tudes of the resulting scattering angles are in better agreement with the measured values, but the slope of the curve is in poorer agreement with the data. This comparison is illustrated in Fig. 3 and is similar to the results of Hortig and Rogge.[1]

VI. CONCLUSIONS

Williams's theory of multiple Coulomb scattering as expressed in Eq. (2) yields rms scattering angles which are smaller than the measured values by a factor of about 1.8 for the systems investigated in this work. The near constancy of this normalization factor indicates that the predictions of Williams's theory as to the variation of the rms scattering angle with beam particle, target material, and target thickness are correct. The results of this work imply that Eq. (2), when multiplied by the empirical correction factor of $(1.8)^2$, can be used to obtain fairly accurate estimates of mean-square scattering angles for sulfur and oxygen ion beams in the target materials investigated and for beam energies ranging from 10 to 110 MeV. This modified equation may also yield useful numbers for other beam particles and target materials which do not differ greatly in their atomic number from those investigated and for moderate extrapolations in beam energy.

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Nuclear-Magnetic-Resonance Measurements in the Rare-Earth Group-V*A* Intermetallic Compounds*

E. D. JONES
Sandia Laboratory, Albuquerque, New Mexico 87115

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The temperature dependences, signs, and magnitudes of the phosphorus, arsenic, antimony, and bismuth nuclear-magnetic-resonance (NMR) Knight shifts in the NaCl-type rare-earth group-V*A* intermetallic compounds have been studied in detail for the temperature range of 1.5–600°K. The Knight shifts in the nonmagnetic compounds, such as LaP, were found to be temperature-independent. For most of the magnetic compounds, such as GdP, the temperature-dependent part of the Knight shift was found to obey a Curie-Weiss law. However, for the praseodymium, samarium, and thulium compounds, the effect of the sixfold cubic crystal-field interaction on the rare-earth ion could not be neglected. An analysis, showing the relationship between the Knight shift and the rare-earth $4f$ paramagnetic susceptibility $\chi_f(T)$, is presented. In this manner, it is shown that detailed information about $\chi_f(T)$ can be derived from an analysis of the NMR data. Furthermore, it is shown that the hyperfine field at the nonmagnetic site in these compounds arises from the spin component **S** of the total angular momentum **J** of the rare-earth ion, and not from the magnetization at the rare-earth site. The s-f exchange energies Γ for these compounds were calculated using the uniform conduction-electron spin-polarization model for the Knight shift. For the rare-earth Group-V*A* intermetallic compounds, Γ was found to be negative (antiferromagnetic) and relatively constant ($\simeq -0.3$ eV) for all of these compounds. Comparisons are made for the s-f exchange energies for all of the various rare-earth intermetallic compounds for which NMR measurements are available. It is again found that Γ is negative and relatively constant in magnitude. For all of these compounds, the total hyperfine field per unit spin S is found to be of the order of -50 kOe. No explanation for this phenomenon is advanced. It is shown that a consistent analysis of the Knight-shift data in terms of the Ruderman-Kittel-Kasuya-Yosida theory is probably impossible. The NMR linewidths δH in the nonmagnetic compounds were found to be in agreement with the calculated dipolar contribution, while for the magnetic compounds, the NMR linewidth δH was found to be due to the presence of demagnetization fields arising from the nonspherical shape of the particles in the powdered samples.

I. INTRODUCTION

THE electrical and magnetic properties of the NaCl-type rare-earth Group-V*A* compounds have been extensively studied by a number of researchers. Generally, it has been found that these compounds exhibit metallic behavior and that their magnetic properties are a result of the presence of the $4f$ electrons. Some of the early x-ray diffraction and magnetic susceptibility measurements were performed by Iandelli.[1,2] Low-temperature neutron diffraction techniques[3] have been used to determine the magnetic structures of some of these compounds. The influence of the crystal-field interaction upon the various types of magnetic order has been studied in detail by Trammell.[4]

Semiempirical extrapolations[5–7] from the known band structures of the III–V and II–VI semiconductors have been used to predict the electrical properties of the rare-earth Group-V*A* compounds. Consequently, the rare-earth Group-V*A* compounds have been classed either as semiconductors or semimetals. Recently, however, self-consistent band-structure calculations have been completed for ScN, ScP, and ScAs.[8] These calculations clearly show that ScP and ScAs are definitely metallic, while ScN is either a semimetal or a narrow band-gap semiconductor. The band structures of ScP and ScAs are similar, the main difference being that the density of states at the Fermi surface is larger for ScAs than for ScP.

Thus, because of the simplicity of their crystal structures (NaCl), their magnetic properties, and their metallic nature, the rare-earth Group-V*A* compounds form an interesting series of intermetallic compounds to study by NMR techniques.

Information concerning the signs, magnitudes, and temperature dependences of hyperfine fields in rare-earth intermetallic compounds is easily obtained from NMR Knight-shift measurements. The first measurement of this kind was performed by Jaccarino *et al.*,[9,10] who measured the aluminum Knight shifts in the rare-earth dialuminides. These authors found that the aluminum Knight shifts were proportional to the paramagnetic susceptibilities $\chi(T)$ of the samples. Consequently, using the uniform conduction-electron spin-polarization model for the Knight shifts, Jaccarino *et al.*[9,10] were able to determine the sign and magnitude of the *s-f* exchange energies. Subsequently, other rare-earth intermetallic compounds have been studied by the NMR technique in an effort to determine the *s-f* exchange energies for these compounds.[11–24]

Generally, the Knight shifts K of the nonmagnetic sites in rare-earth intermetallic compounds are about an order of magnitude larger than the corresponding NMR frequency shifts $(\Delta H/H)$ in rare-earth insulators.[25–27] Since the rare-earth atomic susceptibilities are essentially unaffected by the presence or absence of conduction electrons, the order-of-magnitude difference between K and $\Delta H/H$ implies that the conduction electrons play an important role in determining the magnitude of the resulting hyperfine fields.

The purpose of this paper is to present the results of Knight-shift measurements in the rare-earth Group-V*A* intermetallic compounds. Besides using the Knight-shift data to determine the *s-f* exchange energies and hyperfine fields, it will be shown that a study of the temperature dependence of the Knight-shift data can be used to measure the paramagnetic susceptibilities of these samples. In this manner, rare-earth spin-spin exchange energies, Curie-Weiss temperatures, and crystal-field interactions can be determined. The NMR technique has an inherent advantage over a susceptibility measurement because the presence of other phases, etc., generally do not affect the Knight-shift measurement of the compound being studied.

Section II describes the experimental apparatus and technique used to measure the various NMR Knight shifts. Also described in Sec. II is the technique used to prepare the various samples. A discussion of the contributions to the magnetic susceptibility and Knight shift for a rare-earth intermetallic compound is contained in Sec. III. Section IV contains the experimental results and interpretation of Knight shifts and NMR linewidth measurements in the magnetic compounds are presented in Sec. V. A discussion of the interpretation of the Knight-shift measurements and a summary of all of the NMR data are presented in Sec. VI, while a summary of this paper is contained in Sec. VII.

II. EXPERIMENTAL

The NMR measurements were performed on powdered samples using a variable-frequency induction

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spectrometer and a conventional laboratory electromagnet. Sample temperatures between 90 and 600°K were achieved by use of a Varian V-4540 variable-temperature control unit. For temperatures of 76 and 27°K, liquid nitrogen and neon were used as coolants. Liquid helium was used between 2 and 4°K. The Knight-shift measurements were made at a fixed frequency by sweeping the magnetic field through resonance. For this method, the Knight shift K is defined by $K=(H_L-H_0)/H_0$, where H_L is the Larmor field and H_0 is the magnetic field dependences observed for the Knight shifts. The frequency range for which the various Knight shifts were measured was 2–30 MHz.

The phosphorus Knight shifts were measured with respect to red phosphorus. The arsenic and antimony Knight shifts were measured with respect to one or a combination of the following reference compounds: the proton NMR in H_2O, the deuteron NMR in D_2O, or the lithium NMR in a saturated solution of lithium acetate. The bismuth Knight shifts were measured with respect to the bismuth NMR in a solution of $Bi(NO_3)_3+HNO_3$. The Knight shifts of the two antimony isotopes Sb^{121} and Sb^{123} were found to be the same within experimental error. Therefore, the term antimony Knight shift will generally refer to the Sb^{121} NMR, for which most of the NMR data were taken. The scandium Knight shifts were measured with respect to the scandium NMR in a saturated solution of $ScCl_3$. The lanthanium and yttrium Knight shifts were measured, respectively, with saturated solution of $La(NO_3)_3$ and YCl_3. All of the reference compounds had their published gyromagnetic ratios checked by the proton or deuteron NMR in H_2O-D_2O mixtures. Hence, whenever it proved to be advantageous, the proton or deuteron NMR was sometimes used to measure the resonance field H_0.

The samples were prepared by mixing correct proportions of the elemental materials in a quartz pressure vessel and heating to about 900°C for several days. The exact temperature employed depended upon the two constituents used to make the sample. Under the appropriate conditions, a solid-state diffusion reaction will occur. When necessary, a small excess amount of the group-V*A* element was added to the powder mixture to ensure sample stoichiometry. The samples were then ground into powders, pressed into pellets, and reheated several times to achieve uniformity. Standard x-ray powder diffraction techniques were used to confirm that the samples had the correct NaCl-type crystal structure and lattice constants.[1,2,28–32]

III. CONTRIBUTIONS TO THE SUSCEPTIBILITY χ AND KNIGHT SHIFT K

This section will discuss the various contributions to the paramagnetic susceptibilities and Knight shifts in the rare-earth Group-V*A* intermetallic compounds. The expression "Knight shift" will generally mean the Knight shift of the group-V*A* nucleus, with exceptions as noted.

A. Susceptibility

The partitioning of the various contributions to the magnetic susceptibility will be accomplished by writing an expression for the total susceptibility $\chi(T)$ in the paramagnetic state as

$$\chi(T)=\chi_0+\chi_f'(T), \tag{3.1}$$

where χ_0 and $\chi_f'(T)$ are the respective non-4*f* and 4*f* electronic contributions in these compounds. The term χ_0 contains contributions from the Pauli spin susceptibilities of the *d-p* and *s-p* bands, the orbital susceptibility of the *d-p* and/or *s-p* bands, and the diamagnetic contribution from the ion cores and the filled portion of the *d-p* and/or *s-p* bands. Thus, χ_0 contains all of the contributions to $\chi(T)$ which are found in the "nonmagnetic" compounds such as LaP. This term is, for the compounds discussed in this paper, generally considered to be temperature-independent. Evidence for this phenomenon is presented in Sec. IV.

The term $\chi_f'(T)$ in Eq. (3.1) is the paramagnetic susceptibility of the sample which can be associated with the properties of the 4*f* electrons. There are at least two contributions to $\chi_f'(T)$, and schematically they are referred to as $\chi_f(T)$ and $\chi_{sf}(T)$; $\chi_f(T)$ is the susceptibility of the 4*f* electrons and $\chi_{sf}(T)$ is the *s-f*-exchange enhanced temperature-dependent susceptibility of the conduction-electron bands. Since both contributions, for the simplest of models, have the same temperature dependence, they cannot be distinguished from each other in a susceptibility measurement. Estimates concerning the importance of $\chi_{sf}(T)$ have traditionally been made by noting the difference between the measured number of Bohr magnetons of the sample and the free-ion value. The reason for stressing the importance of distinguishing between $\chi_f(T)$ and $\chi_f'(T)$ is that, as will be shown, the equation for the Knight shift involves only $\chi_f(T)$. It has been common practice to ignore $\chi_{sf}(T)$ in constructing a $K(T)$-versus-$\chi(T)$ diagram in order to obtain information concerning *s-f* exchange energies, etc.; however, from an analysis of susceptibility data (see Sec. V), it appears that $\chi_{sf}(T)$ could be as large as 0.1 $\chi_f(T)$.

Generally, the 4*f* electronic susceptibility $\chi_f(T)$ is temperature-dependent, in most cases obeying a Curie-Weiss law. However, for the praseodymium and thulium Group-V*A* compounds, $\chi_f(T)$ is temperature-independent at low temperatures and is a result of the

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crystal-field interaction giving rise to a nonmagnetic ground state.

B. Knight Shift

The NMR frequency is shifted from the Larmor frequency by an amount $K=(H_L-H_0)/H_0=\Delta H/H$ by interactions between the conduction electrons and the nuclear magnetic dipole moment. The Knight shift $K(T)$ consists of a sum of two terms, the non-$4f$ and $4f$ contributions K_0 and $K_f(T)$, respectively. The contribution K_0 arises from one or a combination of the following interactions: (a) the Fermi contact hyperfine interaction with s-like conduction electrons, (b) a core-polarization type of hyperfine interaction with the d- and/or p-type conduction bands, and (c) a positive orbital hyperfine interaction arising from the same electronic bands which are contributing to the orbital susceptibility. Thus, K_0 is the Knight shift associated with only the conduction-electron bands.

The term $K_f(T)$, due to the presence of the $4f$ electrons, arises from an interaction of the form $A\mathbf{I}\cdot\langle\mathbf{S}\rangle$, where A is a hyperfine interaction constant, $\mathbf{I}$ is the nuclear spin and $\langle\mathbf{S}\rangle$ is the time-averaged value of the rare-earth $4f$ spin component of the angular momentum $\langle\mathbf{J}\rangle$. Experimental confirmation that the hyperfine interaction involves $\langle\mathbf{S}\rangle$ and not $\langle\mathbf{J}\rangle$ has been discussed in the preliminary report[15] on the phosphorus NMR in SmP. This difference between $\langle\mathbf{S}\rangle$ and $\langle\mathbf{J}\rangle$ is important only for the samarium and europium 3+ compounds since $\langle\mathbf{S}\rangle$ is not proportional to $\langle\mathbf{J}\rangle$ for these two rare-earth ions at room temperature.

