the quadrupole coupling. In terms of somewhat more fundamental quantities, the quadrupole frequency is defined as follows:

\[
\nu_Q \equiv \frac{3e^2qQ}{2I(2I-1)\hbar},
\]

(7)

where

\( e = \) electronic charge,
\[ q = \text{electric field gradient}, \]
\[ Q = \text{nuclear quadrupole moment}, \]
\[ h = \text{Planck's constant}. \]

Since \( q \) is often the only unknown on the right side of Equation 7, knowledge about \( q \) will provide information about the electric field gradient at the nucleus.

Substitution of the 2I possible values of \( m \) into Equation 6 generates the NMR quadrupole spectrum which consists of \( 2I+1 \) lines. The line corresponding to the transition frequency \( v(\frac{1}{2} \leftrightarrow -\frac{1}{2}) \) will be referred to as the central line. The remaining NMR lines in the spectrum will be referred to as satellite lines. Comments about the satellite lines will be made later. For the present, attention will just be given to the central line.

Examination of Equation 6 reveals that the central line is unaffected by the first order perturbation, and so only second order perturbation effects need to be considered. It follows from Equation 6 that

\[ v(\frac{1}{2} \leftrightarrow -\frac{1}{2}) = v_o \left[ 1 + \frac{b}{v_o^2} (1-\mu^2)(1-9\mu^2) \right], \]  

(8)

where \( b \) is a convenient experimental parameter which is defined as

\[ b = \frac{v_o^2}{16} \left[ I(I+1) - \frac{3}{4} \right]. \]  

(9)

The effect of the quadrupole interaction in a polycrystalline sample is to broaden the central line. A thorough discussion of the quadrupole
effects in a polycrystalline sample is given by Cohen and Reif (20).

C. The Combined Effects of the Anisotropic Knight Shift and Nuclear Quadrupole Interaction upon the Central Line Shape

The anisotropic Knight shift and nuclear quadrupole interaction both affect the shape of the central line in a polycrystalline sample. The effects of the combined interactions upon the polycrystalline line shape were first analyzed by Jones, et al. (31).

The central transition frequency for a single crystal combining the anisotropic shift and quadrupole interactions can be determined by referring to Equations 5 and 8:

\[ \nu(\frac{1}{2} \leftrightarrow -\frac{1}{2}) = \nu_0 \left[ 1 + \frac{b}{\nu_0^2} (1-\mu^2)(1-9\mu^2) + a(3\mu^2-1) \right]. \]  

An average must be made over all possible crystal orientations in order to determine the polycrystalline shape of the central line.

Jones, et al. (31) show how the averaging process over crystal orientations is done, and they derive the following shape function for the central line:

\[ P(\nu-\nu_0) = \left| \frac{4b}{\nu_0^2} \cdot \mu [ (9\mu^2-5) + \frac{3a\nu_0^2}{2b} ] \right|^{-1}. \]

An examination of Equation 11 reveals that \( P(\nu-\nu_0) \) has two singularities which occur when \( \mu = 0 \) and \( \mu = \mu' = (5/4 - \frac{a\nu_0^2}{6b}). \) In addition, there will be a step at the limiting value of \( \mu = 1. \)
Since $\mu'$ is the cosine of an acute angle, it is defined only when $0 < \mu' < 1$. The anisotropic Knight shift in scandium has been shown to be negative (4), so only the case of negative $\alpha$ will be considered. Combining the restriction on $\mu'$ with the fact that $\alpha$ is negative gives the following restriction on $\nu_0$: $-\frac{8b}{3a} > \nu^2 > 0$. For values of $\nu_0$ outside of this frequency range, the singularity of $\mu'$ is non-existent.

The frequencies at which the singularities and step occur may be found by substituting for $\mu$ in Equation 10:

\[ \nu_H = \nu(\mu = 0) = \nu_0 + \frac{b}{\nu_0} - a \nu_0, \quad (12) \]

\[ \nu_L = \nu(\mu = \mu') = \nu_0 - \frac{16b}{9\nu_0} + \frac{2}{3} \frac{\nu_0}{\nu_0} - \frac{a^2 \nu_0^3}{4b} \left(-\frac{8b}{3a} > \nu^2 > 0\right), \quad (13) \]

\[ \nu_S = \nu(\mu = 1) = \nu_0 + 2a \nu_0. \quad (14) \]

The singularities and step move relative to one another as $\nu_0$ changes. For low values of $\nu_0$, the step is between the two singularities. As $\nu_0$ increases, $\nu_S$ begins to merge with $\nu_L$ until the two cross at $\nu_0 = \sqrt{-\frac{8b}{3a}}$.

For higher frequencies, the line is characterized by just the singularity at $\nu_H$ and the step at $\nu_S$. Jones, et al. (31), give illustrative examples of how the line shape changes as a function of $\nu_0$.

The resonance line width may be defined using Equations 12-14. The restriction on $\nu_L$ requires that two definitions be made.

\[ \Delta \nu_{HL} = \nu_H - \nu_L = \frac{25b}{9\nu_0} - \frac{5a \nu_0}{3} + \frac{a^2 \nu_0^3}{4b}, \quad (r > -\frac{8}{3}) \quad (15) \]

\[ \Delta \nu_{HS} = \nu_H - \nu_S = \frac{b}{\nu_0} - 3a \nu_0, \quad (r < -\frac{8}{3}) \quad (16) \]
The dimensionless parameter $r = \frac{a_{0}^{2}}{b}$ has been introduced here. It is a convenient measure of the relative strengths of the anisotropic Knight shift and the nuclear quadrupole coupling and will be used often in following discussions.

The line width is seen from Equations 15 and 16 to be principally influenced by the quadrupole interaction at low frequencies due to the $\left(\frac{1}{v_{o}}\right)$ dependence. The $\left(v_{o}\right)$ dependence of the line width indicates that it is primarily influenced by the anisotropic Knight shift at high frequencies.

Equations 12 and 13 can also be used to define expressions from which the isotropic Knight shift may be derived. Recalling that $v_{o} = (1 + K_{iso})v_{R}$, it is possible to define the shifts $K_{H}$ and $K_{L}$ as follows:

$$K_{H} = \frac{v_{R} - v_{o}}{v_{R}} = K_{iso} - a + \frac{b}{v_{o}^{2}},$$

$$K_{L} = \frac{v_{R} - v_{o}}{v_{R}} = -K_{iso} - \frac{2}{3} a + \frac{16b}{9a_{o}^{2}} + \frac{a_{0}^{2}v_{R}^{2}}{4b}.$$  \hspace{1cm} (17)

It is possible to define other shifts, but $K_{H}$ and $K_{L}$ were the only two used in this study.

Equations 15-18 suggest the technique for determining $a$, $b$, and $K_{iso}$ from the central line shape data: Determine $\Delta v_{HL}$, $\Delta v_{HS}$, $K_{H}$, and $K_{L}$ at a series of resonance frequencies. Then, make a least squares fit of the appropriate function to the experimental data using $a$, $b$, and
K_{iso} as the variable parameters. The four equations provide a good check of internal consistency.

D. Nuclear Dipole-Dipole Broadening of the Central Line

The analysis of the central line shape will not be complete without the consideration of a basic source of line broadening, the nuclear dipole-dipole interaction. The dipole-dipole interaction of a nuclear spin with its neighboring nuclear spins produces an effective magnetic field at the nuclear site. This effective magnetic field may be slightly greater or less than the applied magnetic field depending upon the relative spin orientations of the neighboring nuclei. Since the nuclear spins in the sample are randomly oriented, there will be a Gaussian distribution of effective magnetic fields which will serve to give the nmr line a Gaussian shape.

The nuclear dipole-dipole interaction is generally the principal source of line broadening in a single crystal. The nmr line at a single crystal orientation will have the symmetric Gaussian shape and a width which is usually on the order of several Oersteds. This dipolar line width may be said to be an intrinsic property of the sample and will be referred to as \( \sigma \).

It is necessary to determine the contribution to the polycrystalline line shape which is made by the dipolar width. Qualitatively, the effect of the dipolar interaction is to "smooth" the line shape defined by the
shape function $P(v-v_o)$. However, more quantitative knowledge of the
dipolar broadening effects is needed.

The line shape, including dipolar broadening, can be generated by
weighting $P(v-v_o)$ with a proper Gaussian shape function and integrating
over all crystal orientations. This is equivalent to assuming that the
nmr line has a Gaussian line shape at every orientation of the single
crystal and then superimposing all of the individual Gaussian lines to
form the composite polycrystalline line shape. The procedure for doing
this is given below.

It is found to be convenient to integrate over a dimensionless
parameter $x$ rather than $\theta$ or $\cos \theta$. Rewriting Equation 10 gives:

$$\frac{(v-v_o)}{v_o^2} = (1- \cos^2 \theta)(1-9\cos^2 \theta) + r(3\cos^2 \theta-1).$$  \hspace{1cm} (19)

The definition of $x$ is

$$x \equiv \frac{(v-v_o)}{v_o^2}. \hspace{1cm} (20)$$

Now Equation 19 can be solved for $\cos \theta$ in terms of the two dimensionless
parameters $x$ and $r$:

$$\cos \theta = \left[ \frac{(10-3r) \pm [(10-3r)^2 + 36(x+r-1)]^{1/2}}{2} \right].$$ \hspace{1cm} (21)

The shape function is given by Equation 11. Rewriting it slightly and
dropping constant terms which are just a vertical scale factor, the
result is $P(x)$:

$$P(x) = \left| \frac{1}{4 \cos \theta (9 \cos^2 \theta-5) + 6r \cos \theta} \right|. \hspace{1cm} (22)$$
where now \( \cos \theta \) is defined by Equation 21.

Considering \( y \) to be a point on the frequency scale in units of \( x \), \( F(y) \) is the value of the dipolar broadened shape function at \( y \):

\[
F(y) = \frac{1}{\alpha \sqrt{\pi}} \int_{x_S}^{x_H} p(x) e^{-(y-x)^2/\alpha^2} \, dx ,
\]

where

\[
x_S = x(\cos \theta = 1) = 2r ,
x_H = x(\cos \theta = 0) = 1-r ,
\alpha = \sigma\nu_c/b = \sigma \sqrt{a/b} ,
\sigma = \text{dipolar line width} ,
\]

The complete line shape is found by evaluating \( F(y) \) for a series of values of \( y \).

Equation 23 was integrated numerically. A program was written for use with the IBM 7074 computer which performed this integration using Gauss' five point quadrature formula (28). Usually, the line shape was generated by evaluating \( F(y) \) for some 60 to 90 values of \( y \).

It is interesting to observe just how much the appearance of the line changes for different values of \( \sigma \). Examples are shown in Figures 1-4 which illustrate the dipolar width effects on the central line shape.

The value of the dipolar width of Sc\(^{45} \) in scandium is approximately 5 Kc/sec, for purposes of comparison with the figures.
Figure 1. The effect of the dipolar line width on the central transition nmr line. In Figures 1-4, the line shapes were generated by numerically integrating Equation 2 of the text. The case for $\alpha = 0$, corresponds to the unbroadened line shape (Equation 11) resulting from the combined electric quadrupole interaction and anisotropic Knight shift interaction. The two values of $\alpha$ given in each figure correspond to dipolar line widths of about 2.0 Kc/sec and 6.0 Kc/sec in the case of the Sc$^{45}$ resonance in the alloys under consideration. The actual dipolar line width of the Sc$^{45}$ nmr line in these alloys is approximately 5.0 Kc/sec which means that the experimentally observed line shape will be similar in appearance to the line shape of the larger value of $\alpha$ in each figure. The parameter $r$ is a convenient measure of the relative strengths of the anisotropic Knight shift and quadrupole interactions. The value of $r = -0.25$ corresponds to a nearly pure quadrupole line shape and would occur at a resonance frequency of about 4.5 Mc/sec in the case of the Sc$^{45}$ resonance.
Figure 2. The effect of the dipolar line width on the central transition nmr line. The line shapes shown in this figure would occur at a resonance frequency of about 9.0 Mc/sec in the case of the $^{45}$Sc resonance in the alloys of interest in this study. It can be seen from the unbroadened line shape that the step ($v_8$) has moved toward the singularity at $v_L$ because of the increased influence of the anisotropic Knight shift interaction. Notice that the experimentally observed line shape appears to be nearly symmetrical for this value of $r$. 
\[ r = \frac{\alpha v_0^2}{b} \]
\[ \alpha = \frac{\sigma}{b/v_0} \]

**Resonance Shape**

- \( \alpha = 1.00 \)
- \( \alpha = 3.00 \)

**Derivative Shape**

- \( \alpha = 1.00 \)
- \( \alpha = 3.00 \)
Figure 3. The effect of the dipolar line width on the central transition nmr line. The singularity at $v_L$ no longer exists for $r = -4$. The unbroadened line shape shows just the step at $v_S$ and the singularity at $v_H$. This value of $r$ corresponds to a resonance frequency of about 18.0 Mc/sec in the case of the Sc$^{45}$ resonance in the alloys under study.
Resonance shape $Q \propto \omega$

$\rho = -4.00$

Derivative shape $C = 2.00$

$\frac{\nu - \nu_0}{\nu_0} = \frac{V}{b}$

$\alpha = 2.00$

Resonance shape $\alpha = 6.00$

Intensity (arbitrary units)

$\frac{\nu - \nu_0}{\nu_0} / \frac{V}{b}$

$\frac{\nu - \nu_0}{\nu_0} / \frac{V}{b}$

$\frac{\nu - \nu_0}{\nu_0} / \frac{V}{b}$

$\frac{\nu - \nu_0}{\nu_0} / \frac{V}{b}$
Figure 4. The effect of the dipolar line width on the central transition nmr line. For this example, the resonance frequency of the Sc$^{45}$ nmr line would be approximately 36 Mc/sec. The line shape is now essentially the same as a line shape resulting solely from an anisotropic Knight shift.
r = \frac{2\nu_0}{b^2}

\sigma = \frac{b}{\nu_0}

\nu = \frac{\nu_0}{b^2}

\nu_0 = \frac{b}{\nu}

\nu_0, \nu_0

Int. (AR. UN.)

Int. (AR. UN.)

Int. (AR. UN.)

Int. (AR. UN.)
A brief consideration of the experimental procedure will indicate why a quantitative knowledge of the dipolar width contribution to the line shape is necessary. Experimentally, one obtains the derivative of the NMR line. The positions of the maximum and minimum of the derivative curve are the directly measured experimental parameters. The extrema of the derivative curve indicate the points of maximum slope of the resonance line. In the absence of the nuclear dipole interaction, the high frequency extremum would correspond to $v_H$ (Equation 12). Similarly, the low frequency extremum would correspond to $v_L$ or $v_S$ (Equations 13 and 14) depending upon the value of $v_o$. The effect of the dipolar interaction in "rounding off" the line shape is to shift the points of maximum slope away from $v_H$, $v_L$, or $v_S$. Consequently, corrections must be made to the experimentally measured parameters in order to use Equations 15-18 correctly in determining $a$, $b$, and $K_{iso}$. It is convenient to express this correction term as a function of $\sigma$ and $v_o$ and to add the functional correction to the expressions for $\Delta v_{HL}^o$, $\Delta v_{HB}^o$, $K^o_H$, and $K^o_L$.

The correction functions associated with the dipolar width were determined through the use of synthetic data. Considering a line shape generated for given values of $r$ and $\sigma$, the points of maximum slope are easily determined from the derivative of this line. Since $r$ is known, $v_H$, $v_L$, and $v_S$ can be calculated in the dimensionless $x$-units. If $r \leq -\frac{8}{3}$, the measured positions of maximum slope are compared with $v_H$ and $v_L$;
and for \( r > -\frac{3}{2} \), the points of maximum slope are compared with \( \nu_H \) and \( \nu_S \).

