LARGE ANISOTROPIC KNIGHT SHIFTS IN INTERMETALLIC COMPOUNDS*

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A variety of intermetallic compounds having electrical properties like those of a metal might be expected to exhibit anisotropy of the Knight shift of the nuclear magnetic resonance of component nuclei. This class of compounds will include those crystallizing with hexagonal or lower symmetry and in addition those crystallizing with cubic symmetry but possessing atoms at sites of less-than-cubic symmetry. Since the nuclei of most of the metals possess electric quadrupole moments, some interference from quadrupole coupling effects may be expected in these situations. In the case of the pure metals, anisotropic Knight shifts have been reported only for cadmium,[1] tin,[2] and thallium,[3] for all of which the nuclear spin is one-half, thereby precluding quadrupolar effects. When both effects are present, the resonance line shape must be investigated as a function of magnetic field strength to determine the individual contributions. This is especially important if the nuclear quadrupole coupling is large enough to give rise to second-order effects.

The cubic Laves phase compounds of the $MgCu_2$ (AB_2) type provide an excellent example of the latter variety mentioned above. In this structure,[4] the Cu or B atoms occupy sites having only axial symmetry, D_{3d}-$\bar{3}m$. The Mg or A atoms are in positions of cubic symmetry, T_d-$\bar{4}3m$. This structure is one of a number in which the average coordination number is $13\frac{1}{3}$, and the compounds exhibit excellent metallic properties except for their brittleness.

In the course of studying the nuclear quadrupole interaction of the B nuclei in cubic Laves phase compounds,[5] we have also observed examples of large anisotropic Knight shifts. With one exception ($MgCu_2$ itself), the observed resonance line shape results from an interplay of the anisotropic Knight shift with the second-order nuclear quadrupole interaction. In a powder sample, each of these effects gives rise to a characteristic line shape.[6] These shapes are, however, qualitatively somewhat similar, so that if the quadrupole interaction is the major effect, the resonance line shape is not significantly altered from that of the quadrupole interaction alone. In the absence of anisotropic Knight-shift broadening, the splitting $\Delta\nu$ between derivative maxima of the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition caused by the nuclear quadrupole interaction in second order is given by[7]

$$\Delta\nu = b/\nu + \sigma, \tag{1}$$

provided that $\sigma \lesssim 0.2\, b/\nu$. Here $b = (25/64)(2I+3) \times e^4q^2Q^2/4I^2(2I-1)h^2$, where e^2qQ/h is the quadrupole coupling in Mc/sec, and 2σ is the linewidth based on the Gaussian shape approximation. For nonconductors, a plot of $\Delta\nu$ vs $(1/\nu)$ yields a straight line from which b and σ may be determined. If anisotropic Knight shift broadening also occurs, the observed $\Delta\nu$ may be represented to a first approximation by

$$\Delta\nu = b/\nu + a\nu + \sigma. \tag{2}$$

In this expression, $a\nu = \Delta\nu_{\parallel} - \Delta\nu_{\perp} = 3\nu\delta_{ax}$, and gives the contribution of the anisotropic Knight shift to the linewidth.[3] For the cases studied here, $\sigma < b/\nu$ or $\sigma < a\nu$, whichever is the more important contribution to $\Delta\nu$ at low or high frequencies. Neglecting σ leads to

$$\nu\Delta\nu = b + a\nu^2, \tag{3}$$

so that $\nu\Delta\nu$ should be linearly proportional to ν^2.

A striking example of this behavior is provided by the Al^{27} resonance in $TmAl_2$. The measured values of the splitting $\Delta\nu$ are shown by the data points in Fig. 1(a), and a plot of the quantity $\nu\Delta\nu$ vs ν^2 for these data is shown in Fig. 1(b), in which the straight line is a least-squares fit of (3) to the points. From this, the nuclear quadrupole coupling and the parameter a are found to be $e^2qQ/h = 3.05$ Mc/sec and $a = 0.0061$. The solid curved line in Fig. 1(a) is drawn using these parameters.

