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Knight Shift Anisotropy in Scandium and Yttrium and Nuclear Quadrupole Coupling in Scandium*

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The anisotropic Knight shift of the Sc^{45} and Y^{89} nuclear magnetic resonances (nmr) in polycrystalline scandium and yttrium metal, respectively, has been observed and measured at room temperature by means of the magnetic field dependence of the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition. The isotropic Knight shift, K_{iso}, is (0.262 ± 0.002) % for scandium and (0.367 ± 0.005) % for yttrium. The axial component of the Knight shift, K_{ax}, is $-(0.024\pm0.002)$ % for scandium and $-(0.026\pm0.002)$ % for yttrium. The scandium nmr spectrum contains a central transition and three pairs of satellite lines, consistent with the $I=\frac{7}{2}$ spin of Sc^{45}. The average spacing of the three pairs of satellites yields a lowest pure quadrupole frequency, $\nu_Q=0.144\pm0.002$ Mc/sec, so that the quadrupole coupling, $e^2Qq/h=2.02\pm0.03$ Mc/sec. Analysis of the central transition splitting yields the same value within the experimental uncertainty.

INTRODUCTION

The nuclear magnetic resonance (nmr) of Sc^{45} in scandium metal affords an excellent example of the manner in which the nuclear resonance line shape changes continuously from that characteristic of quadrupole interaction to that characteristic of anisotropic Knight shift broadening when the resonant nuclei occupy sites of less than cubic symmetry. The full range of line shape behavior is obtained within the range of magnetic field strengths and resonance frequencies typically used in the study of nmr in solids. At a resonance frequency of 2 Mc/sec the central transition of the spectrum is completely split apart by the quadrupole interaction, and at frequencies greater than roughly 20 Mc/sec, the line shape is effectively that of an anisotropic Knight shift broadened line. This latter situation allows the sign of the Knight shift anisotropy to be unambiguously determined as negative. The Knight shift anisotropy in yttrium is also found to be negative.

Blumberg *et al.*[1] were the first to observe the Sc^{45} nmr in scandium metal, although these authors failed to detect any evidence of quadrupole interaction or of Knight shift anisotropy. The value of the isotropic Knight shift obtained by Blumberg *et al.* agrees fairly well with the result of the measurements reported here. Quadrupole effects in the scandium nmr were first reported by Segel and Barnes,[2] who observed two pairs of satellite lines and the behavior of the central transition of the spectrum in the frequency range 3–16 Mc/sec. The work reported herein is an enlargement of that investigation to a wider range of resonance field and frequency, utilizing somewhat better samples of the metal, and provides more reliable values of the quadrupole coupling and Knight shift parameters than were previously obtained.

In the case of yttrium, the nmr of Y^{89} in the metal was first reported by Jones, Graham, and Barnes.[3] These authors failed to measure the axial component of the Knight shift tensor in the polycrystalline (powder) resonance pattern. A contributing factor in this regard is the experimental difficulty in observing the absorption mode signal, which saturates at a relatively low radiofrequency level owing to the small value of the nuclear moment (and correspondingly relatively long relaxation time T_1). We report here additional studies on somewhat purer yttrium, in which, by employing much lower radiofrequency levels than previously, we have observed the anisotropic shape of the absorption mode signal.

EXPERIMENTAL

The scandium and yttrium metal samples used in these studies were produced in the Ames Laboratory by calcium reduction of the metal fluorides and subsequent distillation.[4,5] The metal samples were filed in an argon atmosphere inside a Blickman stainless steel vacuum dry box. In the case of scandium, the filings were sieved to 200 mesh and sealed by welding under vacuum into previously outgassed tantalum crucibles. These crucibles were then sealed into Vycor tubes under helium atmosphere, and these were annealed at 475°C for 12 to 15 h. The yttrium filings (270 mesh) were not annealed. Table I shows the impurity content of the metal used in this investigation, as determined by emission spectroscopic analysis.

Nmr measurements were made with a Varian Associates model V-4200 wide line spectrometer and a Varian 12-in. electromagnet. For magnetic field strengths in the 16–28-kOe range, a Harvey-Wells L-158 15-in.

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[1] W. E. Blumberg, J. Eisinger, V. Jaccarino, and B. T. Matthias, Phys. Rev. Letters **5**, 52 (1960).

[2] S. L. Segel and R. G. Barnes, Bull. Am. Phys. Soc. **7**, 537 (1962).

[3] W. H. Jones, Jr., T. P. Graham, and R. G. Barnes, Acta Met. **8**, 663 (1960).

