incident frequency is Doppler-shifted, two scattering peaks will occur—a peak of width $\Gamma'+\Gamma_\gamma(+)$ at the frequency $\omega_0=(E(+)-E_a)$, corresponding to resonance fluorescence from the symmetric state, and a peak of width $\Gamma'+\Gamma_\gamma(-)$ at the frequency $\omega_0=(E(-)-E_a)$, corresponding to resonance fluorescence from the antisymmetric state. The fact that the radiative widths can be broadened or narrowed in multiatom resonant scattering is a characteristic feature of such scattering and has been discussed by several authors.[18,21,22]

We also note from (B12) and (B14) that it is possible to selectively excite the symmetric or antisymmetric state. If $\mathbf{k}_0\cdot\mathbf{R}_{12}=2n\pi$, then we see that only the symmetric mode will be excited, while if $\mathbf{k}_0\cdot\mathbf{R}_{12}=(2n+1)\pi$, then only the antisymmetric mode will be excited. In particular, if $k_0R_{12}\ll1$, the first term of the bracket in (B14) $\approx4/Q(+)$, while the second term ≈0. Thus if the two atoms are much less than a wavelength apart, the interaction is entirely with the symmetric state. The (partial) radiative width in this case is twice that for a single atom, and the emitted radiation is four times as intense off resonance, and

$$4\left(\frac{\Gamma'+\Gamma_\gamma(b,a)}{\Gamma'+2\Gamma_\gamma(b,a)}\right)^2$$

times as intense at resonance $[\omega_0=E(+)-E_a]$.

The above results are of course intuitively obvious from classical considerations. If two identical multipoles are vibrating in phase with a separation much less than a wavelength, the emitted radiation is of the same multipole order, with field amplitudes twice as large and with radiated intensity four times as great as for a single multipole, and hence the symmetric-state radiative width is $\Gamma_\gamma(+)\approx2\Gamma_\gamma$. However, if the currents are 180° out of phase, then for $k_0R_{12}\ll1$ only higher-order multipole radiation is emitted and $\Gamma_\gamma(-)\approx0$. (For example, two electric dipoles vibrating 180° out of phase become an electric quadrupole current source for $k_0R_{12}\ll1$). If $\mathbf{k}_0\cdot\mathbf{R}_{12}=2n\pi$, then the currents are driven in phase and only the symmetric state is excited, while if $\mathbf{k}_0\cdot\mathbf{R}_{12}=(2n+1)\pi$, then the currents are driven 180° out of phase and only the antisymmetric state is excited.

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Relation between the *g* Shift and Hyperfine Field in Intermetallic Compounds

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The appreciable variation of the gadolinium hyperfine fields from one compound to another in GdX_2 ($X=$Rh, Ir, Mn, Pt, Al) is explained by interaction of the nucleus with the conduction electrons. These electrons are polarized by their exchange interaction with the Gd ion. This interaction was investigated experimentally by measuring the Gd *g* shift by means of electron spin resonance. The *g* shift was found to vary in both magnitude and sign in these compounds. A relation between the Gd hyperfine field and the Gd *g* shift is derived, enabling us to calculate the hyperfine field per spin for 6*s* electrons in $GdPt_2$ to be 2.8×10^6 G.

INTRODUCTION

In a recent letter, Gegenwarth *et al.*[1] reported on the gadolinium hyperfine fields in the magnetically ordered state for several GdX_2 cubic Laves phase compounds. They found that the hyperfine fields vary considerably from one compound to another. According to Gegenwarth, the hyperfine fields in GdX_2 compounds result from two main phenomena: (1) core polarization[2] and (2) interaction with valence electrons.

On the assumption that core polarization remains constant from sample to sample, any variation in the hyperfine fields should be attributed to interaction with the valence electrons. Gegenwarth stressed this point but did not specify the mechanism of the interactions. It is the purpose of this paper to present further experimental results on the GdX_2 compounds and to explain the origin of these hyperfine fields.