We have also observed the anisotropic Knight shift contribution to the splitting $\Delta\nu$ of the Al^{27} resonance in $CaAl_2$ and $YbAl_2$ which have smaller nuclear quadrupole couplings[5] than $TmAl_2$. In the cases of $LaAl_2$ and $CeAl_2$, this contribution to the splitting is not detected. For these, the quadrupole coupling is approximately 4.5 Mc/sec; hence b/ν is presumably still larger than $a\nu$ at the highest frequency at which observations were made. The Cu^{63} and Cu^{65} resonances in the prototype compound $MgCu_2$ also display anisotropic Knight shift broadening. However, in this case, the quadrupole coupling is so small that the ob-

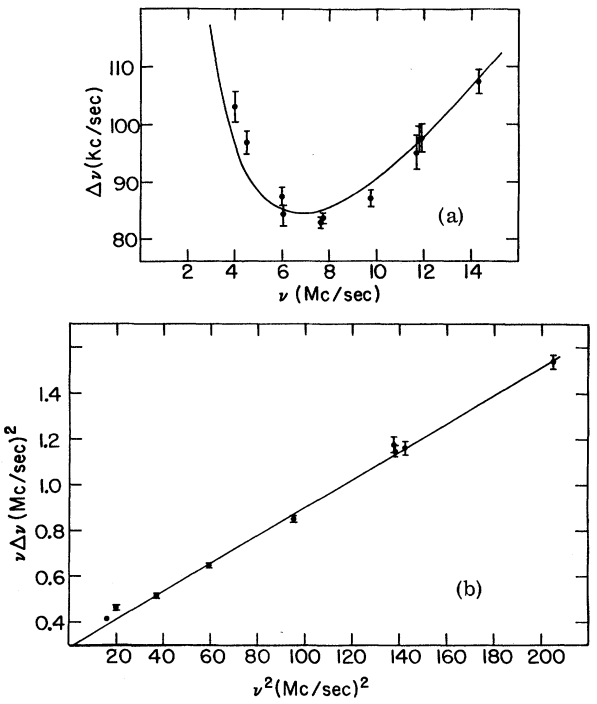

FIG. 1. (a) Resonance linewidth (separation between derivative maxima) as a function of resonance frequency for the Al^{27} resonance in $TmAl_2$. The solid curved line is the straight line of Fig. 1(b). (b) The product $\nu\Delta\nu$ for the data points of Fig. 1(a) as a function of the square of the resonance frequency. The solid line is the least-squares fit of Eq. (3) to the data points.

served splitting is dominated by the anisotropic Knight shift over virtually the entire range of observation.

These experimental results are summarized in Table I. Values of the quantities b/ν and $a\nu$ are given at two resonance frequencies, 4 and 16 Mc/sec. The Van Vleck[8] nuclear dipolar half-linewidth σ (Gaussian approximation) is included for comparison. In addition, the isotropic and axial components, δ_{iso} and δ_{ax}, of the Knight shift tensor[3] and the quadrupole coupling derived from the parameters a and b of Eq. (3) are also given. Besides augmenting the relatively few examples of anisotropic Knight shifts, these results are interesting because they suggest that, in general, several factors combine to cause anisotropy of the shift in the Laves phase compounds. In the cases of $MgCu_2$, $CaAl_2$, and $YbAl_2$, which presumably do not possess ions having unpaired d or f electrons, anisotropy of the p or d character of the conduction band, or of the electron g factor, or of both, must be responsible for the anisotropic shift. On the other hand, a major part of the large anisotropy in the case of $TmAl_2$ very likely arises from the nonisotropic part of the s-f exchange interaction, the isotropic part of which has been shown by Jaccarino et al.[9] to account for the large Knight shifts in the rare-earth-aluminum compounds.

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Table I. Second-order quadrupole and anisotropic Knight shift linewidth parameters for nuclear magnetic resonances in cubic Laves phase compounds. Results for some pure metals are included for comparison.

