

^{31}P NMR studies of transferred hyperfine effects in rare-earth orthophosphates

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Systematic ^{31}P NMR studies at 300 K of the 13 rare-earth phosphates ($R\text{PO}_4$) in the polycrystalline form have revealed the presence of transferred hyperfine effects. Two types of line shapes are broadly encountered: more or less symmetric lines from La to Eu, and asymmetric lines from Gd to Yb, determined by the relative magnitude of the anisotropic interaction and the intrinsic linewidth. The linewidths are in accord with the R^{3+} magnetic moments except for Gd^{3+} , the S -state ion. The powder pattern yields the hyperfine-interaction parameters, viz., the isotropic shift K_{iso} for all the members and the anisotropic shift K_{aniso} for Gd to Yb only. K_{iso} for the first half of the members is an order of magnitude smaller than for the second half of the members and is primarily "contact" in origin, whereas K_{aniso} is determined by the dipolar contribution. Moreover, K_{iso} changes sign at Eu^{3+} and not at Gd^{3+} in consonance with the $\langle S_z \rangle$ values calculated by Golding and Halton, and so their model appears to be applicable to the second-nearest neighbor. The transferred hyperfine effects do seem to indicate a small degree of covalent interaction in these predominantly ionic compounds (f_s varying from 0.001% to 0.015%), but the shift does not appear to support f -electron participation in the covalent bond. Finally, it has been shown that the sign of the shift of the second-nearest neighbor (^{31}P in $R\text{PO}_4$) is opposite to that of the first neighbor and as such differs from those in $3d$ systems.

I. INTRODUCTION

The $R\text{XO}_4$ compounds, where R is a rare-earth ion and X is P, V, or As, have attracted great interest¹⁻³ in recent years. The crystal structure changes⁴ from the monoclinic monazite to the tetragonal zircon as one moves across the series, and the exact point of transition depends on the ratio of the cation-anion radii.⁵ Thus for the phosphates it occurs at Tb, for the vanadates at La, and for the arsenates at Sm. Interestingly, both TbPO_4 (Ref. 4) and LaVO_4 (Ref. 5) have been found to be dimorphic, but SmAsO_4 has, until now, been prepared in the zircon form only. A survey of the literature reveals that the zircons⁶ have been extensively investigated, particularly at low temperatures, in which region they display a variety of phase transitions including magnetic ordering. The zircons, which have attracted particular interest because of their cooperative Jahn-Teller (JT) behavior,³ are the vanadates and arsenates of Tb, Dy, and Tm. Of the phosphates only TbPO_4 seems to exhibit⁷ the cooperative JT effect but a high-temperature phase transition has been observed in GdPO_4 , TbPO_4 , and DyPO_4 from magnetic susceptibility¹ and NMR studies.⁸ This possibly arises from a second-order displacive phase transition due to a soft mode, as has been observed⁹ in $\text{LaP}_5\text{O}_{14}$ and $\text{NdP}_5\text{O}_{14}$.

The basic interest, in this paper, arises from the fact that the rare-earth series provide systems wherein the effect of filling up of the internal $4f$ shell on the chemical, structural, electronic,

and magnetic properties may be observed. Though chemically the rare earths are very similar, the understanding of the bonding situation is of much interest. Even as late as the early sixties, Moeller¹⁰ considered the bonds in rare earths to be purely ionic, but evidence of covalent interaction was forthcoming. Thus volatile rare-earth covalent compounds¹¹ were prepared. Presently, covalency in rare earths is an accepted fact, but the nature of covalent interaction, particularly the question as to whether f orbitals participate¹²⁻¹⁵ in bonding or not, is a highly debatable point.

The $R\text{XO}_4$ compounds are predominantly ionic but possibly with a small admixture of covalency. Ordinary chemical and magnetic methods would not detect such a small covalent admixture and would register it as a purely ionic compound. Nuclear magnetic resonance (NMR), however, provides a very elegant microscopic method of detecting¹⁶ precisely this small covalent admixture even if it be of the order of 0.001%. These effects would influence the NMR shift and relaxation times, and would show up in the line-shape and linewidth studies. Further, the extent of the covalent interaction is expected to change at the structural transition across the series. Interest thus shifts to the effect of this transition on transferred hyperfine parameters. This work is the first systematic NMR study of the whole set of 13 rare-earth phosphates wherein ^{31}P , a spin- $\frac{1}{2}$ nucleus, enabled one to study the magnetic hyperfine interaction without the complications inherent in magnetic-*cum*-quadrupolar hyperfine-interaction effects in vanadates and arsenates.