There have been several proposed mechanisms[10,33–36] for the Knight shift of a nonmagnetic nucleus in rare-earth intermetallic compounds. However, the experimental results presented in this paper are incapable of distinguishing between them. All of the calculations show that an effective hyperfine interaction can be written in the form of $A\mathbf{I}\cdot\langle\mathbf{S}\rangle$, with the origins of the hyperfine coupling constant A varying in detail. For this reason, only the two simplest models will be discussed. The reader is referred[36] to the literature for details concerning the other models. The total Knight shift $K(T)$ is thus given by

$$K(T)=K_0+K_f(T). \tag{3.2}$$

In terms of a hyperfine interaction of the form $A\mathbf{I}\cdot\langle\mathbf{S}\rangle$, the most general expression for $K_f(T)$ is given by

$$K_f(T)=(g_J-1)H^{\mathrm{hf}}\chi_f(T)/Ng_J\mu_B, \tag{3.3}$$

where g_J is the Landé g factor for the rare-earth ion in question, H^{hf} $(=A/\gamma\hbar)$ is the hyperfine field per *unit spin* S, γ is the nuclear gyromagnetic ratio, N is Avogadro's number, μ_B is the Bohr magneton, and $\chi_f(T)$ is expressed in units of emu per mole. The (g_J-1) term in Eq. (3.3) is a result of the projection of $\mathbf{S}$ onto $\mathbf{J}$ for the rare-earth ion. This term could have been incorporated into the definition of H^{hf}, but as will be seen in the discussion of the NMR data (Sec. V), this definition for H^{hf} results in a quantity which has the same sign and essentially the same magnitude for all the compounds. Equation (3.3) is not valid for the samarium and europium compounds, since $\langle\mathbf{S}\rangle\neq(g_J-1)\langle\mathbf{J}\rangle$ at room temperature. The modification of Eq. (3.3) for the samarium and europium compounds is discussed in Sec. V.

It must be again mentioned here that the susceptibility $\chi_f(T)$ appearing in Eq. (3.3) is to be associated only with the properties of the $4f$ electrons and not with the total temperature-dependent susceptibility $\chi_f'(T)$ of Eq. (3.1).

The relationship between $K_f(T)$ and $\chi_f(T)$ given in Eq. (3.3) is valid for any type of material, i.e., insulator or metal, as long as the hyperfine interaction can be written in the form of $A\mathbf{I}\cdot\langle\mathbf{S}\rangle$. Since the compounds discussed in this paper are metallic, a transformation of Eq. (3.3) to metals will now be given in terms of the uniform conduction-electron spin polarization[9,10] and the Ruderman-Kittel-Kasuya-Yosida (RKKY)[33,37,38] models for the Knight shift $K_f(T)$.

In the uniform conduction-electron polarization model[9,10] for rare-earth intermetallic compounds, the conduction-electron spins $\boldsymbol{\sigma}$ are uniformly polarized by an s-f exchange interaction of the form $-\Gamma\mathbf{S}\cdot\boldsymbol{\sigma}$ with the rare-earth spin $\mathbf{S}$. The s-f exchange interaction is thus ferromagnetic for positive and antiferromagnetic for negative Γ. The resulting Knight shift $K_f(T)$ is given by[9,10]

$$K_f(T)=-K_0\Gamma\langle S(T)\rangle/2\mu_BH, \tag{3.4}$$

or in terms of the molar susceptibility $\chi_f(T)$,

$$K_f(T)=(g_J-1)K_0\Gamma\chi_f(T)/2Ng_J\mu_B{}^2. \tag{3.5}$$

The Knight shift $K_f(T)$ in the RKKY theory has been previously calculated[34] with the result

$$K_f(T)=-6\pi Z(g_J-1)\Gamma(0)\chi_f(T)\times\textstyle\sum_R F(2k_FR)/Ng_J\mu_B{}^2, \tag{3.6}$$

where Z is the number of conduction electrons per atom, k_F is the Fermi wave vector, $\Gamma(0)$ is the $\mathbf{k}=0$ value of the s-f exchange energy constant Γ, and

$$F(x)=(x\cos x-\sin x)/x^4. \tag{3.7}$$

Although the RKKY theory is a more realistic calculation than the uniform conduction-electron spin-polarization model, there are difficulties associated with its application. For example, Eq. (3.6) is a result of

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assuming a spherical (free-electron) Fermi surface. The band-structure calculations for the rare-earth Group-VA compounds indicate that the Fermi surface is complicated and nonfree-electron–like. Furthermore, the assumption that $\Gamma(\mathbf{k}-\mathbf{k}')\simeq\Gamma(0)$ implicit in the derivation of Eq. (3.6) has been questioned by a number of authors.[39] Finally, it is to be noted that there are the two unknown parameters k_F and $\Gamma(0)$, in Eq. (3.6), compared to the one parameter in Eq. (3.5). Comparing Eqs. (3.5) and (3.6), it is obvious that a general expression for $K_f(T)$ can be written in the form of Eq. (3.5), i.e., let $-12\pi Z\Gamma(0)\sum F(2k_FR)\rightarrow\Gamma$ in Eq. (3.6). Therefore, in the analysis of the Knight-shift data presented in Sec. V, the uniform polarization *form* for the Knight shift will be used to evaluate Γ. This does not imply that the uniform conduction-electron spin-polarization model is correct (or favored), but rather that it is easier to use a one-parameter theory to analyze the data. When a quantitative theory for the Knight shift becomes available, it will be a simple matter to relate the values for Γ given in this paper to the *product* of the various unknown functions. One of the surprises of using the Knight-shift formula, given by Eq. (3.5), in analyzing the Knight shifts for several types of rare-earth intermetallic compounds is the fact that the values of Γ so obtained are fairly constant[17] for a given rare-earth ion, i.e., independent of the system studied. A discussion of this point and comparisons between the various NMR determined values of Γ are presented in Sec. VI.

Two further contributions to the total Knight shift which have not been discussed thus far are the NMR frequency shift contributions from diamagnetism and demagnetization effects. The *incremental* diamagnetic shift between the reference material used to measure the Knight shift and compound under study is considered to be negligible and therefore its effect will not be considered.

The demagnetization field shift arises from the finite volume magnetization $M_V=\chi_VH_0$ of the sample, and hence the magnetic field inside the sample can be different from the applied field H_0.[40]

For a powdered sample, the demagnetization shift consists of two contributions: one from the over-all shape of the sample and another from the shape of the individual particles (assuming equally shaped particles). In order to determine the importance of the over-all shape of the sample, the phosphorus Knight shift of GdP at 300°K was measured as a function of GdP concentration in a GdP-NaCl powder mixture. Within experimental error, the phosphorus Knight shift was concentration-independent, thereby indicating that the over-all shape of the sample container is not important for these samples.

Since the field shift ΔH [Eq. (3.10)] is proportional to the volume magnetization of the sample, its temperature dependence will be the same as $\chi_f(T)$. For this reason, it will cause an error in the values for Γ (or H^{hf}) presented in Sec. V. An estimate[41] for this error can be made by assuming a worst-case value for the demagnetization field shift of $\Delta H\simeq3\pi M$ in terms of the volume magnetization M. An estimate for $3\pi M$ indicates that the errors to Γ could be about 15%. However, a more realistic estimate is made by using the results of the NMR linewidth studies (see Sec. V for discussion). The NMR linewidth data suggest that $\Delta H\simeq\pi M$, which thus means the maximum error to Γ, due to demagnetization field, is about 5%. Further evidence that demagnetization fields are relatively unimportant can also be obtained from a study of the NMR data in the samarium compounds. Since the Knight shift, due to the $4f$ hyperfine field interaction, is proportional to $\langle S\rangle$ and not χ_f, this Knight-shift contribution will have a different temperature dependence than the demagnetization field shift. The analyses of the NMR data for the samarium compounds presented in Sec. V do not indicate a significant demagnetization field contribution to the total Knight shift. Therefore, the effects of the demagnetization field will also not be included in Eq. (3.2).

Thus, the total Knight shift $K(T)$ is written as

$$K(T)=K_0[1+(g_J-1)\Gamma\chi_f(T)/2Ng_J\mu_B{}^2]. \quad (3.8)$$

From Eq. (3.8) it is obvious that

$$[K(T)-K_0]\propto\chi_f(T), \quad (3.9)$$

and therefore a study of the temperature dependence of the quantity $[K(T)-K_0]$ provides a measurement of the temperature dependence of $\chi_f(T)$. In this manner, the Knight-shift data can be used to measure the paramagnetic susceptibility $\chi_f(T)$ of the rare-earth ion.

Recently,[42] the praseodymium and thulium NMR in PrP, PrAs, TmP, TmAs, and TmSb have been observed and one of the important results is that as a function of temperature, the phosphorus, etc., Knight shifts $[K(T)-K_0]$ are proportional to the praseodymium and thulium NMR frequency shifts. Since the rare-earth NMR frequency shifts are directly proportional to the rare-earth susceptibility $\chi_f(T)$,[42] the measurements clearly show that the function $[K(T)-K_0]$ can indeed be used to measure the temperature dependence of $\chi_f(T)$. Perhaps even more striking is the case of samarium, where Eq. (3.4) would be employed. As

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TABLE I. Observed Knight shifts $K_0(\%)$ in the nonmagnetic rare-earth Group-VA compounds.

Nucleus	Compound P	 As	 Sb	 Bi
Sc^{45}	0.04 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	$\cdots$
Y^{89}	0.11 ± 0.03	0.11 ± 0.03	0.11 ± 0.03	0.11 ± 0.03
La^{139}	0.16 ± 0.01	0.16 ± 0.01	0.17 ± 0.01	$\cdots$
	Sc	Y	La	Lu
P^{31}	0.07 ± 0.01	0.05 ± 0.01	0.06 ± 0.01	0.05 ± 0.01
As^{75}	0.14 ± 0.01	0.16 ± 0.01	0.16 ± 0.01	$\cdots$
$Sb^{121,123}$	0.28 ± 0.01	0.20 ± 0.01	0.29 ± 0.01	$\cdots$
Bi^{209}	$\cdots$	0.27 ± 0.02	$\cdots$	$\cdots$

discussed in detail in Sec. V, the quantity $\langle S_z/H\rangle$ reverses sign at $T\simeq300°K$, as does the Knight-shift function $[K(T)-K_0]$ for these samarium compounds. Thus, for the samarium and europium compounds, the Knight-shift data provide a direct measurement of the temperature dependence of $\langle S_z(T)\rangle$, a quantity which is difficult to measure by other experimental techniques, such as the Mössbauer effect.[43]

Finally, it must be remarked that it appears that the NMR data can be used to measure not only the temperature dependence of $\chi_f(T)$, but its magnitude as well, i.e., using Eqs. (3.2) and (3.3). This is a result of a detailed examination[44] of the praseodymium and thulium NMR data in PrP, TmP, etc., which shows that the effective number of Bohr magnetons for these ions is (to within 1%) *equal* to the free-ion values. Thus, the temperature dependence of the Knight shift completely determines $\chi_f(T)$, while the magnitude of the Knight shift determines H^{hf}, the only unknown left in Eqs. (3.2) and (3.3). Thus, the Knight-shift data presented in Sec. V are, for all practical purposes, essentially susceptibility measurements.

IV. NMR MEASUREMENTS IN NONMAGNETIC COMPOUNDS

This section contains the Knight-shift and NMR linewidth measurements in the nonmagnetic intermetallic rare-earth Group-VA compounds. The phrase "nonmagnetic" refers to the compounds which do not exhibit any $4f$ electronic effects; for example, lanthanum has a $4f^0$ electronic configuration and hence is nonmagnetic.

A. Knight Shifts

The Knight shifts of the various nuclei in the scandium, yttrium, lanthanum, and lutetium phosphides, etc., were measured between 4 and 600°K and within experimental error were found to be temperature-independent. All of the Knight-shift data for these compounds are tabulated in Table I. The lanthanum Knight shift in LaSb has previously been measured by Reddoch and Ritter,[45] and their result of $K^{139}=(0.156\pm0.006)\%$ is in good agreement with the value given in Table I.

The temperature independence of K_0 implies that χ_0 is also independent of temperature. Recently, a large temperature-dependent paramagnetic susceptibility was reported for LaSb.[46] This result is in disagreement with the Knight-shift data reported in this paper. Furthermore, the temperature dependence of $\chi(T)$ for LaP was measured[47] for the same sample for which the Knight shifts were measured, and $\chi(T)$ was found to be essentially temperature-independent, and for LaP, $\chi\simeq-60\times10^{-6}$ emu/mole. Thus, it is felt that the reported temperature dependence to $\chi(T)$ for LaSb is probably a result of impurities. Similar situations for lanthanum and yttrium metal have been noted,[48] i.e., the paramagnetic susceptibility is strongly temperature-dependent while the Knight shift is temperature independent. As discussed in Sec. III, no attempt will be made to analyze the various contributions to K_0; however, a few comments regarding the magnitudes of K_0 are appropriate at this time.

It is interesting to note that the ratio of the arsenic (and antimony) Knight shift K_0 to the phosphorus Knight shift is almost the same as the ratios of the corresponding $3s$, $4s$, and $5s$ atomic hyperfine fields. Using the Si^{28}, Ge^{73}, Sn^{119}, and Pb^{207} atomic hyperfine fields[49] $a(s)$, in order to estimate values for the Group-VA hyperfine fields, gives 1.1, 2.6, 4.3, and 7.2 MG, respectively, for phosphorus, arsenic, antimony, and bismuth. Thus the ratios $K_0{}^{75}/K_0{}^{31}$, $K_0{}^{121}/K_0{}^{31}$, and $K_0{}^{209}/K_0{}^{31}$ of 2.3, 4.7, and 4.7 compare favorably with the respective ratios for $a^{75}(s)/a^{31}(s)$, etc., of 2.4, 3.9, and 6.5. This result suggests that the Knight shifts in the compounds are due to s-like conduction electrons. A similar analysis for the Group-VA hyperfine fields[50] in transition-metal compounds such as MnP, MnAs, and MnSb yields essentially the same conclusions; except for these compounds, the phosphorus Knight shifts are negative.[51]

The magnitudes of the lanthanum and yttrium Knight shifts given in Table I are about a factor of 3 to 4 smaller than measured in the pure metals. For example, in fcc lanthanum,[52] $K^{139}\simeq0.7\%$, while in hexagonal

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[46] E. V. Goncharova, V. P. Zhuze, V. V. Zhdanova, T. B. Zhukova, I. A. Smirnov, and E. V. Shadrichev, Fiz. Tverd. Tela **10**, 1322 (1968) [English transl.: Soviet Phys.—Solid State **10**, 1052 (1968)].