Letting \( \delta \nu_H \), \( \delta \nu_L \), and \( \delta \nu_S \) be the corrections to \( \nu_H \), \( \nu_L \), and \( \nu_S \) respectively, the dipolar corrections to the line width are \( \delta (\Delta \nu_{HL}) = \delta \nu_H + \delta \nu_L \) and \( \delta (\Delta \nu_{HS}) = \delta \nu_H + \delta \nu_S \). Fractional dipolar corrections are then defined as

\[
\frac{\delta \nu_H}{\sigma}, \quad \frac{\delta \nu_L}{\sigma}, \quad \frac{\delta (\Delta \nu_{HL})}{\sigma}, \quad \text{and} \quad \frac{\delta (\Delta \nu_{HS})}{\sigma}.
\]

These fractional dipolar corrections were evaluated for each of several values of \( r \) in the region \(-0.06 \leq r \leq -16.0\).

This constituted the synthetic data.

It was observed from the synthetic data that the fractional dipolar corrections are all complicated functions of both \( \sigma \) and \( r \). No single functional expression appears to be correct for the general case.

Consequently, functions of \( r \) were contrived which approximated the synthetic data for \( \sigma \) between 5.00 Kc/sec and 6.00 Kc/sec, which should correspond to the case of scandium and its alloys. Effort was made to keep the contrived functions as simple as possible while still obtaining a reasonably good approximation to the data. In particular, efforts were made to get a good functional approximation in the region \(-0.10 \leq r \leq -9.0\) which is essentially the region of \( r \) values for which the actual experimental data were taken. For this reason, the \((1/r)\) dependence of \( \frac{\delta \nu_H}{\sigma} \) \( \frac{\delta (\Delta \nu_{HL})}{\sigma} \) should not be taken seriously for \( r \) less than \(-0.05\).

Figures 5-8 show the synthetic data which were of particular interest in this study. The figures also show lines calculated from the functions which were used to approximate the data. Specifically, these functions were
Figure 5. Contribution of the dipolar line width to the position of $v_H$. In Figures 5-8, the synthetic data were obtained in the following way. For each value of $r$ considered, the theoretical line shape (Equation 23) was generated for two values of the dipolar line width, $\sigma$. The two values of $\sigma$ were 5.00 Kc/sec and 6.00 Kc/sec, and it was assumed that $a = -2.0 \times 10^{-6}$ and $b = 2.0 \times 10^{-2}$ (Mc/sec)$^2$, which are approximately the values of $a$ and $b$ appropriate to the Sc resonance in the dilute scandium alloys under study. In this figure, the difference in frequency, $5v_H$, between the singularity at $v_H$ of the unbrodened line and the position of the appropriate extremum of the broadened line derivative was found for each value of $r$ and $\sigma$. The fractional frequency difference, $\frac{5v_H}{\sigma}$, was determined for each value of $\sigma$ and plotted as the synthetic data. The curve which appears in the figure is the theoretical curve given by Equation 24 of the text.
Figure 6. Contribution of the dipolar line width to the position of $\nu_L$. The difference in frequency, $\delta\nu_L$, between the singularity of the unbroadened line at $\nu_L$ and the position of the appropriate extremum of the derivative of the broadened line was determined for each value of $r$ and $\sigma$. The synthetic data consist of the fractional frequency differences, $\frac{\delta\nu_L}{\sigma}$ determined for each value of $\sigma$. The solid line in the figure is the theoretical curve given by Equation 24 of the text.
Figure 7. Contribution of the dipolar line width to the total line width. The frequency difference, $\delta \Delta \omega_{\text{HL}}$, between the line width $\Delta \omega_{\text{HL}}$ of the unbroadened line shape and the frequency difference between the derivative extrema of the broadened line was found for each value of $\sigma$ and the values of $r \leq -2.7$. The fractional differences, $\frac{\delta \Delta \omega_{\text{HL}}}{\sigma}$, are plotted as the synthetic data. The solid line in the figure is the theoretical curve given by Equation 26. The dashed line is the theoretical curve described by Equation 27.
Figure 8. The contribution of the dipolar line width to the total line width. The frequency difference, $\delta \Delta_{HS}$, between the unbroader line width, $\Delta_{HS}$, and the frequency difference between the extrema of the derivative of the broadened line was determined for both values of $\sigma$ at the values of $r \geq -2.7$. The synthetic data are the fractional differences, $\frac{\delta \Delta_{HS}}{\sigma}$. The solid line in the figure is the theoretical curve given by Equation 27. The dashed line represents Equation 26.
\[ \delta v_H = \sigma \left( 0.210 - \frac{0.008}{r} - 0.043r \right), \quad r \geq -\frac{8}{3} \]  
\[ \delta v_L = \sigma \left( 0.370 + 0.0081 r^3 \right), \quad r \geq -\frac{8}{3} \]  
\[ \delta (\Delta v_{HL}) = \sigma \left( 0.580 - \frac{0.008}{r} - 0.043r + 0.0081 r^3 \right), \quad r \geq -\frac{8}{3} \]  
\[ \delta (\Delta v_{HS}) = \sigma \left( 0.290 - \frac{0.680}{r} \right), \quad r < -\frac{8}{3} \]  

Equations 24-27 can now be used to modify Equations 15-18:

\[ \Delta v_{HL} = \sigma \left( 0.580 - \frac{0.008b}{b} - \frac{0.043 av^2}{b} + 0.0081 \left( \frac{av^2}{b} \right)^3 \right) + \frac{25b}{v_o} - \frac{5av^2}{3} + \frac{a^2v^2}{4b}, \quad r \geq -\frac{8}{3} \]  
\[ \Delta v_{HS} = \sigma \left( 0.290 - \frac{0.680b}{b} \right) - \frac{v}{v_o} - 3av_o, \quad r < -\frac{8}{3} \]  

\[ K_H = K_{iso} - a + \frac{b}{v_R^2} + \sigma \left[ \frac{0.210}{v_R^2} - \frac{0.008b}{v_R} - \frac{0.043av_R^3}{b} \right], \]  
\[ K_L = -K_{iso} - \frac{2a}{5} + \frac{16b}{v_R^2} + \frac{a^2v^2}{4b} + \sigma \left[ \frac{0.370}{v_R} + \frac{0.008 la^2v^5}{b^3} \right]. \]

The parameters \( a, b, \) and \( K_{iso} \) were found by making a least squares fit of Equations 28-31 to the experimental data.

**E. Nuclear Dipole-Dipole Broadening of Satellite Lines**

The satellite lines of the nmr quadrupole spectrum can be very useful in determining \( v_Q \). Jones, et al. (31) derive the satellite transition frequencies for a single crystal in which the combined anisotropic Knight shift and quadrupole interactions must be considered.
These transition frequencies, correct to first order perturbation theory, are

\[ \nu(m\leftrightarrow m-1) = \nu_0 \left[ 1 + (3\mu^2 - 1) \left[ a + \frac{1}{2} \left( \frac{\nu_0}{\omega} \right) (m - \frac{1}{2}) \right] \right]. \]  (32)

A singularity in the satellite line shape in the polycrystalline sample occurs for \( \mu = 0 \). From Equation 32, the singularity frequency is

\[ \nu_S(m\leftrightarrow m-1) = \nu_0 \left[ 1 - \left[ a + \frac{1}{2} \left( \frac{\nu_0}{\omega} \right) (m - \frac{1}{2}) \right] \right]. \]  (33)

Let \( m' = n + \frac{1}{2} \) where \( n \) is an integer and \( |m'| \leq 1 \). Then it follows from Equation 33 that

\[ |\nu_S(m\leftrightarrow m-1) - \nu_S(1-m\leftrightarrow m')| = n\nu_q. \]  (34)

Hence, the frequency difference between the singularities of corresponding pairs of satellites is very simply related to the quadrupole frequency.

The spacing between pairs of satellite lines is of major interest. Jones, et al. (31) show that second order effects affect the positions of the satellite lines but the spacing between pairs of satellites remains constant. Therefore, only first order effects need to be considered.

Experimentally, one measures the position of maximum slope of the satellite line which is somewhat removed from the position of the singularity due to the presence of the nuclear dipole-dipole interaction. Consequently a correction due to the dipolar width must be made to the experimentally measured satellite spacing. Again it is necessary to generate the satellite line shape for the polycrystalline sample, taking
into account the effects of the dipolar width.

It is convenient to make the following definition:

$$a' \Xi \left[ a + \frac{1}{2} \left( \frac{\delta}{\delta} \right)^{(m - \frac{1}{2})} \right] v_0 \cdot \quad (35)$$

Now Equation 32 can be written as

$$v(m \geq m - 1) = v_0 + a' (3\mu^2 - 1) \cdot \quad (36)$$

The shape function is found to be (9)

$$P(v - v_0) = \frac{1}{2} \left| \frac{dv}{d\mu} \right|^{-1} = \left| \frac{1}{12a'\mu} \right| \cdot \quad (37)$$

Reference to Equation 36 gives

$$\frac{v - v_0}{a'} = 3\mu^2 - 1 \cdot \quad (38)$$

Let \( \frac{v - v_0}{a'} \) be a dimensionless parameter \( x \). Solving for \( \mu \) gives

$$\mu = \sqrt{1/3(x+1)} \cdot \quad (39)$$

The shape function can now be written in the form:

$$P(x) = \frac{1}{a'} \left| \frac{1}{3a' \sqrt{1+x}} \right| \cdot \quad (40)$$

One is now in a position to generate the dipolar broadened polycrystalline line shape.

Let \( y \) be a value on the frequency scale in units of \( x \). The dipolar broadened line shape function has a value \( F(y) \) at \( y \). As before, \( F(y) \) is determined by weighing \( P(x) \) with an appropriate Gaussian shape function and integrating over all values of \( x \). Here the limits of integration are \( x_1 = x(\mu = 0) = -1 \) and \( x_2 = x(\mu = 1) = +2 \). Therefore,
\[ F(y) = \frac{1}{2\pi \delta \sqrt{6}} \int_{-1}^{+2} \frac{1}{a' \sqrt{x+1}} e^{-\frac{(y-x)^2}{\delta}} \, dx , \quad (41) \]

where
\[ \delta = \sigma / a' , \]
\[ \sigma = \text{dipolar line width}. \]

Equation 41 must be integrated numerically.

The integral for \( F(y) \) was integrated numerically using the IBM 7074 computer. The method of numerical integration was Gauss' five point quadrature formula. Generally, only the shape of the satellite line in the vicinity of the singularity is important, so usually the generated line shape consisted of \( F(y) \) at some 50 - 70 values of \( y \) near \( x = -1 \).

Since the spacing between satellites is seen to be independent of resonance frequency, only the spacing measurement at one frequency is necessary. Consequently, only the dipolar correction at one frequency is necessary, and no dipolar correction functions of \( \sigma \) and \( v_0 \) need to be considered.
III. EXPERIMENTAL METHODS

A. Sample Preparation

The alloys used in this study were prepared by melting the two metals in a nonconsumable electrode arc-melting furnace under an inert gas atmosphere. The buttons were inverted a minimum of five times and remelted each time in order to achieve homogeneity. The spectrographic analyses of the metals used in preparing the alloys appear in Table 1. The alloys were chemically analyzed to determine the concentrations. The solute concentrations, as determined from the analyses (44), are correct to within 0.1 atom percent.

The alloy buttons were filed inside a Blickman stainless steel vacuum dry box under an argon atmosphere. The filings were sieved through a No. 140 mesh sieve, and a permanent magnet with a field of 5231 gauss was used to remove iron filings from the sample. For metal samples, it is necessary that the particle size be sufficiently small to cause skin depth effects to be negligible. An expression for the skin depth is

$$\delta = 5.03 \times 10^{-3} (\rho/\nu)^{1/2},$$

(42)

where

- $\delta$ = skin depth in cm,
- $\rho$ = resistivity in microhm-cm,
- $\nu$ = frequency in Mc/sec.
## Table 1. Impurities in the metals used in preparing the alloys

<table>
<thead>
<tr>
<th></th>
<th>Sc&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Sc&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Y</th>
<th>Zr</th>
<th>Gd</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>1300 ppm</td>
<td>975 ppm</td>
<td>380 ppm</td>
<td>--</td>
<td>1730 ppm</td>
</tr>
<tr>
<td>H</td>
<td>7 ppm</td>
<td>10 ppm</td>
<td>130 ppm</td>
<td>--</td>
<td>1730 ppm</td>
</tr>
<tr>
<td>N</td>
<td>167 ppm</td>
<td>--</td>
<td>175 ppm</td>
<td>10 ppm</td>
<td>245 ppm</td>
</tr>
<tr>
<td>Y</td>
<td>0.01 w/o</td>
<td>0.01 w/o</td>
<td>--</td>
<td>--</td>
<td>&lt; 0.002 w/o</td>
</tr>
<tr>
<td>Tm</td>
<td>&lt; 0.005 w/o</td>
<td>&lt; 0.005 w/o</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Yb</td>
<td>&lt; 0.004 w/o</td>
<td>&lt; 0.004 w/o</td>
<td>--</td>
<td>--</td>
<td>0.01 w/o</td>
</tr>
<tr>
<td>Lu</td>
<td>&lt; 0.005 w/o</td>
<td>&lt; 0.005 w/o</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Er</td>
<td>&lt; 0.01 w/o</td>
<td>&lt; 0.01 w/o</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ca</td>
<td>&lt; 25 ppm</td>
<td>&lt; 25 ppm</td>
<td>&lt; 20 ppm</td>
<td>&lt; 50 ppm</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>Si</td>
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<td>30 ppm</td>
<td>--</td>
<td>&lt; 200 ppm</td>
<td>&lt; 25 ppm</td>
</tr>
<tr>
<td>Fe</td>
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<td>100 ppm</td>
<td>100 ppm</td>
<td>&lt; 1000 ppm</td>
<td>60 ppm</td>
</tr>
<tr>
<td>Ta</td>
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<td>1300 ppm</td>
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<td>--</td>
<td>2500 ppm</td>
</tr>
<tr>
<td>F</td>
<td>--</td>
<td>--</td>
<td>70 ppm</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Mg</td>
<td>--</td>
<td>--</td>
<td>40 ppm</td>
<td>&lt; 200 ppm</td>
<td>--</td>
</tr>
<tr>
<td>Ti</td>
<td>--</td>
<td>--</td>
<td>&lt; 20 ppm</td>
<td>&lt; 1000 ppm</td>
<td>--</td>
</tr>
<tr>
<td>Cr</td>
<td>--</td>
<td>--</td>
<td>60 ppm</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ni</td>
<td>--</td>
<td>--</td>
<td>85 ppm</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Cu</td>
<td>--</td>
<td>--</td>
<td>50 ppm</td>
<td>&lt; 200 ppm</td>
<td>--</td>
</tr>
<tr>
<td>C</td>
<td>--</td>
<td>--</td>
<td>110 ppm</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Sm</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>&lt; 0.02 w/o</td>
</tr>
<tr>
<td>Eu</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>&lt; 0.001 w/o</td>
</tr>
<tr>
<td>Tb</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>&lt; 0.01 w/o</td>
</tr>
<tr>
<td>Al</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>&lt; 50 ppm</td>
<td>--</td>
</tr>
</tbody>
</table>

<sup>a</sup> Scandium metal used in preparing the Sc-Y alloys.

<sup>b</sup> Scandium metal used in preparing the Sc-Zr and Sc-Gd alloys.
To check the particle size to be sure it is sufficiently small, it is necessary to know the skin-depth at the highest frequency at which data were taken and compare this value to the smallest diameter of the largest possible particle in the sample.