Compound and nucleus	b/ν (kc/sec) at 16 Mc/sec	$a\nu$	b/ν (kc/sec) at 4 Mc/sec	$a\nu$	σ (kc/sec)	δ_{iso} %	δ_{ax} %	e^2qQ/h (Mc/sec)
$Mg(Cu^{63})_2$		7.52		1.88	1.97	0.240	0.019	<0.3[a]
$Ca(Al^{27})_2$	9.38	5.70	37.5	1.43	2.15	0.105	0.036	2.19
$Yb(Al^{27})_2$	13.0	6.08	52.0	1.52	2.0	0.110	0.040	2.58
$Tm(Al^{27})_2$	18.1	97.6	72.5	24.4	2.0	-0.55	-0.25	3.05
Cd^{111} b						0.415	0.014	
Sn^{117} c						0.76	0.013	
Tl^{205} d						1.56	0.08	

[a]Estimate based on best fit of data to Eq. (3) in text.
[b]See reference 1.
[c]See reference 2.
[d]See reference 3.

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RELAXATION MECHANISMS IN FERROMAGNETIC RESONANCE

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Up to the present, the agreement between theory and experiment in ferromagnets for the relaxation time, τ_0, of spin waves with zero wave vector (uniform precession) has not been satisfactory, especially in highly polished samples with narrow linewidths.[1] The purpose of this Letter is to report the most recent observations of τ_0 in yttrium iron garnet (YIG), which has the narrowest known ferromagnetic resonance linewidth, and to outline the essential points of a theory which adequately accounts for these observations. The theory is based on the effects of single-ion anisotropy, or local magnetostriction, in a simplified two-sublattice ferrimagnetic model.

The character of τ_0^{-1} in YIG along the [111] crystal axis is as follows:

(i) The magnitude of τ_0^{-1} is 2.4×10^6 sec^{-1} at room temperature and a frequency of 5.7 kMc/sec.

(ii) τ_0^{-1} is proportional to T^n, where $1<n<2$ in the range 150°K to 400°K with the larger values of n corresponding to higher temperatures.[2] (The behavior or τ_0^{-1} below 150°K in the present samples appears to be determined by additional processes other than those considered here, and will be reported on by E. G. Spencer.)

(iii) τ_0^{-1} at room temperature is proportional to frequency, at least for $\nu \geq 3$ kMc/sec.[3]

(iv) τ_0^{-1} at room temperature is nearly proportional to M_S^{-1}, where M_S is the saturation magnetization. This relation was determined by doping YIG with gallium and aluminum, which substitute primarily on tetrahedral sites, and indium, which substitutes on octahedral sites.[4]

The above observations of τ_0^{-1} have been made possible primarily by the following three developments: (1) elimination of the effects of surface roughness, (2) elimination of rare earth impurities,[5] and (3) separation of spin-spin from spin-lattice relaxation effects. These and other related developments will be discussed in detail in a forthcoming paper. At this time we will briefly describe the technique which was used for most of the data.

Schlömann and Morganthaler have shown[6] that growing pairs of spin waves of equal and opposite wave number and frequency $\omega_p/2$ may be excited when an rf field of frequency ω_p with sufficient magnitude is applied parallel to the dc magnetic field, H_{dc}. The threshold rf field is

$$h_{crit} = \omega_p/(\gamma^2\tau_k 4\pi M_S \sin^2\theta_k), \quad (1)$$

where θ_k is the angle between $\vec{k}$ and H_{dc}. Thus the threshold is lowest for $\theta_k = \pi/2$. By measuring h_{crit} as a function of H_{dc}, and using the familiar dispersion relation for spin waves, together with the measured value[7] of the exchange constant D, one can obtain a plot of τ_k^{-1} vs k as shown in Fig. 1. A conventional microwave spectrometer with a critically coupled reflection cavity was used for these experiments.

The data in Fig. 1 can be described by

$$1/\tau_k = (1/\tau_0) + Bk, \quad (2)$$

from $k = 0.35\times10^5$ to 1.55×10^5 cm^{-1}. These data have several important features: (1) τ_0^{-1} obtained by this technique is essentially independent of surface roughness, which is known to affect strongly the ordinary uniform-precession linewidth. Hence τ_0^{-1} must be a property of the bulk material. (2) τ_0^{-1} obtained here is essentially the same as T_{10}^{-1}, the inverse spin-lattice relaxation time of the uniform precession, as measured on the same sample by the frequency modulation technique.[1] (3) For the k numbers involved here, Sparks and Kittel[8] have shown that the k-dependent part of τ_k^{-1} should be linear in k. The observed value of B in Fig. 1 is in approximate agreement with their theory. (The latter point will be considered in more detail separately.)