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A NUCLEAR MAGNETIC RESONANCE STUDY OF
METALLIC SCANDIUM CHLORIDES

Thomas Patrick McMullen

M.S. Thesis Submitted to Iowa State University

Ames Laboratory DOE
Iowa State University
Ames, Iowa 50011

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24

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A nuclear magnetic resonance study of
metallic scandium chlorides

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Thomas Patrick McMullen

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Department: Physics
Major: Solid State Physics

Approved:

Richard E. Barnes
In Charge of Major Work

C. O. Jucius
For the Major Department

P. J. Kanar
For the Graduate College

Iowa State University
Ames, Iowa

1978

A nuclear magnetic resonance study
of metallic scandium chlorides

Thomas Patrick McMullen

Under the supervision of Richard G. Barnes
From the Department of Physics
Iowa State University

The ^{45}Sc nuclear magnetic resonance was studied in samples having the general composition CsSc_xCl_3 ($0.67 \leq x \leq 1.0$) in the $\text{CsCl}-\text{ScCl}_3-\text{Sc}$ system. In particular the structure of CsScCl_3 suggests that it may be a one-dimensional conductor, and an attempt was therefore made to detect the occurrence of a metal-insulator transition of the type characteristic of one-dimensional conductors. Conventional crossed-coil (nuclear induction) techniques were employed. The ^{45}Sc resonance was studied over a wide frequency range (4-24 MHz) at 300K, these measurements yielding the Knight shift and nuclear electric quadrupole coupling parameters. No significant variation in the spectra occurred from 4.2K to 450K, indicating the absence of a metal-insulator transition in this temperature range.

Analysis of the spectra indicates the existence of at least two different Sc sites in the CsSc_xCl_3 samples. The observed spectra of these sites closely match those obtained in the insulating compounds $\text{CsSc}_{2/3}\text{Cl}_3$ and ScCl_3 . Some NMR evidence was found for the occurrence of

a third site, but this resonance is only partially resolved from the other two within a narrow frequency range (20-24 MHz), and it was not possible to draw any firm conclusions regarding its Knight shift and quadrupole coupling parameters. In addition, the NMR spectra definitely reveal the presence of scandium metal in the CsSc_xCl_3 samples, possibly occurring as very finely divided particles. In conclusion, the NMR results are not incompatible with the formation of CsSc_xCl_3 ($0.67 \leq x \leq 1.0$) in which Sc atoms form one-dimensional chains with a random distribution of vacancies, and with Sc metal present as a second phase.

TABLE OF CONTENTS

	Page
CHAPTER I. INTRODUCTION	1
CHAPTER II. THEORY	3
NMR in Solids	3
General theory	3
Quadrupole interactions, dipole interactions, and line shapes	4
Knight shift	14
Saturation and spin-lattice relaxation	16
Phase Transitions in One-Dimensional Conductors	19
Structural Considerations	21
CHAPTER III. EXPERIMENTAL DETAILS	26
Samples	26
Apparatus	30
NMR equipment	30
Cryogenic and high temperature equipment	34
CHAPTER IV. RESULTS AND DISCUSSION	38
General Results	38
Quadrupole Interaction	38
Dipolar Broadening	50
Knight Shift	51
Model Calculations	51
Dipolar broadening	54
Quadrupole coupling	55
Comparison of Spectra and Assignment of Sites	56

	Page
CHAPTER V. CONCLUSIONS	62
REFERENCES	65
ACKNOWLEDGMENTS	68
APPENDIX	69

CHAPTER I. INTRODUCTION

The past several years have seen a great renewal of interest in both magnetic and conducting lower dimensional systems. While the theoretical aspects of one-dimensional conductors have been studied for many years, experimental studies were limited until the organic charge-transfer complexes were first synthesized and found to be anisotropic conductors. Since then many other one-dimensional and quasi-one-dimensional conductors have been synthesized, and a great deal of experimental work has been done to characterize these materials.

Much of the experimental work conducted on the one-dimensional metallic systems has been within the fields of X-ray and neutron diffraction, studies of optical properties such as far infrared transmission and reflectance, thermopower and electrical conductivity measurements, and susceptibility measurements. Nuclear magnetic resonance (NMR) can provide a great deal of information on the electronic and magnetic environment of nuclei, but has been used only sparingly in attempts to characterize one-dimensional conductive materials. Much of the NMR work has been limited to spin $\frac{1}{2}$ nuclei (^{195}Pt and ^1H in KCP, ^1H in the organic charge-transfer salts, and ^{19}F and ^{199}Hg in $\text{Hg}_{2.86}\text{AsF}_6$, a quasi-one-dimensional conductor) (1-4). These studies have provided a great deal of information on the spin-lattice relaxation and conduction mechanisms in these materials and have served to confirm the existence of metal-insulator transitions characteristic of one-dimensional conductors. In studies of spin $\frac{1}{2}$ nuclei, however, no information concerning the electrostatic environment of the nuclei can be obtained.

Pouget et al. (5), have studied the NMR of ^{51}V ($I=7/2$) in the system $\text{V}_{1-x}\text{Cr}_x\text{O}_2$. Their results indicate the existence of three insulating phases, the phases being distinguished by the Knight shifts and quadrupole couplings. The insulating phase extant at temperatures just below the metal-insulator transition reflects two vanadium sites, one site having a negative Knight shift indicative of a localized V^{4+} ion while the second site has a positive shift characteristic of dimerized V^{4+} ions. This dimerization is as expected for a one-dimensional conductor with a half-filled conduction band.

In this study an attempt is made to characterize the environment of ^{45}Sc ($I=7/2$) and to detect the metal-insulator transition in the one-dimensional CsScCl_3 system. Data on the Knight shift, quadrupole coupling, and dipolar broadening deduced from this study are presented, along with possible models to explain the ^{45}Sc NMR spectra in CsScCl_3 . The existence of a metal-insulator transition in this material should result in discontinuities in both the Knight shift and quadrupole coupling as dimerization of ^{45}Sc atoms in the linear chains occurs.

CHAPTER II. THEORY

NMR in Solids

General theory

An important property of many nuclei is the existence of intrinsic angular momentum or spin, denoted $I\hbar$. The magnetic dipole moment of the nucleus may be written as

$$\vec{\mu} = \gamma \hbar \vec{I} \quad (1)$$

where γ is the gyromagnetic ratio and $\hbar$ is Planck's constant divided by 2π . When placed in a magnetic field, $H_0 \hat{z}$, the potential energy of the nuclear dipole moment is given by

$$E_m = -\vec{\mu} \cdot \vec{H} = -\gamma \hbar m H_0 \quad (2)$$

$$m = -I, -I+1, \dots, I-1, I;$$

and the difference in energy between two adjacent levels is given by

$$\Delta E = E_{m-1} - E_m = \gamma \hbar H_0. \quad (3)$$

Thus in a simple system of non-interacting nuclei, the application of magnetic dipole radiation at a frequency

$$2\pi\nu_0 = \Delta E/\hbar = \gamma H_0 \quad (4)$$

would induce transitions between energy levels of the system.

Equation (2) considered only the interaction of an isolated nuclear magnetic dipole moment with an external field $H_0 \hat{z}$, and ignored many other interactions of importance in solids. These interactions are generally perturbations of the Zeeman energies, causing splittings and shifts of the levels described by Equation (2). The Hamiltonian for the complete interaction may be written as

$$H = H_z + H_1 + H_Q + H_{MS}. \quad (5)$$

In this expression H_z is the Zeeman interaction between the nuclear magnetic moment and the applied field H_0 , and H_1 is the interaction of the moment with the oscillating r.f. field H_1 which induces transitions. H_Q is the Hamiltonian for the interaction of the nuclear electric quadrupole moment with the electric field gradient at the nuclear site, and occurs only for nuclei with $I \geq 1$. H_{MS} is the interaction of the nuclear magnetic dipole moment with sample-dependent magnetic fields at the nuclear site. In metals this interaction is between the nucleus and the field induced by the conduction electrons, the effect being known as the Knight shift. The quadrupole and Knight shift terms will be treated in more depth in later sections.