[4] F. H. Spedding and A. H. Daane, J. Metals **6**, 504 (1954).

[5] A. H. Daane, C. Habermann, and D. Dennison, *Proceedings of the Second Rare Earth Conference held at University of Denver, Glenwood Springs, Colorado* (Gordon and Breach Science Publishers, New York, 1961), Vol. III.

TABLE I. Impurity content of the scandium and yttrium metal sample used in the present study, in parts per million by weight, as determined by spectroscopic analysis.

	Impurity element												
Sample	Fe	Ta	C	Al	N	Hg	Si	Cu	Ni	Ca	Cr	O	Ti
Y	159	100	115	⋯	56	30	⋯	⋯	85	30	⋯	100	⋯
Sc[a]	475	240	290	100	100	25	50	100	75	55	75	250	20
Sc[b]	180	1000	⋯	⋯	80[c]	⋯	80	⋯	⋯	320	⋯	1850[c]	⋯

[a] Results reported in Ref. 2 were based on this sample. [b] Used in present study. [c] Based on vacuum fusion analysis.

electromagnet equipped with microshims was used. At these higher field strengths a high-frequency wide-line induction spectrometer developed by one of the authors (D. R. T.) was used for the scandium resonance study.[6]

The magnetic field was precycled to establish a well-defined hysteresis loop for each set of measurements, and the resonances were recorded by scanning the magnetic field at fixed resonance frequency. Calibration of the magnetic field preceded and followed most runs, and was accomplished with the same spectrometers and the nmr of Sc^{45}, Al^{27}, H^2, and K^{39} in appropriate aqueous solutions. Frequency measurements were made with a Computer Measurements Corporation 737CN frequency counter. Magnetic moment values used in the calculations were taken from the tables compiled by Laukien.[7]

In the present experiments on scandium, the full set of $2I-1=6$ satellite lines were observed, consistent with the known spin, $I=\frac{7}{2}$, of Sc^{45}.[7] This improvement over the earlier work[2] in which only two pairs of satellites were detected appears to be due principally to the more careful preparation of the metal filings, as described above. A typical recording of the absorption mode (derivative) signal, showing the three satellite pairs, for a resonance frequency of 10 Mc/sec, is shown in Fig. 1. The central transition of the resonance spectrum is grossly distorted owing to the high level of field modulation needed to bring out the satellite lines, and the latter are shifted from their true positions for the same reason.[8]

The observed satellite intensities fall significantly below the theoretically expected values. For spin $I=\frac{7}{2}$, the relative intensities of the transitions should be 7:12:15:16:15:12:7, whereas what we have observed is more on the order of 0.2:0.7:1.6:16:1.6:0.7:0.2. Actually, the most striking feature of the observed intensities is that the satellites are all much weaker than the central transition, whereas the intensities of the satellites relative to one another are more nearly in keeping with theoretical expectations. The satellite transitions are, of course, much more sensitive to variations in the uniformity of the field gradient tensor, since these transitions reflect the strength of the quarurpole interaction in first order. It is not clear from the present work whether these variations are caused by impurity atoms (see Table I), by unrelieved strains due to the filing operation, or by a combination of these. In the case of indium, although the quadrupole interaction is much stronger than in scandium, the lines have more nearly their theoretical intensities.[9] High-purity indium is, however, readily available, and its low melting temperature implies a low recrystallization temperature—cold work probably annealing at room temperature.

Second-order quadrupole as well as anisotropic Knight shift effects were observed in the central transition of the scandium resonance spectrum. In Fig. 2 are shown several examples of the central transition (derivative) shape, ranging from the quadrupolar dominated splitting at 2 Mc/sec to an anisotropic shift splitting at 23.5 Mc/sec. The results of the central transition measurements are plotted in Fig. 3 as a function of resonance frequency. As is clear from this figure, the minimum in the experimental "width" of the central transition is fairly broad, and this may account some-

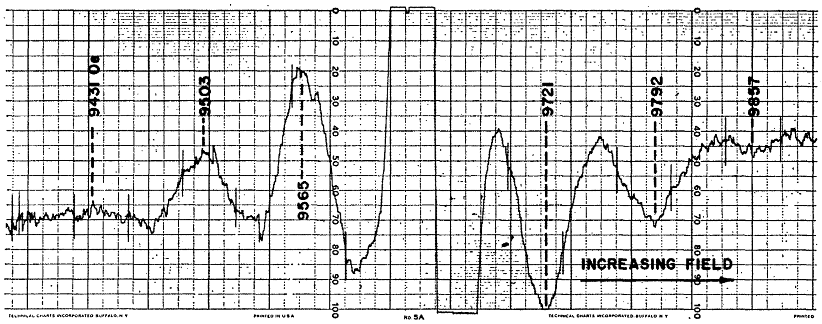

FIG. 1. Absorption mode derivative signal of the Sc^{45} resonance in scandium metal at a resonance frequency of 10 Mc/sec. Three pairs of satellite lines are discernable, the outermost pair being very weak. The central transition of the resonance is grossly distorted by the large modulation amplitude required to reveal the satellite lines, and the latter are shifted from their true positions for the same reason.

