only slightly in structure from each other and having no polarization effects in the substitution. These results are consistent with the dependence of the octahedral cubic field splitting on small variations of lattice spacing, as obtained from pressure data in MgO.[12] They also indicate that the variations of some of the parameters among different hosts are sufficiently large to explain discrepancies between the measured anisotropy constant in YIG and that obtained, assuming that the anisotropy originates in the crystalline field but using spin-Hamiltonian parameters obtained for YGaG. Such results should, hopefully, motivate theoretical calculations of crystal field splitting for the Fe^{3+} ground state in order to elucidate the mechanisms responsible for their existence, thus permitting resonance results on such impurities to be used more efficiently in the study of their environment.

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Nuclear Magnetic Resonance of Indium Metal at 4.2°K*

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The nuclear magnetic resonance spectrum of indium metal power has been measured at twelve magnetic-field points in the range of 17.0 to 30.5 kG at 4.2°K. The analysis of this spectrum gives the isotropic Knight shift as $+0.80\pm0.02\%$, the anisotropic Knight shift as $-0.05\pm0.02\%$, and the nuclear quadrupole spliting parameter ν_q as 1.884 ± 0.002 Mc/sec. All three of these quantities were determined at each of the twelve field points, and no field dependence has been observed in this range.

INTRODUCTION

THE nuclear-magnetic-resonance (NMR) spectrum of indium metal powder has been measured at 4.2°K at magnetic fields ranging from 17 to 30.5 kG as an extension of the earlier measurements of D. R. Torgenson *et al.*[1] The possibility of observing magnetic breakdown and/or de Haas–van Alphen effects at these low temperatures combined with a faster convergence of the perturbation terms suggested the investigation of this higher field region. The availability of other electronic data[2,3] at 4.2°K made this temperature a good choice for comparisons. The isotropic Knight shift, anisotropic Knight shift, and the quadrupole coupling constant have been measured at 12 different field points in this region of 17 to 30.5 kG. The technique used for separating the isotropic Knight shift from the anisotropic Knight shift at a single field point along with the determination of the quadrupole coupling constant at each field point is based on powder pattern line-shape equations given by W. H. Jones *et al.*[4] The experimental determination of these parameters is particularly important in view of recent developments in techniques for the theoretical calculation of energy bands[5] along with new methods for determining the shape and dimensions of the Fermi surface.[6]

THEORY

The NMR spectrum of a metal with $I>\frac{1}{2}$ will, in general, be affected by both the isotropic and the anisotropic Knight shifts and by the presence of quadrupolar interactions. The appropriate Hamiltonian is[7]

$$\begin{aligned}\mathcal{H}=&H_0^{(e)}+H_0^{(n)}+\sum_{i=1}^{n}\beta H_0(L_z^{(i)}+2S_z^{(i)})\\&+\sum_{j=1}^{n}g\mu_0H_0I_z^{(j)}+\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{16\pi}{3}g\mu_0\beta\mathbf{S}^{(i)}\cdot\mathbf{I}^{(j)}\delta(\mathbf{r}_{ij})\\&-2g\mu_0\beta\left[\frac{\mathbf{S}^{(i)}\cdot\mathbf{I}^{(j)}}{r_{ij}^3}-3\frac{(\mathbf{S}^{(i)}\cdot\mathbf{r}_{ij})(\mathbf{I}^{(j)}\cdot\mathbf{r}_{ij})}{r_{ij}^5}\right]\\&+\sum_{q=-2}^{2}(-1)^qQ_q(\nabla E)_{-q},\end{aligned}\tag{1}$$

where $H_0^{(e)}$ is the Hamiltonian for the conduction electrons in the field of the ion cores and $H_0^{(n)}$ is the Hamiltonian for the ion cores. Q_q is the electric quad-

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rupole moment operator and $(\nabla E)_q$ are the field-gradient components as defined by Pound.[8] The contact term in (1) gives rise to the isotropic Knight shift and its effect on a transition is simply to shift the resonance according to

$$\nu_0=(1+k)\nu_R. \tag{2}$$

k is the isotropic Knight-shift parameter, ν_R corresponds to the salt resonance frequency, and ν_0 is the resonance frequency in the metallic environment. The first-order anisotropic Knight shift has been calculated by Bloembergen *et al.*[9] and is given by

$$(E_m-E_{m-1})/h=a\nu_0(3\mu^2-1). \tag{3}$$

a is the anisotropic Knight shift parameter and $\mu=\cos\theta$, where θ is the angle between the external magnetic field and the crystalline axis of symmetry. The second-order anisotropic contribution has been shown to be small.[4]