II. TRANSFERRED HYPERFINE EFFECTS

In a paramagnetic complex, the transferred hyperfine interaction of a ligand nucleus, takes the form¹⁷⁻²⁰

$$\mathcal{H} = -\gamma\hbar I_z H_0 + N' I_z [A'_s + A'_p(3 \cos^2\theta - 1)] \langle S_z \rangle, \quad (1)$$

where θ is the angle between the magnetic field and the symmetry axis of the crystal, A'_s and A'_p are the isotropic and anisotropic parts of the hyperfine coupling tensor, and N' represents the number of nearest magnetic neighbors. The fractional resonance shift k is given by

$$k = k_{\text{iso}} + k_{\text{aniso}}(3 \cos^2\theta - 1), \quad (2)$$

where k_{iso} and k_{aniso} are isotropic and anisotropic shift, respectively. Further, all the paramagnetic centers within the crystal contribute to the local field²¹ H_{loc} which is composed of Lorentz, demagnetization, and dipole fields. The first two act in opposition and the shifts from these factors may cancel out as has been found in rare-earth phosphides.²² The isotropic part of the dipole field is negligible,^{23,24} but the anisotropic contribution is significant²⁵⁻²⁷ in many cases. As such, H_{tot} may be simply written²⁸

$$\vec{H}_{\text{tot}} = \vec{H}_0 + \vec{H}^{\text{hf}} + \vec{H}^d. \quad (3)$$

Further, H^d may be written

$$\vec{H}^d = \alpha(3 \cos^2\theta - 1)\chi_M \vec{H}_0, \quad (4)$$

where α is a constant characteristic of the crystal lattice and χ_M represents the magnetic susceptibility. The anisotropic portion of the hyperfine field is also given by

$$\vec{H}_{\text{aniso}}^{\text{hf}} = A_p(3 \cos^2\theta - 1)\langle S_z \rangle \vec{H}_0. \quad (5)$$

Thus the same functional relationship holds for $H_{\text{aniso}}^{\text{hf}}$ and H^d . Assuming hyperfine and dipolar tensors to be coincident the resonance position in a single crystal is given by

$$\nu = \nu_R [1 + K_{\text{iso}} + K_{\text{aniso}}(3 \cos^2\theta - 1)], \quad (6)$$

where K_{iso} and K_{aniso} contain both the hyperfine and dipolar contributions.

In a polycrystalline specimen, the range of the resonance frequency extends from the minimum to the maximum value of $\nu(\cos\theta)$ of Eq. (6). Thus the intensity maximum occurs at $\theta = 90^\circ$ and the frequency at this point is

$$\nu_1 = \nu_0(1 - a), \quad (7)$$

where $a = K_{\text{aniso}}/(1 + K_{\text{iso}})$ and $\nu_0 = \nu_R(1 + K_{\text{iso}})$. Besides this maximum, there appears a discontinuous step corresponding to $\theta = 0^\circ$ or 180° , and the frequency is

$$\nu_2 = \nu_0(1 + 2a). \quad (8)$$

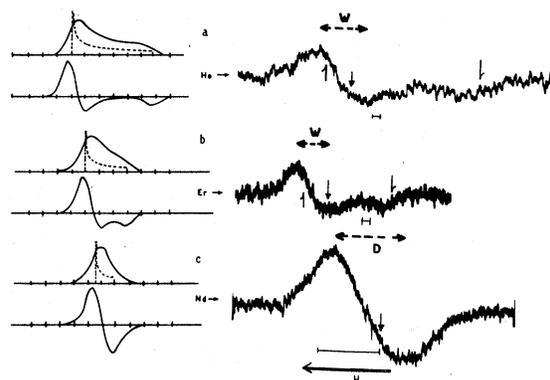


FIG. 1. Powder pattern in presence of anisotropic hyperfine interaction (K_{aniso}). Left—Sobel's calculated absorption lines and their derivatives³⁰ (the dotted line represents the frequency distribution in absence of intrinsic broadening 2β). Right—experimental ³¹P derivative spectra in some rare-earth phosphates. (a) $K_{\text{aniso}} \gg 2\beta$, (b) $K_{\text{aniso}} > 2\beta$, and (c) $K_{\text{aniso}} < 2\beta$. ν_1 and ν_2 positions have been indicated in the spectra by half arrows, together with the standard reference (\dagger). All calibrations (error bars) are equal to 10 kHz. The direction of the scanning magnetic field H has been indicated by the arrow.

Neglecting the effect of line broadening, the spacing between ν_1 and ν_2 could be treated as a measure of the anisotropic shift²⁹ so that

$$|\nu_1 - \nu_2| = 3K_{\text{aniso}}\nu_R. \quad (9)$$

Sobel³⁰ has demonstrated from a numerical calculation that asymmetry in the powder pattern will be prominently exhibited (Fig. 1) only when the strength of this anisotropic interaction is greater than the intrinsic linewidth 2β .