[47] The author is indebted to Dr. G. Booth for performing the susceptibility measurements.

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[49] W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2.

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[51] E. D. Jones, Phys. Rev. **158**, 295 (1967).

[52] D. Zamir and D. S. Schreiber, Phys. Rev. **136**, A1087 (1964).

yttrium,[48] $K^{89}\simeq 0.36\%$. The reduction in the value of Knight shifts between the elemental metals and the Group-V*A* intermetallic compounds is not quantitatively understood. There are several effects which could account for these smaller Knight shifts and two of them are (1) a lower density of states at the Fermi surface, and (2) a reduction in the *s*-character of the conduction-electron bands at the Fermi surface. Indirect evidence that both of these effects are qualitatively important in the Group-V*A* compounds can be found from the band-structure calculations for ScN, ScP, and ScAs.[8] The band structure of fcc scandium metal has also been calculated, and a comparison with the band structures of ScP and ScAs shows that in addition to a reduction in the density of states at the Fermi surface, there exists a partially filled *s* band in fcc scandium which is absent in ScP and ScAs. The *s* bands in ScP and ScAs lie very high above the Fermi energy and hence are empty. The *p* and *d* bands of ScP and ScAs have some *s* character to them, but the amount is small.

From Table I it is evident that the phosphorus and arsenic Knight shifts K_0 are essentially constant across the series from scandium to lutetium. The antimony Knight shift in YSb (measured only at $T=300°\text{K}$) is different from the Knight shifts in ScSb and LaSb. It is not clear to what this difference is due. The measurements of the Knight shifts of the two antimony isotopes in YSb gave identical results.

In the analysis of the Knight-shift data of the magnetic rare-earth compounds, where Eq. (3.8) will be used, it will be assumed that K_0 is constant across the lanthanide series of compounds. Thus, the values for K_0 which will be used for analysis of the NMR data are as follows: $K_0^{31}=(0.06\pm0.01)\%$, $K_0^{75}(0.16\pm0.01)\%$, $K_0^{121,123}=(0.29\pm0.01)\%$, and $K_0^{209}=(0.27\pm0.01)\%$. Evidence that K_0 is also consistent for the other rare-earth compounds is presented in the discussion of the Knight-shift measurements for the samarium compounds in Sec. V.

B. NMR Linewidths

The NMR linewidths δH, defined in this paper as the separation (in gauss) between the absorption derivative extrema, were found to be neither Gaussian nor Lorentzian in shape.

The second-moment contribution to the NMR linewidth due to nuclear dipolar interactions in a powdered sample with the NaCl-type structure has been calculated by McGarvey and Gutowsky[53] and is

$$\langle \Delta H^2\rangle_I = \tfrac{3}{5} f_I \gamma_I^2 \hbar^2 I(I+1)(115.6/a_0^6) + (4/15) f_S \gamma_S^2 \hbar^2 S(S+1)(422.1/a_0^6), \quad (4.1)$$

where f_I and f_S are the fractional concentrations of the nuclear spins I and S, γ_I and γ_S are the respective nuclear gyromagnetic ratios, and a_0 is the lattice constant of the NaCl-type structure. The peak-to-peak NMR linewidth δH is defined by $\delta H = 2\langle \Delta H^2\rangle^{1/2}$, where $\langle \Delta H^2\rangle$ is given by Eq. (4.1).

TABLE II. Observed and calculated NMR linewidth δH in the nonmagnetic rare-earth Group-V*A* compounds.

Compound and nucleus	δH_{obs}(G)	δH_{calc}(G)
Sc^{45}P	5.6	3.3
ScP^{31}	3.6	3.9
Sc^{45}As	4.7	3.0
ScAs^{75}	4.3	3.6
Sc^{45}Sb	3.5	3.0
ScSb^{121}	3.2	3.2
YP^{31}	1.1	0.9
YAs^{75}	1.1	0.8
YSb^{121}	1.3	1.4
YSb^{123}	1.0	1.6
YBi^{209}	1.0	1.5
La^{139}P	5.3	1.5
LaP^{31}	2.1	1.7
La^{139}As	3.2	1.4
LaAs^{75}	2.5	1.6
La^{139}Sb	4.5	1.7
LaSb^{121}	4.2	1.7
LuP^{31}	2.8	2.3

The experimental and calculated values of the NMR linewidths δH are tabulated in Table II. The experimental uncertainties in δH are approximately ±10% and are not indicated in Table II. As can be seen in Table II, there is reasonable agreement between the calculated and measured values of δH. The most serious discrepancies between δH_{obs} and δH_{calc} are generally for these nuclei with electric quadrupole moments, i.e., for $I>\frac{1}{2}$. For these particular nuclei, the presence of strains, vacancies, etc., in cubic crystals can be an important source of line broadening. The yttrium $(I=\frac{1}{2})$ NMR signal-to-noise ratio was small, and therefore a measurement of the NMR linewidth δH was not made. Repeated annealing of the samples at high temperatures did not substantially alter the NMR linewidths.

V. NMR MEASUREMENTS IN MAGNETIC COMPOUNDS

This section contains the Knight-shift and NMR linewidth measurements in the rare-earth Group-V*A* intermetallic compounds which exhibit 4*f* electronic effects.

A. Knight Shifts

For convenience, the Knight-shift data are arranged in the following manner: (1) systems exhibiting Curie-Weiss behavior (Ce, Nd, Gd, Tb, Dy, Ho, Er, and Yb), (2) singlet ground-state systems (Pr and Tm), and (3) manifestations of thermally populated excited states (Sm and Eu).

For the analysis of the Knight-shift data discussed in this section, Eq. (3.8) will be used. The experimentally determined values for the hyperfine field H^{hf} [Eq. (3.3)] will be presented in Sec. VI. For all of the figures, unless otherwise indicated, the experimental uncertain-

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[53] B. R. McGarvey and H. S. Gutowsky, J. Chem. Phys. **20**, 1472 (1952).

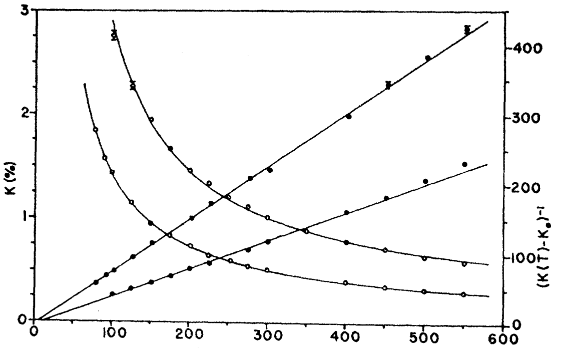

FIG. 1. Temperature dependences of the phosphorus and arsenic Knight shifts $K(T)$ and inverse Knight-shift functions $[K(T)-K_0]^{-1}$ for CeP and CeAs. The upper Knight shift and lower inverse Knight-shift data are for CeAs. The curves drawn through the Knight-shift data are a result of a least-squares fit using a Curie-Weiss law for $\chi_f(T)$ in Eq. (3.8).

ties in the Knight-shift data are equal to or less than the size of the plotted points, with a minimum error of $\pm 0.01\%$.

A summary of all of the NMR-derived parameters given in this section will be presented in Table V, Sec. VI.

1. *Systems Exhibiting Curie-Weiss Behavior*

All of the Knight-shift data which were found to exhibit Curie-Weiss behavior were analyzed by performing a least-squares fit of Eq. (3.8) to the data, using a Curie-Weiss law for $\chi_f(T)$, i.e., $\chi_f(T)=C_M(T-\theta)^{-1}$ with C_M the appropriate molar Curie constant for each rare-earth element. Thus, the solid lines drawn through the data shown in the figures are a result of this least-squares fit.

Cerium. Magnetic susceptibility measurements[54–56] on CeP and CeAs have shown that for $T \gtrsim 100°\text{K}$, the paramagnetic susceptibility $\chi(T)$ obeys a Curie-Weiss law. These measurements were made up to $T \simeq 200°\text{K}$ and the reported Curie-Weiss temperatures θ range from -8–$+5°\text{K}$ for CeP and -21–$-5°\text{K}$ for CeAs. The effective number of Bohr magnetons μ_{eff} derived from these measurements ranges from 2.56 to 2.82 and is to be compared with the Ce^{3+} free-ion value of 2.54. Low-temperature measurements ($T<100°\text{K}$) for these compounds show that $\chi(T)$ exhibits an anomalous temperature dependence which has been attributed to either a temperature-dependent effective $\text{Ce}^{+3} \leftrightarrow \text{Ce}^{4+}$ valency change[57] or to the effect of a crystal-field interaction.[58] Recently,[59] neutron diffraction measurements in CeAs have indicated the existence of a large crystal-field splitting in agreement with the predictions of Ref. 58. Therefore, the low-temperature anomaly seems to be associated with the crystal-field interaction and not with a valency change. The cerium Group-VA intermetallic compounds are found to be type-I antiferromagnets with Neel temperatures T_N of 9, 8, 18, and 25°K, respectively, for CeP, CeAs, CeSb, and CeBi.

The phosphorus and arsenic Knight shifts in CeP and CeAs were measured between 77 and 550°K and the results of these measurements are shown in Fig. 1. As can be seen in Fig. 1, the Knight shifts are positive and strongly temperature-dependent. Also shown in Fig. 1 are the temperature dependences of the Knight-shift functions $[K(T)-K_0]^{-1}$. It is obvious from the data presented in Fig. 1 that the susceptibility $\chi_f(T)$ obeys a Curie-Weiss law in the temperature range for which these measurements were made. Preliminary Knight-shift measurements for $T<77°\text{K}$ indicate that there is a strong deviation from Curie-Weiss behavior in agreement with the susceptibility data.[54–56] The least-squares fit to the Knight-shift data yielded values for Γ and θ as follows: CeP, $\Gamma=-(1.1\pm0.2)$ eV and $\theta=+(3.6\pm1.0)°\text{K}$; CeAs, $\Gamma=-(0.74\pm0.05)$ eV, and $\theta=+(9.9\pm3.0)°\text{K}$. The NMR-derived values for the Curie-Weiss temperatures θ are in disagreement with the susceptibility determined values; however, this could be a result of the limited temperature ranges for which the susceptibility measurements were made ($T<300°\text{K}$).

Neodymium. Magnetic susceptibility measurements[54,56,59–61] ($T<300°\text{K}$) have shown that the paramagnetic susceptibilities $\chi(T)$ of the neodymium compounds obey Curie-Weiss laws. All of the neodymium

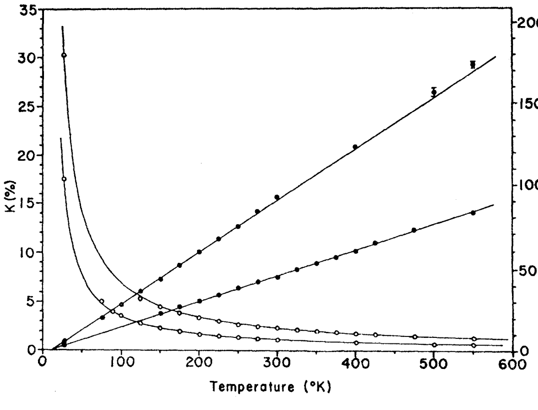

FIG. 2. Temperature dependences of the phosphorus and arsenic Knight shifts $K(T)$ and inverse Knight-shift functions $[K(T)-K_0]^{-1}$ for NdAs and NdP. The upper Knight shift and lower inverse Knight-shift data are for NdAs. The curves drawn through the Knight-shift data are a result of a least-squares fit using a Curie-Weiss law for $\chi_f(T)$ in Eq. (3.8).

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[61] G. Busch, P. Junod, F. Levy, A. Menth, and O. Vogt, Phys. Letters **14**, 264 (1965).

compounds order magnetically[56,60] with ordering temperatures T_N of 11, 11, and 16°K, respectively, for NdP, NdAs, and NdSb. The Curie-Weiss temperatures for NdP and NdAs were reported[56] to be +11 and +4°K, respectively. The effective number of Bohr magnetons μ_{eff} were found from the susceptibility data to be approximately 3.8 compared to the Nd^{3+} free-ion value of 3.62.

The phosphorus and arsenic Knight shifts in NdP and NdAs were measured between 27 and 500°*K* and the data are shown in Fig. 2. Also shown in Fig. 2 are the temperature dependences of $[K(T)-K_0]^{-1}$ for these compounds. The least-squares best fit occurred with $\Gamma=-(0.56\pm0.09)$ eV, $\theta=+(8.9\pm0.2)$°K for NdP, and $\Gamma=-(0.42\pm0.03)$ eV, $\theta=+(5.9\pm0.2)$°K for NdAs. These values for the Curie-Weiss temperatures θ are in good agreement with the susceptibility data results.