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[6] D. R. Torgeson, (to be published).

[7] G. Laukien, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 38, Part 1, pp. 338–376.

[8] R. G. Barnes and L. W. Mohn (to be published).

[9] D. R. Torgeson and R. G. Barnes, Phys. Rev. Letters **9**, 255 (1962).

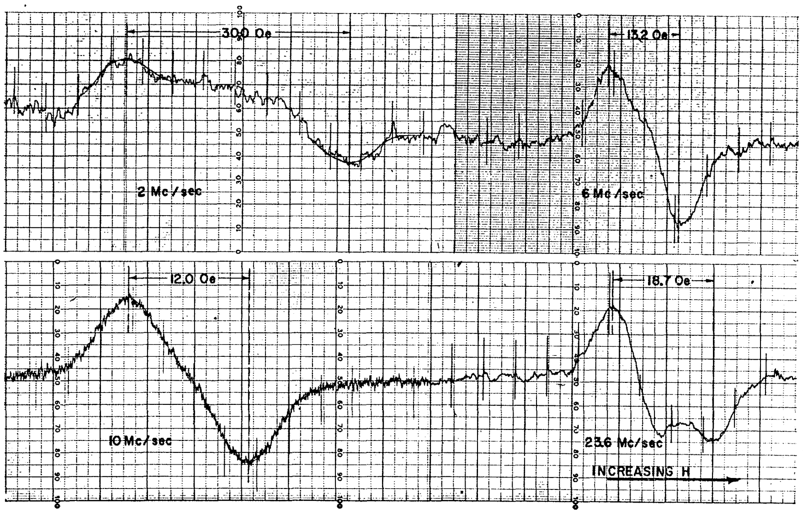

FIG. 2. Representative examples of the absorption mode derivative signal shape of the Sc^{45} resonance central transition in scandium metal, showing the transition from quadrupolar shape at low-resonance frequencies to Knight shift anisotropy at high-resonance frequencies.

what for the original failure to detect the quadrupole and anisotropic shift effects.[1]

In the case of yttrium, the spin of Y^{89} being one-half, quadrupole complications do not arise. Figure 4 shows typical recorded (derivative) tracings of the Y^{89} resonance in the metal. The shape of the derivative signal is that characteristic of Knight shift anisotropy. At constant resonance frequency the additional "bump" occurs on the high-field side of the resonance, indicating that the shift anisotropy is negative. Figure 4(a) was obtained using conventional lock-in techniques, whereas Fig. 4(b) was obtained using the method of continuous averaging.[10] The latter method allows the use of smaller modulation amplitudes [that used in the case of 4(b) is only one-sixth that used in 4(a)] which in the present case would permit a more reliable estimate of the width of the Y^{89} resonance to be made. However, attempts to average over still longer times proved unsuccessful owing to wandering of the oscillator frequency.

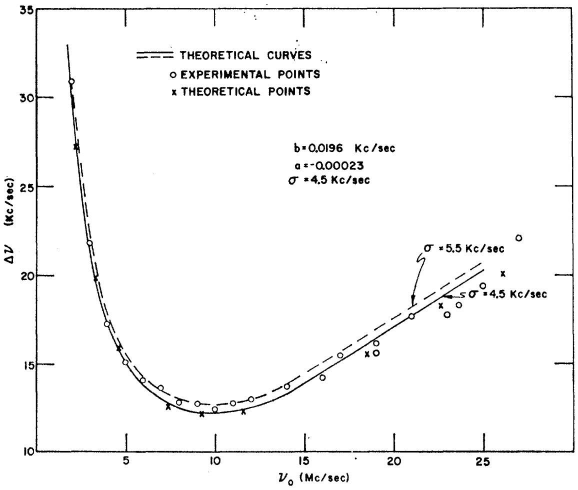

FIG. 3. Splitting of the central transition of the Sc^{45} resonance in scandium metal as a function of resonance frequency. The open circles represent the experimental data, and the crosses represent the splittings measured on computed line shapes (see text). The solid and dashed curves represent Eqs. (2) and (5) of the text [Eq. (5) applies below 15 Mc/sec and (2) applies above 15 Mc/sec], with the linewidth parameter σ being different for the two curves.