No electrical resistivity measurements of the alloys have been made. However, it is possible to argue that for dilute solid solution alloys, the resistivity of the alloys will be significantly greater than the resistivity of the solvent metal. Qualitatively, this occurs because the solute nuclei act as impurities in the metal, disturbing the lattice regularity and serving as scattering centers for the conduction electrons.

A more quantitative argument may be established using Linde's Rule (13). Linde's Rule states that the increase in resistivity for a given atom percent of solute is proportional to the square of the difference in the atomic numbers between solvent and solute. The smallest difference in atomic numbers for the alloys involved in this study is that between scandium and yttrium in the Sc-Y system. Here the increase in resistivity is proportional to $(\Delta)^2$ which should be significant. Moreover, according to Linde's Rule the increase in resistivity will be even greater for the other alloy systems.

Another indication that the resistivity will increase with the addition of solute nuclei to the metal is given by the following equation from alloy theory (13):
\[ \Delta R = kc (1-c), \quad (43) \]

where

\[ \Delta R = \text{increase in resistivity}, \]

\[ k = \text{constant}, \]

\[ c = \text{atom percent of solute}. \]

On the basis of the above arguments, it may be assumed that the resistivities of all the alloys will be greater than that of scandium metal, and in many of the alloys, the resistivity difference may be quite large. Therefore, the resistivity of scandium metal will be used in the skin depth calculations for the check on particle size.

The resistivity of scandium is 66 microhm-cm (56). The highest frequency measurements in this study were made at 27 Mc/sec. Substitution of these values for \( \rho \) and \( \upsilon \) into Equation 42 yields the minimum value for the skin-depth, \( \delta_{\text{min}} = 7.86 \times 10^{-3} \text{ cm} \). For a No. 140 mesh sieve, the sieve opening is \( 1.05 \times 10^{-2} \text{ cm} \). This can be taken as the minimum diameter of the largest particle in the sample. The ratio of the largest particle diameter to the minimum skin depth is 1.34. Chapman, et al. (15) have shown that for this value of the ratio of particle diameter to skin depth no significant skin depth effects occur. Since most of the study was done at frequencies less than 27 Mc/sec and most of the particles were observed to be smaller than No. 140 mesh size, it may be concluded that the particle size of the samples used in this study was sufficiently
The filing process causes strains in the samples which serve to reduce the intensity of the nuclear magnetic resonance lines. The satellite lines in the nmr quadrupole spectrum are particularly sensitive to these strains. In order to relieve these strains, the filings were annealed as follows: The powder sample was sealed in an outgassed tantalum crucible under an atmosphere consisting of a mixture of argon and helium. Since tantalum will burn at 500° C, the crucible was then sealed inside vicor under a helium atmosphere at reduced pressure. The samples were placed inside a Thermolyne Furnace, Model No. F-2025P-1, and heated to temperatures between 500° C and 550° C. These temperatures were maintained for periods of time ranging from $4\frac{1}{2}$ hours to 38 hours. It did not appear that annealing the samples longer than $4\frac{1}{2}$ hours significantly enhanced the resonance line intensities. The filings were removed from the crucible inside the dry box and sealed in test tubes under an argon atmosphere in order to keep sample oxidation to a minimum.

B. Equipment

A Varian Associations wide line crossed-coil (nuclear induction) spectrometer was used to take data at frequencies between 2 Mc/sec and 16 Mc/sec. A high frequency wide line induction spectrometer developed by D. R. Torgeson was used to take data at frequencies between 16 Mc/sec
and 27 Mc/sec. A Varian Associates 12 inch electromagnet was used for work involving fields up to 16 kilogauss, and a Harvey-Wells 15 inch electromagnet model L-158 equipped with micro-shims was used for the work at higher magnetic fields. Frequencies were measured using a Computer Measurements Corporation 737CN frequency counter. Most of the data were taken using a crystal frequency synchronizer also developed by D. R. Torgeson. The synchronizer frequency was set using plug-in crystals made by International Crystal Company. It was possible to stabilize the frequency of the spectrometer within a range of 10 cycles or less for long periods of time using the crystal frequency synchronizer.

Two methods of taking data were used. One method used the conventional lock-in techniques described by Andrew (1) and the Varian Associates manual (60). Most of the linewidth and shift data for frequencies less than 16 Mc/sec were gathered using this method.

The second method which was used involved the technique of continuous averaging (34). Figure 9 is a block diagram of the experimental setup for this method. It may be noted that for the lock-in method mentioned above, the signal from the narrow band amplifier and phase sensitive detector is in the form of a DC voltage and is recorded directly on a strip chart recorder. In this case, a separate mechanism is necessary to scan the magnetic field through the resonance condition.

For the method of continuous averaging it can be seen from Figure 9
Figure 9. Block diagram of the experimental set-up used in the method of continuous averaging.
that the signal from the narrow band amplifier and phase sensitive
detector is fed into the voltage reducer which biases the signal so that
the voltage is always positive. The signal is then fed into a Vidar
Model 241 voltage-to-frequency converter which accurately produces a
pulse train with a repetition rate proportional to the input voltage.
A RIDL 400 Channel pulse height analyzer, Model 34-12B, then counts the
number of pulses produced in a given interval of time and stores the
number of counts in a memory channel. This is essentially a method for
taking a time integral of the voltage over a given interval.

The necessary one-to-one correspondence between channel address and
absolute value of the magnetic field is achieved by driving the magnetic
field with voltage derived from the channel address. The DC buffer
amplifier is used to determine the range of the magnetic field scan and
the direction of the scan, i.e., whether the magnetic field increases
or decreases as the channel address advances. The rate of the magnetic
field scan is determined by the time base generator which advances the
channel address after a pre-set interval of time has elapsed. A typical
interval in which a channel might be open for memory storage is 1/8
second. For this case, the time to make the entire scan will be 50
seconds. When the channel address is advanced from channel 399 to channel
0, an instantaneous change in the output voltage from the analyzer occurs
from its peak value to its initial value. The magnet is not able to follow
such a sudden change in voltage, so time must be allowed for the magnetic field to return to its initial value before the scan is repeated. Otherwise, hysteresis effects will destroy the required one-to-one correspondence between channel address and the absolute value of the magnetic field. The time base generator restart will start the time base generator advancing the channel address again. This trigger pulse is emitted only after a pre-set time interval has elapsed. The various auxiliary units needed for use with the 400-channel analyzer were developed by D. R. Torgeson.

The basic differences between the two methods have been well discussed by Klein and Barton (34). It was found in this study that the method of continuous averaging is in general much more sensitive than the more conventional method. Therefore, the method of continuous averaging was used in the study of quadrupole satellite lines, line width measurements at frequencies greater than 16 Mc/sec and less than 4 Mc/sec, and for line shape studies.

The capability to read out the data from the analyzer in the form of punched paper tape was particularly convenient for making experimental line shape studies. The data are associated with the derivative of the resonance line, and an integration must be performed in order to determine the actual experimental line shape. The data were transferred from punched tape to punched cards and used as the input data for an
IBM 7074 integration program. In this way it took little time and
trouble to determine the actual experimental line shapes for a more
accurate comparison with theoretical line shapes.

C. Procedure for Taking Data

The crossed-coil spectrometer allows one to detect a signal which is
in phase with either $X'$ or $X''$ of the complex nuclear susceptibility (1),

$$X = X' + iX'' .$$

When the signal is in phase with $X''$, the signal is in the absorption
mode. All nmr data in this study were taken in the absorption mode.

All resonances were recorded by scanning the magnetic field at a
fixed resonance frequency. The magnetic field was cycled at least ten
times before each run in order to establish a hysteresis curve. A
calibration of the magnetic field was made before and after each run
using Sc$^{45}$ in a saturated solution of Sc(NO$_2$)$_3$ as the reference. All
Knight shift measurements were made with respect to the nmr of Sc$^{45}$ in
this solution.

Care was taken to keep the peak-to-peak amplitude of the modulation
field less than $\frac{1}{4}$ the apparent line width in order to avoid modulation
broadening effects. Saturation studies were made and a value of the
r.f. power was used for which the signal did not saturate. This is
particularly critical when working with the absorption mode.
When the conventional lock-in method was used to take data, each run consisted of six to eight scans of the spectrum, half with increasing magnetic field and half with decreasing magnetic field. So for this case each datum point is the average of six to eight measurements. When the method of continuous averaging was used, a minimum of 15 scans of the spectrum was made.

The pair of satellite lines of the nmr quadrupole spectrum corresponding to the \((\frac{3}{2} \leftrightarrow \frac{1}{2})\) transition were observed in all alloys with solute concentrations of two atom percent or less. However, for the two atom percent alloys the lines were very weak in intensity. The spacing between each satellite pair was measured in every case in which they could be observed, correcting for the effects of excessive modulation amplitudes (45).
IV. RESULTS

A. Method of Non Linear Least Squares

The experimental results of this study consist of values for the quadrupole frequency, the anisotropic Knight shift, and the isotropic Knight shift for each of the alloys being considered. The values for these hyperfine interaction parameters were determined by fitting Equations 28-31 of Section II. D to the appropriate experimental data. The theoretical curves were fitted to the data by treating the experimental parameters as variable parameters with the best fit being determined by the least squares criterion. A description of the least squares method which was used follows.

The least squares fit was a machine calculation involving the use of an IBM 7074 computer. The program which was used was a non linear least squares program titled NLLS. The theory of NLLS is based upon Gauss' iteration method (28). The original NLLS program was written by Lietzke (40) for use on the IBM 7090 computer. This program was revised for use on the IBM 7074 computer by Christine Hennig of the Ames Laboratories Computer Services. Some further minor revisions were made by the author for convenience of use in this study.

The program NLLS consisted of a main program which actually made the least squares fit and a subprogram which defined the function to be fit. An initial estimate of each of the variable parameters was
required but convergence was usually obtained in less than 10 iterations even for poor initial estimates. It was found to be desirable or necessary in several cases to be discussed later to hold fixed one or more of the parameters which might normally have been varied while making the fit. This capability was present in the final version of NLIS which was used.

B. The Experimental Data

The experimental data are qualitatively similar for all the alloys and so it is possible to make some general comments about them. Data associated with the Sc-Y alloy with 2 atom percent yttrium content will be considered as an illustrative example. These data may be considered typical of the data associated with the rest of the alloys.

The experimental average deviation of a given datum point was between 1% and 2%. For a few alloys with higher solute concentrations the average deviation was somewhat higher since the weaker nmr line intensities introduced greater uncertainty into the measurements. In the figures to be discussed in this section, the uncertainty per datum point is slightly greater than the size of the circles.

The line width of the Sc$^{45}$ central transition is plotted as a function of resonance frequency in Figure 10. Qualitatively, the data are indicative of a combined nuclear quadrupole and anisotropic Knight shift interaction. The increase in line width at low frequencies is due
Figure 10. Experimental line width data. The average deviation of the data shown in Figures 10-12 is approximately twice the radius of the circles. The solid line represents the best fit of Equation 28 to the data as determined by the least squares criterion. The dashed line is the fit of Equation 29 to the high frequency data using the NLLS method.
Sc-Y ALLOY (20% Y)

- EXPERIMENTAL DATA
- THEORY ($\Delta \nu_{pp} = \Delta \nu_{HL}$)
-- THEORY ($\Delta \nu_{pp} = \Delta \nu_{HS}$)
to the nuclear electric quadrupole interaction, while the increase in line width at higher frequencies is characteristic of the anisotropic Knight shift. The presence of a clearly defined minimum in the curve indicates that neither interaction is solely dominant over the entire range of experimentally obtainable operating frequencies. This is a rather unique characteristic of scandium metal and the dilute scandium alloys. The two curves which appear in Figure 10 are the best fit of Equations 28 and 29 to the data as determined by NLLS:

\[
\Delta \omega_{\text{NL}} = \sigma \left[ .580 - \frac{0.008b}{a^2} - \frac{0.043 a^2}{b^2} + 0.0081 \left( \frac{a}{b} \right)^3 \right] \\
+ \frac{25b}{9b_o} - \frac{5a}{3} + \frac{a^2 b^3}{4b}, \quad 0 \leq \omega_o \leq 15 \text{ Mc/sec.} \quad (28)
\]

\[
\Delta \omega_{\text{HS}} = \sigma [0.290 - \frac{0.680b}{a^2} + \frac{b}{\omega_o} - 3a \omega_o, \quad \omega_o \geq 15 \text{ Mc/sec.} \quad (29)
\]

The scatter of the data about the curves may be considered typical of all the alloys.

The \( K_H \) and \( K_L \) data associated with the alloy with 2 atom percent yttrium content are plotted as functions of \( \frac{1}{\omega^2} \) in Figures 11 and 12 respectively. It will be observed that both shifts are nearly linear functions of \( \frac{1}{\omega^2} \). The curve which appears in Figure 11 is the best fit of Equation 30 to the data as determined by NLLS:

\[
K_H = K_{\text{iso}} - a + \frac{b}{\omega^2} + \sigma \left[ \frac{0.210}{\omega R} - \frac{0.008b}{a^2 R} - \frac{0.043a^2}{b R} \right]. \quad (30)
\]

Similarly, the curve in Figure 12 is the "NLLS best fit" of Equation 31.
Figure 11. Example of the experimental $K_H$ data. The solid line is the NLLS fit of Equation 30 to the data.
Sc-Y ALLOY (2.0% Y)

- EXPERIMENTAL DATA
- THEORY
Figure 12. Example of the experimental $K_L$ data. The solid line is the NLLS fit of Equation 31 to the data.
Again the scatter of the data about the theoretical curves may be considered typical. All of the experimental data for the alloys are tabulated in the appendix.

C. Dipolar Line Width

Several limitations in the use of the NLIS program were discovered during the course of this study. Moreover a critical judgment of the values for the experimental parameters of interest was necessary since there were a few serious discrepancies between values of a given parameter found from different types of data associated with the same alloy. The practical problems involved in the evaluation of each parameter will be discussed.

The first parameter of interest is $\sigma$, the dipolar line width. The importance of $\sigma$ in line shape studies was discussed in Section II and may be deduced from Equations 28-31. Initially, it was hoped that an experimental value of $\sigma$ could be found for each of the alloys along with the other hyperfine interaction parameters. However, it was found that the values for $\sigma$ determined with the use of the NLIS program had large uncertainties and could not be considered reliable. A possible reason for this may have been the fact that while the contribution of $\sigma$ to the
theoretical functions is not ignorable, it is also always relatively minor compared to the contributions of the other parameters. In general, it was found that a parameter could be found with good reliability using the NLLS method from functions in which it made a dominant contribution for some range of frequencies. It was decided that since no reliable information about $\sigma$ was possible, the parameter should be held constant during the least squares calculations in order to have a consistent evaluation of the other parameters.

It is necessary to know what the fixed value of the dipolar width should be for each alloy in order to get reliable values for other parameters. Barnes, et al. (4), report a theoretical value of 4.76 Oe and $\sigma$ in scandium metal using equations given by Kambe and Ollom (33) and assuming a Gaussian line shape. This corresponds to a dipolar line width of 4.92 Kc/sec in frequency units.

The experimental nmr line shape of the $^{45}$Sc central transition in scandium metal at a frequency of 25.25 Mc/sec was obtained using the method of continuous averaging and integrating the data stored in the 400 channel analyzer with an integration program written for the IBM 7074 computer. Theoretical line shapes for the central transition at this frequency were generated using the program described in Section II. The values for $a$ and $b$ used in generating the theoretical line shapes were those reported by Barnes, et al. for scandium metal. Line shapes
were generated for dipolar line widths of 4.50 Kc/sec, 5.00 Kc/sec, and 5.50 Kc/sec. The three theoretical lines were normalized to the experimental line shape and the result is illustrated in Figure 13.