Gadolinium. Paramagnetic susceptibility measurements[1,54,56,59,60,62–65] on the gadolinium Group-V*A* compounds have been performed by a number of authors, and all of the results indicate that $\chi(T)$ obeys a Curie-Weiss law. However, the susceptibility determined Curie-Weiss temperature θ and effective number of Bohr magnetons μ_{eff} vary over a range of values. For example, the reported Curie-Weiss temperature θ for GdP ranges between −2 to +41°K. The effective number of Bohr magnetons, reported for these compounds, varies from about 7.7 to 8.2, which is to be compared to the Gd^{3+} free-ion value of 7.94. All of the gadolinium Group-V*A* compounds order magnetically at low temperatures: GdN is a simple ferromagnet with $T_C=72$°K, while the rest are presumably type-II antiferromagnets with Neél temperatures of 15, 25, 28, and 28°K, respectively, for GdP, GdAs, GdSb, and GdBi.

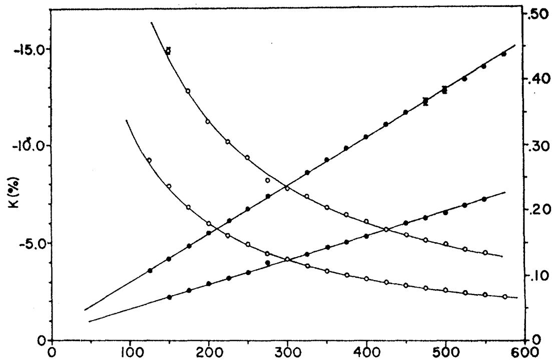

FIG. 3. Temperature dependences of the phosphorus and arsenic Knight shifts $K(T)$ and inverse Knight-shift functions $[K(T)-K_0]^{-1}$ for GdP and GdAs. The upper Knight shift and lower inverse Knight-shift data are for GdAs. The curves drawn through the Knight-shift data are a result of a least-squares fit using a Curie-Weiss law for $\chi_f(T)$ in Eq. (3.8).

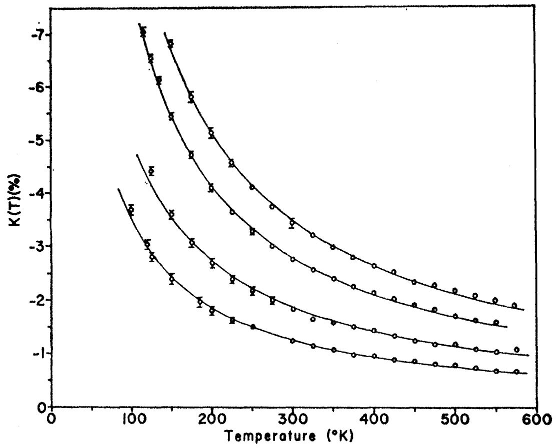

FIG. 4. Temperature dependences of the phosphorus Knight shifts $K(T)$, respectively, from top to bottom, for TbP, DyP, HoP, and ErP. The curves are a result of a least-squares fit of Eq. (3.8) to the Knight-shift data using a Curie-Weiss law for $\chi_f(T)$ for each compound.

Low-temperature x-ray diffraction studies[66] of the exchange-striction–induced lattice distortion and Knight-shift measurements have shown that the sign of the nearest-neighbor exchange interaction in GdP and GdAs is negative (antiferromagnetic) and its volume dependence is also negative.

The phosphorus and arsenic Knight shifts in GdP and GdAs were measured between 125 and 575°K. These results are shown in Fig. 3. Because of the very large NMR linewidths ($\delta H>100$ Oe at 8 MHz), the phosphorus and arsenic NMR were not observed for $T<100$°K. Also shown in Fig. 3 are the temperature dependences of the inverse Knight-shift functions $[K(T)-K_0]^{-1}$. It is to be noted in Fig. 3 that the Knight shifts are now negative (compare with Fig. 1). This result is a consequence of the fact that the Landé *g* factor g_J for gadolinium (and the elements to the right of it on the Periodic Table) have $g_J>1$. The elements to the left of gadolinium have $g_J<1$. Hence, as can be seen in Eq. (3.3), the Knight-shift contribution $K_f(T)$ should reverse sign at gadolinium, assuming the same sign for H^{hf}, i.e., Γ. (The negative Knight shifts in EuP are a result of a different mechanism and are discussed in the paragraphs on europium.)

As can be seen from the figure, there is good agreement between the calculated (solid lines) and observed temperature dependences. The least-squares parameters were Γ and θ, and the best fit for GdP was obtained with $\Gamma=-(0.08\pm0.02)$ eV and $\theta=-(22.4\pm1.2)$°K; for GdAs, with $\Gamma=-(0.28\pm0.02)$ eV and $\theta=-(32.6\pm3.2)$°K.

The least-squares determinations of the Curie-Weiss temperature θ are in agreement with the previously

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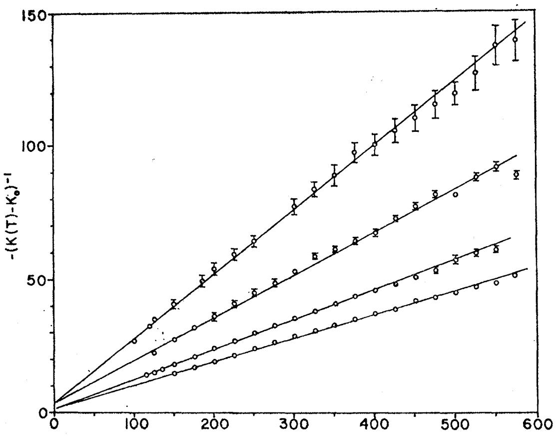

FIG. 5. Temperature dependences of the inverse Knight-shift functions $[K(T)-K_0]^{-1}$ for, from top to bottom, ErP, HoP, DyP, and TbP. The straight lines drawn through the data points are a result of the least-squares program which gave the curves shown in Fig. 4.

quoted values of $\theta(\text{GdP})=-25$°K and $\theta(\text{GdAs})=-35$°K, which were obtained[66] by drawing a straight line through a $[K(T)-K_0]^{-1}$-versus-T plot and extrapolating to zero.

Terbium. Paramagnetic susceptibility measurements[1,56,59,60,62–65] on the terbium Group-V*A* compounds have shown that $\chi(T)$ exhibits Curie-Weiss behavior. The reported values for the Curie-Weiss temperature θ and the effective number of Bohr magnetons vary over a fairly wide range. For example, the reported effective number of Bohr magnetons for TbP range from 9.2 to 9.6, compared with the Tb^{3+} free-ion value of 9.72. All of the terbium Group-V*A* compounds order[3] at low temperatures with transition temperatures of 40, 8, 9, and 10°K, respectively, for TbN, TbP, TbAs, and TbSb.

The nitrogen Knight shift in TbN has been measured[67] at 300 and 77°K; however, an analysis of these data in terms of the uniform conduction-electron spin-polarization model was not made. The method of performing this calculation and the estimate $\Gamma\simeq-0.2$ eV for TbN is presented in Sec. VI.

The phosphorus Knight shift in TbP was measured between 150 and 575°K, and the results are shown in Fig. 4. The temperature dependence of the inverse Knight-shift function $[K(T)-K_0]^{-1}$ for TbP is shown in Fig. 5. The agreement between the measured and calculated (solid lines) temperature dependence of the phosphorus Knight shift in TbP is good. The least-squares parameters Γ and θ for TbP were found to be $\Gamma=-(0.31\pm0.05)$ and $\theta=-(15.6\pm2.8)$°K.

Dysprosium. Paramagnetic susceptibility measurements[1,54,56,59,60,62–65] on the dysprosium Group-V*A* compounds have shown that the susceptibilities $\chi(T)$ obey a Curie-Weiss law. The effective number of Bohr magnetons μ_{eff} and the Curie-Weiss temperature θ vary, respectively, from 9.9 to 10.22 and 2 to 8°K. The dysprosium free-ion value is $\mu_{\text{eff}}=10.64$. These compounds order magnetically[3] at low temperatures, with ordering temperatures of approximately 10°K.

The phosphorus Knight shift in DyP was measured between 100 and 500°K, and the temperature dependence of $K(T)$ is shown in Fig. 4. The temperature dependence of the inverse Knight-shift function $[K(T)-K_0]^{-1}$ for DyP is shown in Fig. 5. The least-square parameters for DyP were found to be $\Gamma=-(0.27\pm0.04)$ eV and $\theta=-(10.5\pm1.6)$°K.

Holmium. Paramagnetic susceptibility measurements[1,54,56,59,60,62–64,68] ($T<300$°K) on the holmium Group-V*A* compounds have shown that the susceptibility $\chi(T)$ obeys a Curie-Weiss law. The reported Curie-Weiss temperature for HoP is of the order of 5°K. The effective number of Bohr magnetons in HoP ranges from 10.2 to 10.4 compared to the Ho^{3+} free-ion value of 10.61. These holmium Group-V*A* compounds order magnetically[3] at low temperatures with transition temperatures T_C of 12, 6, 5, and 6°K, respectively, for HoN, HoP, HoAs, and HoSb. Neutron diffraction studies[3] of HoP in the ordered state show an interesting noncollinear magnetic structure. The Ho^{3+} magnetic moments are aligned ferromagnetically in (111) planes, with the direction of the Ho^{3+} moment alternating from [100] to [010] for alternating (111) sheets. This structure has been subsequently referred to as the HoP-type of magnetic ordering.

The phosphorus Knight shift in HoP was measured between 125 and 550°K and the results are shown in Fig. 4. The temperature dependence of the inverse Knight-shift function $[K(T)-K_0]^{-1}$ for HoP is shown in Fig. 5. The agreement between the calculated (solid lines) and measured Knight shifts is good. The

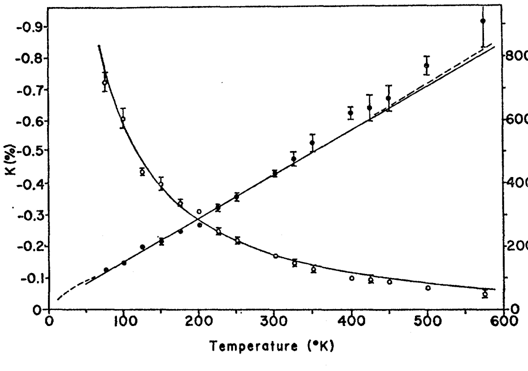

FIG. 6. Temperature dependences of the phosphorus Knight shift $K(T)$ and inverse Knight-shift function $[K(T)-K_0]^{-1}$ for YbP. The solid lines are a result of a least-squares fit of Eq. (3.8) to the Knight-shift data using a Curie-Weiss law for $\chi_f(T)$. The dashed line is the least-squares fit when a crystal-field splitting of $\Delta/k\simeq450$° invoked for the Yb^{3+} ion (see text).

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least-squares parameters for HoP were found to be $\Gamma = -(0.24 \pm 0.04)$ eV and $\theta = -(22.3 \pm 5.9)°\mathrm{K}$.

Erbium. Magnetic susceptibility measurements[1,54,56,59,60,62–64] on the erbium Group-V*A* compounds have shown that the paramagnetic susceptibilities $\chi(T)$ obey a Curie-Weiss law. The reported effective number of Bohr magnetons varies from 9.3 to 10.5 for these compounds, which is to be compared with the Er^{3+} free-ion value of 9.58. The erbium Group-V*A* compounds are observed to order magnetically[3] at low temperatures with transition temperatures of 6, 4, 4, 4, and 4°K, respectively, for ErN, ErP, ErAs, ErSb, and ErBi. The details of the various kinds of magnetic order have been discussed by Child *et al.*[3]

The phosphorus Knight shift in ErP was measured between 100 and 575°K, and the results are shown in Fig. 4. The temperature dependence of the inverse Knight-shift function $[K(T) - K_0]^{-1}$ for ErP is shown in Fig. 5. The least-squares parameters for ErP were found to be $\Gamma = -(0.23 \pm 0.04)$ eV and $\theta = -(14.9 \pm 2.5)°\mathrm{K}$.

Ytterbium. Interpretations of paramagnetic susceptibility measurements of ytterbium Group-V*A* compounds have been based on two assumptions, which are that the susceptibility data exhibit either Curie-Weiss behavior[1,6,28] or effects due to large crystal-field interactions.[63,69] Junod *et al.*[70] have claimed that in order to explain the temperature dependence of their susceptibility data, the effect of the sixfold cubic crystal-field interaction must be included. These data were taken for $T < 300°\mathrm{K}$, and the reported over-all crystal-field splittings were of the order of 400–500°K for YbP and YbAs. Iandelli[1] and Bruzzone *et al.*[28] performed their susceptibility measurements between 77 and 475°K and found Curie-Weiss behavior for $\chi(T)$ over the entire temperature range. Furthermore, the measured effective number of Bohr magnetons is of the order of 4.5, compared to the Yb^{3+} free-ion value of 4.54. For a sixfold cubic crystal-field interaction in these compounds, the expected low temperature ($T \ll \Delta$) effective number of Bohr magnetons is 2.51. However, for $T \simeq 100 - 300°\mathrm{K}$, the effective number of Bohr magnetons is of the order of 4 for $\Delta \simeq 400°\mathrm{K}$. The Curie-Weiss interpretation of the data gave Curie-Weiss temperatures of $\theta \simeq -26$, -30, and $-30°\mathrm{K}$, respectively, for YbP, YbAs, and YbSb.

It is interesting to note here that the ytterbium ion in the ytterbium Group-V*A* intermetallic compounds behaves magnetically as a Yb^{3+} configuration. In other rare-earth intermetallic compounds, such as the monochalcogenides and dialuminides, the ytterbium is nonmagnetic, i.e., the number of $4f$ electrons is given by assuming a Yb^{2+} ion.