In electron spin resonance (ESR), we measure the exchange interactions between the Gd ion and the conduction electrons. Since these interactions are responsible for the variation in the hyperfine fields (as will be explained later), we believe that ESR measurements are best suited to the above-mentioned purpose.

RESULTS AND DISCUSSION

The ESR of gadolinium in powdered samples of GdX_2 ($X=$Rh, Ir, Mn, Pt) and GdN was measured as a function of temperature, from liquid nitrogen to

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[1] R. E. Gegenwarth, J. I. Budnick, S. Skalski, and J. H. Wernick, Phys. Rev. Letters **18**, 9 (1967).

[2] G. T. Rado and H. Suhl, in *Magnetism* (Academic Press Inc., New York, 1965), Vol. AII, p. 237.

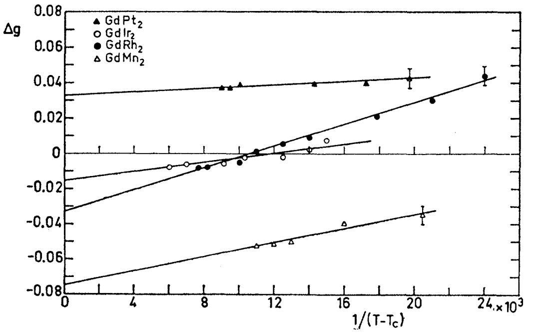

FIG. 1. The g shift of GdX_2 (X=Rh, Ir, Mn, Pt) as a function of $1/(T-T_c)$ in °K^{-1}, where T_c is the paramagnetic Curie temperature and is equal to 70, 75, 90, and 50°K, respectively. The measurements were carried out at 0.8 cm.

room temperature. The apparatus and the technique of measurement have been described elsewhere.[3,4] The measurements were taken at wavelengths of 0.8 and 1 cm. The g shift, Δg, was found to be linear with the susceptibility χ_f. The susceptibility of these compounds was measured as a function of temperature using a vibrating-type magnetometer. The susceptibility reveals a $1/(T-T_c)$ behavior for $T>T_c$. T_c is the paramagnetic Curie temperature.

The Hamiltonian of the Gd ions in an external field, neglecting the terms which do not contribute to the line shift, can be written as[5]

$$\mathcal{H}=g_{\mathrm{Gd}}\beta\sum_n(\mathbf{H}\cdot\mathbf{S}_n)+\sum_{i,n}J(\mathbf{r}_i-\mathbf{R}_n)(\mathbf{s}_i\cdot\mathbf{S}_n), \quad (1)$$

where $J(\mathbf{r}_i-\mathbf{R}_n)$ is the exchange interaction between the Gd spin $\mathbf{S}_n$ located at $\mathbf{R}_n$ and the spin $\mathbf{s}_i$ of the conduction electron located at $\mathbf{r}_i$, g_{Gd} is the ionic g factor, and β is the Bohr magneton. $\mathbf{H}$ is the effective field seen by the Gd ion, and includes the demagnetizing field, apart from the external field.

The second term in the Hamiltonian produces the g shift resulting from interaction with the conduction electrons. This g shift has been calculated by many authors[4] to be

$$\Delta g_0=J\chi^{\mathrm{spin}}/g_e\beta^2N_0, \quad (2)$$

where J is the average exchange interaction, χ^{spin} is the spin susceptibility of the conduction electrons per mole, g_e is the conduction electron g factor, and N_0 is the number of lattice sites per mole.

The first term in Eq. (1) gives the shift caused by demagnetization effects[4] as well as the ordinary g value. This shift is proportional to the susceptibility χ_f, given by the Curie-Weiss law $\chi_f=C/(T-T_c)$.