ANALYSIS OF THE EXPERIMENTAL DATA

Scandium

The extraction of the relevant resonance parameters —isotropic and anisotropic Knight shifts, quadrupole coupling, and linewidth—from the observed spectrum of Sc^{45} in the metal follows closely the methods discussed by Jones *et al.*[11] for the case of combined quadrupole and anisotropic shift interactions. As shown in Ref. 11 the spacings between corresponding satellite pairs are unaffected by the anisotropic shift interaction through the second order of perturbation theory, and are also independent of second-order quadrupole contributions:

$$\nu(-m+1\leftrightarrow -m)-\nu(m\leftrightarrow m-1)=(m-\tfrac{1}{2})\nu_Q. \quad (1)$$

Here, $\nu_Q=3e^2qQ/2I(2I-1)h$ is the lowest frequency "pure quadrupole" transition, and e^2qQ/h is the quadrupole coupling in frequency units. The satellite spacings therefore provide a reliable and direct measure of the quadrupole coupling. In the present case, we obtain for scandium,

$$\nu_Q=0.144\pm0.002 \text{ Mc/sec}$$

from the satellite spacings after correcting for the effect of excessive modulation amplitude.[8] The maximum value of the ratio, $\lambda=\nu_Q/\nu_0$, which measures the relative

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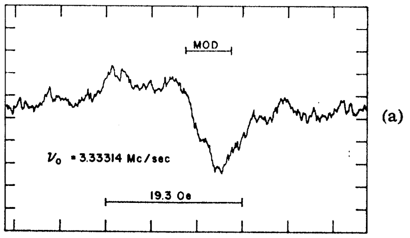
[10] M. P. Klein and G. W. Barton, Jr., Rev. Sci. Instr. **34**, 754 (1963).

[11] W. H. Jones, Jr., T. P. Graham, and R. G. Barnes, Phys. Rev. **132**, 1898 (1963).



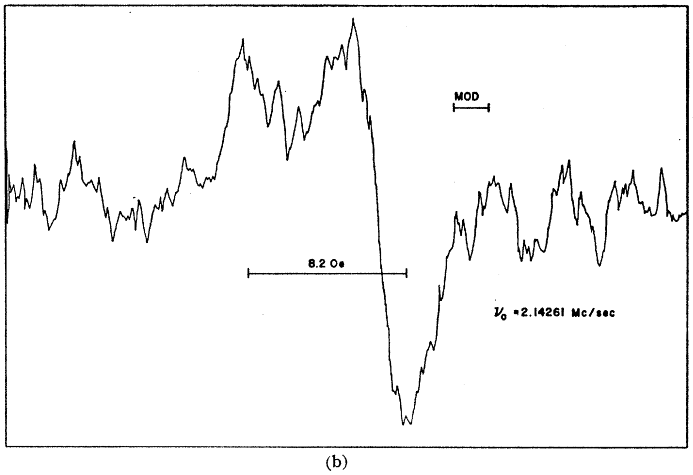


FIG. 4. Absorption mode derivative signal traces of the Y^{89} resonance in yttrium metal, showing the characteristic shape associated with Knight shift anisotropy. (a) Conventional recording made using lock-in technique; the lock-in time constant was 25 sec. (b) Recording made using method of continuous averaging; the total averaging time was 324 min (324 passes), and the modulation amplitude is one-sixth that used in (a). The lock-in time constant was 0.8 sec.

strength of the quadrupole and Zeeman interactions, occurs at the lowest resonance frequency used (2 Mc/sec in this work). With the above value of ν_Q, we have $\lambda = 1/14$ at 2 Mc/sec, hence the methods discussed by Jones *et al.*[11] are entirely adequate for treating the experimental data.