III. EXPERIMENTAL

Rare-earth phosphates constitute a set melting at high temperatures. Attempts at producing good single crystals large enough for NMR work were not very successful.^{1,31} As such, the work reported here is on polycrystalline specimens. The usefulness of investigating powders in the absence of good single crystals has been discussed elsewhere.³² The hydrated phosphates were prepared from a solution following the method of Buyers *et al.*³³ To obtain the anhydrous form, the precipitate was slowly heated to 1000 °C and kept at this temperature for 6 h. The fired samples showed no proton resonance, indicating that the anhydrous form had been obtained. The phosphates³⁴ from La to Tb were obtained in the monazite form and from Dy to Yb in zircon form. Monoclinic rare-earth phosphates found in nature as mineral monazite have a tetramolecular unit cell. The space group is $C_{2h}^5 (P_{21}/n)$ with all atoms in the general posi-

tion. The tetragonal zircon form contains four molecules in the unit cell. The space group is D_{4h}^{19} ($I4/amd$).

NMR measurements were performed using a Varian 2-16-MHz variable-frequency induction spectrometer and a 12-in. electromagnet. Preliminary temperature-variation studies revealed a very poor signal-to-noise ratio, resulting in large errors, particularly for the second half of the members, due to reduction of sample volume. As such, systematic temperature-variation studies of the set were not performed. Shifts were measured with respect to the reference ^{31}P NMR signal in orthophosphoric acid.

Initially the ^{31}P NMR lines were measured with polycrystalline materials contained in spherical bulbs. The first half of the members (La-Eu) presented no difficulty. The signal-to-noise ratio, however, fell abruptly for the second half of the members (Gd-Tm), which exhibited wider lines, particularly at higher-field values. Shifts could not be measured in powders from these poor lines. To overcome this difficulty, cylindrical pressed pellets made of KBr in die were used in place of powder. This enabled the signal-to-noise ratio to increase three to four times the previous value. The traces in powdered and pellet form recorded under identical conditions produced almost the same line shape.

IV. RESULTS

^{31}P NMR in all the 13 rare-earth phosphates exhibits hyperfine-interaction effects, except in the case of La, which is diamagnetic. The shift and linewidth data in the present work are more or less in agreement with the fragmentary NMR data on the RPO_4 system studied by Saji *et al.*² Sobel's³⁰ calculated line shapes together with some of the recorded spectra of RPO_4 are presented in Fig. 1. Following the method of Borsa and Barnes,²⁹ ν_1 and ν_2 of Eqs. (7) and (8) have been located on the derivative spectra only for the highly asymmetric lines. Though only three basic line shapes have been presented in Fig. 1, other intermediate varieties have actually been observed (Fig. 2). The spectra for RPO_4 in the range 4-16 MHz, for all the first half of the members, showed a more or less symmetric line indicating that $K_{\text{aniso}} < 2\beta$, while the line shapes for the second half of the members (Gd-Tm) were found to be highly asymmetric, exhibiting structure in the limit $K_{\text{aniso}} \gg 2\beta$. For YbPO_4 , however, the anisotropic interaction is considerably less, as revealed by the line shape. As the field changes, the spacing between ν_1 and ν_2 varies linearly with the field (Fig. 3). This has been reflected in Fig. 4, where the frequency in-

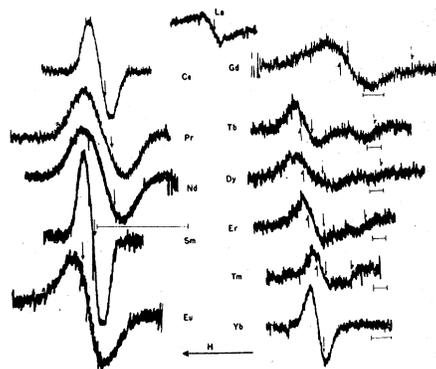


FIG. 2. ^{31}P derivative spectra of the RPO_4 system at 4 MHz (300 K). Symbols same as in Fig. 1.

dependence of the fractional shifts (%) of ν_1 and ν_2 for the second half of the members (Gd-Yb) has been shown. This fact is consistent with the relationship expressed in Eq. (9). Though in the treatment presented here only the effects of hyperfine and dipolar contributions have been taken into account, asymmetry in general may arise from various other factors,^{19,23,24,35-37} e.g., inequivalent lattice sites, g anisotropy, etc. Preliminary temperature-variation studies of our samples showed that the shape of the line remains the same, with only the separation between the humps changing, unlike the observation of Blinc *et al.*³⁷ in the case of ^{19}F NMR. This phenomenon excludes the possibility of the inequivalence of lattice sites being the origin of the asymmetry. Gd, with an isotropic g , has consistently given an asymmetric line³⁸ indicating that g anisotropy is not of primordial importance in determining the asymmetry of the line. Using Eqs. (7)-(9), ν_0 , hence K_{iso} and K_{aniso} , have been estimated (Table I). It is to be noted that the anisotropic shift could not be estimated for the first half of the members with symmetric lines. The situation for the first half of the members is similar to that expressed in Fig. 1(c). Interest-

