

GADOLINIUM HYPERFINE FIELDS

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The Gd hyperfine field, in the magnetically ordered state of several GdX_2 cubic Laves-phase compounds, shows a large variation in magnitude and sign. A comparison of our results with those on other rare-earth systems supports the supposition of a constant $4f$ core-polarization field in the rare earths.

We have measured the gadolinium hyperfine field in the magnetically ordered state at 4.2°K for several GdX_2 ($X = Al, Rh, Pt, Fe, Mn$) intermetallic Laves-phase compounds by nuclear-magnetic-resonance spin-echo techniques. Our results show a large variation in the magnitude of the Gd hyperfine field throughout this series. This is in sharp contrast to the essentially constant value of the Gd hyperfine field previously reported for Gd nuclei in a variety of environments, namely, Gd metal,^{1,2} GdN,³ and Gd^{3+} ions.^{4,5,6} As a result of the earlier investigation, which yielded a field of approximately -340 kOe (the negative sign implying that H_{eff} is directed opposite to the local magnetization), it was believed that the major contribution to the Gd hyperfine field comes from core polarization by the unfilled $4f$ shell. Our results point out the importance of other contributions to the hyperfine field which we will call "valence" polarization.

Our experimental results on the Gd hyperfine fields in the cubic Laves-phase intermetallic compounds and in GdN are summarized in Table I. All of these data were obtained on magnetically ordered samples at 4.2°K in zero applied magnetic field. In these systems, where

the Gd sites have cubic symmetry, the spin-echo spectra showed two maxima of approximately equal amplitude which occur at frequencies in the ratio of the ^{155}Gd and ^{157}Gd nuclear magnetic moments. We note that the magnitude of the Gd hyperfine fields in these samples varies from 103 kOe in $GdRh_2$ to 453 kOe in $GdFe_2$. Furthermore, the sign of the field at Gd in $GdFe_2$, as determined by the frequency shift produced by a static applied magnetic field, is positive with respect to the local magnetization direction. In the light of previous data giving negative fields for Gd^{3+} , this positive field establishes the presence of a large positive contribution in $GdFe_2$ which is presumably due to a significant polarization of the valence electrons. Such a large positive contribution needed to explain our results in $GdFe_2$ has also been found necessary to explain Mössbauer-effect data in other RFe_2 ($R = Tb, Dy, Er, Tm$) compounds. In contrast with this latter series of rare-earth compounds, Gd is expected to have a negligible orbital contribution to the hyperfine field.

In the absence of any orbital contribution to the hyperfine field at a Gd nucleus, the effective field can be written as the sum of two terms:

$$H_{eff} = H_{core} + H_{val},$$

where H_{core} is the contribution due to polarization of the core electrons by the unfilled $4f$ shell and H_{val} is the contribution due to the valence electrons. In writing H_{eff} this way we are assuming that the various mechanisms responsible for valence-electron polarization can be collected into a single term and merely superimposed on a constant core-electron contribution. On the basis of the reported field at the Gd nuclei in Gd metal, GdN, and the Gd^{3+} ion, we put $H_{core} = -340$ kOe. Since $H_{eff} = +453$

Table I. Gadolinium hyperfine fields.

Compound	H_{eff} at 4.2°K (kOe) ^a
$GdAl_2$	-170
$GdRh_2$	-103
$GdPt_2$	180 ^b
$GdFe_2$	+453
$GdMn_2$	285 ± 30^b
GdN	370 ^b

^a $a\mu(^{157}Gd) = 0.32\mu_N$.

^bThe signs of these fields are uncertain but are believed to be negative.

kOe in GdFe_2 , H_{val} must be of the order of 800 kOe in that compound. It is significant that the hyperfine fields at Tb, Dy, Tm, and Er, in TbFe_2 ,⁷ DyFe_2 ,⁸ TmFe_2 ,⁹ and ErFe_2 ,¹⁰ respectively, are also about 800 kOe higher than in the corresponding pure metals Tb,⁷ Dy,⁸ Tm,¹¹ and Er.¹² Since the fields in these metals are already large and positive because of the orbital contribution, there is no change in the sign of the hyperfine field in going from the pure metals to the $R\text{Fe}_2$ systems as occurs in going from Gd metal to GdFe_2 . It is interesting to note that the numerical difference between the metal and $R\text{Fe}_2$ hyperfine fields for these systems is essentially independent of the large variation of the orbital contribution to the hyperfine field. This suggests that the polarization mechanism responsible for this difference is confined to the valence ($5d$, $6s$) electrons of these rare earths, and that the outer electrons are weakly coupled to the $4f$ electrons. It is probable that the mechanism responsible for this difference in hyperfine fields is the same as that responsible for the high Curie temperatures of all of these $R\text{Fe}_2$ compounds as compared with the metals, and could be caused by overlap of d -character electron wave functions localized about the rare earth and iron sites, respectively. The importance of the d character of the valence electrons in Gd metal has already been demonstrated in the recent band-structure calculation of Dimmock and Freeman,¹³ and we would expect the d character of the conduction band to be especially important in the $R\text{Fe}_2$ systems.

In Fig. 1 we compare the hyperfine field at Dy nuclei as determined by Mössbauer experiments¹⁴ with our Gd nmr results in the rare-earth Laves-phase systems as a function of R - R nearest neighbor (n.n.) distance (normalized to the Gd-Gd n.n. distance in GdAl_2). The similarity in the variation of the rare-earth hyperfine fields in these two series of Laves-phase compounds suggests that (1) the $4f$ orbital contribution (which is the dominant contribution in the Dy compounds and is negligible in the Gd compounds) is essentially unchanged throughout each series and is largely determined by the crystal symmetry, and therefore (2) the $4f$ core-polarization field H_{core} is also constant throughout each series. This similar variation of the Gd and Dy fields in the presence of the large difference in the absolute magnitude of their respective hyperfine fields

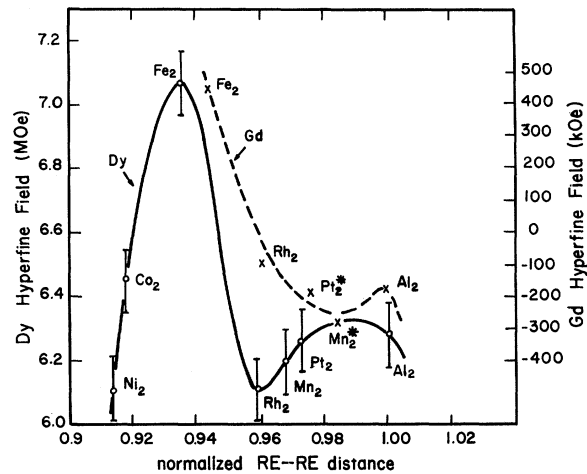


FIG. 1. Dy and Gd hyperfine fields as a function of the rare-earth separation, normalized to that in GdAl_2 . The asterisks indicate that the signs of the GdPt_2 and GdMn_2 fields are uncertain but are believed to be negative.

(6.2 MOe in Dy compounds and 0.34 MOe in the Gd compounds) strongly supports the constancy of the $4f$ core-polarization field in the rare earths and emphasizes the importance of "valence" electron polarization.

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