Quadrupole interactions, dipole interactions, and line shapes

If the nucleus being studied possesses an electric quadrupole moment, eQ , the interaction of this moment with the electric field gradient at the nuclear site will alter the NMR lineshape. If the quadrupole interaction energy is much smaller than the Zeeman energy, the quadrupole interaction can be treated as a perturbation of the Zeeman levels, the perturbation order depending on the relative strengths of the two interactions. It has been necessary to use fourth order perturbation to explain the NMR spectrum of ^{115}In in indium metal (6), but in this study second order perturbation theory is sufficient.

The electric field gradient is generally a second rank symmetric tensor (6 independent components) which can be diagonalized in the principal axes system such that only three independent terms are necessary to describe the gradient. Further, since the gradient arises

from charges external to the nucleus, Laplace's equation

$$\nabla^2 V = V_{xx} + V_{yy} + V_{zz} = 0 \quad (6)$$

must apply, hence only two independent parameters are necessary to describe the electric field gradient. By convention these parameters are defined by

$$eq \equiv V_{zz} = \frac{\partial^2 V}{\partial z^2} \quad (7)$$

and

$$\eta \equiv \frac{V_{xx} - V_{yy}}{V_{zz}} \quad (8)$$

with $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. Thus the z-axis of the principal axes system is chosen such that the gradient is largest along this axis. The asymmetry parameter, η , is always in the range $0 \leq \eta \leq 1$ and is zero if the z-axis coincides with an n-fold rotation axis of the crystal with $n > 2$ (7). Based on the assumed crystal structure of CsScCl_3 , only the $\eta=0$ case will be treated.

The Hamiltonian for the quadrupole interaction with $\eta=0$ may be written as (8)

$$H_Q = \frac{e^2 q Q}{4I(2I-1)} [3I_z^2 - I(I+1)] \quad (9)$$

where eQ is the nuclear electric quadrupole moment, I is the nuclear spin, and I_z is the spin component along the electric field gradient z-axis. When this interaction is treated to second order as a perturbation of the Zeeman levels, the transition frequencies for a single crystal may be written as (9)

$$\begin{aligned} \nu_{m \leftrightarrow m-1} = & \nu_0 + \frac{1}{2} \nu_Q (3\mu^2 - 1)(m - \frac{1}{2}) + \frac{\nu_Q^2}{32\nu_0} (1 - \mu^2) \times \\ & \{ [102m(m-1) - 18I(I+1) + 39]\mu^2 - [6m(m-1) - 2I(I+1) + 3] \} \end{aligned} \quad (10)$$

where $\mu = \cos \theta$ and θ is the angle between the applied field axis and the z-axis of the electric field gradient. In this expression $\nu_Q = 3e^2qQ/2I(2I-1)h$ is the pure quadrupole resonance frequency and provides a measure of the strength of the quadrupole interaction.

In a polycrystalline powder essentially all values of θ are present and the powder pattern will reflect an average over all orientations. In the experimental absorption derivative spectrum the features most easily seen will be the singularities of the central ($m=\frac{1}{2} \leftrightarrow m=-\frac{1}{2}$) transition and the locations of the satellite ($m \leftrightarrow m-1$, $m \neq \frac{1}{2}$) transitions. Cohen and Reif (7) show that the satellite intensity is maximum for $\theta=90^\circ$, so that satellite peaks appear at frequencies

$$\nu_{m \leftrightarrow m-1} = \nu_0 - \frac{1}{4}\nu_Q(2m-1) - \frac{\nu_Q^2}{16\nu_0} \left\{ 3m(m-1) - I(I+1) + \frac{3}{2} \right\}, \quad (11)$$

$m \neq \frac{1}{2}$

Equation (11) indicates that to second order the satellites of the powder pattern will be asymmetrically displaced about the central transition. The separation between equivalent opposite peaks is not affected by the second order term, this separation being

$$\nu_{-m+1 \leftrightarrow -m} - \nu_{m \leftrightarrow m-1} = \frac{1}{2}\nu_Q(2m-1), \quad m \neq \frac{1}{2}. \quad (12)$$

In terms of the magnetic field when operating at constant frequency, this expression may be written as

$$H_{-m+1 \leftrightarrow -m} - H_{m \leftrightarrow m-1} = \frac{\nu_Q}{2\gamma} (2m-1), \quad m \neq \frac{1}{2}; \quad (13)$$

therefore, measuring the satellite separation will yield the value of the quadrupole frequency.

It is clear from Equation (10) that the central transition is not affected by the first order perturbation. When second order terms are

included, however, there is both a shift in the resonance and a splitting of the spectrum. Cohen and Reif (7) show that the central transition powder pattern maxima will appear at frequencies corresponding to $\cos \theta = 0$ and $\cos^2 \theta = 5/9$;

$$\nu_{\frac{1}{2}}^I \leftrightarrow -\frac{1}{2} (\cos \theta = 0) = \nu_o + \frac{\nu_Q^2}{16\nu_o} [I(I+1) - \frac{3}{4}] \quad (14a)$$

$$\nu_{\frac{1}{2}}^{II} \leftrightarrow -\frac{1}{2} (\cos^2 \theta = \frac{5}{9}) = \nu_o - \frac{\nu_Q^2}{9\nu_o} [I(I+1) - \frac{3}{4}]. \quad (14b)$$

Setting $I=7/2$, these expressions become

$$\nu^I = \nu_o + \frac{15}{16} \frac{\nu_Q^2}{\nu_o} \quad (15a)$$

$$\nu^{II} = \nu_o - \frac{5}{3} \frac{\nu_Q^2}{\nu_o} \quad (15b)$$

The splitting of the central transition is given by

$$\Delta\nu_Q \equiv \nu^I - \nu^{II} = \frac{125}{48} \frac{\nu_Q^2}{\nu_o} \quad (16)$$

or

$$\Delta H_Q = \frac{125}{48} \frac{\nu_Q^2}{\nu_o} \quad (17)$$

Measuring the splitting of the central transition provides a second means of determining the quadrupole frequency.

The experimental parameter extracted from quadrupole perturbed NMR measurements is the quadrupole interaction strength expressed by the frequency

$$\nu_Q = \frac{3e^2qQ}{2I(2I-1)h} = \frac{e^2qQ}{14h} \quad (18)$$

for $I=7/2$. The quadrupole interaction or "coupling" involves only the product of the electric field gradient, eq , and the nuclear electric quadrupole moment, eQ . The quadrupole moment of ^{45}Sc is accepted to be $|Q|=0.22 \times 10^{-24} \text{ cm}^2$, allowing a determination of an experimental value for eq , the field gradient at the nuclear site.

In metals the electric field gradient (efg) may be written as (10)

$$eq = eq_{latt}(1-\gamma_{\infty}) + eq_{loc}(1-R_Q). \quad (19)$$

The first term in this expression is the efg due to neighboring atoms considered as point charges, the factor $(1-\gamma_{\infty})$ accounting for the enhancement of this efg by the closed shell electrons of the metal nucleus.

This effect, Sternheimer antishielding (11), results from distortion of the electronic charge distribution by both the nuclear quadrupole field and the field gradient due to the neighboring ions. In the case of the Sc^{3+} ion, the calculated free ion value is $(1-\gamma_{\infty}) \cong 11$ (12).

The second term in Equation (19) is the contribution to the efg due to the local valence and conduction electrons, corrected by a factor to account for shielding by the inner core electrons. This correction is always much smaller than the correction factor for shielding by outer electrons, and is always in the range $0 \leq 1-R_Q \leq 1$ (13).