The Knight shift parameters (as well as the quadrupole coupling) may be determined from the behavior of the central transition ($m = +\frac{1}{2} \leftrightarrow m = -\frac{1}{2}$) of the resonance spectrum. It is clear from the derivative line shapes shown in Fig. 2 that the shape of the central transition is dominated by the quadrupole interaction at low frequencies and by the anisotropic Knight shift at high frequencies. Since the data extend well into the anisotrpic shift region, a value of the shift anisotropy can be obtained from the high-frequency behavior. For $I = \frac{7}{2}$ this splitting is given by[11]

$$\Delta\nu_{\mathrm{HS}} = (15/16)\nu_Q^2 \nu_R^{-1} - 3a\nu_R, \qquad (2)$$

so that

$$\nu_R^{-1}\Delta\nu_{\mathrm{HS}} = (15/16)(\nu_Q/\nu_R)^2 - 3a. \qquad (3)$$

Here, $a = K_{\mathrm{ax}}/(1+K_{\mathrm{iso}}) \cong K_{\mathrm{ax}}$ in the present case since the value of K_{iso} is less than one percent. Thus, for all practical purposes, we may take $a = K_{\mathrm{ax}}$. Borsa and Barnes[12] have shown that for anisotropic Knight shift broadening the static (zero-field) broadening may be neglected when $3a\nu_R \gtrsim 3.5\sigma$ where σ is the static broadening. A plot of $\nu_R^{-1}\Delta\nu_{\mathrm{HS}}$ versus ν_R^{-2} for the data above 15 Mc/sec yields the value

$$K_{\mathrm{ax}} = -(0.0232 \pm 0.0014)\%$$

from the intercept at $\nu_R^{-2} = 0$.

The shift of the high-frequency side of the resonance K_H is given for all values of the relative strength parameter, $r = (16/15)a(\nu_R/\nu_Q)^2$, within the range of frequencies investigated, by[11]

$$K_H = K_{\mathrm{iso}} - a + (15/16)(\nu_Q/\nu_R)^2. \qquad (4)$$

The values of K_H are plotted versus ν_R^{-2} in Fig. 5, for the data in the range 4–15 Mc/sec. Determination of the shift from the 2 and 3 Mc/sec data was not reliable. The straight line in Fig. 5 is the least-squares best fit to the data points. From the intercept at $\nu_R^{-2} = 0$, we have

$$K_{\mathrm{iso}} - a = 0.286\%.$$

The slope of the line yields

$$\nu_Q = 0.143 \text{ Mc/sec}.$$

A separate determination of ν_Q and a was also made from the measured splittings at low frequencies. For frequencies within the range $0 < \nu_H^2 \leq -5\nu_Q^2/2a$ (and with $a < 0$), the central transition splitting $\Delta\nu_{\mathrm{HL}}$ is given by[11]

$$\Delta\nu_{\mathrm{HL}} = \frac{25}{9}\frac{b}{\nu_R} - \frac{5}{3}a\nu_R + \frac{a^2\nu_R^3}{4b} + \frac{\sigma}{2}. \qquad (5)$$

A least-squares fit by computer (IBM 7074) of this

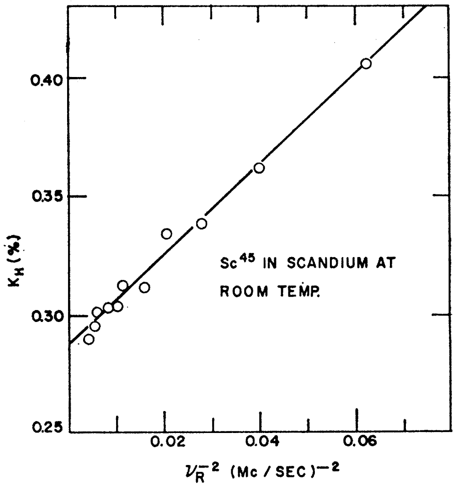


FIG. 5. Plot of shift of high-frequency peak of resonance K_H versus reciprocal square of resonance frequency ν_R^{-2}. The straight line is the least-squares fit to the data points.

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[12] F. Borsa and R. G. Barnes, J. Phys. Chem. Solids **25**, 1305 (1964).

TABLE II. Summary of experimental Knight shift and quadrupole coupling measurements on scandium.

Method	ν_Q (Mc/sec)	K_{ax} %	K_{iso} %
Satellite spacings	0.144		
Central transition			
1) High-frequency data		-0.0232	
2) Low-frequency data	0.146	-0.0245	
3) K_H versus ν_R^{-2}	0.143		$+0.286+K_{\text{ax}}$
Final results	0.144 ± 0.002	-0.024 ± 0.002	$+0.262$ ± 0.004

equation to the 2–15-Mc/sec data yielded the following values:

$$a=K_{\text{ax}}=-(0.0245\pm0.002)\%,$$
$$\nu_Q=0.146\pm0.002\ \text{Mc/sec},$$
$$\sigma=4.22\ \text{kc/sec}.$$