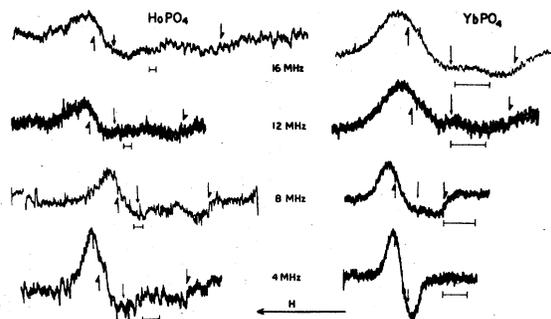


FIG. 3. ^{31}P derivative spectra of HoPO_4 and YbPO_4 at various frequencies (300 K). Symbols same as in Fig. 1.

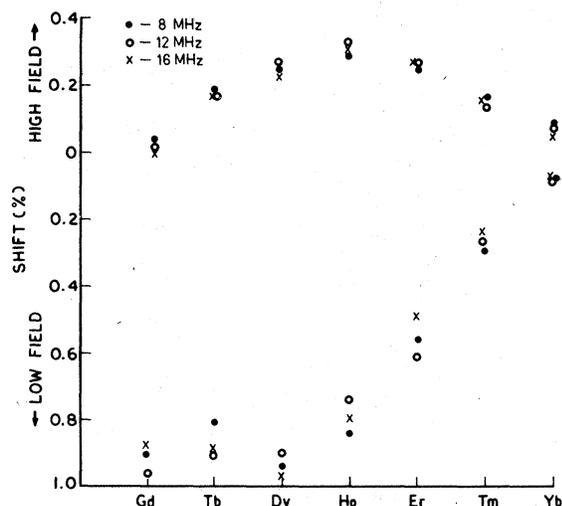


FIG. 4. Fractional shifts of ν_1 (upper points) and ν_2 (lower points) of ^{31}P for the second half of the phosphates (Gd–Yb) at various resonance frequencies.

ingly, the isotropic shift is an order of magnitude smaller for the first half of the members (f^n , $n < 7$) as compared to that of the second half of the members (f^n , $n \geq 7$).

A comparative study of the linewidths in the powdered form across the phosphate series is confronted with difficulties in the definition of the linewidth. For the symmetric lines, the distance D [Fig. 1(c)] is taken as the linewidth. This straightforward definition does not apply to the asymmetric case. Nevertheless, the distance W , as shown in Figs. 1(a) and 1(b), has been considered as a measure of linewidth for comparison purposes. Thus W is a complicated function of the intrinsic

TABLE I. ^{31}P shifts in rare-earth phosphates.^a Sign convention of the shifts: Positive shift indicates shift towards low field, negative shift indicates shift towards high field.

R^{3+}	Structure	K_{iso} (%)	K_{aniso} (%)
Ce	Monoclinic	-0.01 ± 0.003	
Pr		-0.02 ± 0.005	
Nd		-0.03 ± 0.005	
Sm		-0.005 ± 0.003	
Eu		$+0.03 \pm 0.005$	
Gd		$+0.30 \pm 0.01$	0.32 ± 0.02
Tb		$+0.27 \pm 0.01$	0.37 ± 0.02
Dy	Tetragonal	$+0.10 \pm 0.01$	0.40 ± 0.02
Ho		$+0.09 \pm 0.005$	0.33 ± 0.02
Er		$+0.05 \pm 0.005$	0.28 ± 0.02
Tm		$+0.05 \pm 0.005$	0.17 ± 0.02
Yb		-0.01 ± 0.003	0.06 ± 0.005

^a LaPO_4 exhibits zero shift with respect to the reference orthophosphoric acid.

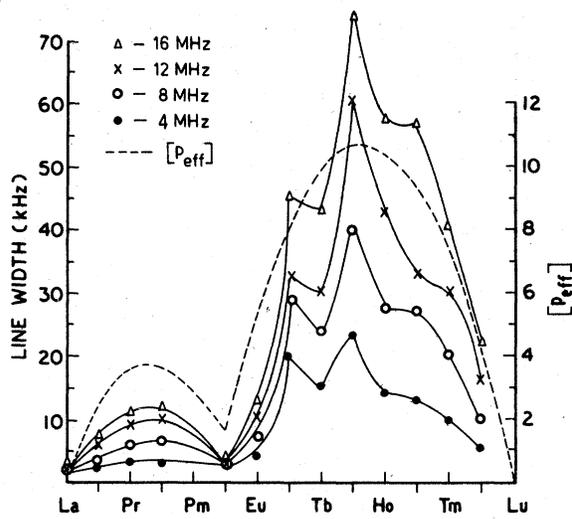


FIG. 5. ^{31}P linewidths as a function of resonance frequency across the rare-earth series. The dotted curve represents the effective magnetic moment P_{eff} .