It will be observed from Figure 13 that the theoretical line shape with a dipolar width of 5.00 Kc/sec most closely corresponds to the experimental line shape. Consequently, the theoretical dipolar line width must be a good approximation to the actual line width. All least squares calculations were made with $\sigma$ held constant at a value determined by the Kambe and Ollum equations. The values for $\sigma$ actually used in the least squares calculations were rounded off to the nearest 0.1 Kc/sec for convenience. It was found that the values for the other parameters were not affected for variations in $\sigma$ up to 0.2 Kc/sec. The values of $\sigma$ used in the least squares calculations for each alloy are tabulated with the final values of the other parameters.

D. Quadrupole Interactions

Several parameters have been introduced in this study to describe the quadrupole interaction. A summary of the definitions of these parameters may be helpful in avoiding possible confusion in the use of terms. The most basic parameter is the quadrupole coupling defined as $\frac{e^2Qq}{\hbar}$ and usually expressed in frequency units. It is somewhat more convenient for purposes of discussion to describe the quadrupole interaction by $v_Q$, which will always be referred to in this study as the
Figure 13. Comparison of an experimental Sc$^{45}$ nmr line shape in scandium metal with several theoretical line shapes. The experimental line shape (solid line) was found in the following way. The method of continuous averaging was used to obtain data associated with the derivative of the Sc$^{45}$ resonance line for a resonance frequency of 25.25 Mc/sec. These data were read out of the 400 channel analyzer on to punched tape which could be used in conjunction with the IBM 7074 computer to integrate the derivative data and obtain the shape of the resonance line. The theoretical line shapes were generated by numerically integrating Equation 23 for values of a and b appropriate to the Sc$^{45}$ resonance in scandium metal and three different values of the dipolar line width, $\sigma$. These synthetic line shapes were normalized to the experimental line shape and are presented in the figure for comparison with the experimental line shape.
PURE SCANDIUM
(25.25 Mc/SEC.)

EXPERIMENT - SOLID LINE
THEORY

- \( \sigma' = 4.50 \text{ Kc/SEC} \)
- \( \sigma' = 5.00 \text{ Kc/SEC} \)
- \( \sigma' = 5.50 \text{ Kc/SEC} \)
The quadrupole frequency is a convenient definition associated with first order perturbation calculations. A third parameter is \( b \), a convenient definition used in second order perturbation expressions:

\[
b = \frac{15}{16} v_Q^2.
\]

Since Equations 28-31 are second order expressions, \( b \) is the parameter involved in the NLIS calculations. However, the \( v_Q \) corresponding to the value of \( b \) found by the NLIS method will be the number which will be tabulated and discussed in the following.

Three values for the quadrupole frequency for each alloy were determined using the NLIS analysis of the \( \Delta \omega_{HL}, K_L \), and \( K_H \) data. An additional value was found for nine of the alloys from the quadrupole satellite spacings. All of these results are tabulated in Table 2.

Data which were used by Barnes, et al. (4), in the study of scandium metal were made available for reanalysis. The results of this reanalysis of the scandium metal data also appear in Table 2. The reanalysis somewhat modified the values for the hyperfine interaction parameters reported by Barnes, et al., but as will be seen, the changes were small.

Some comment should be made about the fact that the high frequency line width data was not used to evaluate \( v_Q \). This is due to the fact
Table 2. Values of the hyperfine interaction parameters found from the various sets of data

<table>
<thead>
<tr>
<th>Alloy (Atom Percent)</th>
<th>$\Delta v_{HL}$ Data</th>
<th>$v_Q$ (Mc/sec)</th>
<th>$K_L$ Data</th>
<th>$K_H$ Data</th>
<th>Satellite</th>
<th>$\Delta v_{HL}$ Data</th>
<th>$\Delta v_{HS}$ Data</th>
<th>$K_{iso}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc Metal</td>
<td>0.142</td>
<td>0.144</td>
<td>0.128</td>
<td>0.141 ± 0.002</td>
<td>-2.20</td>
<td>0.255</td>
<td>0.253</td>
<td></td>
</tr>
<tr>
<td>0.5 Zr</td>
<td>0.137</td>
<td>0.135</td>
<td>0.139</td>
<td>0.147 ± 0.002</td>
<td>-2.40</td>
<td>-2.19</td>
<td>0.250</td>
<td>0.248</td>
</tr>
<tr>
<td>1.0 Zr</td>
<td>0.135</td>
<td>0.141</td>
<td>0.129</td>
<td>0.151 ± 0.003</td>
<td>-2.38</td>
<td>-2.24</td>
<td>0.249</td>
<td>0.248</td>
</tr>
<tr>
<td>2.0 Zr</td>
<td>0.137</td>
<td>0.144</td>
<td>0.127</td>
<td>0.153 ± 0.004</td>
<td>-2.29</td>
<td>-2.17</td>
<td>0.253</td>
<td>0.251</td>
</tr>
<tr>
<td>4.0 Zr</td>
<td>0.138</td>
<td>0.149</td>
<td>0.104</td>
<td></td>
<td>-2.25</td>
<td>-2.21</td>
<td>0.253</td>
<td>0.249</td>
</tr>
<tr>
<td>8.0 Zr</td>
<td>0.132</td>
<td>0.135</td>
<td>0.118</td>
<td></td>
<td>-2.28</td>
<td>-2.53</td>
<td>0.243</td>
<td>0.239</td>
</tr>
<tr>
<td>14.2 Zr</td>
<td>0.152</td>
<td>0.155</td>
<td>0.149</td>
<td></td>
<td>-2.62</td>
<td></td>
<td>0.232</td>
<td>0.230</td>
</tr>
<tr>
<td>0.5 Y</td>
<td>0.135</td>
<td>0.137</td>
<td>0.131</td>
<td>0.147 ± 0.002</td>
<td>-2.41</td>
<td>-2.24</td>
<td>0.249</td>
<td>0.247</td>
</tr>
<tr>
<td>1.0 Y</td>
<td>0.130</td>
<td>0.133</td>
<td>0.121</td>
<td>0.149 ± 0.003</td>
<td>-2.36</td>
<td>-2.24</td>
<td>0.246</td>
<td>0.242</td>
</tr>
<tr>
<td>2.0 Y</td>
<td>0.129</td>
<td>0.132</td>
<td>0.121</td>
<td>0.158 ± 0.004</td>
<td>-2.31</td>
<td>-2.21</td>
<td>0.243</td>
<td>0.242</td>
</tr>
<tr>
<td>5.0 Y</td>
<td>0.125</td>
<td>0.129</td>
<td>0.116</td>
<td></td>
<td>-2.25</td>
<td>-2.23</td>
<td>0.233</td>
<td>0.232</td>
</tr>
<tr>
<td>10.0 Y</td>
<td>0.121</td>
<td>0.130</td>
<td>0.108</td>
<td></td>
<td>-2.09</td>
<td>-2.07</td>
<td>0.222</td>
<td>0.222</td>
</tr>
<tr>
<td>0.5 Gd</td>
<td>0.133</td>
<td>0.135</td>
<td>0.131</td>
<td>0.148 ± 0.002</td>
<td>-2.59</td>
<td>-2.48</td>
<td>0.248</td>
<td>0.247</td>
</tr>
<tr>
<td>1.0 Gd</td>
<td>0.129</td>
<td>0.129</td>
<td>0.133</td>
<td>0.150 ± 0.003</td>
<td>-2.74</td>
<td>-2.69</td>
<td>0.242</td>
<td>0.242</td>
</tr>
<tr>
<td>2.0 Gd</td>
<td>0.140</td>
<td>0.137</td>
<td>0.135</td>
<td>0.162 ± 0.004</td>
<td>-2.83</td>
<td>-3.11</td>
<td>0.245</td>
<td>0.245</td>
</tr>
<tr>
<td>4.0 Gd</td>
<td>0.133</td>
<td>0.129</td>
<td>0.140</td>
<td></td>
<td>-4.76</td>
<td>-4.41</td>
<td>0.241</td>
<td>0.230</td>
</tr>
</tbody>
</table>

\(^a\)Results from the reanalysis of the data provided by Barnes, et al. (4).
that $\Delta \omega_{LS}$ is dominated by the anisotropic Knight shift term which has a linear frequency dependence. The quadrupole interaction term makes only a small contribution due to its $\frac{1}{e}$ dependence. As indicated in previous discussion, this means that no reliable value for $b$ and hence $\nu_Q$ could be derived from the NLLS calculation.

The splitting of the quadrupole satellites should yield the most reliable values for $\nu_Q$, since the spacings between pairs of satellites were shown to be simple multiples of $\nu_Q$ in Section II. E. This is true provided the electric field gradient is axially symmetric, which is the case for scandium metal. Barnes, et al. (4) reported that the satellite spacings yielded a value of $(0.144 \pm 0.002) \text{Mc/sec}$ for $\nu_Q$ in scandium metal. This value had been corrected for excessive modulation effects, but no correction had been made for the effect of the dipolar line width of the satellites on the apparent value of $\nu_Q$.

The "satellite spacing" value for $\nu_Q$ reported by Barnes, et al., was corrected for dipolar broadening effects. This corrected number appears in Table 2. The correction was made as follows. A dipolar line width of 4.00 Kc/sec was assumed for the satellites. This value for $\sigma$ was used in generating synthetic dipolar broadened satellite lines for several values of $\nu_Q$ using the method described in Section II. The spacings between the derivative maxima of these synthetic lines were measured to determine the apparent $\nu_Q$ value. These would correspond to
the values of \( \nu_0 \) determined from the direct experimental measurement of
the satellite spacings. It was found that for \( \nu_0 = 0.141 \text{ Mc/sec} \) the
apparent value of \( \nu_0 \) would be very close to 0.144 Mc/sec. Using this
result, the value of \( \nu_0 \) reported by Barnes, et al., was reduced to
(0.141 \( \pm \) 0.002) Mc/sec. This should be more nearly the correct value for
\( \nu_0 \) in scandium metal.

E. Isotropic and Anisotropic Knight Shifts

The NLLS analysis of the \( \Delta \nu_{\text{HL}} \) and \( \Delta \nu_{\text{HS}} \) data was used to find \( a, \)
the anisotropic Knight shift. These data yielded two values for \( a \) for
each alloy which are tabulated in Table 2. The \( K_L \) and \( K_H \) data could not
be used to find \( a \). Again, the reason is the fact that \( a \) makes only a
relatively small contribution to Equations 30 and 31 and so large
uncertainties are involved in using the NLLS analysis to determine \( a \)
from these data.

The isotropic Knight shift, \( K_{\text{iso}} \), was extracted from the \( K_L \) and
\( K_H \) data. The value for \( a \) found from the \( \Delta \nu_{\text{HL}} \) and \( \Delta \nu_{\text{HS}} \) data was held
fixed during the NLLS calculation. The internal consistency between the
two values for \( K_{\text{iso}} \) found from these data was in general very good, as
can be seen in Table 2.
F. Final Results

The final values which were determined for the hyperfine interaction parameters for each alloy are tabulated in Table 3. A general discussion of these values and the estimated errors follows. First, however, some comment will be made about the three sets of values for scandium metal which also appear in Table 3.

The first set consists of the numbers reported by Barnes, et al. (4). The second set are those values found in this study from a reanalysis of the "Barnes" data. The differences between these two sets are seen to be small and are within the estimated experimental errors. The third set are values determined from extrapolations to zero solute concentration for each alloy system. It was found that there was good agreement between the three extrapolated values for each parameter. The extrapolated values of the hyperfine interaction parameter for "pure" scandium agree well with those found from data associated with scandium metal. The differences may be a reflection of a difference in quality between the scandium used in the scandium metal study and the scandium used in the preparation of the alloys for this study.

The final values for a and K_{iso} are the averages of the two results for each parameter which appear in Table 2. This is not true in the case of the quadrupole frequency. A discussion of how the final values of \nu_{Q} were decided follows.
<table>
<thead>
<tr>
<th>Alloy (Atom Percent)</th>
<th>( v_0 ) (Mc/sec)</th>
<th>( a \times 10^4 )</th>
<th>( K_{iso} ) (Kc/sec)</th>
<th>( \sigma ) (Kc/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc Metal (^a)</td>
<td>0.144 ± 0.002</td>
<td>-2.4 ± 0.2</td>
<td>0.262 ± 0.004</td>
<td>4.22</td>
</tr>
<tr>
<td>Sc Metal (^b)</td>
<td>0.142 ± 0.002</td>
<td>-2.2 ± 0.1</td>
<td>0.253 ± 0.003</td>
<td>5.00</td>
</tr>
<tr>
<td>Sc Metal (^c)</td>
<td>0.135 ± 0.003</td>
<td>-2.35 ± 0.04</td>
<td>0.248 ± 0.003</td>
<td>5.00</td>
</tr>
<tr>
<td>0.5 Zr</td>
<td>0.136 ± 0.002</td>
<td>-2.30 ± 0.04</td>
<td>0.249 ± 0.003</td>
<td>5.00</td>
</tr>
<tr>
<td>1.0 Zr</td>
<td>0.138 ± 0.003</td>
<td>-2.31 ± 0.04</td>
<td>0.248 ± 0.003</td>
<td>5.00</td>
</tr>
<tr>
<td>2.0 Zr</td>
<td>0.140 ± 0.003</td>
<td>-2.23 ± 0.04</td>
<td>0.252 ± 0.003</td>
<td>5.00</td>
</tr>
<tr>
<td>4.0 Zr</td>
<td>0.142 ± 0.003</td>
<td>-2.23 ± 0.04</td>
<td>0.251 ± 0.003</td>
<td>4.80</td>
</tr>
<tr>
<td>8.0 Zr</td>
<td>0.134 ± 0.003</td>
<td>-2.40 ± 0.08</td>
<td>0.241 ± 0.003</td>
<td>4.60</td>
</tr>
<tr>
<td>14.2 Zr</td>
<td>0.154 ± 0.003</td>
<td>-2.62 ± 0.10</td>
<td>0.231 ± 0.003</td>
<td>4.40</td>
</tr>
<tr>
<td>0.5 Y</td>
<td>0.136 ± 0.002</td>
<td>-2.32 ± 0.03</td>
<td>0.248 ± 0.003</td>
<td>5.00</td>
</tr>
<tr>
<td>1.0 Y</td>
<td>0.132 ± 0.002</td>
<td>-2.30 ± 0.03</td>
<td>0.244 ± 0.003</td>
<td>5.00</td>
</tr>
<tr>
<td>2.0 Y</td>
<td>0.132 ± 0.002</td>
<td>-2.26 ± 0.03</td>
<td>0.242 ± 0.003</td>
<td>5.00</td>
</tr>
<tr>
<td>5.0 Y</td>
<td>0.127 ± 0.002</td>
<td>-2.24 ± 0.03</td>
<td>0.232 ± 0.003</td>
<td>4.75</td>
</tr>
<tr>
<td>10.0 Y</td>
<td>0.126 ± 0.003</td>
<td>-2.08 ± 0.03</td>
<td>0.222 ± 0.003</td>
<td>4.50</td>
</tr>
<tr>
<td>0.5 Gd</td>
<td>0.131 ± 0.002</td>
<td>-2.54 ± 0.04</td>
<td>0.248 ± 0.003</td>
<td>5.00</td>
</tr>
<tr>
<td>1.0 Gd</td>
<td>0.133 ± 0.003</td>
<td>-2.72 ± 0.04</td>
<td>0.242 ± 0.003</td>
<td>5.00</td>
</tr>
<tr>
<td>2.0 Gd</td>
<td>0.135 ± 0.003</td>
<td>-2.97 ± 0.10</td>
<td>0.245 ± 0.003</td>
<td>5.00</td>
</tr>
<tr>
<td>4.0 Gd</td>
<td>0.140 ± 0.003</td>
<td>-4.50 ± 0.15</td>
<td>0.236 ± 0.003</td>
<td>5.00</td>
</tr>
</tbody>
</table>

\(^a\) Results reported by Barnes, et al. (4).