The task then is to determine eq_{latt} and eq_{loc} . Considering neighboring atoms as point charges, eq_{latt} may be written, for $\eta=0$ only, as (14)

$$q_{latt} = \sum_i z_i \frac{3\cos^2\theta_i - 1}{r_i^3} \quad (20)$$

where z_i is the net charge at the i th lattice point, r_i is the distance from the lattice point to the nucleus, and θ_i is the angle between the efg axis and the vector $\vec{r}_i$. Evaluation of the contribution to the efg from the valence and conduction electrons is not as straightforward, and may be written as (10)

$$q_{loc} = q^0 + q' + q''. \quad (21)$$

The q^0 and q'' terms are connected to the behavior of all occupied conduction electron states while the q' term results only from those states near the Fermi surface. A theoretical treatment of the terms requires a knowledge of the density of states at the Fermi surface as well as a knowledge of the conduction band character. These terms will not be examined further in this study.

A nucleus in a solid experiences not only the applied magnetic field $H_0 \hat{z}$, but also a local field at its site due to the magnetic moments of neighboring nuclei. This local field ($H_{loc} \approx \mu/r^3$) is typically about 1 Oe in magnitude and may oppose or add to the applied field. Thus the resonance frequency of a given nuclear isotope will vary over a range of about $\Delta\nu \approx 100 \gamma/2\pi$ Hz.

In terms of the second moment of the line shape function, the dipole-dipole broadening may be written for a polycrystalline sample as (15)

$$\langle \Delta\omega^2 \rangle_I = \frac{3}{5} \gamma_I^4 \hbar^2 I(I+1) \sum_j \frac{1}{r_j^6} \quad (22a)$$

for contributions from like nuclei and as

$$\langle \Delta\omega^2 \rangle_S = \frac{4}{15} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \sum_{j,k} \frac{1}{r_{jk}^6} \quad (22b)$$

for contributions from unlike nuclei. These equations must further be modified due to the presence of quadrupole coupling (16, Ch.4). For the central transition the second-moment contribution due to the dipole interaction between like nuclei located in equivalent sites may be written as

$$\langle \Delta\omega^2 \rangle = F_L(I) \gamma_I^4 \hbar^2 \frac{9}{5} \sum_j \frac{1}{r_j^6} \quad (23)$$

where

$$F_L(I) = \frac{4}{27} I(I+1) + \frac{2I^2(I+1)^2 + 3I(I+1) + \frac{13}{8}}{18(2I+1)} \quad (24)$$

For $I=7/2$ the ratio $3F_L(I)/I(I+1)$ is 881/756, so Equation (22a) becomes

$$\langle \Delta \omega^2 \rangle_I = \frac{881}{80} \gamma_I^4 \hbar^2 \sum_j \frac{1}{r_j^6} . \quad (25)$$

Equation (22b) describing broadening due to interaction between unlike nuclei is not changed in the presence of quadrupole coupling. Abragam (16, Ch.4) also treats the modification of the second moment due to interactions between like nuclei located at inequivalent sites, but this term will not be needed.

Combining equations (22b) and (25) the total second moment contribution due to dipolar interactions may be written as

$$\begin{aligned} \langle \Delta H^2 \rangle_d &= \sum_i \langle \Delta H^2 \rangle_i \\ &= \frac{881}{80} \gamma^2 \hbar^2 \sum_j \frac{1}{r_j^6} + \frac{4}{15} \hbar^2 \sum_{\ell} \gamma_{\ell}^2 [S_{\ell}(S_{\ell}+1)] \sum_k \frac{1}{r_{jk}^6} \end{aligned} \quad (26)$$

where r_j is the distance between like nuclei, r_{jk} is the distance between unlike nuclei, and ℓ denotes a particular nucleus different from that under investigation. The peak-to-peak width of the absorption derivative due to dipole interactions is then given by (17)

$$\Delta H_{pp} = 2 \langle \Delta H^2 \rangle_d^{1/2} \quad (27)$$

assuming that the resonance has a Gaussian shape.

If the single crystal resonance were a sharp line the resulting second-order quadrupole broadened central transition line shape for the powder sample would be as shown in Figure 2-1 (18). This line shape is smoothed by the dipole-dipole interaction, the experimental method employed in this study yielding the derivative of this broadened absorption line as shown. Extracting the values of ν_Q , η , and 2σ , the dipolar broadening parameter, is then a formidable task. The methods

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Fig. 2-1. Second-order quadrupole splitting of the central transition of ^{55}Mn in $\beta\text{-Mn}$ (18).
The curve is the experimental absorption derivative showing the effect of dipolar broadening superimposed on the quadrupole lineshape.

used to obtain these parameters from the central transition absorption derivative are discussed by several authors (19-21).

With $\eta=0$ the polycrystalline line shape for the central transition has been shown to be (19)

$$g(\nu) = \frac{(5+3x)^{-\frac{1}{2}} + (5-3x)^{-\frac{1}{2}}}{4x} \quad \text{for } \nu_0 - \frac{16A}{9} \leq \nu \leq \nu_0, \quad (28a)$$

$$= \frac{1}{(5+3x)^{\frac{1}{2}} 4x} \quad \text{for } \nu_0 \leq \nu \leq \nu_0 + A \quad (28b)$$

$$= 0 \quad \text{elsewhere;} \quad (28c)$$

where

$$x = \left[\frac{16}{9} + \frac{\nu - \nu_0}{A} \right]^{\frac{1}{2}}$$

and

$$A = \frac{I(I+1) - \frac{3}{4}}{16\nu_0} \left[\frac{3e^2 q Q}{2I(2I-1)h} \right]^2$$

$$= \frac{15}{16} \frac{\nu_Q^2}{\nu_0} \quad \text{for } I = 7/2.$$

These expressions assume that the single crystal line shape is a delta function. If the single crystal line is assumed to be Gaussian due to dipolar broadening, the polycrystalline line shape is given by the convolution of the Gaussian with the line shape function,

$$A(\nu) = \int_{-\infty}^{\infty} g(\nu') \exp \left[-\frac{(\nu - \nu_0 - \nu')^2}{2\sigma^2} \right] d\nu', \quad (29)$$

while the derivative of $A(\nu)$ is actually observed,

$$A'(\nu) \propto \int_{-\infty}^{\infty} (\nu - \nu_0 - \nu') g(\nu') \exp \left[-\frac{(\nu - \nu_0 - \nu')^2}{2\sigma^2} \right] d\nu'. \quad (30)$$

Baughner et al. (21) have evaluated this derivative for several values of the ratio $\Delta\nu_Q/2\sigma \leq 20$. By matching the observed derivative spectra to computer generated spectra, estimates of the ratio $\Delta\nu_Q/2\sigma$ can be obtained.

Knight shift

In metals the magnetic field experienced by the nucleus may have an additional contribution due to the polarization of unpaired conduction electron spins by the applied magnetic field. In the absence of quadrupole effects this will lead to resonance at a frequency ν_m rather than at ν_r , where ν_r is the resonance frequency in a diamagnetic reference compound. The Knight shift is defined as

$$K = \frac{\nu_m - \nu_r}{\nu_r} = \frac{H_r - H_m}{H_m}, \quad (31)$$

where the first equality applies for resonance in a constant magnetic field and the second applies for resonance at constant frequency.

In the transition metals the Knight shift arises from three sources: the s-electron contact interaction, polarization of the core s-electrons by d- and f-conduction electron interactions, and interaction of the nuclear spin moment with the d- and f-electron orbital moment. In general the Knight shift may be written

$$K(T) = K_s + K_{cp}(T) + K_o \quad (32)$$

where the temperature dependence of the total shift is dominated by the core polarization term.

The shift due to the contact interaction may be written (22)

$$K_s = \frac{8\pi}{3} \chi_p \langle |\psi_s(0)|^2 \rangle_{FS}, \quad (33)$$

where χ_p is the Pauli paramagnetic spin susceptibility per atom and $\langle |\psi(0)|^2 \rangle_{FS}$ is the electronic probability density at the nucleus averaged over conduction electron states at the Fermi surface. This contribution leads to an isotropic, temperature independent Knight shift.