width 2β and K_{aniso} . Figure 5 shows the dependence of the linewidth on the number of f electrons at various frequencies, and reveals a parallelism between it and the value of the magnetic moment of the rare earth, similar to the case of ^{19}F NMR in rare-earth fluorides.³⁹ It is interesting to find that this parallelism holds despite the structural transition at terbium in the phosphate series. This indicates that the anisotropic shift due to dipolar interaction is the dominant term in determining the linewidth in powders, according to the relationship obtained from Eqs. (3), (4), and (6)

$$K_{\text{aniso}} \propto \alpha \chi_M \propto \alpha \bar{\mu}, \quad (10)$$

where $\bar{\mu} = \mu_0^2 H_0 / 3k_B T$ is the average static component of the magnetic moment μ_0 . Further, since $\bar{\mu}$ is proportional to the applied magnetic field, the approximate linear dependence of the linewidth on the resonance frequency is quite understandable. There is, however, a consistent discrepancy in the linewidth of GdPO_4 , which is always greater than that of TbPO_4 , whereas μ_0 of Gd^{3+} is less than that of Tb^{3+} . The linewidth in a paramagnetic specimen is characterized by a correlation time τ_c . This τ_c is longest in Gd^{3+} , an S-state ion. Accordingly, in rare-earth phosphides, Myers and Narath⁴⁰ found the T_1 values of ^{31}P to be $6 \mu\text{sec}$ for the Gd compound compared to $77 \mu\text{sec}$ for the Tb compound. Coming to TbPO_4 , the ^{31}P linewidth is expected to increase marginally because of the larger value of the magnetic moment of Tb^{3+} . However, the increase in the intrinsic width of the ^{31}P line in GdPO_4 as expected from the S character, may more than overcompensate the en-

hancement due to the anisotropic broadening in TbPO_4 . Hence the width $W(\beta, K_{\text{aniso}})$ of GdPO_4 becomes greater than that of TbPO_4 as observed experimentally.

V. DISCUSSION

A. Isotopic shift

The isotopic shift consists of the Fermi contact and the dipolar terms (pseudocontact). The contact shift⁴¹ in rare-earth compounds reverses its sign only once across the series, unlike the dipolar shift which alternates its sign in a manner predicted by Bleaney.⁴² The sign reversal in rare-earth solids across the series was first reported by Jaccarino *et al.*⁴¹ for ^{27}Al NMR in rare-earth aluminides at Gd (Eu^{3+} was not studied). Jaccarino *et al.* related the observed nature of the shifts to the fact that $J = L - S$ in the first half of the series and $J = L + S$ in the second half. Thus the hyperfine interaction (contact part) involves the spin S rather than the total angular momentum J and the interaction takes the form $A\vec{I} \cdot \vec{S}$. Further, the magnitude of S is proportional to the magnitude of J except for Sm^{3+} and Eu^{3+} compounds.²² Accordingly, the sign reversal is expected to occur at the half-filled-shell ion, i.e., at Gd^{3+} but in many systems^{43,44} the change in the sign of the shift occurs at Eu. In the case of Eu, the low-lying excited states contribute appreciably to the average magnetic moment. As a result, the simple formulation $J = L - S$ fails to explain the observed facts. In the RPO_4 system studied here, the sign reversal does occur (Table I) at Eu, indicating that the shifts are predominantly contact in origin.

Golding and Halton⁴⁵ have shown that the NMR shifts in rare-earth complexes of nuclei like ^{14}N and ^{17}O which occur in ions having a lone pair of electrons and directly bonded to the rare-earth ion, are predominantly contact in origin. Thus

$$\Delta H = H_0 K_{\text{iso}} = A_s \langle S_z \rangle / g_N \beta_N, \quad (11)$$

where g_N, β_N are the nuclear gyromagnetic ratio and the nuclear magneton, respectively, $\langle S_z \rangle$ is the average z component of the rare-earth spin, and A_s is the coupling constant. The calculated $\langle S_z \rangle$ values of Golding and Halton explain the sign reversal of the ^{17}O shifts at Eu, as $\langle S_z \rangle$ itself changes sign at Eu^{3+} .