\(^b\) Results of the reanalysis of the data provided by Barnes, et al.

\(^c\) Extrapolated values from the results of this study.
It was indicated during the discussion of the quadrupole frequency results that the most reliable value for $v_Q$ in scandium metal was that found from the quadrupole satellite spacing. For scandium metal, the agreement between $v_Q$ found using the NLLS analysis and $v_Q$ found from the satellite spacings is excellent. However, the satellite spacing values for $v_Q$ in the alloys are in poor agreement with those found from the NLLS analysis. This may be seen in Table 2. Consequently, a decision must be made as to the relative credibility of the two methods of analysis before a final value can be assigned to the quadrupole frequencies of the alloys.

Consider the electric field gradient of scandium metal. In the ideal case, the exact symmetry of the lattice and the presence of just one type of nucleus would serve to establish the sharply defined electric field gradient which is assumed to exist in making electric quadrupole perturbation calculations. Real metals, however, have strains and impurities present to some degree which will have the effect of changing the one sharply defined electric field gradient to a distribution of electric field gradients. If one assumes that the strains and impurities are randomly distributed throughout the metal, one might expect the electric field gradient distribution to be Gaussian and centered on the value occurring in the ideal case. A separate study is in progress to determine what effects such a distribution of field gradients would have.
on nmr lines. While the study is not yet complete, it has been found that several effects do occur which have important implications for this study.

The electric field gradient distribution effects are being studied as follows. Line shapes are generated with the IBM 7074 computer for a distribution of $\nu_Q$ values. Each line shape is then multiplied by an appropriate Gaussian weighing factor and the line shapes are superimposed to give a composite nmr line. Composite nmr lines are generated for Gaussian distributions of different widths. Changes in intensities and apparent $\nu_Q$ values are then determined as a function of Gaussian distribution width. The study includes effects upon both the central transition line and the satellite lines.

It was found that an electric field gradient distribution has a much greater effect on the satellites than on the central transition line. This would be expected since the satellites are a first order perturbation phenomenon, whereas the central transition is only affected in second order. For a given Gaussian distribution of field gradients, the intensities of the satellite lines are reduced to a much greater extent than the intensity of the central line. This may explain why the experimental intensities of the satellite lines relative to the central transition are observed to be much less than the intensities predicted from perturbation theory for a number of hexagonal metals, e.g. scandium (4), beryllium (37), technecium (32). More important for this study is
the fact that the apparent value for $v_Q$ found from the satellite spacings increases significantly as the distribution width increases.

Now consider the case of the scandium alloys. The introduction of solute ions into the lattice must cause an additional distribution of electric field gradients. For a Gaussian distribution, this would be reflected in an increase in the distribution width. Such an increase in the gradient distribution could largely account for the rapid decrease in the satellite intensities with increasing solute concentrations observed for the alloys in this study. It would also mean that the values for $v_Q$ measured from the satellite spacings in the alloys are too high and that a correction for the field gradient distribution effect is necessary.

While the observed effects should be true qualitatively for any distribution of field gradients, one cannot be certain that the correct distribution is Gaussian. In short, there is not enough information about the actual distribution of field gradients and the corresponding quantitative effects presently available with which to make adequately the necessary corrections to the apparent quadrupole frequency. On the other hand, an electric field gradient distribution which has a profound effect on the satellite lines will have a very small effect upon the central transition line. Consequently, it is not so important to worry about the corrections to $v_Q$ found from the NLLS analysis of the data associated with the splitting of the central line. Therefore, the NLLS analysis was the
sole method used for the determination of the quadrupole frequency in the alloys.

The reliability of the values for $v_q$ found from the $K_H$ data is questionable. It will be observed from Table 2 that while agreement between the $\Delta v_{HL}$ and $K_L$ results was generally good, the $K_H$ data quite consistently yielded significantly lower quadrupole frequency values. Since this was also true for scandium metal for which the other three values of $v_q$ were in excellent agreement, it was decided that the $K_H$ data not be used in the final evaluations of the quadrupole frequency for scandium metal and the Sc-Y and Sc-Zr alloys. The values for the Sc-Gd alloys will be considered in the discussion of that system in the next section.

The error limits which appear in Table 3 are generally on the order of $1\%$ to $2\%$. These error limits seemed to be reasonable after a consideration of data point scatter, the standard deviations for the parameters as found from the NLLS calculations, and the estimated effects of the approximations made for the dipolar line width. The estimated errors are somewhat larger for the alloys with higher solute concentrations since the weaker nmr line intensities in these alloys introduced greater uncertainty into the experimental measurements.
V. DISCUSSION OF RESULTS

A. The Sc-Y System

The characteristics of the electronic structure of yttrium appear to be surprisingly different from those of scandium. Ostensibly, scandium and yttrium should be very much alike. They are the first members of the first and second transition groups respectively, with the same electronic valence configuration. Yet, scandium seems to behave more like lanthanium, the first element in the third transition series, than yttrium. The differences between scandium and yttrium have been indicated through several previous studies.

One such study was that made by Segel (52) on the Sc-Y system for alloys with 33% Y content and greater. Segel's results were briefly commented upon in the Introduction, and it will be recalled that he observed an increase in the value of the electric quadrupole coupling at the Sc site of more than two-fold. This was unexpected since the lattice contribution to the electric field gradient remains essentially constant over most of the Sc-Y system.

Magnetic susceptibility and Knight shift studies indicate another difference between scandium and yttrium. It will subsequently be shown that the isotropic Knight shift is closely related to the susceptibility of a metal. Studies of the susceptibility of scandium (17) (24), yttrium (25), and lanthanium (41) indicate that for all three metals the total
susceptibility has a negative temperature dependence. The magnetic susceptibility for each of the three metals increases in a linear fashion with decreasing temperature.

Blumberg, et al. (10) report that the Knight shifts of scandium and lanthanum also increase in a linear fashion with decreasing temperature. On the other hand, Segel (52) measured a decrease in the Knight shift of Y in yttrium metal as the temperature is lowered. Hence, it would seem that scandium is more like lanthanum than yttrium.

It must be pointed out that one should be careful about the interpretation of these reported variations in Knight shifts with temperature. For all three metals, the isotropic Knight shift was assumed to be the measured parameter. However, neither Blumberg, et al. nor Segel considered the presence of the anisotropic Knight shift in making their measurements. Thus, the parameter which was measured was probably an "average" Knight shift, \( K_{av} \) which may be represented as some linear combination of the isotropic Knight shift, \( K_{iso} \) and the anisotropic Knight shift, \( K_{ax} \). For example, one might define

\[
K_{av} = mK_{iso} + nK_{ax},
\]

where \( m \) and \( n \) are parameters which may be functions of both temperature and resonance frequency.

Consequently, one should be careful about interpreting the temperature dependence of \( K_{av} \) as the temperature dependence of \( K_{iso} \) for these three metals, since it cannot be assumed that \( K_{ax} \) is temperature
Barnes, et al. (3) found \( K_{ax} \) of Sn\(^{119} \) to be strongly temperature dependent in \( \beta \)-tin and in the intermetallic compounds PrSn\(_3\), NdSn\(_3\), and LaSn\(_3\). They also found \( K_{ax} \) of Cd\(^{113} \) to be temperature dependent in Cd metal. These are the only reported temperature studies of the anisotropic Knight shift, but they do indicate that the possibility of the temperature dependence of \( K_{av} \) being caused wholly or in part by a temperature dependent \( K_{ax} \) must be considered. Moreover, the problem of correctly extracting the hyperfine interaction parameters from nmr data in scandium and lanthanum is further complicated by the presence of a quadrupole interaction. One cannot discard the possibility that the reported temperature dependence of \( K_{av} \) for these two metals is influenced by a temperature dependent quadrupole coupling. Blumberg, et al. did not consider the presence of the quadrupole interaction in making their Knight shift measurements.

It has been necessary in the following discussions of the experimental results to use the reported temperature dependence of scandium. Care will be taken to indicate when one should distinguish between \( K_{iso} \) and \( K_{av} \) and when statements must be of a qualified nature until proper temperature studies of the Knight shift in scandium and yttrium metals have been made. The discussion of the results for the Sc-Y system will begin with a consideration of the isotropic Knight shift.

The first reported measurement of the isotropic Knight shift was by
Knight (36), who found that the resonance frequency of Cu in copper metal was higher than its resonance frequency in CuCl. Knight also reported a similar effect on the resonant frequency in Li, Na, Al, and Ga metals. Since that time a similar shift in frequency has been observed for more than a score of other metals.

The first theoretical explanation of the Knight shift was made by Townes, et al. (59). The theory as advanced by Townes, et al., gives good agreement with the qualitative and quantitative experimental observations on non-transition metals and is based upon the paramagnetism associated with the s-type conduction electrons. It has been found that this theory is incomplete for purposes of explaining the Knight shift in transition metals, but nevertheless, it is basically correct and is necessary for an understanding of the Knight shift. Knight (35), Rowland (49), and Slichter (54) fully discuss the Knight shift and associated theory for non-transition metals.

Townes, et al., formulate their theory on the assumption that the isotropic Knight shift results from the s-state hyperfine interaction between the nuclear moment and the unpaired conduction electrons at the nuclear site. In the absence of an external magnetic field, the electron spins have no preferential orientation. The nuclear moment in experiencing coupling to many random spins has a resultant magnetic coupling of zero. The application of a magnetic field to the sample polarizes
the unpaired electron spins in the direction of the magnetic field. Since the spin orientation is no longer random, the resultant magnetic coupling is no longer zero, resulting in an effective magnetic field at the nuclear site which is larger than the applied field. Since the degree of spin polarization is proportional to the strength of the magnetic field, the additional increment to the field will be proportional to the applied field.

The fact that the effective magnetic field is larger than the applied field implies that the resonance frequency in a metal will be greater than in a reference solution or diamagnetic salt for a given value of magnetic field. Conversely, for constant frequency, the magnetic field required for resonance will be lower in the metal than in the reference. Exceptions to this general rule exist, but only for some transition metals.

Consideration of the s-state hyperfine interaction leads to the following expression for the relative Knight shift:

\[
K_{iso} = \frac{\nu - \nu_R}{\nu_R} \cdot \frac{H - H_R}{H_R} = \frac{3}{2} \chi_p \nu_o < |\psi(0)|^2 >_F,
\]

where

\( \nu_o \) = resonance frequency in the metal,

\( \nu_R \) = resonance frequency in the reference sample,

\( H_o \) = resonance field in the metal,

\( H_R \) = resonance field in the reference sample,

\( \chi_p \) = electron spin susceptibility in c.g.s. volume units,
\[ V_o = \text{atomic volume}, \]
\[ \psi(o) = \text{value at the nucleus of the wave function normalized over } V_o \]

for an electron at the Fermi surface.

The quantity \( < |\psi(o)|^2 >_F \) is the average probability density of conduction electrons at the nucleus. It is non-zero only for s-type conduction electrons.

Pauli's (47) expression for the paramagnetic susceptibility for weakly interacting electrons is useful:

\[ \chi_p = \beta^2 N(E_F), \tag{45} \]

where \( \beta = \text{Bohr magneton}, \)
\[ N(E_F) = \text{Density of one-electron states per unit volume and energy at the Fermi surface}. \]

Substituting into Equation 44 gives:

\[ \frac{\Delta \mu}{V_R} = \frac{\Delta N}{H_R} = 8 \pi \frac{\beta^2 V_o N(E_F)}{2} < |\psi(o)|^2 > _F. \tag{46} \]

Equation 46 is often a more useful form of the isotropic Knight shift since information about the density of states at the Fermi surface can be derived from specific heat measurements.

The electronic specific heat is important at very low temperatures. The electronic specific heat, \( C_e \), is linearly related to the absolute temperature through the electronic specific heat coefficient, \( \gamma \).
Sommerfeld (55) derived an expression for $\gamma$ in terms of the density of states:

$$\gamma = \left( \frac{C_e}{T} \right) = \frac{n^2 k^2}{3} N(E_F),$$  \hspace{1cm} (47)

where

$$k = \text{Boltzmann's constant.}$$

Knowledge of how $\gamma$ changes then gives one an opportunity to deduce how $< |\psi(0)|^2 | \psi_F >$ changes from changes in the Knight shift.

The paramagnetism of the s-type conduction electrons is actually just one of several mechanisms involved in the isotropic Knight shift, but for non-transition metals the contributions from these other sources are negligible. This is not the case for transition metals and so these other contributions to the Knight shift must be considered in a discussion of scandium, yttrium, and zirconium metals. Specifically, the Knight shift in transition metals is written (Clogston, et al. (18)):

$$K_{\text{iso}} = K_s + K_d + K_o,$$  \hspace{1cm} (48)

where $K_s$ is the contribution from the paramagnetism of the s-type conduction electrons discussed above, $K_d$ is the result of core polarization of the inner electrons by the d-type conduction electrons, and $K_o$ is a contribution from the orbital momentum of the d-electrons. The terms $K_d$ and $K_o$ will be briefly considered.

The expression for $K_{\text{iso}}$, equation 44, indicates that the Knight shift is proportional to the density probability for s-electrons at the
nucleus. Specifically, only the s-electrons at the Fermi surface are considered in Equation 44. The s-electrons in the filled inner shells also have a non-zero probability of being at the nucleus. However, in general, these electrons are paired and the contribution from spin-up electrons exactly cancels the contribution from spin-down electrons. Cohen, et al. (20), show that these inner s-electrons do contribute to the Knight shift via exchange polarization with the d-electrons at the Fermi surface. The spins of the non s-conduction electrons become polarized and interact with the spins of the core s-electrons with the result that the core electrons are no longer exactly paired off and are hence capable of contributing to the hyperfine contact term. A useful expression for $K_d$ is given by Butterworth (14):

$$K_d = \left( \frac{8\pi}{3} \right) \psi_d V_o < |\rho(o)| >_d , \quad (49)$$

where

$$< |\rho(o)| >_d = \text{net unpaired spin density at the nucleus due to one d-spin averaged over the d-states at the Fermi surface},$$

$$\psi_d = \text{spin susceptibility of the 3d electrons per unit volume},$$

$$V_o = \text{atomic volume}.$$ 

This term makes a negative contribution to the Knight shift and is temperature dependent. In manganese and platinum, the core polarization term is dominant and accounts for the observed negative Knight shifts.
in these transition metals (30) (50).

The contribution of the orbital magnetic moment of the electrons to the electronic paramagnetism was neglected in the initial Knight shift theory because of the "quenching" effect by the crystal fields. However, Kubo and Obata (38) show that for metals with degenerate and partly filled non-s bands there is a second order perturbation contribution of the orbital magnetic moment to the paramagnetic susceptibility which may not be negligible compared with the spin susceptibility. The second order term is the metal analogue of the so-called temperature-independent Van Vleck susceptibility for non-metals.

The second order contribution of the orbital moments is negligible compared to the spin paramagnetism contribution in paramagnetic salts. In metals, however, the spin paramagnetism is reduced by the factor $(\frac{T}{T_0})$ where $T_0$ is a degeneracy temperature. The contributions from the spin paramagnetism and the orbital moment became comparable not because the second order perturbation term becomes large but because of the drastic reduction in the spin paramagnetism. If the electron orbital moments contribute significantly to the electronic paramagnetism, they must also contribute to the Knight shift.