We assume that the g shift which results from interaction with the conduction electrons, Δg_0, does not depend on temperature. This assumption is justified in view of the large variation of demagnetization shift with temperature. Therefore we can find Δg_0 by plotting the gadolinium shift, Δg, as a function of $1/(T-T_c)$ and extrapolating to $1/(T-T_c)=0$ (Fig. 1). The value of the g shift obtained by this extrapolation was found to be the same for both wavelengths.

It was found that Δg_0 was *positive* for GdPt$_2$. This indicates a positive exchange interaction between the Gd ion and the conduction electrons. In the case of GdX_2 (X=Rh, Ir, Mn), Δg_0 was found to be *negative*, indicating a negative exchange interaction. A possible mechanism for this negative interaction has been suggested by many authors.[6] Previous ESR results of Gd in metals have shown that the exchange interaction of Gd with the s band is always positive. The interaction with the d band was found to be negative.[7] Therefore, for GdX_2 (X=Rh, Ir, Mn) the dominant contribution to the g shift comes from interaction with the d electrons; for GdPt$_2$ the g shift is the result of interaction with s electrons.

The exchange interaction between the Gd ion and the conduction electrons produces polarization of the conduction band. This polarization causes a hyperfine field via the hyperfine interaction $A(\mathbf{I}\cdot\mathbf{s})$ between the nuclear spin $\mathbf{I}$ and the spin $\mathbf{s}$ of the conduction electron.

By a simple calculation shown in the Appendix, we obtain for this hyperfine field[5]

$$H_1^{\mathrm{hf}}=\frac{1}{g_e^2\beta^2N_0}\frac{A}{g_I\mu_I}J\chi^{\mathrm{spin}}\langle S\rangle, \quad (3)$$

where $g_I\mu_I$ is the nuclear magnetic moment, $\langle S\rangle$ is the expectation value of the Gd spin, and A is the hyperfine constant.

We distinguish between two hyperfine fields which result from interaction with the conduction bands. One is due to the conduction electrons which are polarized by the Gd ion of the same nucleus and is given by Eq. (3). The other is caused by the conduction electrons which are polarized by the surrounding gadolinium ions.

The second hyperfine field was calculated by Yosida[8] for a spherical Fermi surface to be

$$H_2^{\mathrm{hf}}=-\frac{9\pi}{2}\frac{z^2A}{g_I\mu_I}\frac{J}{E_F}|\langle S\rangle|\sum_n F_n, \quad (4)$$

where $E_F=\hbar^2k_F^2/2m$ is the Fermi energy for the conduction electrons, and z is the number of conduction electrons per Gd atom.

F_n is given by the formula

$$F_n=\frac{2k_FR_n(\cos 2k_FR_n)-\sin(2k_FR_n)}{(2k_FR_n)^4}, \quad (5)$$

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[3] J. B. Mock, Rev. Sci. Instr. **31**, 551 (1960).

[4] M. Peter, D. Shaltiel, J. H. Wernick, H. J. Williams, J. B. Mock, and R. C. Sherwood, Phys. Rev. **126**, 1395 (1962).

[5] For simplicity, we assumed a single-band model for the conduction electrons. A two-band (i.e., s and d bands) model would not change our qualitative results.

[6] M. Peter, J. Dupraz, and H. Cottet, Helv. Phys. Acta **40**, 301 (1967).

[7] D. Shaltiel, J. H. Wernick, H. J. Williams, and M. Peter, Phys. Rev. **135**, 1346 (1964).

[8] K. Yosida, Phys. Rev. **106**, 893 (1957).

where R_n represents the position of the gadolinium ions. Since k_F is not known, we have calculated $\sum_n F_n$ as a function of k_F, summed over the nine Gd nearest neighbors. The atomic distances were calculated using x-ray data.[9] Assuming the free-electron model and one electron per Gd atom, we found $k_F = 0.82 \times 10^8$ cm^{-1} and the corresponding value of $\sum_n F_n$ to be -0.4×10^{-2}. Hence, the value of H_2^{hf} is 15% of that of H_1^{hf}. Other approximations reveal that H_2^{hf} is always less than 50% of H_1^{hf}. We therefore consider the hyperfine field due to interaction with conduction electrons, $H_{\text{ce}}^{\text{hf}}$, to be the sum of H_1^{hf} and H_2^{hf}.