The core polarization contribution results from unpairing of the inner shell s-electrons via an exchange interaction with d- and f-character conduction electrons (23,p.3). This contribution is generally negative and is temperature dependent for d- and f-electrons in a narrow conduction band.

The orbital contribution results from a coupling of the nuclear spin moment to the orbital magnetic moment of d- and f-electrons. This contribution is very important in transition metals and is generally temperature independent. Unlike the contact interaction shift, this contribution is independent of the density of states at the Fermi level (23,p.12).

The Knight shift is not generally isotropic, but has components K_x , K_y , and K_z ; x, y, and z usually referring to the principal axes system of the crystal lattice. In the case of axial symmetry only two components are required to define the shift. By convention these components are defined as the isotropic shift, K_{iso} , and the axial or anisotropic shift, K_{ax} ;

$$K_{iso} = \frac{1}{3}(K_{\parallel} + 2K_{\perp}) \quad (34a)$$

$$K_{ax} = \frac{1}{3}(K_{\parallel} - K_{\perp}) \quad (34b)$$

where $K_{\parallel} = K_z$ and $K_{\perp} = K_x = K_y$. For ^{45}Sc in scandium metal the values are $^{45}K_{iso} = 0.262\%$ and $^{45}K_{ax} = -0.048\%$ (24). The effect of the Knight shift on the lineshapes and splittings in NMR spectra is treated by several authors (9,25-27)..

Saturation and spin-lattice relaxation

In order to detect the resonance effect there must be a net absorption of power from the applied r.f. field. Consider a simple spin $\frac{1}{2}$ system which has energy levels at $E_0 \equiv E_{m=+\frac{1}{2}} = -\gamma\hbar H_0/2$ and $E_1 \equiv E_{m=-\frac{1}{2}} = \gamma\hbar H_0/2$. The Boltzmann factor gives the equilibrium occupations,

$$\frac{n_1}{n_0} = e^{-\Delta E/kT} = e^{-\gamma\hbar H_0/kT} \quad (35)$$

where n_i is the occupation of level i . Applying a perturbing field, the time rate of change of the population of level 0 is given by

$$\frac{dn_0}{dt} = n_1 W_{10} - n_0 W_{01}, \quad (36)$$

where W_{ij} is the probability per second of inducing a transition from level i to level j . From time-dependent perturbation theory the two transition probability rates can be shown to be equal (28) and Equation (36) becomes, with $W_{10}=W_{01}=W$,

$$\frac{dn_0}{dt} = W(n_1 - n_0). \quad (37)$$

The solution of this equation is

$$n = n_e e^{-2Wt}, \quad (38)$$

where $n(=n_0 - n_1)$ is the population difference at time t and n_e is the thermal equilibrium population difference for the system. In a solid there is an interaction of the spin system with the lattice (as well as with neighboring spins). The lattice acts as a thermal reservoir, accepting energy as the spins relax to lower energy states. The population difference due to this process is (15,p.7).

$$n = n_e (1 - e^{-t/T_1}) \quad (39)$$

where T_1 is the spin-lattice relaxation time and n_e is the thermal equilibrium population difference for the relaxation process with no applied r.f. field. Combining the effects of the applied oscillating field and spin-lattice relaxation gives the steady state population difference,

$$n_s = \frac{n_e}{1+2WT_1} \quad (40)$$

and the time rate of energy absorption by the system is given by

$$\frac{dE}{dt} = nh\nu_o W = \frac{n_e h\nu_o W}{1+2WT_1} \quad (41)$$

If $2WT_1 \ll 1$ the energy absorption is proportional to the transition probability per second, W , which in turn is proportional to the photon density of the oscillating field. Thus, for $2WT_1 \ll 1$, the rate of energy absorption may be written as

$$\frac{dE}{dt} \propto n_e h\nu_o \rho \propto n_e h\nu_o H_1^2 \quad (42)$$

where ρ is the photon density and H_1 is the magnitude of the oscillating magnetic field. The signal strength is seen to be proportional to the square of the magnitude of the applied r.f. field. Saturation occurs when $2WT_1 \geq 1$, causing the time rate of energy absorption to be independent of the magnitude of the applied oscillating field. A qualitative measure of T_1 can be obtained by progressive saturation in which the signal strength is measured for several values of the magnitude of the r.f. field, H_1 . Nuclei with short T_1 would be found to saturate at relatively higher magnitudes of the field due to the fast relaxation of the moment to lower energy states. A completely quantitative measurement of T_1 is usually not possible using the saturation method because

the perturbation calculation is not valid for high values of H_1 . Equation (40) was obtained by assuming only a small change in the population difference due to the action of the perturbing field H_1 . As H_1 is increased this assumption is no longer valid and Equation (40) no longer applies.

The effective or total spin-lattice relaxation rate,

$$\frac{1}{T_1} = \sum_i \frac{1}{T_i}, \quad (43)$$

expresses the contribution of all mechanisms to the effective spin-lattice relaxation time. In metals there are generally four important sources of spin-lattice relaxation (29): the existence of paramagnetic impurities, the diffusion of metal ions through the crystal lattice, the interaction of the nuclei with the conduction electrons, and the interaction of the quadrupole moment with the electric field gradient modulated by thermal motion of the lattice. It can be assumed that the first two effects are absent in this study.

It is very difficult to write an exact expression for the contributions of the contact and quadrupole interactions to the relaxation rate. Generally the Korringa relation (30) is used to relate the spin-lattice relaxation rate to the Knight shift, but this relationship is not valid for the case of large quadrupole interaction. It is expected that the quadrupole relaxation mechanism will dominate, and no theoretical estimates of spin-lattice relaxation times by this mechanism are available. Abragam (16, Ch.9) discusses the mechanisms leading to spin-lattice relaxation in solids.

Phase Transitions in One-Dimensional Conductors

Peierls (31) first pointed out that a strictly one-dimensional metallic system is inherently unstable, undergoing a lattice transformation to form an insulating state at $T = 0$ K. In a linear chain of atoms separated by a distance c , the basis cell in reciprocal space is the interval

$$-\frac{\pi}{c} < k < \frac{\pi}{c}$$

If every r th atom is displaced, the lattice vector is increased to rc and the basis cell becomes

$$-\frac{\pi}{rc} < k < \frac{\pi}{rc}$$

This displacement can be treated as a perturbation on the periodic potential of the undistorted lattice, producing band gaps (Figure 2-2) at the edge of the reduced cell. The average value of the electron energy in states directly above and below the gap is unchanged to first order and the total electron energy will not be changed by the distortion if the bands above and below the gap are both filled. If the gap occurs near the Fermi surface, however, the result of the distortion will be a net reduction in the total electron energy.

The energy change will be greatest for small values of r , the most favorable case for one electron per atom ($r=2$) leading to dimerization of the atoms in the chain and a gap in the energy at wavevector $k = \pi/2c$. For a one-third filled or one-quarter filled band the distortion will be a trimerization or tetramerization, respectively, as has been observed in many of the organic charge transfer salts (32). The result of the

distortion is a transition from a metallic to an insulating state at $T = 0$ K for an isolated, rigid lattice. In the case of linear chains coupled in three-dimensions, the results are modified and lead to a transition at $T > 0$ K.

Fröhlich (33) showed that a Peierls transition will lead to a coupled electronic and ionic charge density wave (CDW) in a 1-D system in which the ions are considered as a uniform charge background (jellium model). In this model the electrons carry the ionic charge density wave, resulting in the energy gap also being carried in the frame of the moving electrons. As in the BCS theory of superconductivity this leads to a dynamic state in which no scattering of electrons by phonons or impurities can occur and should lead to superconductivity in a 1-D metal. In a real system, however, the CDW is pinned by impurities (34) resulting in finite values of the conductivity. Three-dimensional ordering has the effect of phase-locking the CDW in adjacent chains, also resulting in reduced conductivity. Further, if the CDW and lattice are commensurate, the CDW will be pinned in the lattice (analogous to standing waves) reducing the dc conductivity to zero. This occurs at a temperature T_c , the metal-insulator transition temperature.