Butterworth (14) also gives an expression for the orbital contribution to $K_{iso}$:

$$K_o = 2 \langle r^{-3} \rangle_d \chi_0/N,$$

(50)
where

\[ \chi_o = \text{orbital contribution to molar susceptibility}, \]
\[ N = \text{Avogadro's number}, \]
\[ r = \text{d-electron radius}, \]
\[ < r^{-3} > = \text{average over the d-electrons}. \]

Marshall and Johnson (42) give an expression for \( \chi_o \) for d-electrons:

\[ \chi_o \sim \left( \frac{c_s^2}{2\Delta} \right) n (10-n), \]  

(51)

where \( \Delta = \text{energy parameter} \sim \text{width of the d band} \). The contribution from \( K_o \) is always positive. The exact calculation of \( \chi_o \) and \( < r^{-3} > \) is very difficult and requires a rather exact knowledge of the electronic wave functions. However, estimates of \( K_o \) have been made and it is found that \( K_o \) is especially important in the early transition metals and must be taken into consideration (18).

The interpretation of the isotropic Knight shift results for the three alloy systems studied requires a knowledge of the relative contributions of \( K_s, K_d, \) and \( K_o \) to \( K_{iso} \) in scandium metal. The Knight shift is obviously closely associated with the magnetic susceptibility. Clogston, et al. (18), give an expression showing the close relationship between \( K_{iso} \) and \( \chi \):

\[ K_{iso} = \alpha(s)\chi_s + \alpha(d)\chi_d + \alpha(o)\chi_o, \]  

(52)

where \( \chi_s \) and \( \chi_d \) are spin paramagnetic susceptibilities of s and d-electrons respectively, and \( \chi_o \) is the orbital susceptibility discussed
Gardner and Penfold (24) analyzed susceptibility data and the data on the temperature dependence of $K_{av}$ of Sc$^{45}$ reported by Blumberg, et al. (10), to determine the various quantities in Equation 52. On this basis, they find $\alpha(0) = 13$ and $\chi_0 = 95 \times 10^6$ emu/g-atom. This corresponds to a value for $K_0$ of .12% which is almost half of the total measured Knight shift. Gardner and Penfold had a more difficult time deciding upon values for $\alpha(s)$, $\alpha(d)$, $\chi_s$, and $\chi_d$.

The temperature dependence of the Knight shift is usually associated with $K_d$. However, the temperature dependence of $K_d$ is opposite to that observed for $K_{av}$ in scandium. Clogston, et al. (18), attribute the temperature dependence to $K_o$ in the case of scandium, but Gardner and Penfold rejected this on the grounds that it would require an improbable band structure. Instead, they argued that $K_s$ is the temperature dependent term made possible by a thorough mixing of s and d wave functions in the conduction band. Consequently, the choice of $\alpha(s)$ and $\alpha(d)$ will determine $\chi_s$ and $\chi_d$ since the sum of $\chi_s$ and $\chi_d$ is constant for a given temperature. Gardner and Penfold set the following limits on $\alpha(s)$ and $\alpha(d)$, $156 > \alpha(s) > 109$, $-11.5 < \alpha(d) < 0$.

Gardner and Penfold also analyzed $T_\perp$ data furnished them by Butterworth in a private communication. The values which they derived from these data were $\alpha(s) \sim 150$, $\alpha(d) \sim -5$, and $\alpha(0) \sim 13$. These
results correspond to $K_s = 0.22\%, K_d = -0.09\%$, and $K_o = +0.12\%$. Masuda (43) made an independent analysis of $K_{av}$ in scandium metal from another set of TT data. His values were $K_s = 0.15\%, K_d = -0.04\%$, and $K_o = 0.14\%$. These values fall in the range for $a(s)$, $a(d)$, and $a(o)$ indicated by Gardner and Penfold, and they correspond quite well to the results from the Butterworth data.

It must be emphasized that the analyses of the Knight shift in scandium by Gardner and Penfold and Masuda involved the interpretation of the susceptibility and relaxation time data in terms of $K_{av}$ rather than $K_{iso}$. Thus, one should be somewhat careful in using their results. The values of $K_o$ are probably good. Thus, the use of $K_{av}$ rather than $K_{iso}$ should only affect the relative values of $K_s$ and $K_d$ and not their sum. The isotropic Knight shift of the Sc-Y alloys will be discussed on this basis.

The isotropic Knight shift data from Table 3 for the Sc-Y alloy system are plotted as a function of yttrium concentration in Figure 14. It will be observed that the Sc$^{45}$ Knight shift decreases monotonically with Y concentration and within experimental uncertainty the decrease is linear. For purposes of determining just what is changing, the following expression for $K_{iso}$ which is equivalent to Equations 48 and 52 should be considered:

$$K_{iso} = N(E_F) \left[ A < |\psi(\phi)|^2 > F - B < |\rho(\phi)| > d \right] + K_o,$$

(53)
Figure 14. The isotropic and anisotropic Knight shift results for the Sc-Y alloy system. The solid lines only serve to indicate the linear nature of the variations in the two parameters.
Sc-Y ALLOY SYSTEM

- $K_{iso}$
- Anisotropic Knight Shift

Y Concentration (Atom per Cent)
where $N(E_F), \langle |\psi(o)|^2 \rangle_F, \langle |\rho(o)|^2 \rangle_d$ and $K_o$ have been defined previously and $A$ and $B$ are constants. One arrives at Equation 53 in the following way: Given $K \propto \langle |\psi(o)|^2 \rangle_F$ and $K \propto \langle |\rho(o)|^2 \rangle_d$ and that the total spin susceptibility is $\chi^e_F = \chi^s_s + \chi^d_d$, which in turn is proportional to $N(E_F)$, it is permissible to write $K_s = N(E_F)A \langle |\psi(o)|^2 \rangle_F$ and $K_d = -N(E_F)B \langle |\rho(o)|^2 \rangle_d$ where $A$ and $B$ are proportionality factors. The negative sign was introduced in $K_d$ to emphasize the fact that $K_d$ makes a negative contribution to $K_{iso}$. The important factor $\langle r^{-3} \rangle$ which appears in $K_o$ is an average over all d-electrons and not just those at the Fermi surface; hence $K_o$ may be considered independent of $N(E_F)$.

The density of electron states at the Fermi surface, $N(E_F)$, may be found from the electronic specific heat coefficient using Equation 47. Montgomery and Pells (46) report that $\gamma$ for scandium is 11.3 $\text{mj}/\text{K}^2\text{-g}$ atom. However, Gardner and Penfold (24) indicate that in a private communication from Montgomery and Pells, they were informed that the value for $\gamma$ actually ranged between 10 $\text{mj}/\text{K}^2\text{-g}$ atom and 11 $\text{mj}/\text{K}^2\text{-g}$ atom depending upon the sample of scandium metal used. Betterton and Scarbrough (8) in their study of Sc-Zr alloys report the electronic specific heat coefficient of Sc to be 10.7 $\pm$ 0.1 $\text{mj}/\text{K}^2\text{-g}$ atom. The value for $\gamma$ given by Betterton and Scarbrough will be the value used in this analysis. Montgomery and Pells also found the value for $\gamma$ for yttrium to be 10.2 $\pm$ 0.1 $\text{mj}/\text{K}^2\text{-g}$ atom.
Segel (52) observed a monotonic decrease in the density of states between Sc and Y using data associated with the isotropic Knight shifts of both Sc and Y. If one assumes that $\gamma$ decreases linearly from 10.7 mj/$^\circ$K g atom to 10.2 mj/$^\circ$K g atom, then it will have decreased by $\frac{1}{2}\%$ with 10 atom-percent yttrium content. However, since the reported uncertainty in $\gamma$ is $1\%$, for all practical purposes $\gamma$ and hence $N(E_F)$ remains constant for the Sc-Y alloys considered in this study.

It was stated in connection with Equation 53 that $A$ and $B$ were constants. Actually, this statement must be qualified somewhat. First, $A$ and $B$ both have a volume dependence associated with $V_0$. The atomic volume increases by approximately $3\%$ in going from scandium metal to ten atom percent yttrium content. Hence $A$ and $B$ will also increase by somewhat less than $3\%$ due to the volume dependence.

A second qualification has to do with electron-electron interactions. If one considers the effect of electron-electron interactions, it is found that (53):

$$\chi^e_p = \chi_p \frac{\phi}{1-\phi N(E_F)},$$

(54)

where

$$\chi_p = \text{Pauli susceptibility of Equation 45},$$

$$\phi = \text{interaction parameter}.$$

Gardner and Penfold (24) found from an analysis of the susceptibility data for scandium metal, that $\phi = 0.091$ ev in scandium. Gardner, et al. (25),
report that $\phi = 0.029$ ev in yttrium metal. Using the specific heat data to calculate $N(E_F)$ it is found that the denominator of Equation 54 increases from 0.60 for scandium metal to 0.87 for yttrium metal. If one assumes a uniform change in $\phi$, then this term increases by about 4% across the concentration region being considered. This term is a common denominator factor of both $A$ and $B$ as Equation 53 is written, and so $A$ and $B$ should decrease in value by somewhat less than 4% due to the electron-electron interaction. However, the volume and interaction effects tend to cancel each other, and so to a good approximation $A$ and $B$ may be considered constant in this analysis.

The term $K_o$ is principally dependent upon $< r^{-3} >$ which is quite sensitive to changes in the state wave functions. It is very difficult to determine $< r^{-3} >$ for the alloys and it will be assumed that it remains constant in the alloy region of interest. It might be commented that if $< r^{-3} >$ does change, it will probably decrease in value since the atomic radius of yttrium is larger than that of scandium. For this analysis, $K_o$ will be considered constant.

The two variable quantities remaining in Equation 53 with regard to the Sc-Y system are $< |\psi(o)|^2 >_F$ and $< |\rho(o)|^2 >_d$. The decrease in $K_{iso}$ can be interpreted on the basis of a change in the conduction electrons from an $s$-character to a $d$-character. Such a change would decrease the probability density, $< |\psi(o)|^2 >_F$, for an electron at the Fermi surface.
to be at the nucleus. It would also increase the degree of core polarization and hence increase $|\rho(o)|^a$. Both changes would have the effect of reducing $K_{iso}$.

The anisotropic Knight shift data from Table 3 which are associated with the Sc-Y system are plotted as a function of Y concentration in Figure 14. It will be observed that the absolute value of $a$ also decreases linearly, within experimental error, with increasing yttrium content. Segel's data was available for reanalysis using the MLHS method, and it was found, as he had reported, that the absolute value of $a$ continues to decrease in essentially a linear fashion until it becomes zero for the alloy with approximately 85 atom percent yttrium content. The anisotropic Knight shift then becomes positive and begins to increase in absolute value.

From Section II. A it will be recalled that the anisotropic Knight shift could be written as:

$$ a = \beta^2 N(E_F) V_0 q_F, $$  \hspace{1cm} (55)

where

$N(E_F)$ = density of electron states at the Fermi surface per unit energy and volume,

$V_0$ = atomic volume,

$q_F$ = electric field gradient due to a non-s electron at the Fermi surface.
From the discussion of $K_{iso}$, $N(E_F)$ and $V_o$ can be considered essentially constant for the alloys considered in this study. Therefore, the important term in Equation 55 is $q_F$. The fact that $a$ is negative implies that $q_F$ is negative. Negative $q_F$ implies that at the Fermi surface the electron charge distribution is greater in the directions perpendicular to the symmetry axis. The fact that $a$ becomes more positive with increasing yttrium content indicates that $q_F$ is becoming more positive. Hence the electron charge distribution at the Fermi surface is changing into the configuration where it is greatest in the direction of the symmetry axis. From Segel's data it appears that this redistribution of the charge density continues across the system; the distribution becoming symmetric at about 85 atom percent yttrium content. Some of the implications of the change in $a$ will be considered in the discussion of the electric quadrupole interaction.

The effective electric field gradient (e.f.g.) at a nuclear site in a non-cubic metal is the sum of two terms. One of the terms is the e.f.g. due to the positive ions making up the lattice. This term includes the enhancement due to the Sternheimer antishielding effect. There is also a contribution arising from the e.f.g. due to the non-$s$ electrons in the conduction band. It is possible to calculate the lattice contribution quite accurately but the theoretical calculation of the e.f.g. due to the conduction electrons is much more difficult and
requires precise knowledge of the band structure and electron wave functions involved. Generally, the e.f.g. of the conduction electrons must be estimated by taking the difference between the measured total electric field gradient and the calculated lattice field gradient.

It has been pointed out (27) (58) that the nmr experiment can only determine the magnitude of the field gradient and not the sign and that ambiguity arises in the determination of the sign and magnitude of the conduction electron contribution if the lattice e.f.g. is less than the total e.f.g. in magnitude. In such a case, the e.f.g. of the electrons may simply add to the lattice gradient or it may have the opposite sign of the lattice e.f.g. and a magnitude equal to the sum of the lattice and measured field gradients. Barnes, et al. (4), show that this ambiguity arises in scandium metal where the calculated electric field gradient due to the lattice is 44% of the total measured field gradient. It might be hoped that the relative signs of the two contributions to the total field gradient could be deduced from an observation of how the three e.f.g.'s vary relative to each other in dilute scandium alloys.

The lattice contribution to $q$, the electric field gradient, can be calculated from the following formula for the hcp structure (21):

$$q(\text{lattice}) = (0.0065 - 4.3584 \frac{c}{a} - 1.633)/a^3,$$

(56)

where $c$ and $a$ are the usual lattice parameters associated with the hcp lattice. Values for $c$ and $a$ for the alloys of the Sc-Y system may be
determined from the study on the system by Beaudry and Daane (6).

The electric quadrupole coupling constant due to the lattice is given by

\[
\left( \frac{e^2 q Q}{h} \right)_L = \frac{e^2 Z q \text{(lattice)} Q (1 - \gamma^\infty)}{h},
\]  

where

- \( e \) = electronic charge,
- \( Z \) = degree of ionization,
- \( Q \) = nuclear quadrupole moment,
- \( \gamma^\infty \) = Sternheimer antishielding factor.

For scandium, the following values of the various terms in Equation 57 will be used:

\[ Z = 3, \]

\[ \gamma^\infty = -7; \quad (27) \]

\[ Q = -0.22 \text{ barn.} \quad (28) \]

The quadrupole coupling constant determined experimentally is given by

\[
\left( \frac{e^2 q Q}{h} \right)_{\text{exp}} = 14v \nu.
\]  

The values for \( \nu \) which were used are in Table 3.