The GdX_2 compounds are ferromagnetic in the ground state. Thus, the effective exchange interaction between the Gd ions, i.e., the Ruderman-Kittel interaction,[10] is ferromagnetic and negative. Since this interaction is proportional to $\sum_n F_n$, with a positive constant of proportionality, $\sum_n F_n$ must always be negative.

While the sign of the g shift depends only on the sign of the exchange interaction J, the sign of the hyperfine field H_1^{hf} depends on the product of J and A, and the sign of H_2^{hf} depends on the sign of the product $-A \times J \times \sum_n F_n$. Since $\sum_n F_n$ is negative, the sign of both H_1^{hf} and H_2^{hf}, in our case, should be the same.

The contribution of the core polarization to the hyperfine field, $H_{\text{core}}^{\text{hf}}$, is believed to be constant in all the GdX_2 compounds. The value of $H_{\text{core}}^{\text{hf}}$ is equal to the hyperfine field in Gd^{+3} (or in GdN) which is -340 kG.[11] Therefore the hyperfine field resulting from interaction with the conduction electrons, $H_{\text{ce}}^{\text{hf}}$, can be calculated by subtracting the value -340 kG from the total hyperfine field. In Table I, the extrapolated g shift Δg_0 is compared with the hyperfine field $H_{\text{ce}}^{\text{hf}}$ obtained by the method described above.

TABLE I. Comparison between hyperfine fields and the g shifts resulting from interaction with conduction electrons.

Compound	H^{hf} (kG)	$H_{\text{ce}}^{\text{hf}} = H^{\text{hf}} - H_{\text{core}}^{\text{hf}}$ (kG)	Δg_0 [a]
GdAl$_2$	-170	$+170$	-0.018
GdRh$_2$	-100	$+240$	-0.033
GdPt$_2$	-180[b]	$+160$	$+0.032$
GdMn$_2$	-285[b]	$+80$[c] ($+625$[d])	-0.075
GdIr$_2$	···	···	-0.015
Gd^{+3}	-340	0	-0.008[e]
GdN	-370	~ 0	0

[a] Measured with respect to the free-electron g factor.

[b] Sign was not measured but is believed to be negative (by Gegenwarth *et al.*).

[c] Obtained by Gegenwarth *et al.*

[d] This value was obtained by assuming that the sign of H^{hf} is positive.

[e] Measured by R. Lacroix, Helv. Phys. Acta **30**, 374 (1957).

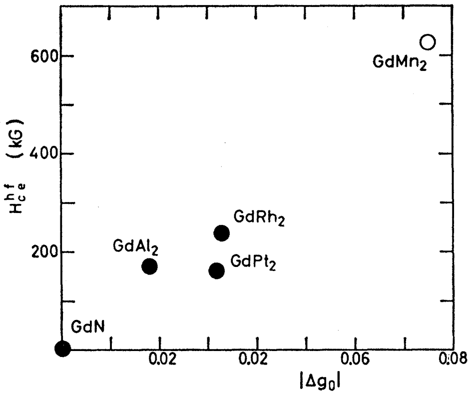

FIG. 2. The hyperfine field resulting from interaction with the conducting electrons, $H_{\text{ce}}^{\text{hf}}$, versus the absolute value of Δg_0 for the various compounds. The hyperfine field $H_{\text{ce}}^{\text{hf}}$ for GdMn$_2$ here has the assumed value of 650 kG.