The plots (Fig. 6) of the experimental ^{31}P shifts of RPO_4 versus the calculated values⁴⁵ of $\langle S_z \rangle$ are basically linear, according to Eq. (11). Linear plots indicate that the contact interaction is the dominant one in spite of P not being directly bonded to the R^{3+} ion. The shifts fit into two separate straight lines corresponding to two different types of crystal structure of the RPO_4 (monoclinic form

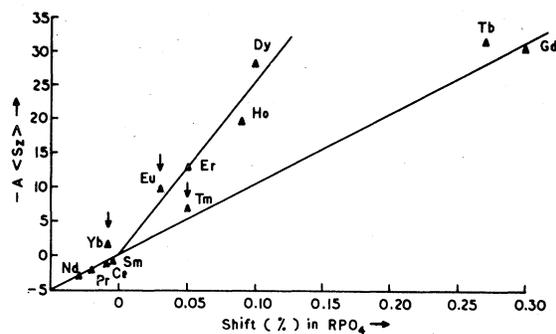


FIG. 6. Plot of Golding and Halton's calculated $-A \langle S_z \rangle$ values ($A = 3 k_B T / \mu_B H$) of rare-earth ions⁴⁵ against experimental ^{31}P shifts in RPO_4 system.

for La-Tb and tetragonal form for Dy-Yb). The strength of the hyperfine interaction is thus different in the two forms, being stronger in the monoclinic form ($A_s/g_N \beta_N \sim 1.3$ and 0.54 kOe for the monoclinic and tetragonal forms, respectively). This fact may be correlated with shorter P-O distances in the monazites ($R_{\text{P-O}} = 1.57-1.54 \text{ \AA}$ for La-Nd) compared with those obtained in the zircon form ($R_{\text{P-O}} = 1.69-1.67$ for Tb-Yb). The slow variation of the distances reflects the contraction in the lanthanides, which, however, could not be discerned in the shift data for the two crystal forms. However, the proportionality of the shifts to $\langle S_z \rangle$ is not very satisfactory for some members, the major departure being the case of YbPO_4 which exhibited a small negative shift (Table I) instead of the expected positive shift. This may be due to residual interactions, viz., dipolar (pseudocontact) and local-field interactions. The departure from a linear plot in a few cases, as indicated by arrows in Fig. 6, may also be attributed to these interactions. Shifts in Sm^{3+} in the present case and in other systems^{22,46-48} have been found to be almost negligible. White and Van Vleck⁴⁹ showed that S in the case of Sm^{3+} results from the superposition of a temperature-dependent and a temperature-independent component, which cancel each other at room temperature, resulting in a negligible shift. The ^{31}P chemical shifts in the RPO_4 series are expected to be the same for all the members. Vanishingly small shifts in diamagnetic La and paramagnetic Sm compounds indicate that this contribution is almost negligible.

The shifts presented so far are the experimentally observed shifts. An attempt has been made to get an idea of the local-field contribution to these shifts. Neglecting the pseudocontact part, the experimental fractional shift may be expressed as

$$\Delta H/H = A_1 \langle S_z \rangle + B_1 \chi_M, \quad (12)$$

where B_1 represents the sum of the numerical factors for the Lorentz, demagnetization, and dipole contribution, and the A_1 term represents the contact contribution. The observed shifts for two rare earths with an expected small dipolar contribution have been chosen to fit Eq. (12). This minimizes the error arising from the neglect of the pseudocontact term in the estimated A_1 and B_1 values. The constant B_1 , which depends on the lattice parameter as well as on the shape of the particles and of the container, is found to be of negative sign for both the zircon and the monazite forms and $B_1\chi_M$ is an order of magnitude smaller than $A_1\langle S_z \rangle$. This local-field contribution if taken into account, however, leads to an improvement, viz., the small anomalous negative ³¹P shift in YbPO₄ changes sign and becomes positive (0.004%), in line with the other members of the second half of the series.

The contact shift is related to the hyperfine field²² H^{hf} by

$$H^{hf} = K_{iso} \frac{Ng_J\beta}{(g_J - 1)\chi_M(T)}, \quad (13)$$

where g_J in the Landé g factor for the rare-earth ion in question, $H^{hf} = A_s/\gamma\hbar$ is the hyperfine field per unit spin, γ is the nuclear gyromagnetic ratio, and N is Avogadro's number. In the absence of $K_{iso}(T)$ data at various temperatures, Eq. (13) has been utilized to estimate H^{hf} from K_{iso} and χ_M at a particular temperature. The susceptibilities of these compounds have been found to be very close^{2,22} to the ionic values which have been used in the calculation of the hyperfine fields (Table II), since χ_M data for the whole set of RPO_4 's are not available. However, Eq. (13) is not valid for Sm and Eu compounds since $\langle S \rangle \neq (g_J - 1)\langle J \rangle$ at room temperature. These values agree in order of magnitude with those calculated from Fig. 6. However, it is to be noted that the values obtained from the formulation of Golding and Halton are the average values for the monazite and the zircon series, whereas Table II presents minor individual variations in the H^{hf} values.