The phosphorus Knight shift in YbP was studied between 76 and 575°K, and the results are shown in Fig. 6. Also shown in Fig. 6 is the temperature dependence of the inverse Knight-shift function $[K(T) - K_0]^{-1}$ for YbP. The Knight-shift data were analyzed for two cases: (1) a large crystal-field interaction $\Delta/k \simeq 450°\mathrm{K}$, with exchange, and (2) Curie-Weiss behavior for $\chi_f(T)$. A least-squares fit of Eq. (3.8) to the Knight-shift data for case (1) is shown in Fig. 6 as the dashed line. The variable parameters were θ and Γ with $\Delta/k = 450°\mathrm{K}$. If the over-all crystal-field splitting Δ was allowed to vary, the least-squares fit yielded inconclusive results because of a large error to Δ. Thus, the crystal-field splitting reported by Junod *et al.*[70] was used as a fixed parameter and the best fit occurred with $\theta = +(11 \pm 50)°\mathrm{K}$ and $\Gamma = -(0.23 \pm 0.04)$ eV.

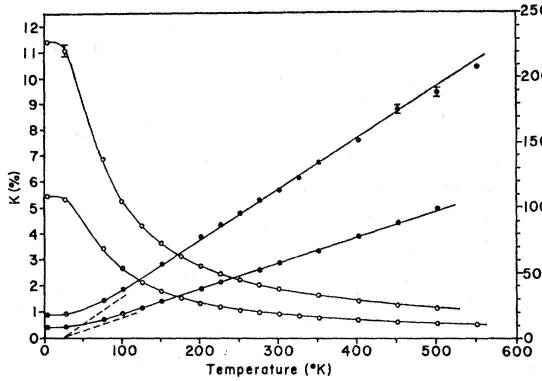

FIG. 7. Temperature dependences of the phosphorus and arsenic Knight shifts $K(T)$ and inverse Knight-shift functions $[K(T) - K_0]^{-1}$ for PrP and PrAs. The upper Knight shift and lower inverse Knight-shift data are for PrAs. The curves are a result of a least-squares fit of Eq. (3.8) to the Knight-shift data, using Eq. (5.1) for $\chi_f(T)$.

The solid curves in Fig. 6 are the result of assuming a Curie-Weiss law for $\chi(T)$. It is evident that the Curie-Weiss or the crystal-field forms for the Knight shift yield negligible differences. Apparently, these Knight-shift data do not extend to high enough (or low enough) temperatures to differentiate between the two cases. The best fit for the Curie-Weiss form for the susceptibility occurred with $\theta = -(11 \pm 8)°\mathrm{K}$ and $\Gamma = -(0.24 \pm 0.04)$ eV.

An expression for $\chi_f(T)$, showing the effect of the crystal-field interaction, will not be presented since there is no unique fit to the Knight-shift data for either type I or II.

The differences in the s-f exchange energy, calculated for the two different forms for the susceptibility, are small. Thus, it appears that in order to assess the importance of the crystal-field interaction in YbP, more Knight-shift and/or paramagnetic susceptibility data must be taken at both lower and higher temperatures.

2. *Singlet Ground-State Systems*

Praseodymium. Magnetic susceptibility measurements[54–56,59,61,70,71] between 4 and 300°K on the praseo-

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[69] J. F. Miller and R. C. Himes, in *Rare Earth Research*, edited by E. V. Kleber (The Macmillian Co., New York, 1961).

[70] P. Junod, A. Menth, and O. Vogt, Phys. Letters **23**, 626 (1966).

[71] D. P. Schumacher and W. E. Wallace, J. Appl. Phys. **36**, 984 (1965).

dymium compounds show that at high temperatures, the paramagnetic susceptibilities $\chi(T)$ obey Curie-Weiss laws, while at low temperatures, $\chi(T)$ is temperature-independent. Since the Pr^{3+} ground state $({}^3H_4)$ has an integer J, Kramer's theorem does not apply and hence the crystal-field interaction can give rise to a singlet ground state. As is well known, a Van Vleck temperature-independent magnetization can be induced in the singlet ground state at low temperature. The paramagnetic susceptibility data for PrP and PrAs have been analyzed, including the effect of the crystal-field interaction.[55,56,70] The over-all crystal-field splittings (Δ/k) were found to be in the range of 150–250°K. Tsuchida and Wallace[54,55] also included an exchange interaction in the analysis of their susceptibility data and found that $\theta \simeq -4$ and -8°K, respectively, for PrP and PrAs. The effective number of Bohr magnetons μ_{eff} were of the order of 3.8, which is to be compared to the Pr^{3+} free-ion value of 3.58.

The praseodymium NMR in PrP and PrAs have been previously reported[42] for the temperature range of 1–76°K. The temperature dependences of the praseodymium NMR frequency shifts $(\Delta H/H)$ were found to be the same as the phosphorus and arsenic Knight shifts over the same temperature range, thus showing that the nonmagnetic constituent Knight shift, such as phosphorus, is proportional to the rare-earth $4f$ electronic susceptibility.

The phosphorus and arsenic Knight shifts $K(T)$ in PrP and PrAs were measured between 1 and 600°K and these results are shown in Fig. 7. Also shown in Fig. 7 are the Knight-shift functions $[K(T)-K_0]^{-1}$ plotted as a function of temperature. The Knight-shift data at low temperatures are temperature-independent, in accord with expectations based on the susceptibility data.

In order to use Eq. (3.8) to fit the Knight-shift data, an expression for $\chi_f(T)$ for a Pr^{3+} ion in a fourth-order sixfold cubic crystal-field will now be given. Penny and Schlapp[72] have calculated $\chi_f(T)$ for this case and including exchange

$$\chi_f(T)=C_M\{[T/f(T)]-\theta\}^{-1}, \tag{5.1}$$

where $C_M=1.60$ for the Pr^{3+} ion and

$$f(T)=A(T)/B(T), \tag{5.2}$$

with

$$A(T)=\frac{360}{7}+\left(\frac{y}{2}+\frac{1647}{28}\right)e^{-(7/27)y}-\frac{432}{5}e^{-(12/27)y}+\left(\frac{25}{2}y-\frac{477}{20}\right)e^{-y} \tag{5.3}$$

and

$$B(T)=(20/3)y(1+3e^{-(7/27)y}+2e^{-(12/27)y}+3e^{-y}), \tag{5.4}$$

where $y=\Delta/kT$ and Δ is the over-all crystal-field splitting.

A least-squares fit of Eq. (3.8) to the Knight-shift data in PrP and PrAs was accomplished using the expression for $\chi_f(T)$ given in Eq. (5.1) with Δ, θ, and Γ as variable parameters. The curves drawn through the data shown in Fig. 7 are least-squares fits giving parameters for PrP of $\Delta/k=(523\pm14)$°K, $\theta=+(21.5\pm1.2)$°K, $\Gamma=-(0.68\pm0.11)$ eV, and for PrAs, $\Delta/k=(491\pm7)$°K, $\theta=+(19.5\pm1.2)$°K, and $\Gamma=-(0.50\pm0.03)$ eV.

The dashed-line portions of the $[K(T)-K_0]^{-1}$-versus-temperature graphs of Fig. 7 are the expected temperature dependences for a Curie-Weiss law only. The Curie-Weiss temperatures θ for PrP and PrAs are thus seen to be positive and of the order of 20°K. From Fig. 7 it can be seen that if a straight line were drawn *through* the high-temperature $[K(T)-K_0]^{-1}$ data and extrapolated to low temperatures, smaller values of θ would result for both PrP and PrAs. Furthermore, if only the data for $T<300$°K were used in a similar manner, negative values for the Curie-Weiss temperatures θ would result. Thus, if this procedure is used to determine the Curie-Weiss temperatures θ for PrP and PrAs, erroneous conclusions regarding the magnitude of the over-all crystal-field splitting Δ can result. When the $T=0$°K value for the paramagnetic susceptibility, which depends only upon Δ and θ [see Eq. (5.1)], is used, the negative Curie-Weiss temperatures θ will result in a smaller value for Δ than for positive values of θ. Thus, the difference between the Knight shift and paramagnetic susceptibility determined values for the over-all crystal-field splitting Δ is probably a result of the smaller temperature range for which the susceptibility measurements were made. It should be remarked here that a straight line *can* be drawn in a $K(T)$-versus-$\chi(T)$ graph for PrP and PrAs. This result indicates that the above conclusions regarding the magnitudes of θ and Δ are valid.

Thulium. Of all the rare-earth VA intermetallic compounds, the magnetic properties of the thulium compounds probably have been studied the most extensively. Paramagnetic susceptibility measurements[1,2,56,59,61,70,71,73–77] on these thulium compounds have shown that for the room-temperature region $\chi(T)$ obeys a Curie or Curie-Weiss law, while at low temperatures $\chi(T)$ is temperature-independent. This temperature independence for $\chi(T)$ is also easily understandable in terms of a singlet ground state which is a result of the sixfold cubic crystal-field interaction upon the Tm^{3+} ${}^3H_6$ ground state.

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[72] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932).

[73] B. R. Cooper, I. S. Jacobs, R. C. Fedder, J. S. Kouvel, and D. P. Schumacher, J. Appl. Phys. **37**, 1384 (1966).

[74] G. Busch, A. Menth, O. Vogt, and F. Hulliger, Phys. Letters **19**, 622 (1966).

[75] B. R. Cooper, Phys. Letters **22**, 24 (1966).

[76] B. R. Cooper, Phys. Letters **22**, 244 (1966).

[77] O. Vogt, and B. R. Cooper, J. Appl. Phys. **39**, 1202 (1968).

It is interesting to note here that the thulium Group-V*A* compounds do not order magnetically, while the analogous $J=6$ terbium and holmium compounds do order. This effect has been attributed[78] to the small $S=1$ spin component of J for thulium compared to the $S=3$ and $S=2$ spin components of J for terbium and holmium, respectively. Thus, since the exchange energy between rare-earth spins is proportional to $(\mathbf{S}\cdot\mathbf{S})$, the exchange energy for thulium is expected to be about a factor of 9 smaller than for terbium. Cooper[78] has analyzed in detail the conditions for magnetic ordering in these thulium compounds in the presence of large crystal-field interactions.

Cooper[75] has also performed an analysis of the TmP, TmAs, and TmSb paramagnetic susceptibility data in terms of a crystal-field interaction model. Excellent agreement between the calculated and observed temperature dependence of the paramagnetic susceptibility of a single crystal of TmSb was obtained using an over-all crystal-field splitting $\Delta/k=225°\text{K}$.[79] For TmSb, there was no indication from the paramagnetic susceptibility data that there was any significant exchange interaction, i.e., the high-temperature susceptibility exhibited Curie-law behavior. For the compounds TmP and TmAs, Cooper[75] found values for Δ/k of 246 and 274°K, respectively. Previous resonance studies in the thulium Group-V*A* compounds have consisted of (a) nitrogen NMR in TmN,[67] (b) Tm^{3+} electron spin resonance in an excited crystal-field state in TmN,[80] and (c) thulium NMR data in TmP, TmAs, and TmSb.[42] The nitrogen NMR data[67] in TmN were not analyzed; however, the calculation for $\Gamma\simeq-0.1$ eV in terms of the uniform polarization model for TmN is presented in Sec. VI.

Before presenting the results of the Knight-shift measurements, it is convenient at this time to write an expression for $\chi(T)$ which includes crystal-field effects. Neglecting exchange interactions for the present, a calculation gives, assuming only fourth-order crystal-field terms,

$$\chi_f(T)=(2Ng_J^2\mu_B^2/Z)[\chi_0e^{-E_0/kT}+\chi_1e^{-E_1/kT}+\chi_2e^{-E_2/kT}+\chi_3e^{-E_e/kT}+\chi_4e^{-E_4/kT}+\chi_5e^{-E_5/kT}], \quad (5.5)$$

where

$$\chi_0=14/(E_1-E_0), \quad (5.6)$$

$$\chi_1=\frac{1}{4kT}+\frac{24.92}{E_2-E_1}+\frac{0.58}{E_4-E_1}-\frac{14}{E_1-E_0}+\frac{2}{E_5-E_1}, \quad (5.7)$$

$$\chi_2=\frac{3.79}{kT}-\frac{24.92}{E_2-E_1}+\frac{5.29}{E_4-E_2}+\frac{4.42}{E_3-E_2}+\frac{0.18}{E_5-E_2}, \quad (5.8)$$

$$\chi_3=9.58/(E_4-E_3)-4.42/(E_3-E_2), \quad (5.9)$$

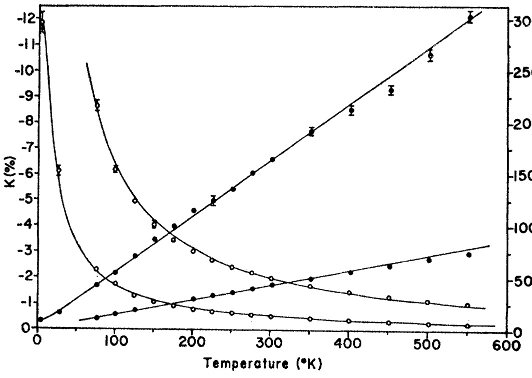

FIG. 8. Temperature dependences of the phosphorus and antimony Knight shifts $K(T)$ and inverse Knight-shift functions $[K(T)-K_0]^{-1}$ for TmP and TmSb. The upper Knight shift and lower inverse Knight-shift data are for TmSb. The curves are a result of a least-squares fit of Eq. (3.8) to the Knight-shift data using Eq. (5.5) for $\chi_f(T)$.

$$\chi_4=\frac{0.37}{kT}-\frac{0.58}{E_4-E_1}-\frac{5.29}{E_4-E_2}-\frac{9.58}{E_4-E_3}+\frac{25.82}{E_5-E_4}, \quad (5.10)$$

$$\chi_5=-0.18/(E_5-E_2)-25.82/(E_5-E_4)-2/(E_5-E_1), \quad (5.11)$$

and

$$Z=e^{-E_0/kT}+3e^{-E_1/kT}+3e^{-E_2/kT}+e^{-E_3/kT}+3e^{-E_4/kT}+2e^{-E_5/kT}, \quad (5.12)$$

where E_0, E_1, E_2, E_3, E_4, and E_5 are the energies of the Γ_1, Γ_4, $\Gamma_5^{(2)}$, Γ_2, $\Gamma_5^{(1)}$, and Γ_3 crystal-field states of the Tm^{3+} $^3H_6$ ion. The calculation for $\chi_f(T)$ is based on the energy eigenvalues and eigenfunctions given by Lea, Leask, and Wolf.[81] The order of the energy levels for a sixfold cubic crystal-field interaction is such that $E_0<E_1<E_2$, etc. The over-all crystal-field splitting Δ is defined as $\Delta=E_5-E_0$.