CONCLUSIONS

Table I shows that the hyperfine field $H_{\text{ce}}^{\text{hf}}$ is always *positive*. This agrees with our expression for $H_{\text{ce}}^{\text{hf}}$, Eqs. (3) and (4), for the following reasons:

(1) The g shift of GdX_2 (X = Rh, Ir, Mn) was found to be *negative* (Table I). Since according to Shaltiel *et al.*,[7] interaction of a Gd ion with an almost full d band is always negative, we expect that the dominant contribution to the g shift and the hyperfine field comes from interaction with the d electrons. Jaccarino *et al.*[12] showed that the hyperfine field per spin, $A/g_I\mu_I$, due to the d electrons is negative. Therefore the product $A \times J$ should be positive leading to a positive H_1^{hf}. Since for ferromagnetic metals $\sum_n F_n$ is always negative, H_2^{hf} should also be positive, making $H_{\text{ce}}^{\text{hf}}$ positive.

(2) Susceptibility measurements of LaPt$_2$ have shown that it is diamagnetic[13] and that its susceptibility does not depend on temperature. This indicates that the d band is filled. Assuming the electronic structure in LaPt$_2$ is similar to that of GdPt$_2$, we conclude that there is only an s-band contribution to the g shift and hyperfine field. Since the hyperfine field per spin, $A/g_I\mu_I$, for interaction with s electrons is always positive, and our result for Δg_0 in GdPt$_2$ is also positive, the product $A \times J$ is therefore positive. This shows that the hyperfine field $H_{\text{ce}}^{\text{hf}}$ in GdPt$_2$ must also be positive, in agreement with the experimental results.

We found the g shift in GdN to be close to zero. This agrees with measurements of resistivity and magnetic properties.[14] These measurements indicate that the conduction bands in GdN are only slightly populated,

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[9] V. B. Compton and B. T. Mathias, Acta Cryst. **12**, 651 (1959); A. E. Dwight, Trans. Am. Soc. Metals 53, 479 (1961).

[10] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), p. 364.

[11] W. Low and D. Shaltiel, J. Phys. Chem. Solids **6**, 315 (1958).

[12] V. Jaccarino, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964,* (Institute of Physics and The Physical Society, London, 1965), p. 377.

[13] H. J. Williams and R. C. Sherwood (unpublished).

[14] R. Didchenko and E. P. Gortsens, J. Phys. Chem. Solids **24**, 867 (1963).

and therefore the contribution to the g shift of $\chi^{\rm spin}$ is negligible. For the same reason we conclude that the contribution of the conduction electrons to the hyperfine field is also negligible. This is in agreement with Eq. (5) and also confirms the assumption of Budnick and his collaborators that core polarization is the only source of the hyperfine field in GdN.

Figure 2 indicates that the hyperfine field $H_{\rm ce}^{\rm hf}$ increases with the increase of the g shift. Table I shows that the g shift Δg_0 of $\mathrm{GdMn_2}$ is large and negative. Therefore, if we adopt the band model, the hyperfine field $H_{\rm ce}^{\rm hf}$ should also be large. From this point of view, we expect the hyperfine field of Gd in $\mathrm{GdMn_2}$ to be 650 kG rather than 80 kG as assumed by Gegenwarth *et al.* However, susceptibility measurements[15] indicate the possibility of an antiferromagnetic ordering between the Gd and the Mn localized moments. In analogy with previous arguments, assuming that the Gd and Mn moments are subject to the Ruderman-Kittel interaction, one can show that the Mn produces a negative hyperfine field on the Gd nuclei, thereby reducing the total hyperfine field $H_{\rm ce}^{\rm hf}$. This will be in agreement with the small value of 80 kG assumed by Gegenwarth for $H_{\rm ce}^{\rm hf}$ in $\mathrm{GdMn_2}$.

It will be very interesting to determine the sign of the total hyperfine field of Gd in $\mathrm{GdMn_2}$. This compound is being further investigated.