Lee, Rice, and Anderson (34) speculate that the Peierls-Fröhlich mechanism is strong enough in many chain materials that the lattice distortions are locked-in, resulting in an insulating material when a conductor might be expected. They predict that due to the relative strength of the commensurability energy for a half-filled band, many of these materials will not exhibit metallic character.

A further treatment of metal-insulator transitions is given by Mott (35) and Hubbard (36) in which electron-electron repulsive interactions are included. In this model the transition is driven by electron correlation effects rather than by inherent lattice instability. The Hamiltonian for the interaction may be written (37)

$$H = -t \sum_{\sigma} (a_{\sigma}^{\dagger} b_{\sigma}^{-} + b_{\sigma}^{\dagger} a_{\sigma}^{-}) + U(n_{a\uparrow} n_{a\downarrow} + n_{b\uparrow} n_{b\downarrow}) , \quad (44)$$

where t is the transfer integral (a measure of the attraction of an electron on one atom for another atom) and U measures the Coulomb repulsion of two electrons in the same orbital state. The a 's and b 's are creation and destruction operators for electrons with spin σ on atoms a and b . If $t \ll U$ the electrons are localized and the material is an insulator, whereas with $t \gg U$ the electrons become delocalized resulting in conduction. A metal-insulator transition is observable with decreasing temperature if $t \approx U$.

Structural Considerations

Goodenough (38) has discussed the conducting properties of compounds of the transition metals in terms of a critical internuclear separation, $D_c(n,1)$. If the separation of the transition metal atoms is less than the critical distance, the electrons will be delocalized and the result will be metallic behavior. For separations greater than this critical distance, the electrons are expected to be localized, resulting in an insulating state. The values of the critical radii have been given for transition metal oxides and sulfides but have not been discussed for the transition metal chlorides. The critical radii, however, are dependent on the electronegativity of the ligand, with lower electronegativity

Fig. 2-2. Peierls distortion effects in 1-D conductors.

(a) Band gap formation due to Peierls distortion of a linear chain of atoms with a half-filled conduction band; (b) density of states per unit energy per spin (39).

resulting in a larger minimum value of the separation required to yield metallic behavior (39). Since the electronegativity of chlorine is between the values given for sulfur and oxygen (3.0, 2.5, and 3.5, respectively) (40), the critical separation is expected to be bounded by those for metal sulfides and oxides. Based on the analytical results of Goodenough shown in Figure 2-3, the critical radius for ^{45}Sc in chlorine octahedra should be in the range 1.6-2.1 $\text{\AA}$. The projected scandium-scandium distance in CsScCl_3 is about 3.0 $\text{\AA}$, well within the metallic limits.

A compound which is isostructural with CsScCl_3 is BaVS_3 (Figure 2-4) in which the vanadium atoms form conducting chains within the sulfur octahedra. In this compound the vanadium is in the formal oxidation state IV, isoelectronic with Sc^{2+} . A metal-insulator transition has been reported at 68K (39) accompanied by a structural transition from hexagonal to orthorhombic symmetry, but it is not known whether this transition may be described as resulting from one-dimensional effects.

Fig. 2-3. The analytical values of the critical radii for 3d and 4d transition metal sulfides and oxides (38).

Fig. 2-4. The linear chain structure of $[\text{VS}_3^{2-}]_n$ chains in BaVS_3 (39).

CHAPTER III. EXPERIMENTAL DETAILS

Samples

All samples used in this investigation, as well as X-ray analyses thereof, were obtained from Mr. K. Poeppelmeier of the Solid State Chemistry Group (Ames Lab-ERDA and Iowa State University). The samples of main interest in this study are listed in Table 3-1; other samples studied include ScCl_3 , Sc_2Cl_3 , Sc_2O_3 and $\text{Cs}_3\text{Sc}_2\text{Cl}_9$. No impurity analysis is available for any of these samples.

Samples A-E are the product of a reaction of a 3:2 mole ratio of CsCl and ScCl_3 with excess scandium metal. Sample F was formed using the proper mole ratio of CsCl , ScCl_3 , and Sc_2Cl_3 in an attempt to insure the reaction of all scandium metal. Both methods result in the formation of blue-black polycrystals which grind to a blue-gray powder. On the basis of simple d.c. resistance measurements the material appears to be a metallic conductor. X-ray analysis of a single crystal from sample D1 indicates that the structure is of the hexagonal perovskite type, space group D_{6h}^4 ($P6_3/mmc$), with $a = 7.35\text{\AA}$ and $c = 6.05\text{\AA}$. A projection of the structure onto the $(11\bar{2}0)$ plane is shown in Figure 3-1, where the chain-like structure of the scandium atoms is immediately evident. The quasi-one-dimensional nature of the structure is the result of the short Sc-Sc intrachain distance of $3.02\text{\AA}$ compared with the interchain distance of $7.35\text{\AA}$. The intrachain scandium separation is smaller than the separation of nearest neighbors in scandium metal, which is $3.26\text{\AA}$ in the hcp form (41). No evidence of superlattice structure was found in either the 0.8 or the 1.0 compounds, indicating that no periodic vacancies occur in the metallic chains.

Table 3-1. Constituent and annealing data for CsSc_xCl₃ samples

Sample	Equation	Weights	Annealing Temperature (°C)	Time (days)	K. Poepellmeier's Reference Number
A	CsSc _{1.0} Cl ₃	Incorrect Stoichiometry			Sc35
B	CsSc _{.816} Cl ₃	Made with scandium strips			Sc41
C	CsSc _{1.0} Cl ₃ + Sc powder	0.300g Sc 1.130g CsCl 0.673g ScCl ₃	700	3	Sc46
D1	CsSc _{1.0} Cl ₃	0.100g Sc 1.123g CsCl 0.673g ScCl ₃	700 850 Cool to < 500°C in 3 hours	7 2	Sc65
D2			700	7	
D3			700 Cool at 1.25°C/hr to 25°C	0	
E1	CsSc _{0.8} Cl ₃	0.054g Sc 1.531g CsCl 0.917g ScCl ₃	700 850 Cool to < 500°C in 3 hours	7 2	Sc66
E2			700	7	
F	CsSc _{1.0} Cl ₃	2.578g ScCl 0.771g ScCl ₃ 2.000g Sc ₂ Cl ₃	700 Cool at 6°C/hr to 25°C	3	

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Fig. 3-1. Projection of the structure of CsScCl_3 on the $(11\bar{2}0)$ plane.

It is interesting to compare the compounds in the region from $x = 0.67$ to $x = 1.0$ (i.e., from $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ to CsScCl_3). The compound $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ is a white, insulating material with structure of the space group D_{3d}^6 ($R\bar{3}c$), with $a = 12.71\text{\AA}$ and $c = 18.11\text{\AA}$. Figure 3-2 shows the relationship between the unit cells of $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ and CsScCl_3 . In $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ every third scandium atom is missing from the chain, with the two atoms on either side displaced slightly inward toward the vacancy. By filling these vacancies the structure of CsScCl_3 can be obtained with a subsequent reduction in the size of the unit cell. X-ray analysis indicates that there is only a slight expansion of the lattice accompanying the addition of the scandium. From structural considerations alone one expects $a = \sqrt{3}a'/3 = 7.34\text{\AA}$ and $c = c'/3 = 6.04\text{\AA}$ to be the lattice parameters for CsScCl_3 , compared with the experimental values given above (42).

Apparatus

NMR equipment

The experimental spectra for this investigation were obtained using conventional nuclear induction (crossed-coil) methods (43) with averaging of a number of scans to achieve a better signal-to-noise ratio. All spectra were taken at constant frequency while sweeping the magnetic field. Three different electromagnets were used, a Varian 15", Magnion 9 $\frac{1}{2}$ ", and Varian 6" covering a magnetic field range from 4kOe to 25kOe; while a Torgeson spectrometer (44) was used at all operating frequencies (4 - 24MHz). A block diagram of the apparatus is shown in Figure 3-3.