The phosphorus, arsenic, and antimony Knight-shift data in TmP, TmAs, and TmSb are shown in Figs. 8 and 9. The inverse temperature dependence of the Knight-shift functions $[K(T)-K_0]^{-1}$ are also shown in Figs. 8 and 9. The arsenic NMR in TmAs was observable at 4°K; however, for some inexplicable reason, the phosphorus NMR could not be observed below 27°K in two different samples of TmP. The expected (see Sec. V B on linewidths) phosphorus NMR linewidth at $T=4°\text{K}$ and $H\simeq1$ kOe is such that the NMR should be observable; in fact, its NMR linewidth should be less than the arsenic NMR linewidth observed under similar conditions.[82]

In order to obtain a meaningful interpretation of the TmP Knight-shift data in terms of the crystal-field interaction, low-temperature phosphorus NMR data is required. As previously mentioned, the temperature

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[78] B. R. Cooper, Phys. Rev. **163**, 444 (1967).

[79] O. Vogt and B. R. Cooper, J. Appl. Phys. **39**, 1202 (1968).

[80] B. R. Cooper, R. C. Fedder, and D. P. Schumacher, Phys. Rev. Letters **18**, 744 (1967).

[81] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

[82] The expected phosphorus NMR linewidth at 4°K is about 100 G.

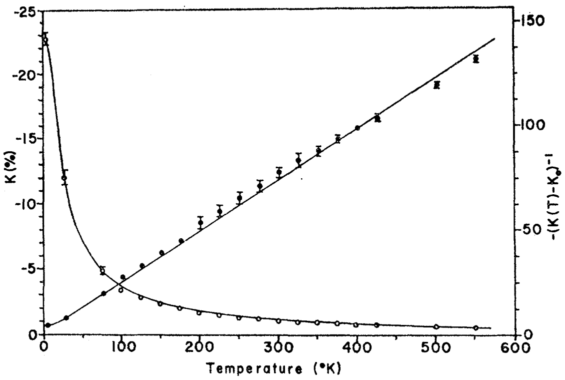

FIG. 9. Temperature dependences of the arsenic Knight shift $K(T)$ and inverse Knight-shift function $[K(T)-K_0]^{-1}$ in TmAs. The curve (and straight line) drawn through the Knight-shift data is a result of a least-squares fit of Eq. (3.8) using Eq. (5.5) for $\chi_f(T)$.

dependence of the thulium and arsenic NMR frequency shifts in TmAs were found to be equal,[42] within experimental error. Therefore, a knowledge of the temperature dependence of the thulium NMR frequency shift and also the phosphorus Knight shift at 27°K can be used to predict the 4°K phosphorus Knight shift. Since the antimony NMR was not observed for $T<76$°K, a similar extrapolation procedure could not be made.

The solid lines drawn through the TmSb Knight-shift data in Fig. 8 are a result of a least-squares fit of Eq. (3.8) to the data with $\chi_f(T)$ being given by Eq. (5.5) and $\Delta/k=225$°K. Since the temperatures for which the antimony Knight shifts were measured did not extend to low enough temperatures, no attempt was made in the least-squares program to use Δ as a variable parameter. Thus, Cooper's[75] value of $\Delta/k=225$°K was used, and the least-squares fit gave $\Gamma=-(0.15\pm0.01)$ eV and $\theta=-(0.5\pm10.0)$°K for TmSb.

The solid lines drawn through the TmP and TmAs data in Figs. 8 and 9 are a result of the same least-squares fit, however, with Δ and Γ as variables. The best fit for TmP was $\Delta/k=(244\pm34)$°K and $\Gamma=-(0.19\pm0.03)$ eV, while for TmAs, $\Delta/k=(284\pm53)$°K and $\Gamma=-(0.16\pm0.01)$ eV. As can be seen from Figs. 8 and 9, the agreement between the observed and calculated Knight shifts in these compounds is good.

Including an exchange interaction did not appreciably alter the results; for example, for TmAs it was found $\theta=(0\pm3)$°K. The Knight shift derived values for Δ and θ for these compounds are in good agreement with Cooper's[75] susceptibility derived values.

3. *Manifestations of Thermally Populated Excited States*

Samarium. Paramagnetic susceptibility measurements[1,54] on SmP, SmAs, SmSb, and SmBi have been performed; however, no attempt was made to analyze these data in terms of crystal-field interactions, etc. Since the energy separation between the two lowest spin-orbit J states is approximately 1500°K, it has been shown by White and Van Vleck[83] that $\langle S_z(T)/H\rangle$ is not proportional to the paramagnetic susceptibility $\chi_f(T)$. Hence, the Knight-shift measurements, which are proportional to $\langle S_z(T)\rangle$, will not measure the same quantity as the paramagnetic susceptibility data. However, all of the parameters necessary to analyze the susceptibility data are also determined from an analysis of the Knight-shift data, and therefore the two different kinds of experimental measurements can complement each other.

White and Van Vleck[83] were also the first to note that the expectation value of the Sm^{3+} spin $\langle \mathbf{S}(T)\rangle$ will reverse sign at $T\simeq300$°K. This reversal in the sign of $\langle \mathbf{S}(T)\rangle$ results from the fact that the spin component of the Sm^{3+} ${}^6H_{7/2}$ excited state is antiparallel to the applied magnetic field. Hence, these two principal contributions to $\langle \mathbf{S}(T)\rangle$ will cancel at some temperature T. This expectation was verified by the preliminary

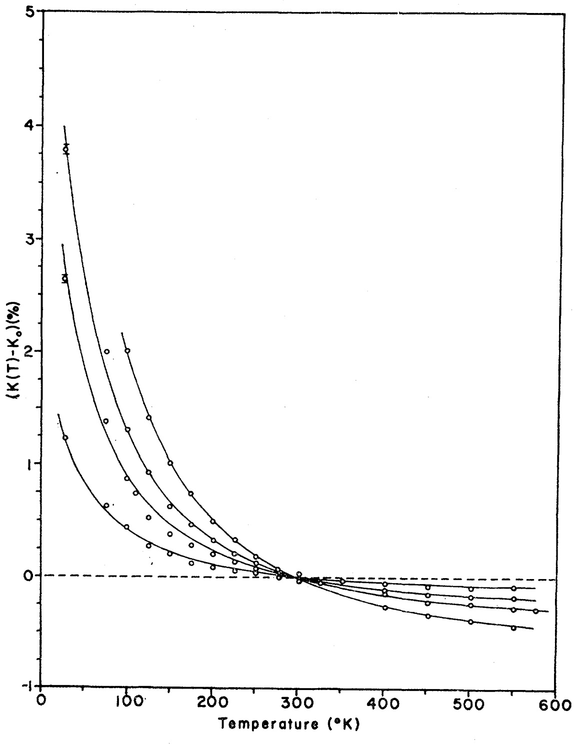

FIG. 10. Temperature dependences of the phosphorus, arsenic, antimony, and bismuth Knight shifts in SmP, SmAs, SmSb, and SmBi. The order, from top to bottom, for the curves in the positive Knight-shift region of the figure is, respectively, for SmBi, SmSb, SmAs, and SmP. For the negative Knight-shift region of the figure the order from top to bottom is reversed. In order to show the reversal at $T\cong300$°K for $K_f(T)$, the Knight shift K_0 was subtracted from $K(T)$ for each compound. The solid curves drawn are a result of a least-squares fit of Eqs. (5.13) and (5.16) to the Knight-shift data.

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[83] J. A. White and J. H. Van Vleck, Phys. Rev. Letters **6**, 412 (1961).

Knight-shift data in $SmAl_2$,[84] and also in the samarium Group-V*A* intermetallic compounds.[15]

Before presenting the Knight-shift data, an expression for $\langle \mathbf{S}(T)\rangle$ will be given. Neglecting, for the moment, crystal-field interactions, a first-order calculation for the Sm^{3+} average spin $\langle \mathbf{S}\rangle$ gives

$$\langle S_z(T)\rangle/\mu_B H = Z^{-1}\left\{\frac{25}{7kT}-\frac{120}{7E_1}+e^{-E_1/kT}\right.$$
$$\left.\times\left[\frac{1144}{189kT}+\frac{120}{7E_1}-\frac{728}{27(E_2-E_1)}\right]+\cdots\right\}, \tag{5.13}$$

where

$$Z=6+8e^{-E_1/kT}+\cdots, \tag{5.14}$$

and where $E_1/k \simeq 1500°K$ and $E_2/k \simeq 3400°K$ are the energies of the first- and second-higher-lying J states measured with respect to the $^6H_{5/2}$ ground state. The sign convention used in Eq. (5.13) is for $\langle S_z\rangle$ parallel to H taken to be positive. Note that the coefficients of the first two terms of Eq. (5.13) have opposite signs and to lowest order, $\langle \mathbf{S}\rangle = 0$ for $T \simeq 300°K$.

The effect of a sixfold cubic crystal-field interaction is to split the $^6H_{5/2}$ Sm^{3+} ground state into two energy levels: a doublet (Γ_7) and a quartet (Γ_8). Therefore, to lowest order, the effect of the crystal-field interaction is to multiply the first T^{-1} term in Eq. (5.13) by a function $f(T)$, where

$$f(T)=\frac{5+26e^{-x}+(32/x)(1-e^{-x})}{21(1+2e^{-x})}, \tag{5.15}$$

with $x=\Delta/kT$ and Δ the energy separation between the doublet (Γ_7) and quartet (Γ_8) energy levels. For the case where the doublet lies lowest in energy, x is positive; if the quartet is lowest, x is negative.

TABLE III. Temperature-dependent Knight shifts $[K(T)-K_0]$ normalized to 100°K for SmP, SmAs, SmSb, and SmBi.

T (°K)	SmP	SmAs	SmSb	SmBi
100	1.00	1.00	1.00	1.00
125	0.61	0.60	0.71	0.70
150	0.46	0.44	0.48	0.50
175	0.27	0.32	0.36	0.37
200	0.18	0.23	0.25	0.24
225	0.11	0.15	0.16	0.16
250	0.01	0.08	0.10	0.09
275	0.00	0.01	0.05	0.04
300	0.00	0.00	0.02	−0.02
325	···	−0.03	···	−0.03
350	−0.08	···	···	···
400	−0.14	−0.14	−0.12	−0.13
450	−0.21	−0.18	−0.18	−0.17
500	−0.23	−0.21	−0.22	−0.19
550	−0.22	−0.22	−0.22	−0.22

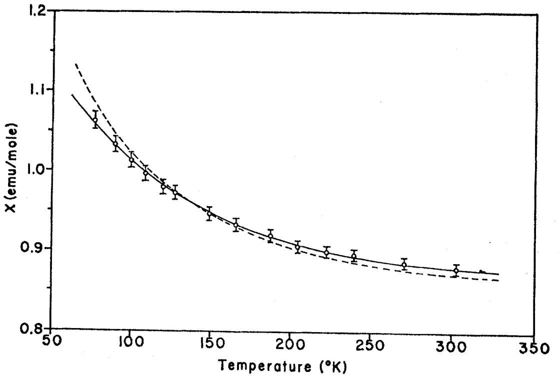

FIG. 11. Temperature dependence of the paramagnetic susceptibility $\chi(T)$ for SmAs. The dashed line is the best-fit curve using the Knight-shift–determined parameters for Δ and E_1 and Eq. (5.18). The solid line is a least-squares fit of Eq. (5.18) to the susceptibility data with variable parameters μ_{eff} and Δ.

Therefore, for the samarium (and europium) Group-V*A* compounds, the Knight shift $K(T)$ is given by

$$K(T)=K_0[1-\Gamma\langle S(T)\rangle/2\mu_B H], \tag{5.16}$$

with $\langle S(T)\rangle$ for the samarium compounds given by Eq. (5.5). Because $\langle \mathbf{S}(T)\rangle = 0$ at $T \simeq 300°K$, the crossover point provides a reasonable estimate for K_0, since $K(T)=K_0$ at $T \simeq 300°K$.

Figure 10 shows the temperature dependences of the Knight shifts in SmP, SmAs, SmSb, and SmBi in the range of 27–550°K. In order to emphasize graphically the reversal in the sign of the Knight-shift contribution $K_f(T)$ at $T \simeq 300°K$, the Knight-shift contribution K_0 for each compound has been subtracted from $K(T)$. As is evident from Fig. 10, the values for K_0 derived from the nonmagnetic compounds (Sec. IV) are reasonable. Furthermore, as seen in Table III, the Knight shifts for these compounds have essentially identical temperature dependences between 100 and 600°K. Thus, these Knight-shift data provide evidence that the assumption concerning the constancy of K_0 across the rare-earth series of compounds is not unreasonable.

The Knight-shift data shown in Fig. 10 were analyzed in the following manner. The energy separation E_1 between the $J=\frac{5}{2}$ and $J=\frac{7}{2}$ states of the S Sm^{3+} ion is not expected to vary significantly between the various compounds. Thus, a least-squares fit of Eq. (5.13) and (5.16) to the data was performed for each compound with variable parameters Γ, E_1, and Δ. Since the value for E_1 depends critically upon the choice of K_0 [note that the condition $K(T)=K_0$ at $T \simeq 300°K$ determines E_1], the Knight shifts K_0 were allowed to vary within their specified error limits. In this manner, the dependence of E_1 on K_0 was determined for each compound. The average value for all of the compounds $[E_1/k = (1405 \pm 15)°K]$ was then taken to be the same for SmP, SmAs, SmSb, and SmBi. The least-squares fit of Eq. (5.16) to the NMR data was then rerun with variable parameters Γ and Δ.