The effect of the quadrupolar term in (1) on a particular nuclear transition from a state m to a state $m-1$ is given to third order[10] by

$$\nu_{m\leftrightarrow m-1}=\nu_0+\tfrac{1}{2}\nu_q(3\mu^2-1)(m-\tfrac{1}{2})+(\nu_q^2/32\nu_0)(1-\mu^2)[\{102m(m-1)-18I(I+1)+39\}\mu^2$$
$$-\{6m(m-1)-2I(I+1)+3\}]+(\nu_q^3/192\nu_0^2)(2m-1)(1-\mu^2)[\mu^4\{387I(I+1)-1225m(m-1)-783\}$$
$$+\mu^2\{252I(I+1)+660m(m-1)+504\}+\{9I(I+1)-15m(m-1)-18\}], \tag{4}$$

where

$$\nu_q\equiv 3e^2qQ/2I(I-1)\hbar.$$

The splitting as a result of (4) for a $I=\frac{9}{2}$ spin system is shown in Fig. 1. Combining (2), (3), and (4) gives the expression for a nuclear transition from a state characterized by a nuclear spin projection number m to a state of $m-1$, correct to first order in the anisotropic Knight shift and correct to third order in the quadrupole term as

$$\nu_{m\leftrightarrow m-1}=\nu_0+\tfrac{1}{2}\nu_q(3\mu^2-1)(m-\tfrac{1}{2})+a\nu_0(3\mu^2-1)+(\nu_q^2/32\nu_0)(1-\mu^2)[\{102m(m-1)-18I(I+1)+39\}\mu^2$$
$$-\{6m(m-1)-2I(I+1)+3\}]+(\nu_q^3/192\nu_0^2)(2m-1)(1-\mu^2)[\mu^4\{(387I(I+1)-1225m(m-1)-783\}$$
$$+\mu^2\{252I(I+1)+660m(m-1)+504\}+\{9I(I+1)-15m(m-1)-18\}]. \tag{5}$$

EXPERIMENTAL DESCRIPTION

The NMR measurements were made at constant magnetic field. A variable-frequency marginal oscillator, similar to the Pound-Knight oscillator,[11] was employed. The frequency was controlled through the use of a variable-capacity silicon diode in the tank circuit. Detection was with a conventional narrow-band phase-sensitive detector and was displayed on a recording potentiometer. Sinusoidal magnetic modulation was used with a peak-to-peak amplitude of 100 G.

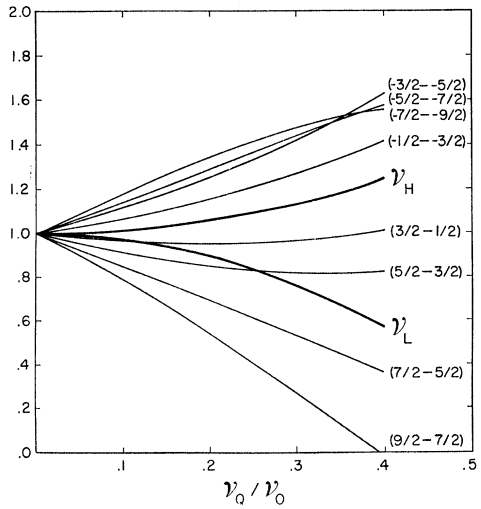

FIG. 1. The splitting of an NMR line as a function of the relative quadrupole perturbation (ν_q/ν_0) for an $I=\frac{9}{2}$ system.

A reference was imbedded in the center of the indium sample and its NMR frequency was used to determine the magnetic field at the site of the indium. In the 17 to 21 kG region, ^{63}Cu metal powder was used as a reference. In the higher field region, 21 to 30 kG, the reference was ^{6}Li metal powder. The long-term stability (12h) of the magnet is the limiting factor in determining the magnetic field at the site of the indium. The narrow linewidths of the reference allowed the magnetic fields to be measured to within less than 1 G. The magnetic field was observed to drift a maximum of 3 G at 30 kG over a 12-h period; a characteristic drift over this interval was 1 G. The field was measured with the reference at the beginning and again at the end of each indium field point. The precision of the experiment is

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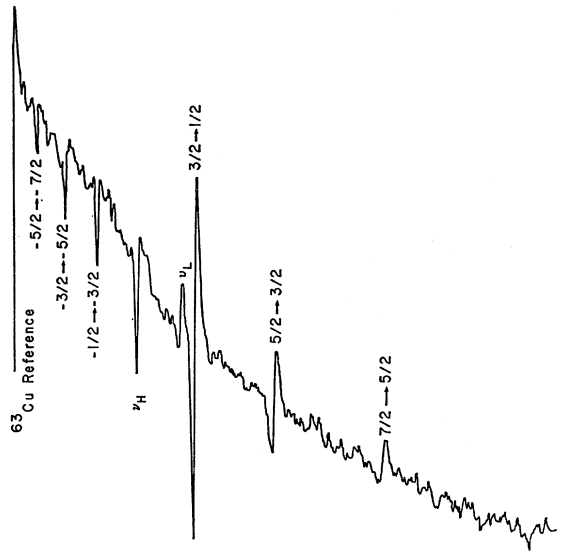

FIG. 2. A recorder trace of the partial NMR spectrum of indium metal powder at 4.2°K and 16 Mc/sec.

limited by the indium linewidth, about 30 G, resulting in uncertainties of 3 kc/sec at 24 Mc/sec for the indium lines.