The total hyperfine field⁵⁰ in the case of magnetic saturation is given by

$$H'^{hf} = H^{hf}(g_J - 1)J. \quad (14)$$

H'^{hf} in the case of RPO_4 is shown in Fig. 7. Though Eq. (14) qualitatively explains the dependence of H'^{hf} on the rare-earth ion, it cannot explain its detailed behavior.

However, to obtain an idea of the covalent admixture, the fractional unpairing f_s of phosphorous 3s electrons may be calculated using the relation⁵¹

$$f_s = (2S/N')(A_s/A_{3s}). \quad (15)$$

The fractional unpairing of the 3s orbital at the

TABLE II. ³¹P hyperfine field (H^{hf}), the hyperfine constant (A_s), and the fractional unpairing (f_s) in rare-earth phosphates. $A_{3s}(\text{P}) = 0.564 \text{ cm}^{-1}$ (Mays, Ref. 52). f_s was calculated using Eq. (15) with $N' = 6$.

	H^{hf} (KOe)	A_s (10^{-5} cm^{-1})	f_s (%)
Ce	1.29	7.41	0.00219
Pr	0.84	4.82	0.00285
Nd	0.82	4.60	0.00153
Sm
Eu
Gd	1.26	7.23	0.0149
Tb	1.26	7.23	0.0128
Dy	0.47	2.75	0.0040
Ho	0.55	3.17	0.0037
Er	0.44	2.56	0.0022
Tm	0.86	4.95	0.0029
Yb	-0.53 ^a	-3.05 ^a	...

^aThe negative sign for Yb is discussed in the text.

phosphorous site is presented in Table II. It is seen that the magnitude of f_s is rather small, corroborating the predominantly ionic nature of the rare-earth-phosphate bond. Interestingly, this is at least an order of magnitude smaller than the bond in LiMnPO₄.⁵²

B. Anisotropic shift

In most of the paramagnetic complexes, it has been found^{25,53} that $K_{aniso}^{hf} < K_{iso}^{hf}$. In some cases, however, the experimentally observed large anisotropy has been attributed¹⁶ almost entirely to the dipolar

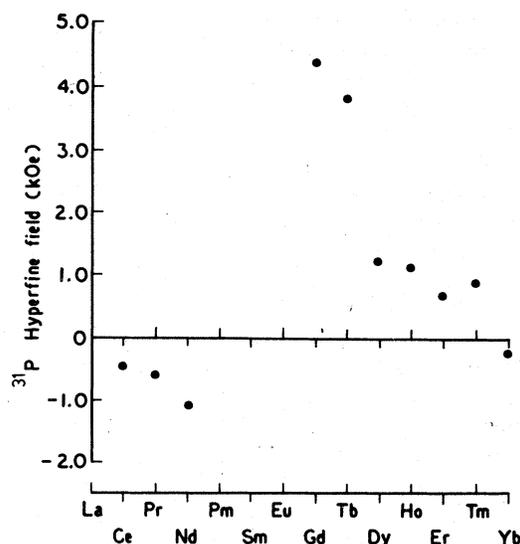


FIG. 7. Variation of the ³¹P hyperfine field H'^{hf} across the rare-earth-phosphate series.

field, i.e., $K_{\text{aniso}}^{\text{exp}} \sim K_{\text{aniso}}^{\text{dip}}$. In the present case, also, $K_{\text{aniso}}^{\text{exp}} > K_{\text{iso}}$. This indicates that the anisotropy of the dipole field dominates over that of the hyperfine field. From Eqs. (4) and (5) it is, in principle, possible to have an estimate of the dipolar and hyperfine contribution to $K_{\text{aniso}}^{\text{exp}}$ with the help of calculated $\langle S_z \rangle$ and χ_M values. A rough estimate suggests the dipolar contribution to be an order of magnitude greater than the hyperfine one. A separate hyperfine term A_p gives the fractional $3p$ unpairing from the relation⁵²

$$f_p = (2S/N')(A_p/A_{3p}). \quad (16)$$

This value is $\sim 0.0001\%$, again corroborating a small covalent admixture.

C. Bonding

As $4f$ electrons in rare-earth ions (R^{3+}) are well shielded by $5s$ and $5p$ core electrons, covalency involving direct participation of $4f$ electrons is expected to be of lesser importance. The observed magnitude and sign of the ^{17}O shifts in aqueous rare-earth complexes points to the fact that a very weak covalent bond is formed between oxygen $2s$ and rare-earth $6s$ orbitals, the $4f$, $5d$, and $5p$ orbitals probably have less effect on bonding. Golding and Halton⁴⁵ have examined the consequences of the direct participation of the $4f$ electrons of the rare earth on the sign of the shift by incorporating the orbital-reduction factor. The predicted wrong sign of the shift for f^5 configuration rules out any significant direct bonding with f electrons. Freeman and Watson⁵⁴ postulated an exchange-polarization mechanism (in which calculation electrons of different spins are allowed different radial wave functions) to explain the magnetic interaction of the rare-earth Gd^{3+} ion with its neighbors F^- in GdF_3 . They found that the spin-polarized functions predict that the Gd^{3+} ion, as seen by a nearest-neighbor F^- ion, appears in its transferred hyperfine interaction to have its spin antiparallel to the spin of the Gd^{3+} ion. The direct $4f$ contribution is thus very small and effects of the polarized outer shell ($5s, 5p$) play the dominant role.