The curves drawn through the data in Fig. 10 are a result of the least-squares fit with the following parameters: for SmP, $\Delta/k = (130 \pm 11)°K$, $\Gamma = -(0.35 \pm 0.06)$

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[84] V. Jaccarino, quoted by Ref. 83.

eV; for SmAs, $\Delta/k=(118\pm13)$°K, $\Gamma=-(0.28\pm0.02)$ eV; for SmSb, $\Delta/k=(122\pm8)$°K, $\Gamma=-(0.22\pm0.01)$ eV; for SmBi, $\Delta/k=(121\pm18)$°K, and $\Gamma=-(0.36\pm0.01)$ eV. These results are tabulated for convenience in Table V, Sec. VI.

The effect of including an exchange interaction between the Sm^{3+} spins in Eq. (5.13) was investigated; however, the results were insensitive to this interaction. For example, for SmP, the molecular field approximated exchange energy was found to be $\lambda\mu_B/k\simeq+(1.0\pm10)$°K. Since the errors in $\lambda\mu_B/k$ were very large, this interaction will not be considered. The insensitivity of the Knight-shift data to the exchange interaction is probably due to the fact that insufficient data were taken for $T\ll\Delta/k$. Evidence that the exchange interaction is important at low temperatures is offered by the preliminary observation[44] that these compounds magnetically order at $T\simeq3$°K.

It should be mentioned here that the expectation value of the angular momentum component $\langle\mathbf{L}\rangle$ of the total angular momentum $\langle\mathbf{J}\rangle$ also reverses sign as a function of temperature for the same reason that $\langle\mathbf{S}\rangle$ does. To lowest order, a calculation for $\langle L_z\rangle$ gives

$$\langle L_z\rangle=-\mu_B H(10/7kT-20/7E_1). \tag{5.17}$$

The minus sign indicates that the temperature-dependent ${}^6H_{5/2}$ ground-state contribution to $\langle\mathbf{L}\rangle$ is antiparallel to the applied magnetic field H, i.e., parallel to $\mathbf{J}$. Equation (5.17) shows that $\langle\mathbf{L}\rangle=0$ at $T=\frac{1}{2}E_1$, or about 700°K, which is significantly different from the temperature at which the Knight shifts reverse sign (Fig. 10). Hence, the Knight shifts do not have any substantial contribution due to the orbital angular momentum $\langle\mathbf{L}\rangle$, but rather involve only the spin component $\langle\mathbf{S}\rangle$ of the total angular momentum $\langle\mathbf{J}\rangle$.

An expression for the paramagnetic susceptibility $\chi_f(T)$ for a Sm^{3+} ion and a cubic crystal-field interaction has been previously calculated,[83] with the result that for relatively low temperatures ($T<350$°K)

$$\chi_f(T)=C_M\left[\frac{f(T)}{T}+\frac{12}{E_1/k}\right], \tag{5.18}$$

where $C_M=0.089$ for the Sm^{3+} $J=\frac{5}{2}$ ground state and the effect of the crystal-field interaction is contained in $f(T)$ [Eq. (5.15)].

The paramagnetic susceptibility for SmAs was measured[47] as a function of temperature between 77 and 300°K; and the results, corrected for diamagnetism ($\chi_{\mathrm{dia}}\simeq-60\times10^{-6}$ emu/mole for SmAs),[85] are shown in Fig. 11. The experimental uncertainties were conservatively estimated to be ±2% of the total susceptibility $\chi(T)$. The dashed curve drawn through the data shown in Fig. 11 is a least-squares fit of Eq. (5.18) to the data with a single variable parameter μ_{eff} [$C_M=\mu_{\mathrm{eff}}^2\mu_B^2J(J+1)/3k$]; the other parameters E_1 and Δ were fixed as determined by the NMR measurements. The effective number of Bohr magnetons $\mu_{\mathrm{eff}}=(0.81\pm0.03)$ for SmAs is to be compared to the free-ion ground-state value of 0.845. Presumably, the difference between the free-ion and experimentally observed values of μ_{eff} are due to the temperature-dependent contribution to the susceptibility arising from the s-f exchange-induced conduction-electron spin polarization. The agreement, using NMR-determined parameters for E_1 and Δ, between the calculated and measured susceptibilities is fair. As a further check, the least-squares fit of Eq. (5.18) to the paramagnetic susceptibility data was rerun, letting both μ_{eff} and Δ be variable parameters. The results of this calculation are shown in Fig. 11 as the solid curve. The best-fit parameters were $\Delta/k=(187\pm10)$°K and $\mu_{\mathrm{eff}}=(0.82\pm0.01)$. Because of the rather small temperature interval for which the susceptibility data were taken, it is impossible to assess at the present time the reason for the different values of Δ/k obtained from the Knight-shift and susceptibility measurements.

Europium. The magnetic properties of the Eu^{3+} spin system have attracted considerable interest since the early work of Van Vleck and his collaborators.[85–87] This interest is due to the fact that the Eu^{3+} ground state is a singlet (${}^7F_0$), and the first excited (${}^7F_1$) spin-orbit state is approximately 500°K above the ground state. To date, there do not exist any magnetic susceptibility measurements on EuP. Since the preliminary NMR work on EuP was reported,[22] further Knight-shift measurements have been made and these results, together with a least-squares fit of the theoretical expression for $\langle\mathbf{S}(T)\rangle$ of the Eu^{3+} ion, will be presented.

Neglecting the cubic crystal-field interactions for the $J=2$ state (the effect of which has been shown previously to be negligible for EuP for $T<600$°K), the average value of the Eu^{3+} spin $\langle S_z(T)\rangle$ is calculated to be

$$\frac{\langle S_z\rangle}{\mu_B H}=-(2ZE_1)^{-1}\left[\frac{16+(3y-1)e^{-y}+(15y-5/3)e^{-3y}+\cdots}{1+(\lambda\mu_B/E_1Z)[16+(y-1)e^{-y}+(5y-5/3)e^{-3y}+\cdots]}\right], \tag{5.19}$$

where

$$Z=1+3e^{-y}+5e^{-3y}+\cdots, \tag{5.20}$$

and where $y=E_1/kT$, E_1 is the energy of the ${}^7F_1$ state measured with respect to the Eu^{3+} ${}^7F_0$ ground state, and $\lambda(=H_{\mathrm{ex}}/\langle S\rangle)$ is the molecular field parameter for the exchange energy ($E_{\mathrm{ex}}=2\mu_BH_{\mathrm{ex}}S$). For the analysis

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[85] J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

[86] A. Frank, Phys. Rev. **48**, 765 (1935).

[87] W. P. Wolf and J. H. Van Vleck, Phys. Rev. **130**, 1361 (1963).

of the data presented in this paper, the Landé interval rule has been assumed to be valid. It is to be noted in Eq. (5.19) that the direction of the Van Vleck temperature-independent field induced spin in the $J=0$ ground state is antiparallel to the external field.

The phosphorus Knight shift in EuP was measured between 100 and 600°K. Because of the presence of a small amount of ferromagnetic EuO in the sample, the phosphorus NMR was not observed below 77°K. The measured phosphorus Knight shifts are plotted as a function of temperature in Fig. 12. The solid line drawn through the data in Fig. 12 is a result of a least-squares fit of Eqs. (5.16) and (5.19) to the data with variable parameters E_1, λ, and Γ. The best-fit parameters are $E_1/k=(470\pm19)$°K, $\lambda\mu_B/k=+(6.5\pm1.6)$°K, and $\Gamma=-(0.40\pm0.06)$ eV. The value for the energy separation E_1 is in good agreement with the results of susceptibility measurements in other Eu^{3+} compounds.[88] One interesting aspect of the fit shown in Fig. 12 is the apparent constancy of the s-f exchange energy Γ for the different J states. The Knight-shift measurements suggest that Γ is independent of J for intermetallic compounds, and hence Eq. (5.16) is valid as it is written. Another consequence of the good agreement between the calculated and observed temperature dependence of the phosphorus Knight-shift data is that the postulate of an Eu^{3+} ion EuP is substantiated. The nomenclature for the valence does not mean to imply that the charge of the europium ion is +3, but rather that the total number of f electrons is given by assuming this ionicity. Generally, europium seems to favor a $4f^7$ configuration (Eu^{2+}); however, for the rare-earth Group-V*A* compounds, it appears that the number of $4f$ electrons of all the rare-earth elements is given by assuming a +3 valence.

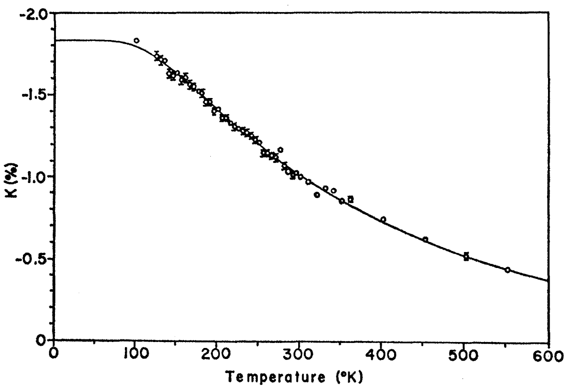

FIG. 12. Temperature dependence of the phosphorus Knight shift in EuP. The curve is a result of a least-squares fit of Eqs. (5.16) and (5.19) to the knight-shift data.

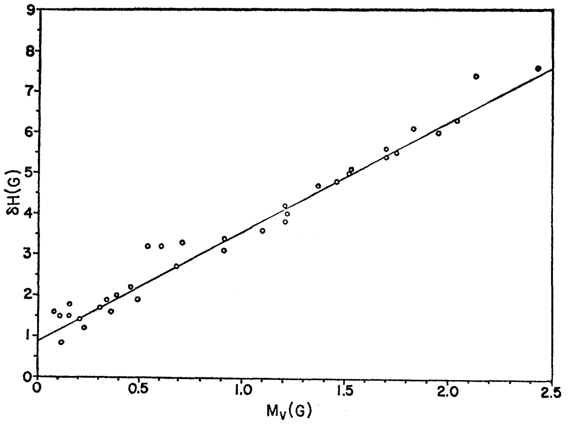

FIG. 13. Phosphorus NMR linewidth δH in CeP plotted as a function of the volume magnetization M_V for various temperatures and magnetic fields.

B. NMR Linewidths

The NMR linewidths in the magnetic rare-earth Group-V*A* compounds were found to be temperature- and magnetic-field–dependent. An analysis of these temperature and field dependences showed that the NMR linewidth δH is proportional to the magnetization of the sample, indicating that the source of the linewidth is probably due to demagnetization field effects. An example of the dependence of δH upon the volume magnetization $M_V=\chi_V H$ is shown in Fig. 13, where the phosphorus NMR linewidth δH in CeP was measured for a range of temperatures and magnetic fields. The slope of the straight line drawn through the data is 3.0, while the intercept at $M_V=0$ is $\delta H\simeq1$ G, which is in reasonable agreement with the NMR linewidths for the lanthanum compounds given in Table II. The NMR linewidths in the other rare-earth compounds were observed to behave in a similar manner to CeP. The characteristics of these NMR linewidths are generally as follows: (1) As the temperature is lowered the NMR linewidth δH increases since χ generally increases. and (2) for fixed temperature the NMR linewidth δH narrows with decreasing magnetic field. Thus, since $\chi_V\propto T^{-1}$, at lower temperatures the increased signal-to-noise ratio of the NMR signal amplitude is offset by an increasing NMR linewidth δH. A graphic example of these two competing effects has been previously reported for $GdAl_2$, where the aluminum NMR was fairly narrow at 600°K but unobservable at 300°K.[14]

Table IV contains a tabulation of the NMR linewidth data for the compounds which were studied in detail. It is evident from Table IV that the NMR linewidths are roughly given by the relationship $\delta H\simeq\pi M_V$. Thus, corrections to the measured Knight shift due to demagnetization effects are negligible. For example, in PrAs where $\alpha=6.3$, the maximum demagnetization field contribution to the arsenic Knight shift K is approximately 2.5% of K, which is less than the errors quoted for Γ of PrAs. Since the phosphorus Knight shifts are about one-half of the arsenic Knight shifts, for the same rare-earth element, the maximum errors to Γ are about 5%.

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[88] J. H. Van Vleck, J. Appl. Phys. 39, 365 (1968).

TABLE IV. NMR linewidth parameters in the magnetic rare-earth Group-VA intermetallic compounds.

Compound and nucleus	Slope $\alpha = \delta H/M_V$
CeP^{31}	3.0
PrP^{31}	4.5
PrAs^{75}	6.3
NdP^{31}	3.1
YbP^{31}	3.5

VI. DISCUSSION

A summary of the various Knight-shift parameters, obtained from an analysis of the NMR data of Sec. V, is given in Table V. Columns 1, 3, and 4 of the table are the NMR-determined Curie-Weiss temperatures θ, over-all crystal-field splittings Δ, and s-f exchange energies Γ. Columns 2 and 5 are the exchange energies $(\lambda\mu_B/k)$ and hyperfine fields per unit spin, H^{hf}.

The exchange energies $(\lambda\mu_B/k)$ listed in Table V have been calculated from the respective Curie-Weiss temperatures θ using the relationship

$$\theta = -\tfrac{2}{3}(g_J-1)^2(\lambda\mu_B/k)J(J+1). \tag{6.1}$$

No adjustments have been made for the number of neighbors contributing to the total exchange energy. The reason for the neglect of the number of neighbors is that it is not clear how many neighbor shells for rare-earth metals should be included in the definition of the Curie-Weiss temperature θ. In general, $\theta \propto \sum z_j J_j$, where z_j is the number of neighbors in the jth shell with an exchange energy J_j. From Eq. (6.1) it can be seen (remembering the standard sign conventions for θ) that $\lambda\mu_B/k<0$ means a net antiferromagnetic exchange interaction, while $\lambda\mu_B/k>0$ means a net ferromagnetic exchange interaction. The primary purpose for tabulating the various values for $\lambda\mu_B/k$ is to allow comparisons to be made with the $\lambda\mu_B/k$ values obtained from analysis of the EuP Knight-shift data where the exchange interaction could not be simply written in the form of a Curie-Weiss temperature θ.