Frequencies were measured on a Hewlett Packard model 524C frequency counter. The frequency measurements were accurate to within 100 cps.

The sample was the same as the one used for the pure nuclear-quadrupole-resonance (NQR) measurement.[12] About 6 g of metal powder consisting of 2-μ-diam spheres was mixed with an equal volume of quartz powder. The size and uniformity of the particles were monitored with an oil-immersion microscope. The indium used was purchased from the Indium Corporation of America with a reported purity of 99.999%. The sample contained both In^{113} and In^{115} in their natural isotopic abundances. A partial spectrum at 16 Mc/sec is shown in Fig. 2.

ANALYSIS OF SPECTRUM

In a polycrystalline sample the line shape is, following Cohen and Reif,[13]

$$p(\nu-\nu_0)=\tfrac{1}{2}|d\nu/d\mu|_{\cdot}^{-1} \tag{6}$$

Now (5) is of the form

$$\nu=A\mu^6+B\mu^4+C\mu^2+D, \tag{7}$$

where A, B, C, and D depend both on the I and m values of the transition and on the three parameters k, a, and ν_q. The third-order quadrupole term in (5) vanishes for the $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition and for that case (7) reduces to

$$\nu=B'\mu^4+C'\mu^2+D' \tag{8}$$

and

$$d\nu/d\mu=4B'\mu^3+2C'\mu. \tag{9}$$

Therefore, (6) has a pole at $\mu=0$ which is identified as ν_H and a pole at $\mu=\mu'$ identified as ν_L. The resonance at $\mu=0$ is always observable, but the resonance at $\mu=\mu'$ may or may not correspond to a real value of $\theta(-1\leqslant\mu\leqslant1)$. The ν_L resonance can be observed if

$$-8b/3a\geqslant\nu_0^2\geqslant0 \text{ for } a<0;\ 0\leqslant\nu_0^2\leqslant10b/3a \text{ for } a>0, \tag{10}$$

where $b=\frac{3}{2}\nu_q^2$. In indium, in the region of 16 to 26 Mc/sec, condition (10) is met for $m=\frac{1}{2}$ and correspondingly two resonances are observed. The absorption curve, resulting from (6), exhibits considerable asymmetry. The measurement of the position of the poles for these lines depends on the asymmetry and was performed following a method outlined by Williams.[14] To third order the resonance frequencies corresponding to the $\nu_{1/2\leftrightarrow-1/2}$ transition are

$$\nu_H=\nu_0+b/\nu_0-a\nu_0, \tag{11}$$

$$\nu_L=\nu_0-16b/9\nu_0+2a\nu_0/3-a^2\nu_0^3/4b. \tag{12}$$

The experiment involves the measurement of specific lines in the indium spectrum at twelve different values of magnetic field ranging from 16 to 30.5 kG. The lines selected were ν_H, ν_L, and $\nu_{3/2\leftrightarrow1/2}$. The expression for $\nu_{3/2\leftrightarrow1/2}$ follows from (5) and is

$$\nu_{3/2\leftrightarrow1/2}=(1-a)\nu_0-\frac{\nu_q}{2}+\frac{21\nu_q^2}{16\nu_0}-\frac{129\nu_q^3}{64\nu_0^2}. \tag{13}$$

The resonance frequencies of these three lines as a function of magnetic field are shown in Fig. 3. By ex-

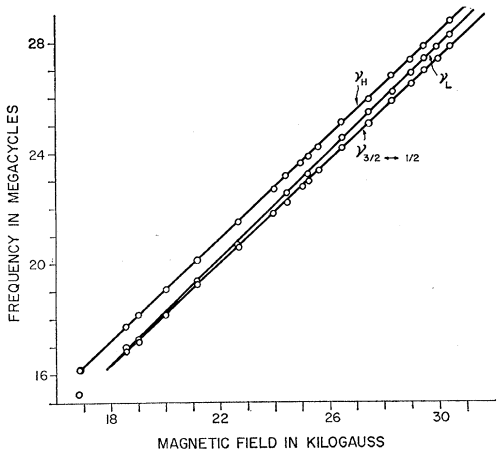

FIG. 3. A plot of ν_H, ν_L, and $\nu_{3/2\leftrightarrow1/2}$ as a function of magnetic field between 16.0 and 30.5 kG.