The sample was placed in a Varian 4230B crossed-coil probe and centered in the most homogeneous part of the magnetic field. The d.c.

Fig. 3-2. The structures of (a) $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ and (b) CsScCl_3 viewed along and perpendicular to the c-axis (42). The dots in the side views represent the scandium atoms in the chains.

Fig. 3-3. Block diagram of the continuous-wave NMR spectrometer used in this study.

magnetic field was modulated via a set of Helmholtz coils in the probe at a frequency of 80 Hz which was provided by the reference signal of a Princeton Applied Research JB-4 Lock-In Amplifier. The modulation amplitude was controlled by a Varian 4250A sweep unit. The constant frequency r.f. signal was generated using a crystal oscillator stable to a few parts in 10^7 , with amplitude controlled by an external attenuator (coarse) and a potentiometer in the spectrometer (fine). Peak-to-peak r.f. fields ($2H_1$) of 0 to 1 Oe were attainable. All frequency measurements were made using either a CMC 880B or Monsanto 110B frequency counter.

The magnetic field was swept using the channel address voltage from a RIDL 34-27 400 channel analyzer. After being amplified and offset (45) this voltage was used to drive the external sweep of the magnet power supply. The magnetic field within the sweep range was thus directly proportional to the data channel address over field sweeps of a few hundred oersteds. The sweep rate was inversely proportional to the sampling time per channel which was set by an external time base generator. An independently adjustable delay allowed stabilization of the magnetic field after each sweep.

The signal from the receiver coil was amplified and detected and the audio component (at 80 Hz) was input to the lock-in amplifier, producing a d.c. signal proportional to the derivative of the resonance signal. A voltage-to-frequency converter allowed the signal to be digitized and stored in the memory of the 400 channel analyzer, multiple passes through the resonance being used to increase the signal-to-noise ratio of the spectra. For monitoring the data and producing a hard

copy of the spectra, an oscilloscope and an x-y recorder were connected to the 400 channel analyzer.

Magnetic field calibration was accomplished using an aqueous solution of $^{27}\text{AlCl}_3$ ($\gamma_{\text{Al}} = 1.109404 \text{ MHz/kOe}$). The magnetic field was set using address selection on the analyzer and the aluminum resonance was centered using a Tektronix 191 or Hewlett-Packard 606A variable frequency signal generator. The channel address and resonance frequency were then recorded on the trace of the spectrum. The magnetic fields for critical points of the sample spectra were determined assuming a linear sweep between the ^{27}Al calibration points.

Cryogenic and high temperature equipment

Several spectra were obtained at both 77 K and 4.2 K by immersing the sample in liquid nitrogen or liquid helium baths. The liquid nitrogen was contained in a simple finger dewar which allowed up to about twelve hours run time between fills. The liquid helium was contained in a double glass dewar as shown in Figure 3-4. The surrounding nitrogen bath reduced heat leakage to the helium bath which permitted run times of up to eight hours between helium transfers.

A few spectra were obtained at temperatures above 300 K using a nitrogen gas flow apparatus as shown in Figure 3-5. In this investigation it was necessary to keep the sample tube sealed, so the monitoring thermocouples were placed outside the sample tube and slightly above and below the sample region, the lower thermocouple being used as a reference for the temperature control apparatus. The nitrogen gas was heated by passing it over a 5Ω heater, the power input to the heater being controlled by the potentiometer output through a null detector and tempera-

Fig. 3-4. Cross-sectional view of the glass liquid helium dewar.

Fig. 3-5. Construction of the variable temperature gas-flow apparatus used in this study. In the experiments described in the text the sample tube is sealed and the thermocouples are located just above and below the sample tube.

ture control unit. No attempt was made to monitor the gas flow rate so that some uncertainty concerning temperature stability resulted. However, experience has shown that the sample temperature is stable to well within ± 5 K under these operating condition.

CHAPTER IV. RESULTS AND DISCUSSIONS

General Results

Representative derivative spectra obtained in this study are shown in Figure 4-1. Table 4-1 lists the range of operating frequencies and temperatures covered for each sample. At lower applied fields three resonances are well-resolved indicating the existence of at least three different ^{45}Sc sites in the samples. The first site is represented by the peaks E and H, the extrema of a quadrupole split central transition. Site 2 is seen as the narrow line (FG) and reflects only a weak quadrupole interaction at this site. This resonance is resolved from the site 1 resonance only at $\nu_0 \gtrsim 20\text{MHz}$ in the CsSc_xCl_3 samples. Site 3, line ABC, is a metallic type site with a Knight shift approximately equal to that in scandium metal. This resonance was most prominent in sample F, the only sample which did not contain scandium metal as an initial component.

There were no apparent differences in the main features of the spectra from 4.2 K to 450 K. There were slight variations in the quadrupole parameters, but this effect did not change the character of the spectra.

Spectra of the ^{133}Cs resonance indicate a single ionic site with no Knight shift and no quadrupole coupling. No satellites were seen and no cesium metal ($K \approx 1.49\%$) was detected by NMR.

Quadrupole Interaction

Site 1 shows the largest quadrupole interaction of the three sites, it being necessary to use second-order perturbation theory to account for

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Fig. 4-1. Representative NMR derivative spectra of ^{45}Sc in CsScCl_3 ,
sample F.

Table 4-1. Ranges of operating frequencies and temperatures of ^{45}Sc and ^{133}Cs spectra obtained in this study.

SAMPLE	T(K)	ν_o (MHz)											
		4	6	7	8	10	12	14	16	18	20	22	24
A	298					X	X				X		
B	298					X	X	X	X	X	X	X	X
		Satellites											
	77						X		X			X	
C	298												X
D1	298	X	X		X		X		X	X	X	X	X
	77								X			X	
D2	298	X		X	X			X	X	X	X	X	X
		Satellites											
													X
D3	298				X	X		X	X				X
E1	298		X		X	X	X						X
E2	446								X				
	406												X
	390								X				
	349												X
	298	X	X	X	X			X	X	X	X	X	X
	77			X	X	X		X	X	X	X	X	X
	4.2							X	X	X	X	X	X
F	298				X		X		X	X	X		X
		Satellites											
	77								X		X		X
$\text{Cs}_3\text{Sc}_2\text{Cl}_9$	298						X		X			X	X
	77												X
ScCl_3	298								X			X	X
Sc Metal	298												X
Sc_2Cl_3	298						X		X				X
$\text{Sc}_7\text{Cl}_{10}$	298				X			13					X
Cs in B	298						11						
D3	298		4.5				11						
E2	298						11						
E2		Satellites											
								12.5					

the features of the spectra. Using the method of Creel et al. (25), a graph of the effective gyromagnetic ratio, γ_{eff} , of the powder pattern singularities versus the inverse square of the resonance field strength (Figure 4-2) yielded a measure of both the quadrupole coupling constant and the Knight shift. Assuming axial symmetry ($\eta=0$), the positions of the powder pattern singularities are given by

$$\gamma_E = \gamma_o (1 + K_{\perp}) + \frac{15}{16} \frac{\nu_Q^2}{\gamma_o H^2}, \quad (45a)$$

and

$$\gamma_H = \gamma_o \left[1 + \frac{5K_{\parallel} + 4K_{\perp}}{9} \right] - \frac{5}{3} \frac{\nu_Q^2}{\gamma_o H^2}. \quad (45b)$$

The values obtained for ν_Q from this analysis are shown in Table 4-2.

A second measure of the quadrupole interaction is given by Equation (17), indicating that the slope of a graph of the splitting of the central transition versus the inverse of the operating frequency will yield a measure of ν_Q . This graph is shown in Figure 4-3. Also, the satellite splitting will yield a further measure of ν_Q as indicated by Equation (13). The satellite spectra for sample F and scandium metal are shown in Figure 4-4.