Recently, McGarvey¹⁴ has interpreted the ^{19}F hyperfine interaction in Yb^{3+} -doped alkaline-earth fluorides in terms of f -electron participation in the bond. Undoubtedly, Yb^{3+} is an exceptional case, and the recent tendency is to invoke mixed-valence characteristics⁵⁵ to explain its behavior. Recently, however, Mustafa *et al.*⁵⁶ have invoked simultaneously f -electron participation and exchange polarization to interpret the ^{19}F shifts in ErF_3 . However, to date the experimental data on the whole series seem to uphold the charge-transfer or polarization mechanism involving the outer

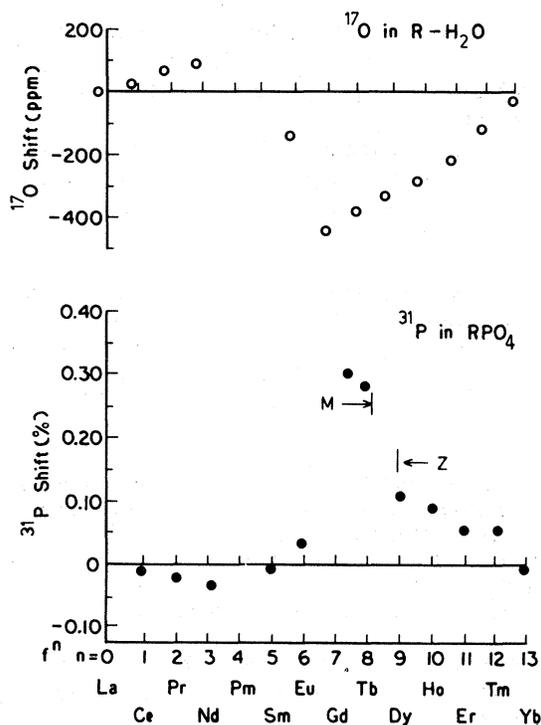


FIG. 8. Sign reversal of the shift of ligand nuclei for rare-earth systems. ^{17}O (nearest neighbor) shifts in rare-earth aqueous complexes in solution (upper) and ^{31}P (next-nearest neighbor) shifts in polycrystalline RPO_4 (lower). M , monoclinic; Z , tetragonal.

$6s$ and possibly the $5s$ and $5p$ orbitals, but not the $4f$ orbitals. As a matter of fact, covalency effects have been demonstrated from infrared studies⁵⁷ of YPO_4 (the diamagnetic analog of the zircon phosphates) which does not have any f electron.

The result of the present investigation which deals with second-nearest-neighbor hyperfine interaction is now examined in the light of the above theories. The sign of the isotopic shift of the ligand nuclei in rare-earth phosphates is opposite to that of nuclei which are directly attached to the R^{3+} ion (Fig. 8), whereas in the case of transitional metal compounds both the first-^{16,58} and the second-nearest-neighbor⁵² ligand nuclear resonance is shifted in the same direction. However, the sign of the shifts of ^{17}O and of the coupled proton (second-nearest neighbor) in water molecules the aqueous Gd^{3+} complex⁵⁹ has been found to be the same. Thus the bonding situation in the O-H bond seems to be different from that of the O-P bond in rare-earth phosphates. It may be mentioned that the O-H bond involves an $s-p$ hybrid σ bond with no π contribution to the ligand hyperfine interaction, whereas this is not the case in the PO_4 group. In the P-O bond of the PO_4 group the alternation of the shifts of P and O may be due to

the electron correlation effect,⁶⁰ the effect which explains the alternation of the ligand shifts in a number of aromatic compounds where π bonding is present.

Golding and Halton's expression⁴⁵ for the shift applied to the directly bonded ligand nucleus, but apparently the same formulation could explain the ³¹P shifts across the rare-earth series for the second-nearest-neighbors. The theory of Freeman and Watson has shown that the rare-earth ions may appear to their neighbor as having negative spin

(i.e., antiparallel to the 4f spin direction), but the experimental results in this oxysalt RPO₄ show that a parallel spin is transferred to the second-nearest ligand atom, viz. the phosphorous.

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