Table 4 contains values calculated for the quadrupole coupling constant due to the lattice and the measured quadrupole coupling constant for each Sc-Y alloy. It also contains the values for \( a \) and \( b \) used for each alloy and the two quantities \( \Delta_1 \) and \( \Delta_2 \):
\[ \Delta_1 = \left| \frac{e^2 q Q}{h} \right|_{\text{exp}} + \left| \frac{e^2 q Q}{h} \right|_L \]

\[ \Delta_2 = \left| \frac{e^2 q Q}{h} \right|_{\text{exp}} - \left| \frac{e^2 q Q}{h} \right|_L . \]

Table 4. Quadrupole coupling constants for Sc-Y alloys

<table>
<thead>
<tr>
<th>Alloy (a/o Y)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>( \frac{e^2 q Q}{h} ) Latt (Mc/sec)</th>
<th>( \frac{e^2 q Q}{h} ) Expt (Mc/sec)</th>
<th>( \Delta_1 ) (Mc/sec)</th>
<th>( \Delta_2 ) (Mc/sec)</th>
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<tbody>
<tr>
<td>0.5</td>
<td>3.315</td>
<td>5.276</td>
<td>0.931</td>
<td>1.904</td>
<td>2.835</td>
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<td>0.937</td>
<td>1.848</td>
<td>2.785</td>
<td>0.923</td>
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<td>0.936</td>
<td>1.820</td>
<td>2.756</td>
<td>0.884</td>
</tr>
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<td>5.0</td>
<td>3.332</td>
<td>5.300</td>
<td>0.951</td>
<td>1.778</td>
<td>2.729</td>
<td>0.827</td>
</tr>
<tr>
<td>10.0</td>
<td>3.350</td>
<td>5.325</td>
<td>0.957</td>
<td>1.764</td>
<td>2.721</td>
<td>0.807</td>
</tr>
</tbody>
</table>

The experimental quadrupole coupling constant, \( \left( \frac{e^2 q Q}{h} \right)_{\text{exp}} \), is plotted in Figure 15 as a function of yttrium content. The decrease in the coupling constant with increasing yttrium content is somewhat unexpected and will be commented upon later. Segel (52) had reported a sharp increase in the coupling constant and a reanalysis of his data using the NLLS method affirmed the fact that \( \left( \frac{e^2 q Q}{h} \right) \) increases more than two-fold across the system. Moreover, additional data were available for an alloy with 20 atom percent yttrium content, making it possible to determine one additional value of the quadrupole coupling constant. More data should be taken for the higher concentration alloys before
Figure 15. The electric quadrupole coupling data for the Sc-Y alloy system. The \( \frac{e^2 q Q}{h} \) \_EXPERIMENT are the experimentally determined values of the electric quadrupole coupling constant. The \( \frac{e^2 q Q}{h} \) \_LATTICE are the values of the contribution of the ions in the lattice to the quadrupole coupling constant, and are calculated in accordance with the discussion in the text.
Sc-Y SYSTEM

- $\frac{e^2 q Q}{h}$ EXPERIMENT
- $\frac{e^2 q Q}{h}$ LATTICE

Y CONCENTRATION (ATOM PER CENT)

CONCENTRATION (ATOM per cent)
quantitative statements are possible, in the opinion of the author. However, it appears that the quadrupole coupling constant of scandium changes smoothly across the system, decreasing slightly for dilute alloys to a minimum of 1.76 Mc/sec at about 10 atom percent yttrium content and then increasing again to an extrapolated value of about 5.2 Mc/sec in yttrium metal. Before considering the implications of this change in the coupling constant, it is necessary to relate the anisotropic Knight shift to the quadrupole contribution of the conduction electrons.

Equation 55 relates the anisotropic Knight shift to the average electric field gradient due to a non-s electron at the Fermi surface. The electric field gradient due to the conduction electrons considered above is an average over all electrons in the conduction band. Borsa and Barnes (12) show that if one assumes that the electron wave functions are constant across the conduction band, then

\[ q_{c.e.} = Z q_F \]

where \( q_{c.e.} \) is \( q \) due to all the conduction electrons and \( Z \) is the number of electrons in the conduction band. It is found that calculating \( q_F \) and \( q_{c.e.} \) using the electronic specific heat coefficient to determine \( N(E_F) \) gives values which are much higher than those observed experimentally, even assuming that the lattice and conduction electron field gradients have opposite signs. The reasons for this discrepancy are not known. However, it does seem that a relationship does exist between the
variations in the anisotropic Knight shift and variations in the conduction electron electric field gradient.

An attempt will be made to determine the relative signs of the lattice and conduction electron electric field gradients from the variations in $a$, the anisotropic Knight shift. Since the quadrupole coupling constant is directly related to the electric field gradient, changes in the coupling constant should reflect changes in the field gradient. The two quantities $\Delta_1$ and $\Delta_2$ were defined above and values for the alloys are tabulated in Table 4. The quantity $\Delta_1$ corresponds to the contribution of the electrons to the quadrupole coupling constant when the signs of the electron and lattice field gradients are opposed. Conversely, $\Delta_2$ corresponds to the conduction electron contribution when the field gradient signs are the same. Figure 16 shows a plot of $\Delta_1$ and $\Delta_2$ as a function of concentration.

Recalling $\frac{a}{\sqrt{N(E_F)}} \propto q_F \propto \frac{e^2qQ}{h}$, the calculation of the variation in the coupling constant of the conduction electrons was made as follows:

$$\frac{e^2qQ}{h} (\text{Alloy}) = (0.5)^X \frac{a(\text{Alloy})}{a(0.5)} \times \frac{V_o(0.5)}{V_o(\text{Alloy})},$$

where

$$\frac{e^2qQ}{h} (\text{Alloy}) = \text{conduction electron contribution to the coupling constant in a given alloy},$$

$$\Delta (0.5) = \text{respective value of } \Delta_1 \text{ or } \Delta_2 \text{ in the alloy with 0.5}$$
Figure 16. Comparison of $\Delta_1$ and $\Delta_2$ for the Sc-Y alloy system. The parameters $\Delta_1$ and $\Delta_2$ are defined in the text. The parameter $\Delta_1$ represents the case in which the signs of the electric field gradients due to the conduction electrons and the lattice ions are opposite. The quantity $\Delta_2$ is representative of the assumption that the signs of the electric field gradients of the conduction electrons and lattice ions are the same. The values of $(\Delta_1)^{\text{EXPT}}$ were determined by adding the observed quadrupole coupling constants to the calculated quadrupole coupling constant due to the lattice. Subtracting the calculated values of the lattice coupling constant from the observed coupling constant values yielded values for $(\Delta_2)^{\text{EXPT}}$. The values for $(\Delta_1)^{\text{CALC}}$ and $(\Delta_2)^{\text{CALC}}$ were calculated from Equation 60 in the text, and indicate how $(\Delta_1)^{\text{EXPT}}$ and $(\Delta_2)^{\text{EXPT}}$ for the alloy with 0.5 atom percent Y content vary due to changes in the anisotropic Knight shift. The choice of the alloy with 0.5 atom percent Y content as the alloy for which the calculated values of $\Delta_1$ and $\Delta_2$ are equal to the experimental values was arbitrary.
atom percent Y content,

\[ a(\text{Alloy}) = \text{value of } a \text{ in the alloy}, \]

\[ a(0.5) = \text{value of } a \text{ in the alloy with 0.5 atom percent } Y, \]

\[ V_o(0.5) = \text{value of } V_o \text{ in the alloy with 0.5 atom percent } Y, \]

\[ V_o(\text{Alloy}) = \text{atomic volume in the alloy}. \]

In these calculations \( N(E_F) \) was considered constant over the region of interest, but variations in \( V_o \) were considered using the atomic volume data for scandium and yttrium reported by Spedding, et al. (57). The values for \( \Delta_1 \) and \( \Delta_2 \) calculated in this way are also plotted in Figure 16 for comparison with the experimental values. Unfortunately, no final conclusions can be drawn from these results, though it appears that the correlation between experimental and calculated values of \( \Delta_1 \) is better than for \( \Delta_2 \). This would imply that the conduction electron e.f.g. is opposed in sign to the lattice field gradient.

Consider, however, the quadrupole results for the entire Sc-Y system. If \( q_F \) is truely reflective of the conduction electron e.f.g., then it would appear that the conduction electron field gradient steadily decreases in magnitude as one adds Y to the system. This is implied from the anisotropic Knight shift results discussed above. Consequently, the magnitude of the quadrupole coupling contribution of the conduction electrons would also decrease and become essentially zero at about 85\% Y content. This would imply that the pronounced increase in
the quadrupole coupling was due to a change in the lattice contribution, most likely through a change in $\gamma_0$ since $q(\text{lattice})$ remains essentially constant.

Supposing that the lattice and conduction electron e.f.g. are opposed in sign, the sign of the measured e.f.g. would be the same as the e.f.g. of the conduction electrons because the lattice e.f.g. is smaller than the observed e.f.g. The decrease in $q_0$ would result in a net decrease in the magnitude of the measured e.f.g. across the system if $\gamma_0$ is constant in magnitude. The two-fold increase in the observed e.f.g. cannot be accounted for by a decrease in $\gamma_0$. An increase in the magnitude of $\gamma_0$ would result in an observed quadrupole coupling which decreases to a value of zero and then increases again with the change of sign.

Now if the e.f.g. of the conduction electrons has the same sign as the e.f.g. of the lattice, the observed variation in \( \frac{e^2q_0}{h} \) could be explained as follows: The initial decrease in the coupling constant is caused in part at least by the decrease in $q_{c.e.}$. The minimum and sharp increase in the value of \( \frac{e^2q_0}{h} \) may be caused by a sharp increase in the magnitude of the Sternheimer antishielding factor. The increase in $\gamma_0$ would have to be great enough to counter balance the decrease in $q_{c.e.}$ and result in a net increase in the measured $q$ but this may not be unreasonable especially in light of the other alternatives. These arguments would then lead one to conclude that the signs of $q_{c.e.}$ and
Zirconium is the second element in the second transition series and thus has one more d-electron than yttrium. Presumably, this extra d-electron will enter the conduction band when zirconium is alloyed with scandium. It might be expected that this extra electron in the conduction band will cause changes in the hyperfine interaction parameters in the Sc-Zr system which are quite different from those observed in the Sc-Y system. Different effects were observed, as the following discussion indicates.

The isotropic Knight shift data for the Sc-Zr system, tabulated in Table 3, is plotted in Figure 17 as a function of zirconium concentration. Initially, up to two or three atom percent zirconium concentration, $K_{iso}$ appears to remain constant or to increase slightly. Betterton and Scarbrough (8) observed a rather sharp decrease in the electronic specific heat coefficient and hence in $N(E_F)$ for the Sc-Zr alloy system as zirconium is added to scandium metal. A slight increase in $K_{iso}$ would consequently imply a possible increase in $< |\psi(o)|^2 >_F$, referring to Equation 53. An increase in $< |\psi(o)|^2 >_F$ would, in turn, imply that the additional electrons were entering the conduction band with mainly s-character, indicating a slight increase in the height of the s-band at the Fermi surface. The isotropic Knight shift must be analyzed further.
Figure 17. The isotropic and anisotropic Knight shift results for the Sc-Zr alloy system. The solid lines are only drawn to indicate the trends in the variations of the parameters.
Sc-\MakeLowercase{Er} SYSTEM

\begin{itemize}
  \item $K_{iso}$
  \item Anisotropic Knight Shift
\end{itemize}

\textbf{Er CONCENTRATION (ATOM PER CENT)}

$K_{iso}$ (%) vs Er CONCENTRATION (ATOM PER CENT)
before any speculation is possible about the change in $K_{iso}$ for concentrations of more than three atom percent Zr content.

Further analysis of $K_{iso}$ necessitates referring again to Equation 53 and the related discussion:

$$K_{iso} = N(E_F)[A < |\psi(\alpha)|^2> - B < |\rho(\alpha)|^2>^d + K_0.$$  \hspace{1cm} (53)

The two factors A and B were observed to be functions of $V_o$, the atomic volume, and $\phi$, an electron-electron interaction parameter. The atomic volume of zirconium differs by less than $6\%$ from the atomic volume of scandium, so $V_o$ may be considered to be essentially constant in the region of zirconium concentration being studied.

The term which is significant with respect to $\phi$ is $(1 - \phi N(E_F))$ which is in the denominator of A and B. No information about $\phi$ was found for zirconium. If one considers $\phi$ to remain constant at the scandium value, then A and B will decrease by about 10\% across the region of interest due to the effect of the decreasing density of states upon $(1 - \phi N(E_F))$. The decrease in A and B will be even greater if the value of $\phi$ for zirconium is near the value for yttrium, which is about 1/3 the value of $\phi$ in scandium. An increase in $\phi$ will slow the rate of decrease of A and B. However, since the information about how $\phi$ may be changing is not available, A and B will be considered constants for the purpose of analysis. Possible consequences of non-constant A and B will be considered later.
Several values for $K_0$ in scandium metal were given in the discussion of $K_{iso}$ for the Sc-Y system. Gardner and Penfold (24) estimated that $K_0 \approx 0.12\%$ from susceptibility and relaxation time data. Since they analyzed their data assuming $K_{iso} = 0.24\%$ rather than the better value of $0.25\%$, their estimate may be slightly low. Masuda (43) estimated $K_0 = 0.14\%$ from relaxation time measurements, getting a value of $0.25\%$ for the total average Knight shift. For purposes of this discussion, $K_0$ will be estimated to be $0.13\%$ and will be considered constant for the alloys being studied. The constant value $K_0 = 0.13\%$ was subtracted from the measured $K_{iso}$ for each alloy and values of $(K_{iso} - K_0)$ for each alloy are tabulated in Table 5.

Consideration of Equation 53 shows that $(K_{iso} - K_0)$ has an explicit dependence upon $N(E_F)$. For this analysis, only changes in $N(E_F)$ are important and these changes are directly reflected in the variation of $\gamma$, the electronic specific heat coefficient. Values of $\gamma$ for each alloy were found by interpolation from the electronic specific heat data for the Sc-Zr system reported by Betterton and Scarbrough (8). These specific heat values are also tabulated in Table 5.

Values for $(K_{iso} - K_0)_{calc}$ were obtained in the following way: The calculated value of $(K_{iso} - K_0)$ was set equal to the experimental value for the alloy with two atom percent zirconium content. Then for a given alloy,
\[(K_{\text{iso} - K_o})_{\text{Alloy}} = (K_{\text{iso} - K_o}(2.0) \times \frac{\gamma(\text{Alloy})}{\gamma(2.0)}), \]

where

- \((K_{\text{iso} - K_o})_{\text{Alloy}}\) = calculated value of \((K_{\text{iso} - K_o})\) for a given alloy,
- \((K_{\text{iso} - K_o}(2.0))\) = experimental value of \((K_{\text{iso} - K_o})\) for 2.0 atom percent Zr,
- \(\gamma_{\text{Alloy}}\) = electron specific heat coefficient for the alloy of interest,
- \(\gamma(2.0)\) = electron specific heat coefficient for 2.0 atom percent Zr.

The results are tabulated in Table 5.

Table 5. Isotropic Knight shift data for the Sc-Zr System

<table>
<thead>
<tr>
<th>Alloy (a/oZr)</th>
<th>((K_{\text{iso} - K_o})_{\text{exp}}) (%)</th>
<th>((K_{\text{iso} - K_o})_{\text{calc}}) (%)</th>
<th>(\gamma) ((\text{mJ}/\text{K}^2\cdot\text{g atom}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.119</td>
<td>0.124</td>
<td>10.65</td>
</tr>
<tr>
<td>1.0</td>
<td>0.118</td>
<td>0.124</td>
<td>10.60</td>
</tr>
<tr>
<td>2.0</td>
<td>0.122</td>
<td>0.122</td>
<td>10.44</td>
</tr>
<tr>
<td>4.0</td>
<td>0.121</td>
<td>0.119</td>
<td>10.15</td>
</tr>
<tr>
<td>8.0</td>
<td>0.111</td>
<td>0.112</td>
<td>9.60</td>
</tr>
<tr>
<td>14.2</td>
<td>0.101</td>
<td>0.103</td>
<td>8.80</td>
</tr>
</tbody>
</table>

Figure 18 is a plot of \((K_{\text{iso} - K_o})_{\text{exp}}\) and \((K_{\text{iso} - K_o})_{\text{calc}}\) as functions of zirconium concentration.