Site 2 shows only a small quadrupole interaction, the line splitting being only marginally dependent on the value of the applied magnetic field strength. It is appropriate only to set an upper limit for the quadrupole frequency based on the slope of ΔH versus $1/\nu_o$. This limit is given in Table 4-2. The broadening in lower applied fields may be due to the need to use higher modulation amplitudes to obtain good signal-to-noise ratios.

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Fig. 4-2. Effective gyromagnetic ratio versus inverse square of the resonance field strength for ^{45}Sc in CsScCl_3 . The upper and lower lines are least square fits to the data from peaks E and H (Fig. 4-1) in sample E1.

Table 4-2. Measured values of ν_Q and K in CsSc_xCl_3 .

Site	Sample	T(K)	ν_Q (MHz) (± 0.01 except where noted)			
			ν vs $1/H^2$	ΔH vs $1/\nu_0$	Satellites	Average
1	F	298	0.420 ± 0.02	0.443	0.421	0.428
	D2,E1	298	0.415	0.421	0.410	0.415
		77	0.421 ± 0.02	0.428	-	0.425
		4.2	0.438 ± 0.03	0.443	-	0.441 ± 0.02
2	D2,E1	298	-	< 0.113	-	< 0.113
		77	-	< 0.159	-	< 0.159
		4.2	-	< 0.074	-	< 0.074
3	F	298	-	-	0.147	0.147

Knight shifts (%)						
Site	Sample	T(K)	$K_{\parallel} (\pm 0.02)$	$K_{\perp} (\pm 0.02)$	$K_{\text{iso}} (\pm 0.01)$	$K_{\text{ax}} (\pm 0.005)$
1	F	298	0.019	0.032	0.023	-0.004
	D2,E1	298	0.016	0.025	0.019	-0.003
		77	0.029	0.027	0.028	-0.001
		4.2	0.016	0.022	0.018	-0.002
2	F	298	-	-	0.019	-
	D2,E1	298	-	-	0.030	-
		77	-	-	0.043	-
		4.2	-	-	0.027	-
3	F	298	0.278	≤ 0.211	≤ 0.256	≤ -0.022

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Fig. 4-3. Line width versus inverse of ^{45}Sc resonance frequency for sites 1 and 2 in samples D2 and E1.

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Fig. 4-4. The ^{45}Sc inner satellite spectra of Sc metal and CsScCl_3 . The Sc^{3+} dimer is assigned to the site 1 resonance while the other peaks result from scandium metal.

In the frequency range of 12-24MHz the site 3 resonance line shape is dominated by the Knight shift and no measurement of the quadrupole interaction could be obtained by analyzing the central transition. At 8MHz the spectra obtained are extremely difficult to analyze due to the superposition of resonance peaks from different sites. A measure of ν_Q was obtained from the satellite spectra, Figure 4-4, yielding a value equal to that in scandium metal. The satellite spectra were complicated by the fact that at least two satellite sets were seen, with the first satellite ($\frac{1}{2} \leftrightarrow \frac{3}{2}$) from site 3 hidden by the central transition from site 1. The close match of the other observed satellites indicates, however, that the quadrupole coupling must be identical to that in scandium metal.

Dipolar Broadening

Site 2 exhibits only a small quadrupolar contribution to the width and can be considered as essentially a dipolar broadened line with some artificial broadening due to overmodulation. The width and gyromagnetic ratio compare favorably with that of ^{45}Sc in ScCl_3 . A plot of the linewidth versus the operating frequency is shown in Figure 4-3.

Site 1 exhibits a quadrupole split shape with dipolar broadening superimposed. Using the measured value of the quadrupole frequency, a measure of the splitting of the central transition due to quadrupole coupling may be obtained from (21)

$$\Delta\nu_Q = \nu_Q^2 \left[I(I+1) - \frac{3}{4} \right] \frac{\eta^2 + 22\eta + 25}{144\nu_0} \quad (46)$$

Matching the derivative spectra to the lineshape library of Baugher

et al. (21) as shown in Figure 4-5 indicates that site 1 has axial symmetry ($\eta=0$) with $\Delta\nu_Q/2\sigma \cong 4.0$ at 24MHz. Using Equation (46) and $\nu_Q = 0.415\text{MHz}$, the estimated value of the dipolar broadening, 2σ , is 4.7 kHz or about 4.5 Oe.

The effect of dipolar interactions on the site 3 line is limited to smoothing of the asymmetric lineshape. An estimate of the magnitude of 2σ has not been made.

Knight Shift

Sites 1 and 2 show negligible Knight shifts, indicating either that the scandium atoms at these sites are not involved in the conduction mechanism, or that the conduction band character is other than that of s-electrons. The Knight shift obtained for scandium at site 1 using Equations (45a,b) is given in Table 4-2. The value of the Knight shift for site 2 is based on the extrapolated value of the gyromagnetic ratio at infinite applied field.

Site 3 exhibits a Knight shift similar to that in scandium metal. The form of the resonance derivative, however, differs somewhat from that seen in scandium metal (24). The values given in Table 4-2 are thus limits based on the locations of the low field singularity and what is assumed to be the high field step.

Model Calculations

It is not feasible to make accurate calculations of the expected dipolar broadening and quadrupole couplings due to the lack of knowledge of the exact structure of the samples. It was expected that CsScCl_3 would have only one scandium site, while at least three sites are clearly

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Fig. 4-5. Comparison of the ^{45}Sc central transition in CsScCl_3 with the computer generated pattern for $\eta = 0$ and $\Delta Q/2\sigma = 4.0$. The match is only approximate due to the superposition of another resonance on what appears (at 24 MHz) to be a single quadrupole broadened resonance. Note that here the magnetic field increases to the left.

seen in the NMR spectra of the samples. Further, it was expected that $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ would have a single scandium site, but the sample again shows spectra of three sites with the resonances differing only in intensity from those seen in CsScCl_3 .

Dipolar broadening

Using Equations (26) and (27) an estimate can be made of the contribution of the dipolar interactions to the line width for several assumed structures. Since two relatively abundant chlorine isotopes occur in the ratio $3(^{35}\text{Cl}):(^{37}\text{Cl})$, the relative amounts of the isotopes should be accounted for in the calculations. The values of constants used in these calculations are listed in the Appendix.

The calculation for CsScCl_3 assumed that the structure is as shown in Figure 3-1 with contributions from the two nearest neighbor scandium atoms, the six nearest neighbor chlorine atoms (with appropriate factors to account for the differing isotopes), and the six nearest neighbor cesium atoms, which make only a minor contribution to the second moment.

The structure of $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ was assumed equivalent to that of CsScCl_3 except that only one nearest neighbor scandium is included in the calculation. This affects only the scandium contribution to the second moment. The dipolar second moment in ScCl_3 was calculated using only the six nearest neighbor chlorine atoms, with all other contributions assumed to be negligible.

Table 4-3 compares the theoretical dipole broadening to the measured dipole contribution to the line width. The poor agreement between theoretical and measured values is due in part to the use of only nearest neighbors in the calculations. The measured ScCl_3 line width was assumed

to be totally due to dipolar broadening, but it is expected that some quadrupolar coupling exists. There is also some uncertainty in matching the site 1 spectrum with the lineshape library (Figure 4-5) due to the superposition of the site 2 resonance on the site 1 spectrum.

Table 4-3. Theoretical versus measured dipolar broadening

	Theoretical Second Moment (Oe^2)				Linewidth (Oe)	
	Sc	^{35}Cl	^{37}Cl	Cs	Theory	Measured
CsScCl_3	1.17	0.13	0.09	0.01	2.37	-
ScCl_3	-	0.13	0.09	-	0.94	2.5
$\text{Cs}_3\text{Sc}_2\text{Cl}_9$	0.59	0.13	0.09	0.01	1.81	4.5

Quadrupole coupling

There are many difficulties inherent in making theoretical calculations of the electric field gradients at nuclear sites based on structural information alone. While the ionic lattice contribution is given by Equation (20), this is not necessarily the major contribution to the total efg. Indeed, the conduction electron contribution may be opposite in sign as well as one or two orders of magnitude greater than the lattice contribution. Further, Equation (20) assumes an ionic structure, an assumption which is not easily justified if directed covalent bonds are present, as might be expected in these compounds. Consequently, lacking detailed knowledge of the electronic structure and band character of these materials, attempts to calculate the electric field gradients

appear unlikely to yield useful results. Any agreement between theoretical and experimental results would be fortuitous.