The results of these several methods of analysis are collected in Table II. We take as our final results for scandium:

$$\nu_Q=0.144\pm0.002\ \text{Mc/sec},$$
$$K_{\text{ax}}=-(0.024\pm0.002)\%,$$
$$K_{\text{iso}}=+(0.262\pm0.004)\%.$$

Yttrium

The determination of the shift tensor components in the case of axially symmetric shift anisotropy from measurements made on powder samples has been recently discussed by Borsa and Barnes.[12] The overall splitting between the outer peaks of the Y^{89} absorption derivative signal, δH_{msl}, was measured as a function of the applied external field, H_0, in the range $H_0=10$ to 19.1 kOe. Recordings of the resonance made at lower field strength generally did not resolve the splitting. The high-field splittings are a linear function of the applied field strength, leading to the result:

$$K_{\text{ax}}=-(0.026\pm0.002)\%.$$

In measuring the isotropic shift the N^{14} resonance in HNO_3 was used as a convenient standard. The ratio $\nu(N^{14})/\nu(Y^{89})$ was first determined, using a saturated solution of YCl_3:

$$\nu(N^{14})/\nu(Y^{89})=1.47462\pm0.00004.$$

Using the above value, we obtain for the isotropic Knight shift of Y^{89} in yttrium,

$$K_{\text{iso}}=(0.367\pm0.005)\%.$$

The difference between this value and that previously reported[3] arises principally from the fact that in the earlier measurements the anisotropic shape of the resonance was not resolved.

STATIC (DIPOLAR) LINE BROADENING

Both Sc^{45} and Y^{89} are 100% abundant isotopes, so that the indirect exchange interaction between unlike nuclei cannot contribute to the static line breadth.[13] On the other hand, the pseudodipolar interaction between like nuclei may contribute. Neglecting these effects altogether, the calculated nuclear dipolar second moment for the Y^{89} resonance in yttrium is 0.48×10^{-2} Oe^2, so that the linewidth is on the order of 0.15 Oe. In the case of scandium, the dipolar second moment appropriate to the central transition must be determined from the more complex formula given by Kambe and Ollam,[14]

$$\langle\Delta H^2\rangle_{\text{av}}=F_L(I)\gamma^2\hbar^2\textstyle\sum_k b_k^2\,, \tag{6}$$

where $F_L(I)$ is a complicated function of the spin I.[14] Using (6) we obtain $\langle\Delta H^2\rangle_{\text{av}}=5.65$ Oe^2 for the central transition of the Sc^{45} resonance in scandium, and assuming that the line shape is Gaussian, the width (between points of maximum slope) is $\delta H_{\text{msl}}=4.76$ Oe.

In the case of yttrium no definitive experimental value of δH has been obtained. The modulation amplitude required to record reliable derivative traces of the absorption mode signal (see Fig. 4) in all cases exceeds considerably the calculated value of δH_{msl}. (The modulation amplitude is, however, less than the splitting due to the Knight shift anisotropy, so that the determination of the latter quantity is not affected by this factor.) It is clear from the continuous averaging traces [Fig. 4(b)] that the linewidth is less than one oersted. For scandium, the experimental δH_{msl} lies in the range 4.2–5.5 Oe, being perhaps closer to the 4.2 Oe value. In Fig. 3 the dashed and solid curves represent Eq. (5) for frequencies below 15 Mc/sec and Eq. (2) for those above 15 Mc/sec, with $a=-0.023\%$ and $\nu_Q=0.1446$ Mc/sec. For the dashed curve, $\sigma=\delta H_{\text{msl}}=5.5$ kc/sec, and for the solid curve, $\delta H_{\text{msl}}=4.5$ kc/sec. Also, as mentioned in connection with the determination of the Knight shift parameters, a least-squares fit of (5) to the splitting data below 15 Mc/sec yields $\delta H_{\text{msl}}=4.22$ kc/sec. Thus, we conclude that nondipolar interactions are not needed to account for the static line broadening of the Sc^{45} resonance in scandium.

This conclusion (in the case of scandium) was also substantiated by the results of a calculation of the shape of the central transition of the resonance spectrum for a powder specimen. Assuming that the line shape appropriate to each individual single crystallite in the specimen is Gaussian, the distribution function which describes the dependence of the central transition frequency on the angle θ between the external magnetic field and the crystal symmetry axis [Eq. (20) of Ref. 11] in the case of combined quadrupole and anisotropic shift interactions has been weighted with the Gaussian to give the actual absorption envelope. This calculation

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[13] N. Bloembergen and T. J. Rowland, Acta Met. 1, 731 (1953).