Consideration of Table 5 and Figure 18 reveals that the agreement
Figure 18. Study of the quantity \((K_{iso} - K_0)\) in the Sc-Zr alloy system. The terms \(K_{iso}\), isotropic Knight shift, and \(K_0\), the orbital contribution to the isotropic Knight shift, are discussed in the text. The term \((K_{iso} - K_0)_{\text{EXPT}}\) was found by subtracting \(K_0 = 0.12\%\) from the experimentally determined values for \(K_{iso}\). The calculated values, \((K_{iso} - K_0)_{\text{CALC}}\), were found from Equation 61 in the text, and represent how the value for \((K_{iso} - K_0)_{\text{EXPT}}\) for the alloy with 2 atom percent Zr content changes due to the change in the density of electron states at the Fermi surface. The value of \((K_{iso} - K_0)_{\text{CALC}}\) for the alloy with 2 atom percent Zr was arbitrarily chosen to be equal to the corresponding value of \((K_{iso} - K_0)_{\text{EXPT}}\).
Sc-Zr SYSTEM

\[ (K_{ISO} - K_0)^{EXPT} \]
\[ (K_{ISO} - K_0)^{CALC} \]

\[ (K_{ISO} - K_0)^{EXPT} = (K_{ISO} - K_0)^{CALC} \]

Zr CONTENT (ATOM PER CENT)

12.0 14.0 16.0 18.0 20.0 22.0 24.0 26.0 28.0 30.0

.130

.120

.110

.100

0.0 2.0 4.0 6.0 8.0 10.0 12.0 14.0
between the experimental and calculated values of \((K_{iso} - K_0)\) is very good, especially for alloys with zirconium concentrations greater than two atom percent. These results indicate that within the experimental uncertainty and considering the approximations made above, \([A|\psi(o)|^2_F - B|\rho(o)|^2_d]\) is constant with the possible exception of the alloys with less than two atom percent zirconium content. If \(A\) and \(B\) do remain essentially constant, then one can draw the conclusion that the character of the electrons and their wave functions at the Fermi surface remain undisturbed with the addition of the extra electron to the conduction band. If \(A\) and \(B\) are actually decreasing due to electron-electron interactions as discussed above, then \(<|\psi(o)|^2_F\) and \(<|\rho(o)|^2_d\) must be changing so as to keep the total expression in brackets constant. This latter alternative seems unlikely, but not impossible.

The anisotropic Knight shift data are plotted in Figure 17 as a function of zirconium content. The behavior of \(a\) in the Sc-Zr system is very much different from the behavior of \(a\) in the Sc-Y system. Initially, the anisotropic Knight shift magnitude decreases approximately as the density of states decreases indicating that \(q_F\) remains nearly constant. However, the increase in the magnitude of \(a\) for concentrations greater than about four atom percent zirconium content indicates a rather rapid increase in \(q_F\). This should imply a substantial change in the conduction electron s and d character at the Fermi surface.
From the discussion of the isotropic Knight shift, it will be recalled that the variation in $K_{iso}$ does not appear to indicate such a change in the wave character of these electrons. Moreover, the apparent anomalous behavior of $K_{ax}$ does not seem to be manifested in the variation of the quadrupole coupling constant, as will be pointed out in the discussion of that parameter.

One explanation for the apparently strange behavior of the anisotropic Knight shift might be that the measured parameter is not $K_{ax}$, as defined previously. If another type of interaction is present which has the effect of broadening the resonance line in direct proportion to the magnetic field, then it may be difficult to separate the effects of this interaction from those of the anisotropic Knight shift. One interaction of this sort results from indirect coupling of nuclei with localized ionic spins through the conduction electrons. This coupling will be discussed more fully in connection with the Sc-Gd system. However, this only occurs for cases in which the solute has a localized electronic moment, such as the rare earth elements with an incomplete f-shell and certain other transition elements. Zirconium has no such moment in zirconium metal. However, ZrZn$_2$ was observed to be ferromagnetic (39). So it may be possible to have a localized moment in the Sc-Zr alloys, though the specific heat work of Betterton and Scarbrough did not indicate that this was the case. At present, the apparent variation in $q_F$ is
The quadrupole coupling constant data are plotted in Figure 19 as a function of concentration. The contribution to the quadrupole coupling constant from the lattice was calculated for each alloy using Equations 56 and 57. In making these calculations, the data pertaining to the lattice parameters were taken from Beaudry and Daane (6). Also, the values \( \gamma_\infty = -7 \), \( Z = 3 \), and \( Q = -0.22 \) barn were used in the calculations with Equation 57. These results are tabulated in Table 6, and are plotted in Figure 19.

Table 6. Quadrupole coupling data for Sc-Ar alloys

<table>
<thead>
<tr>
<th>Alloy (a/cZr)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>( \frac{e^2qQ}{h} ) exp (mcps)</th>
<th>( \frac{e^2qQ}{h} ) Lattice (mcps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>3.313</td>
<td>5.274</td>
<td>1.904</td>
<td>0.938</td>
</tr>
<tr>
<td>1.0</td>
<td>3.313</td>
<td>5.274</td>
<td>1.932</td>
<td>0.945</td>
</tr>
<tr>
<td>2.0</td>
<td>3.312</td>
<td>5.269</td>
<td>1.960</td>
<td>0.961</td>
</tr>
<tr>
<td>4.0</td>
<td>3.311</td>
<td>5.263</td>
<td>1.988</td>
<td>0.993</td>
</tr>
<tr>
<td>8.0</td>
<td>3.309</td>
<td>5.252</td>
<td>1.876</td>
<td>1.048</td>
</tr>
<tr>
<td>14.2</td>
<td>3.305</td>
<td>5.236</td>
<td>2.156</td>
<td>1.118</td>
</tr>
</tbody>
</table>

In Figure 19, the lattice contribution is plotted such that the lattice e.f.g. has the same sign as the observed e.f.g. Since the magnitude of the lattice field gradient is about half that of the total field gradient, plotting the lattice contribution in this way also implies that the lattice e.f.g. has the same sign as the conduction electron.
Figure 19. The electric quadrupole coupling constant results for the Sc-Zr alloy system. The \( \frac{e^2 q Q}{h} \) _EXPT_ are the experimentally determined values of the electric quadrupole coupling constant. The \( \frac{e^2 q Q}{h} \) _LATTICE_ represent the contribution to the coupling constant from the ions in the lattice; the discussion of how these values are calculated appears in the text. The solid lines indicate qualitatively how the two quantities are changing and have no theoretical significance.
Sc-Zr SYSTEM

- $\frac{c^2qQ}{h}$ _EXPT_
- $\frac{c^2qQ}{h}$ _LATTICE_

**Zr CONCENTRATION (ATOM PER CENT)**

**Mic/SEC**
field gradient. It can be seen from a study of Figure 19 and Table 6, that the increase in the observed quadrupole coupling can be accounted for, within the experimental uncertainties, by the increase in the lattice quadrupole coupling. This implies two things.

First, the signs of the conduction electron and lattice electric field gradients are the same. This was also implied by the Sc-Y data. Second, the conduction electron contribution appears to remain essentially constant. There is no reflection of the strange behavior of the anisotropic Knight shift in the behavior of the quadrupole coupling. Even if one were to argue that the contribution from the lattice should be reversed, the resulting apparent variation in the conduction electron contribution could not be accounted for by the apparent variation in \( q_p \) and presumably \( q_{c.e.} \).

C. The Sc-Gd System

Gadolinium is a rare earth element with a half-filled f-shell and a valence configuration identical to that of scandium and yttrium. The effect of the unfilled f-shell on the Sc\(^{15}\) resonance is very striking. The scandium resonance line is broadened by the addition of Gd very quickly so that only alloys with less than four atom percent gadolinium content were studied. Also, there was much less information about gadolinium of the type which could be correlated with the NMR results available. For these reasons, the discussion of the Sc-Gd system will
be somewhat shorter than for the other two alloy systems.

The isotropic Knight shift is plotted in Figure 20 as a function of gadolinium concentration. The Knight shift appears to decrease monotonically in an essentially linear manner. This appears to be the typical behavior for $K_{\text{iso}}$ of the solvent in dilute alloy systems based upon the observation of the Sc-Y system in this study and upon the observations of Drain (22) and Webb (61), among others. Since gadolinium is ferromagnetic below room temperature, electronic specific heat data is not available. Hence, no correlation between variations in $K_{\text{iso}}$ and variations in the density of states can be made.

The anisotropic Knight shift data for the Sc-Gd system are plotted on Figure 21. It will be observed that there is a very dramatic increase in the apparent value of $\alpha$. This apparently large increase in $\alpha$ can be explained in the following way:

The gadolinium ions have a localized magnetic moment due to the half-filled $f$-shell. The direction of this moment continuously changes due to the effects of spin-lattice and spin-spin interactions. For very rapid changes as compared with the spin-spin relaxation rate of the nuclei the nuclei will experience an effective magnetic field on the order of $\mu/r^3$. Here $\mu$ is given by

$$\mu_z = g\beta S B_0 \left( \frac{g\beta S H}{T} \right),$$

where
Figure 20. The isotropic Knight shift and quadrupole coupling results for the Sc-Gd alloy system. The solid lines only indicate the apparent linearity in the variations of the two parameters.
Sc-Gd SYSTEM

Sc-Gd SYSTEM

\( \frac{e^2 q Q}{\hbar} \)

\( K_{iso} \) (%)

Gd CONCENTRATION (ATOM PER CENT)
Figure 21. The anisotropic Knight shift results for the Sc-Gd alloy system.
Sc-Gd SYSTEM

- ANISOTROPIC KNIGHT SHIFT

Gd CONCENTRATION (ATOM PER CENT)
\( \bar{\mu}_z \) = component of \( \bar{\mu} \) in the z-direction,

\( g \) = spectroscopic splitting factor,

\( \beta \) = Bohr magneton,

\( S \) = spin of solute ion core,

\( B_S \) = Brillouin function,

\( H \) = Resonant value of the magnetic field,

\( T \) = absolute temperature.

The distance between the solvent and solute nuclei is \( r \). The solvent resonance line is broadened by an amount proportional to \( \bar{\mu}_z \), and through the Brillouin function, the broadening will be proportional to \( H/T \).

Behringer (7) and Chapman and Seymour (16) have observed this effect on the copper resonance line for Cu-Mn alloys with dilute Mn concentrations.

The contribution to the line width from the localized moment on the Gd ion will be directly proportional to \( H \) at a given temperature. Consequently, since \( K_{ax} \) also has a direct magnetic field dependence, the effects of the two interactions are inseparable in a study made at one temperature. That is, the apparent value of \( a \) found from the analysis of the line width is actually the value of a quantity which is the combined result of the anisotropic Knight shift interaction and the localized moment interaction. Since the line width due to the localized moment is also a function of \( 1/T \), it should be possible to separate the two effects by making a temperature study of the shift parameters of the system.
The quadrupole frequency data in Table 2 indicate the bad scatter in the results obtained from the different width and shift measurements. Averaging the $\Delta \omega_{HL}$ and $K_L$ data results, as was done in the other two cases, results in a series of points which are quite widely scattered and which do not lend themselves to meaningful analysis. It was rather surprising that the results derived from the $K_H$ data show a smooth variation in $\nu_Q$ with concentrations. Since the validity of the $K_H$ data results is questionable in the other systems, it must also be questioned for the Sc-Gd system. However, the quadrupole coupling constants of the Sc-Gd system derived from the $K_H$ data are plotted in Figure 20 for the sake of discussion.

The coupling constant is observed to increase in essentially a linear fashion with Gd content. An increase in the lattice contribution also occurs, on the basis of lattice parameter data for the Sc-Gd system (5). This may imply, as in the cases of the Sc-Zr and Sc-Y systems, that the sign of the e.f.g. of the lattice is the same as that of the conduction electrons.
VI. SUMMARY

Values for three hyperfine interaction parameters associated with the nuclear magnetic resonance of Sc\(^{45}\) were extracted from resonance line width and shift data associated with alloys in the Sc-Y, Sc-Zr, and Sc-Gd systems. The method of extracting these parameters involved the use of machine calculated synthetic data for comparison of theoretical and experimental line shapes and line widths and the use of a non-linear least squares technique. This analysis is more complete and accurate than any which have been made previously on similar non-cubic metals, and it is felt that the values of the parameters which were found can be accepted with considerable confidence. Moreover, this type of analysis of nmr data should prove useful in the study of other non-cubic alloy systems.

The isotropic Knight shift results together with electronic specific heat results from other sources were used in making deductions about the wave character of the electrons at the Fermi surface in the Sc-Y and Sc-Zr alloys. The effect of alloying Y with Sc appears to be that of changing the electrons from an s-character to a d-character. On the other hand, the conduction electron wave functions appear to remain relatively unchanged when Zr is alloyed with Sc. The lack of density of states data for the Sc-Gd system precludes a similar analysis of \( K_{iso} \) for that system. However, the isotropic Knight shift is observed
to decrease linearly in the Sc-Gd system in accord with the observed $K_{iso}$ dependence of solvents in other solid solution alloy systems.

The effects of alloying the three solutes with scandium were quite different with regard to the anisotropic Knight shift. The addition of yttrium to scandium causes the anisotropic Knight shift, and hence the electric field gradient due to the electrons at the Fermi surface to decrease in magnitude monotonically. The anisotropic Knight shift of scandium behaves in an anomalous manner with the addition of zirconium. It decreases slightly and then increases in magnitude at a rather rapid rate. The change in $a$ was not reflected in variations of $K_{iso}$ nor in the quadrupole coupling. Another interaction such as indirect coupling with magnetic ions via conduction electrons may be required to explain the behavior of the anisotropic Knight shift in the Sc-Zr system. The anisotropic Knight shift increases very rapidly with the addition of gadolinium. This increase is explained on the basis of an interaction of the Sc nuclei with the localized moment on the Gd ions.

The electric quadrupole coupling results for each alloy system are consistent with the assumption that the electric field gradient due to the conduction electrons has the same sign as that due to the ions in the lattice. However, one cannot absolutely rule out the possible alternative assumptions which have been discussed.
A temperature study of the nuclear magnetic resonance of Sc\(^{45}\) in these three alloy systems would be helpful. The use of the method of analysis of the nmr data described in this study should determine if the temperature dependence of \(K_{av}\) is due to a temperature dependent \(K_{iso}\), a temperature dependent \(K_{ax}\), or both. Consequently, such a study should help to establish better the magnitudes of the various contributions to the isotropic Knight shift. A temperature study would also help determine the true anisotropic Knight shift for the Sc-Gd system and may help to explain the behavior of the anisotropic Knight shift in the Sc-Zr system.
VII. LITERATURE CITED


VIII. ACKNOWLEDGEMENTS

The author wishes to thank Dr. R. G. Barnes for suggesting this problem and to express his sincere appreciation to him for his encouragement, interest, and guidance during the course of this study.

Mr. B. Beaudry and Mr. P. Palmer are thanked for preparing the alloys used in this study and for their advice concerning techniques for annealing the samples. Thanks are also extended to members of Analytical Chemistry Group I and Spectrochemistry Group I for their analyses of the alloys. The assistance of Mrs. C. A. Hennig and Mrs. M. K. Rhyne of the computer services group in solving several programming problems is gratefully acknowledged.

The author wishes to thank Dr. S. Segel and Mr. D. R. Torgeson for making their data on the $^{45}$Sc nmr in Sc-Y alloys and scandium metal available for reanalysis with the NLLS method. He would also like to thank Mr. R. Lecander for many interesting discussions and for making one of his revised computer programs available for use in the line shape analysis.

Finally, the author wishes to acknowledge the great importance of the continuing love and morale support provided by his wife and two daughters during the period of this study.
IX. APPENDIX
Table 7. Line width data (in Kc/sec) for the Sc-Zr alloy system. The data given in Tables 7-15 include the average deviations in the experimental measurements.

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Table 9. Line width data (in Kc/sec) for the Sc-Gd alloy system

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Table 10. K_2 data (in %) for the Sc-Zr alloy system.
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<td>0.377 ± 0.013</td>
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<td>0.354 ± 0.023</td>
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<td>0.443 ± 0.035</td>
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Table 11. \( K_H \) data (in %) for the Sc-Y alloy system

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Table 13 (Continued)

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<td>Frequency (Mc/sec)</td>
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Table 15. \( K_\alpha \) data (in \%) for the Sc-Gd alloy system

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