As shown above, both $H_1^{\rm hf}$ and Δg_0 result from exchange interaction between the Gd ion and the conduction electrons. By substitution of Eq. (3) in Eq. (4), we obtain the relation between the g shift and $H_1^{\rm hf}$:

$$H_1^{\rm hf}=\left(\frac{\Delta g_0}{g}\right)\left(\frac{A}{g_I\mu_I}\right)\langle S\rangle\left(\frac{\chi_1^{\rm spin}}{\chi_2^{\rm spin}}\right), \qquad (6)$$

where $\chi_1^{\rm spin}$ and $\chi_2^{\rm spin}$ are the susceptibilities of the conduction bands at the temperatures at which the hyperfine field and the g shift were measured, respectively.

Equation (6) also represents the relation between the hyperfine field $H_{\rm ce}^{\rm hf}$ and the g shift, Δg_0, if and only if $H_1^{\rm hf}\gg H_2^{\rm hf}$ (as the numerical calculation above has shown).

Assuming that this condition holds, one can find the hyperfine field per spin, $A/g_I\mu_I$, for the various compounds. For example, we have shown that for $\mathrm{GdPt_2}$ the hyperfine field $H_{\rm ce}^{\rm hf}$ results from interaction with the s band. For such a band $\chi_1^{\rm spin}=\chi_2^{\rm spin}$, since the spin susceptibility does not change with temperature. Using $H_{\rm ce}^{\rm hf}=+160$ kG, $\Delta g_0=+0.032$ and $\langle S\rangle=\frac{7}{2}$, we obtain from Eq. (6) $A/g_I\mu_I=2.8\times10^6$ G. This value agrees closely with the estimate of Gossard *et al.*[16] for the 6*s* electrons contribution in rare-earth compounds.

Shaltiel *et al.*[17] have investigated the magnetic properties of intermetallic compounds using EPR and NMR techniques. They were able to relate the EPR and NMR results, and thereby obtain information on the magnetic properties of the system which could not have been obtained by means of just one of these techniques. We therefore see that investigating the same compounds using both techniques yields additional information on the origin of magnetic interactions.

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APPENDIX

The exchange interaction between the Gd ion and the conduction electrons $J(\mathbf{S}\cdot\mathbf{s})$ produces an exchange field $H^{\rm ex}$ on the s electrons, which is given by $H^{\rm ex}=J\langle S\rangle/g_e\beta$. This exchange field polarizes the conduction band. The polarization M can be written

$$M=\chi^{\rm spin}H^{\rm ex}=\frac{J\langle S\rangle}{g_e\beta}\chi^{\rm spin}.$$

On the other hand, this polarization is equal to $g_e\beta N_e\langle s\rangle$, and therefore $\langle s\rangle$, the expectation value of the electron spin, is found to be

$$\langle s\rangle=\chi^{\rm spin}\frac{J}{g_e^2\beta^2N_e}\langle S\rangle,$$

where N_e represents the number of conduction electrons per mole.

The polarization of the conduction electroms, M, causes a hyperfine field on the nuclear spin $\mathbf{I}$ via the hyperfine interaction $A(\mathbf{I}\cdot\mathbf{s})$. This hyperfine field is obtained from the equation $\sum_i A(\mathbf{I}\cdot\mathbf{s}_i)=g_I\mu_I(\mathbf{I}\cdot\mathbf{H}_1^{\rm hf})$ to be $H_1^{\rm hf}=(A/g_I\mu_I)z\langle s\rangle$, where z is the number of conduction electrons interacting with each spin $\mathbf{I}$. Substituting the value of $\langle s\rangle$ found above in the formula for $H_1^{\rm hf}$ we get

$$H_1^{\rm hf}=\frac{A}{g_I\mu_I}\frac{1}{g_e^2\beta^2N_0}J\chi^{\rm spin}\langle S\rangle,$$

where N_0 $(N_0=N_e/z)$ is the number of lattice sites per mole.

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