[14] K. Kambe and J. F. Ollom, J. Phys. Soc. Japan 11, 50 (1956).

TABLE III. Atomic s-electron hyperfine constant, electronic specific heat, etc., and experimental and theoretical ratios of the isotropic Knight shifts of scandium, yttrium, and lanthanum.

	$a(s)$[a] (cm^{-1})	γ[b] (mJ/mole deg^2)	K_{iso} (%)	g_I[c]	Exp	Theory[d]
Sc	0.082	11.3	0.262	1.357		
Y	0.031	10.2	0.367	0.2736		
La	0.101	10.1	0.685	0.7937		
$K_{\text{Sc}}/K_{\text{Y}}$					0.60	0.59
$K_{\text{Sc}}/K_{\text{La}}$					0.32	0.53
$K_{\text{Y}}/K_{\text{La}}$					0.54	0.9

[a] Calculated from data tabulated in National Bureau of Standards Circular 467 using standard relations given, for example, in H. Kopfermann, *Nuclear Moments* (Academic Press Inc., New York, 1958).
[b] H. Montgomery and G. P. Pells, Proc. Phys. Soc. (London) **78**, 622 (1961).
[c] Reference 7 in text.
[d] Calculated assuming that $\xi_{\text{Sc}} = \xi_{\text{Y}} = \xi_{\text{La}}$.

has been made in the manner described elsewhere.[12] The splittings of the absorption lines so calculated were than measured, and the results are shown on Fig. 3 by the crosses. Very good agreement with the experimental data is obtained.

DISCUSSION

Knight Shifts

Scandium and yttrium are both simple hexagonal close-packed metals. In this, they differ somewhat from lanthanum, which although electronically similar, takes on a variant of the hcp structure.[15] In other respects also, these two metals more closely resemble the heavy rare earths which also take on the simple hcp structure. All three elements (Sc, Y, La) have the same atomic configuration, s^2d. No evidence of magnetic ordering has been detected in either scandium or yttrium (or lanthanum), and it appears that both metals exhibit simple Pauli paramagnetism.

The isotropic Knight shift can be expressed as

$$K = [a(s)/2gI\beta]\chi_P\xi, \tag{7}$$

where for brevity we drop the subscript "iso." Here, $a(s)$ is the hfs constant for s electrons in the free atom, g_I is the nuclear g factor, β the Bohr magneton, χ_P the Pauli susceptibility per gram-atom, and $\xi = \langle|\Psi_s(0)|^2\rangle_F/|\Psi_s(0)|_A{}^2$, where $\langle|\Psi_s(0)|^2\rangle_F$ is the average over the Fermi surface of the probability for an electron in an S state to be found at the nuclear site and $|\Psi_s(0)|_A{}^2$ is the corresponding probability in the free atom. We may compare the ratio, $K_{\text{Sc}}/K_{\text{Y}}$, determined from our experimental shift values with that given by (7). To do this, we assume that the Pauli susceptibility is proportional to the electronic specific heat γ, so that

$$\frac{K_{\text{Sc}}}{K_{\text{Y}}} = \frac{a(s)_{\text{Sc}}}{a(s)_{\text{Y}}} \frac{g_I(\text{Y})}{g_I(\text{Sc})} \frac{\gamma_{\text{Sc}}}{\gamma_{\text{Y}}} \frac{\xi_{\text{Sc}}}{\xi_{\text{Y}}}.$$

The various relevant parameters are listed in Table III. Assuming that $\xi_{\text{Sc}} = \xi_{\text{Y}}$, we obtain from the above equation

$$(K_{\text{Sc}}/K_{\text{Y}})_{\text{theory}} = 0.587,$$

whereas our measured shift values yield

$$(K_{\text{Sc}}/K_{\text{Y}})_{\text{exp}} = 0.6.$$

The near equality of these values confirms the assumption that $\xi_{\text{Sc}} = \xi_{\text{Y}}$, and shows that the band structures of these two metals must be very similar.

The shifts in scandium and yttrium may also be compared in this same way with the shift in lanthanum. In this case, the agreement between theoretical and experimental values of the shift ratios is not nearly so good. The parameter values involved and the values of the ratios are tabulated in Table III.