Comparison of Spectra and Assignment of Sites

Figure 4-6 shows the spectra of sites 1 and 2 in CsScCl_3 and $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ at 24MHz. The narrow resonance which is resolved in $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ is not seen in CsScCl_3 above about 20MHz, probably because of its lower relative intensity in those samples. As seen in Figure 4-7, this narrow resonance closely matches that seen in ScCl_3 and on this basis has been assigned to an isolated Sc^{3+} ion in a chlorine octahedron. The quadrupole-split line of site 1 can then be reasonably assigned to paired Sc^{3+} ions characteristic of the $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ structure.

The Knight shifted resonance appears to be due to scandium metal present in the samples. The Knight shift and quadrupole coupling (derived from the satellite spectra) measured in CsScCl_3 match those measured in scandium metal to within the experimental uncertainty. It would be tempting to assign this line to chains of scandium as shown in Figure 3-1, but such an assignment would require that the spectral parameters (ν_Q and K) of such scandium chains be identical to those in scandium metal, which appears highly unlikely.

There is some indication that a fourth site exists in sample F, as shown by peak D in Figure 4-1. Detailed analysis of this resonance has not been possible due to the small frequency range over which it appears isolated from the other resonances (20-24MHz). Again, it would be attractive to have a broad line present in the spectrum that could be assigned to ^{45}Sc located in Sc^{2+} ions, analogously to ^{51}V in the

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Fig. 4-6. Comparison of the ^{45}Sc spectra of sites 1 and 2 obtained in CsScCl_3 (F) to the spectrum of $\text{Cs}_3\text{Sc}_2\text{Cl}_9$. The metallic resonance seen in sample F is not included within the field range scanned here. The narrow central line in the $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ spectrum is apparently due to broken Sc^{3+} dimers.

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Fig. 4-7. Comparison of the ^{45}Sc spectra of sites 1 and 2 in CsScCl_3 to the spectrum in ScCl_3 .

$V_xCr_{1-x}O_2$ case (5). However, such a resonance ought also to exhibit a negative Knight shift, and this appears impossible for feature D.

Spectra of Sc_2Cl_3 and Sc_7Cl_{10} were also obtained but did not match any of the spectral features prominent in the $CsScCl_3$ samples.

CHAPTER V. CONCLUSIONS

The NMR measurements on the CsSc_xCl_3 samples indicate the existence of at least three ^{45}Sc sites in these samples; the sites being assigned to isolated Sc^{3+} , paired Sc^{3+} , and metallic scandium. On this basis it must be concluded that the samples are most probably mixtures of several phases rather than single-phase. The composition of the mixture cannot be specified with quantitative precision since NMR provides only a qualitative measure of relative amounts when complex spectra occur. The strength of the signals indicates, however, that significant amounts of metallic scandium occur in sample F, where this resonance was studied most closely. Other samples showed lesser amounts of this metal resonance, in most cases the signal being barely above noise levels.

If scandium metal exists in the samples in significant amounts, then it is not unreasonable to expect that $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ may also exist in the samples. This conclusion is born out by the close match of the site 1 spectrum to the $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ spectrum. The existence of the line assigned to ScCl_3 in both CsScCl_3 samples and the $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ sample is not unreasonable, indicating simply the breaking of some number of ^{45}Sc pairs in the structure.

It should be noted that it would be difficult to distinguish between paired Sc^{3+} ions in $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ and paired Sc^{3+} ions in CsSc_xCl_3 based solely on ^{45}Sc NMR. This comment would hold for Sc^{3+} ions in ScCl_3 and isolated Sc^{3+} ions in CsSc_xCl_3 as well. Thus the spectra obtained from CsScCl_3 may be due to chains of Sc^{3+} ions in which a large number of vacancies occur randomly. The relative intensities of the

resonances indicate, however, that there are many more isolated and paired Sc^{3+} ions than Sc^{3+} ions within chains of three or more, assuming that such chains would be responsible for another undetected ^{45}Sc NMR spectrum characteristic of a 1-D structure.

No temperature dependence was seen from 4.2 K to about 450 K in the paired and isolated Sc^{3+} resonances of sites 1 and 2, respectively, beyond what might be expected due to lattice dimension changes on cooling and heating. In addition, the metallic resonance in sample F was studied at 77 K and 298 K. No differences in the spectra were detected at those temperatures. Thus it can definitely be concluded that no metal-insulator phase transitions, such as might be characteristic of a 1-D conducting system, occurs in the range 77 K to 298 K, and probably does not occur in the full range 4.2 K to 450 K.

Although these results may not completely exclude the occurrence of one-dimensional CsScCl_3 in the samples, they do clearly indicate that the bulk sample cannot be characterized as single-phase and that CsScCl_3 may not even be present. While the characteristics of the ^{45}Sc spectrum expected from CsScCl_3 cannot be completely specified in advance, it might be expected by analogy to the cases of $\text{Hg}_{2.86}\text{AsF}_6$ and $\text{V}_x\text{Cr}_{1-x}\text{O}_2$ (4,5) that in the metallic phase the Knight shift would be different from that in scandium metal and probably negative. Furthermore, since the structure of CsScCl_3 is distinguishable from that of both $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ and ScCl_3 , a different quadrupole coupling is reasonably anticipated. It seems most unlikely that both the Knight shift and quadrupole coupling of ^{45}Sc in CsScCl_3 would be completely identical to those of one of the other phases.

Alternatively, if the CsScCl_3 phase exists in these samples, its ^{45}Sc spectrum must be masked by the spectra of the other phases. This possibility also appears strained in that it would require rather remarkable coincidence of spectral features over the entire frequency range investigated as well as at various temperatures. It would also mean that the intensity of the hypothesized CsScCl_3 spectrum would have to be very weak, indeed, compared to the three observed spectra.

In conclusion, it appears that all of the ^{45}Sc spectra obtained can be accounted for in terms of the spectra of the compounds $\text{Cs}_3\text{Sc}_2\text{Cl}_9$, ScCl_3 , and scandium metal, present in various proportions in multiphased mixtures. No ^{45}Sc spectrum has been obtained which can reasonably be assigned to the hypothesized 1-D conducting compound CsScCl_3 .

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APPENDIX

This appendix lists the values of various constants used in calculations.

Data on Nuclear Species

<u>Isotope</u>	<u>Abundance (%)</u>	<u>Spin (I)</u>	<u>γ (MHz/kOe)</u>	<u>References</u>
^{45}Sc	100	7/2	1.0343	23
^{35}Cl	75.4	3/2	0.4172	23
^{37}Cl	24.6	3/2	0.3472	23
^{133}Cs	100	7/2	0.5585	23

Interatomic Distances ($\text{\AA}$)

	<u>Sc-Cl</u>	<u>Sc-Sc</u>	<u>Cs-Cs</u>	
ScCl_3	2.58	-	-	46
CsScCl_3	2.54	3.02	3.90	-

Sternheimer Antishielding

$$\gamma_{\infty}(\text{Sc}^{3+}) = -10 \quad 12$$

Spectral Parameters for ^{45}Sc in Scandium Metal

$$\begin{aligned} \nu_Q &= 0.144 \pm 0.002 \text{ MHz} & 24 \\ K_{\text{iso}} &= 0.26 \pm 0.004\% & 24 \\ K_{\text{ax}} &= -0.02 \pm 0.002\% & 24 \end{aligned}$$