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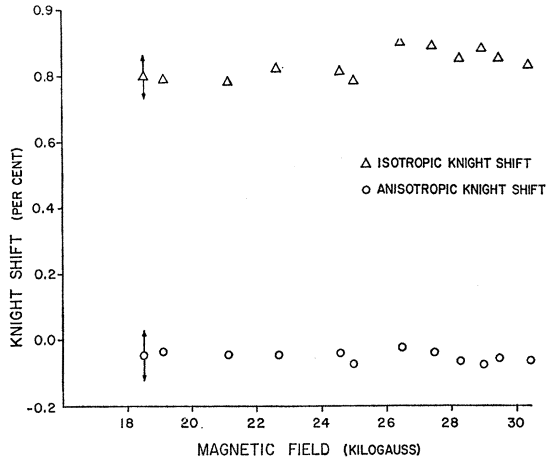

FIG. 4. Experimental results for k and a at 12 different values of magnetic field.

amining three or more lines at a given field, it is possible to separate the three parameters k, a, and ν_q. The results, shown in Fig. 4, give the experimental values for k and a as a function of external field. There is no apparent field dependence and the average values over the region are found to be

$$\text{isotropic Knight shift}=0.0080\pm0.0002,$$

$$\text{anisotropic Knight shift}=-0.0005\pm0.0002.$$

By eliminating $k-a$ from (11) and (13), a cubic equation in ν_q is developed according to

$$\frac{129\nu_q^3}{64\nu_R(1+k)^2}-\frac{3\nu_q^2}{16(1+k)}-\frac{\nu_q\nu_R}{2}+\nu_R(\nu_H-\nu_{3/2\leftrightarrow1/2})=0. \quad (14)$$

The cubic term is a result of third-order perturbation

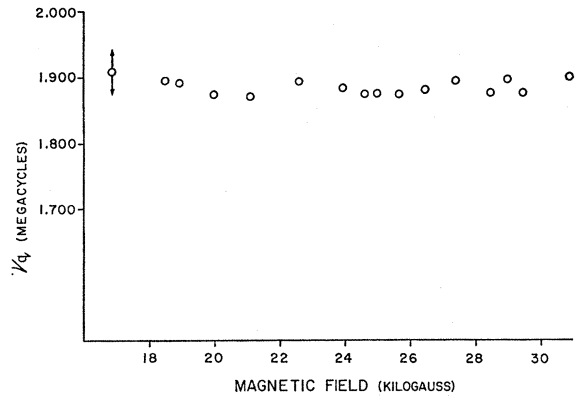

FIG. 5. Experimental results for ν_q at 16 different field points.

theory and is small but important. ν_q was evaluated by the use of (14) at each of 17 field points and the results are shown in Fig. 5. Again there is no apparent field dependence and the average value over the field range investigated is

$$\nu_q=1.885\pm0.002 \text{ Mc/sec},$$

in good agreement with the pure quadrupole measurement[12] of 1.886±0.003 Mc/sec.

CONCLUSIONS

There is no evidence of either magnetic breakdown or de Haas–van Alphen effects in the magnetic region investigated. The isotropic Knight shift is in close agreement with the room-temperature measurement as is to be expected. A recent theoretical calculation of the isotropic Knight shift[15] using the orthogonalized plane-wave method has yielded a value of $k=0.82\%$. This general agreement indicates that other contributions to the isotropic Knight shift arising from core polarization [16,17] and orbital motion of band electrons[18,19] are either individually small or combine in such a way as to cancel. The value of the anisotropic Knight shift is sufficiently different from the room-temperature value to deserve comment. The quadrupole frequency, which is a measure of the interaction of the quadrupole moment of the nucleus with the quadrupole moment of the entire electronic system, increases with decreasing temperature. This can be at least partially explained by motional averaging at the higher temperature; however, the shift is so large (around 30% between room temperature and helium temperatures) that it is likely that the electronic distribution is also changing in a way such as to increase the coupling. Although the anisotropic Knight shift depends only on the quadrupole moment of the electrons around the Fermi surface, one may expect that their distribution would also change in a manner such as to increase the anisotropic coupling. Since a decrease is observed, other mechanisms may be involved. The small absolute value of the anisotropic Knight shift is in agreement with current band-structure calculations which indicate an almost spherical Fermi surface.[15] An important extension of this work is a similar experiment in a single crystal which will give more direct information about the anisotropic Knight shift.

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