Quadrupole Coupling

In general, the total effective electric field gradient (efg) at a nuclear site in a noncubic metal is considered to result from the addition of the efg due to the lattice of ion cores (enhanced by the Sternheimer antishielding effect) and the efg due to the non-s-character of the conduction electrons. The contribution, in the case of scandium, which arises from the lattice of ion cores may be estimated as follows: interpolating in de Wette's results[16] for the hcp structure with the lattice parameters of scandium,[4] $a = 3.3090$ Å, $c = 5.2733$ Å, $c/a = 1.5936$, yields the value, $q_{\text{hcp}} = 1.494 \times 10^{22}$ cm^{-3}. The Sternheimer antishielding factor γ_∞ has been estimated to be approximately -7,[17] and the quadrupole moment of Sc^{45} has been obtained from an atomic beam experiment to be $Q(\text{Sc}^{45}) = 0.22$ b[18] (uncorrected for Sternheimer shielding effects). Combining these values we have for the lattice contribution to the quadrupole coupling:

$$e^2Qq_{\text{hcp}}(1-\gamma_\infty)/h = 0.92 \text{ Mc/sec}.$$

This value is 44% of the experimental value obtained

TABLE IV. Summary of nuclear quadrupole couplings and related quantities for the metals scandium, yttrium, and lanthanum.

	Sc^{45} in scandium	Sc^{45} in yttrium	La^{139} in lanthanum
e^2qQ/h[a] (Mc/sec)	2.02	5.20[b]	1.41[c]
Q (barns)	-0.22[d]	-0.22[d]	$+0.21$[e]
$\lvert q_{\text{exp}}\rvert$ (10^{22} cm^{-3})	26.4	67.8	19.3
$q_L(1-\gamma_\infty)$ (10^{22} cm^{-3})	12.0	13.1	38.3

[a] Room temperature values.
[b] References 2 and 19 in text.
[c] Reference 20 in text.
[d] Reference 18 in text.
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in the present work. In this respect, scandium is typical of most metals, in that the calculated lattice contribution is usually less (in magnitude) than that observed. On this account, it cannot be decided whether the conduction-electron contribution to the coupling aids or opposes that of the lattice.

In Table IV are compared the quadrupole couplings and total effective field gradients observed in scandium, yttrium, and lanthanum. Although Y^{89} has no quadrupole moment, the quadrupole coupling of Sc^{45} has been measured for various compositions in the Sc-Y solid solution system, including 10% Sc-90% Y.[2,19] The coupling increases monotonically with yttrium content, and the extrapolated value at 100% yttrium is 5.20 Mc/sec. Table IV also lists the lattice contribution to the total efg, $q_L(1-\gamma_\infty)$, for each of these metals. Two features of the values shown in the table are of interest to us:

(1) Only in the case of lanthanum is the calculated lattice gradient greater than the observed total magnitude. As discussed elsewhere,[20] this means that in this case the conduction electron and lattice contributions to the total efg must be opposed.

(2) The near equality of the lattice contributions to the efg in scandium and yttrium, coupled with the very different quadrupole couplings observed, suggests that the electronic contributions in these two cases are very different. This conclusion is difficult to reconcile with the results of the Knight shift measurements which indicate very similar band structures for these two metals. It may be that the Sternheimer factor γ_∞ for the scandium ion is quite sensitive to its environment, and that this is the major source of the increase in coupling of Sc^{45} in yttrium. However, a change on the order of a factor of two seems surprising. We propose to discuss this matter more thoroughly in connection with other results on the Sc-Y alloy system.[19]

Investigation of the temperature dependence of the Knight shift parameters of these metals and comparison with the magnetic susceptibilities should prove worthwhile. Blumberg *et al.*[1] noted strong temperature dependences of the shifts in scandium (and in cubic lanthanum), but these were not resolved into their isotropic and axial components. More recently, Masuda has measured the spin-lattice and spin-spin relaxation times in scandium by pulse methods, finding $T_1T=0.11$ sec°K in the range 1.5–77°K.[21] These measurements were made at a fixed frequency of 10 Mc/sec, and the Knight shift anisotropy and quadrupole coupling were evidently not noted. Masuda has estimated,[21] on the basis of comparing his measured T_1 with a calculated value for the orbital contribution to the relaxation, that the orbital interaction is mainly responsible for the spin-lattice relaxation, and that the orbital and direct contact interaction contributions to the Knight shift are about equal. In so doing he has assumed that the electrons at the Fermi surface are essentially entirely of d character. It would appear to us, in view of our own measurements, and in view of the extreme difficulty of obtaining scandium which is not contaminated by iron and tantalum (in particular), as well as by oxygen, that any such conclusions must be regarded as of a very tentative nature.

Note added in proof. There is an error in the inset of Fig. 3. $b=0.0196$ Kc/sec, should be $b=0.0196$ Mc/sec.

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