TABLE V. Summary of Knight-shift parameters for the rare-earth Group-VA intermetallic compounds.

Compound	θ (°K)	$\lambda\mu_B/k$ (°K)	Δ/k (°K)	Γ (eV)	H^{hf} (kOe)
CeP	3.6±1.0	−30	···	−1.1 ±0.2	−57
CeAs	9.9±3.0	−83	···	−0.74±0.05	−102
PrP	21.5±1.2	−40	523±14	−0.68±0.11	−35
PrAs	19.5±1.2	−37	491± 7	−0.50±0.03	−69
NdP	8.9±0.2	− 7	···	−0.56±0.09	−29
NdAs	5.9±0.2	− 5	···	−0.42±0.03	−58
SmP	···	···	130±11	−0.35±0.06	−18
SmAs	···	···	118±13	−0.28±0.02	−39
SmSb	···	···	122± 8	−0.22±0.01	−54
SmBi	···	···	121±18	−0.36±0.01	−84
EuP	···	9	···	−0.41±0.07	−21
GdP	−22.4±1.2	2	···	−0.37±0.06	−19
GdAs	−32.6±3.2	3	···	−0.28±0.02	−39
TbP	−15.6±2.8	2	···	−0.31±0.05	−16
DyP	−10.5±1.6	2	···	−0.27±0.04	−14
HoP	−22.3±5.9	7	···	−0.24±0.04	−12
ErP	−14.9±2.5	9	···	−0.23±0.04	−12
TmP	···	···	255±92	−0.19±0.03	−10
TmAs	···	···	284±53	−0.16±0.01	−22
TmSb	···	···	225	−0.15±0.01	−37
YbP	−30.0±3.0	14	···	−0.27±0.04	−14

TABLE VI. Ratio of the s-f exchange energies Γ for the phosphides and arsenides.

Element	$\Gamma(\mathrm{As})/\Gamma(\mathrm{P})$
Ce	0.67±0.11
Pr	0.74±0.13
Nd	0.75±0.13
Sm	0.80±0.14
Gd	0.75±0.13
Tm	0.80±0.14

The values for the over-all crystal-field splittings Δ, listed in column 4 of Table V, clearly show that there is no simple dependence upon lattice constant a_0, as previously reported.[56]

It is not understood why the Curie-Weiss temperature reverses sign in going from the light to the heavy rare-earth compounds. At first glance, it is tempting to attribute this change in sign to the RKKY mechanism. Recently, Darby and Taylor[89] have used this approach and claimed to have found that the number of conduction electrons per atom Z for these compounds is a constant; and, hence, changes in the sign of the Curie-Weiss temperature θ are due to lattice-constant differences. This result is, however, inconsistent with the underlying principles of the RKKY theory. An expression for the Curie-Weiss temperature θ can be easily derived from the RKKY theory with the result[34]

$$k\theta = -3\pi^2 Z^2 \Gamma(0)^2 (g_J-1)^2 J(J+1) E_f^{-1} \times \textstyle\sum_m F(2k_F R_m), \tag{6.2}$$

where E_f is the Fermi energy, R_m is the distance between rare-earth ions, and $F(x)$ is given by Eq. (3.7). For a spherical (free-electron) Fermi surface, for which the RKKY theory is applicable, the product $k_F R_m$ is independent of the lattice constant a_0 since $k_F \propto a_0^{-1}$ and $R_m \propto a_0$. Thus, for a fixed number of conduction electrons per atom Z, the function $\sum F(2k_F R_m)$ is independent of the lattice constant a_0. Hence, for the RKKY model, the sign of the Curie-Weiss temperature is fixed and cannot reverse sign, by changing the lattice constant. Therefore, it must be concluded that the interpretations that Darby and Taylor[89] have presented are invalid, and an explanation for this phenomenon must await further theoretical considerations.

It thus appears that there does not exist any correlation between the Knight-shift data and the Curie-Weiss temperature θ using the RKKY model. This conclusion is based on the fact that the reversal in the sign of the Knight shift can be understood in terms of the Landé g factor, while reversal in the sign of the Curie-Weiss temperature is not understood.

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[89] M. I. Darby and K. N. R. Taylor, Phys. Letters **14**, 179 (1965).

TABLE VII. Comparison of s-f exchange energies Γ for various rare-earth intermetallic compounds as calculated using the uniform conduction-electron spin-polarization model for the Knight shifts. The values for Γ are expressed in units of electron volts.

	P[a]	As[a]	Sb[a]	Bi[a]	N[b]	Al_2 [c]	Al_3 [d]	B_6 [e]	Pt_2 [f]	Pt_5^{I} [g]	Pt_5^{II} [g]	Sn_3 [h]
Ce	−1.1	−0.74	⋯	⋯	⋯	−0.63	−0.41	⋯	−0.09	−0.05	−0.3	−0.14
Pr	−0.68	−0.50	⋯	⋯	⋯	−0.48	−0.35	∼−0.1	−0.1	−0.02	−0.5	−0.09
Nd	−0.56	−0.42	⋯	⋯	⋯	−0.38	−0.22	⋯	−0.08	−0.03	−0.5	−0.06
Sm	−0.35	−0.28	−0.22	−0.36	⋯	⋯	−0.21	⋯	⋯	⋯	⋯	⋯
Eu	−0.41	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯
Gd	−0.37	−0.28	⋯	⋯	⋯	−0.31	−0.23	∼−0.1	⋯	⋯	⋯	⋯
Tb	−0.31	⋯	⋯	⋯	−0.2	−0.28	−0.22	⋯	⋯	⋯	⋯	⋯
Dy	−0.27	⋯	⋯	⋯	⋯	−0.25	−0.24	⋯	⋯	⋯	⋯	⋯
Ho	−0.24	⋯	⋯	⋯	⋯	−0.38	−0.20	⋯	⋯	⋯	⋯	⋯
Er	−0.23	⋯	⋯	⋯	⋯	−0.30	−0.18	⋯	⋯	⋯	⋯	⋯
Tm	−0.19	−0.16	−0.15	⋯	−0.1	−0.29	⋯	⋯	⋯	⋯	⋯	⋯
Yb	−0.27	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯

[a] This work.
[b] Reference 76.
[c] References 9, 10, 14, and 17.
[d] References 19–21, and 23.
[e] Reference 11.
[f] Reference 24.
[g] Reference 24.
[h] References 12, 13, and 16.

The hyperfine fields per unit spin H^{hf} listed in column 5, Table VII, are defined by Eq. (3.3). An examination of the Knight shifts defined by Eqs. (3.3) and (3.5) shows that the hyperfine field H^{hf} and the s-f exchange energy Γ are related by

$$H^{\mathrm{hf}}=K_0\Gamma/2\mu_B. \tag{6.3}$$

The results of using the values for the s-f exchange energies and Eq. (6.3) to give H^{hf} are tabulated in Table V. As can be seen, using Eq. (3.3) as a definition for the hyperfine field H^{hf} results in a quantity which has the same sign (negative) for all of the rare-earth Group-VA compounds, regardless of the Landé g factor g_J. However, it must be stressed at this point, that the definition for the hyperfine field H^{hf} does not depend on the model chosen for the origin of the Knight shift while the values listed for Γ are model-dependent. Thus, Eq. (6.3) should be regarded as an expression relating the uniform conduction-electron spin-polarization s-f exchange energy Γ to the hyperfine field H^{hf} and not the reverse.

The total hyperfine field per unit spin H^{hf} is thus found to point in the same direction as the spin component of the total angular momentum $\mathbf{J}$ (opposite direction to the spin magnetization). Usually, a negative hyperfine field implies a negative Knight shift; however, for the case of the rare-earth intermetallic compounds, an understanding of the sign definition used for the hyperfine field H^{hf} is a prerequisite before predictions are made concerning the signs of prospective Knight shifts.

The Knight-shift–determined s-f exchange Γ for the rare-earth Group-VA intermetallic compounds is given in Table V, column 4. An examination of the values of Γ for the various compounds reveals an interesting result. This is shown in Table V, which lists the ratio of the arsenic to the phosphorus s-f exchange energies $\Gamma(\mathrm{As})/\Gamma(\mathrm{P})$ for the various rare-earth ions. As can be seen from Table VI, the ratios $\Gamma(\mathrm{As})/\Gamma(\mathrm{P})$ for the rare-earth ions are relatively constant, the average being 0.75±0.05. It thus appears that the s-f exchange energies, defined by the uniform conduction-electron spin-polarization form for the Knight shift, are simply related to each other in going from the rare-earth phosphides to the arsenides. In view of the similar band structures of ScP and ScAs, perhaps this result is not too surprising. A similar analysis of the antimonides cannot be performed at the present time due to an insufficient amount of antimony NMR data.

To date, Knight-shift measurements have been reported[10–24] for the following series of rare-earth intermetallic compounds (X=rare-earth): $X\mathrm{Al}_2$, $X\mathrm{Al}_3$, $X\mathrm{As}$, $X\mathrm{B}_6$, $X\mathrm{Bi}$, $X\mathrm{N}$, $X\mathrm{P}$, $X\mathrm{Pt}_2$, $X\mathrm{Pt}_5$, $X\mathrm{Sb}$, and $X\mathrm{Sn}_3$. For all of these intermetallic compounds, the reported Knight shifts are *positive* for the light and *negative* for the heavy rare earths. The one exception to this empirical result is the aluminum Knight shift in SmAl_2 reported by Buschow[21] *et al.* These authors' results, however, disagree with the earlier aluminum Knight-shift measurements in SmAl_2 by Jaccarino,[84] whose observation of a Knight-shift sign reversal is in agreement with the prediction of White and Van Vleck[83] (and also with the results of the Knight-shift measurements for the samarium compounds reported in Sec. V of this paper).

Table VII gives a summary of the s-f exchange energies derived from the uniform conduction-electron spin-polarization form for the Knight shift, for all of the published NMR data in the various rare-earth intermetallic compounds. For the $X\mathrm{Pt}_5$ compounds,[24] there are two nonequivalent platinum sites labeled I and II. There seems to be some discrepancy[11,17] regarding the magnitude of K_0 in the $X\mathrm{Al}_2$ compounds. The s-f exchange energies listed in Table VII for the $X\mathrm{Al}_2$ compounds are based on a value for $K_0\simeq0.05\%$.

Before discussing Table VII, the analysis of the nitrogen NMR data[67] in TbN and TmN leading to values for the s-f exchange energy will be presented. In order to calculate the s-f exchange energy Γ from the Knight-shift data [Eq. (3.8)], the Knight-shift K_0

TABLE VIII. Comparison of measured values of H^{hf}, the total hyperfine fields per unit spin S, for the various rare-earth intermetallic compounds listed in Table VII. The units are kOe.

	P	As	Sb	Bi	N	Al_2	Al_3	B_6	Pt_2	Pt_2^{I}	Pt_5^{II}	Sn_3
Ce	-57	-102	...	...	...	-28	-20	...	-54	-44	-27	-77
Pr	-35	-69	...	...	...	-21	-17	-1.3	-57	-20	-47	-50
Nd	-29	-58	...	...	...	-16	-11	...	-48	-26	-39	-33
Sm	-18	-39	-54	-84	...	...	-10	...	...	...	...	...
Eu	-21	...	...	...	...	...	...	...	...	...	...	...
Gd	-19	-34	...	...	...	-13	-11	-1.0	...	...	...	...
Tb	-16	...	...	...	-17	-12	-11	...	...	...	...	...
Dy	-14	...	...	...	...	-11	-12	...	...	...	...	...
Ho	-12	...	...	...	...	-16	-10	...	...	...	...	...
Er	-12	...	...	...	...	-13	-9	...	...	...	...	...
Tm	-10	-22	-37	...	-9	-12	...	...	...	...	...	...
Yb	-14	...	...	...	...	...	...	...	...	...	...	...

must be known. Unfortunately, the nitrogen NMR has not been studied in LaN or an equivalent nonmagnetic rare-earth nitride. Recently, however, the nitrogen and phosphorus Knight shifts in the NaCl-type intermetallic compounds ThN and ThP have been measured,[90] with the result $K^{14}=(0.11\pm 0.02)\%$ and $K^{31}=(0.044\pm 0.002)\%$. Since the phosphorus Knight shift in ThP is nearly equal to the Knight shifts measured in the nonmagnetic rare-earth phosphides (Table I), it is not unreasonable to assume that the nitrogen Knight shift in LaN will also be about the same as the ThN Knight shift. Thus, the XN s-f exchange energies were calculated using $K_0^{14}\simeq 0.1\%$.

From Table VII it appears that the s-f exchange energies Γ are relatively unchanged for the various series of rare-earth intermetallic compounds. No attempt will be made in this paper to speculate about the various mechanisms which might predict this result; however, a few comments are appropriate at this time.

It is to be noted that the s-f exchange energies for the XSn$_3$, XPt$_2$, and XPt$_5$ compounds are about an order of magnitude smaller than calculated for the other rare-earth compounds. This difference could be removed (if desired) by noting that for platinum compounds (and possibly tin) there can exist large orbital contributions to the Knight shift K_0 which, to first order, are not affected by the s-f exchange process, and hence the K_0 used in Eq. (3.5) should not include this contribution. Another similar situation, which would also lead to erroneous results, is to consider the effect of two conduction bands, say p-like and d-like, with one band interacting mainly with the $4f$ electrons and the other band interacting mainly with the nuclear moment of the nonmagnetic ion. Thus again, for this situation, the measured K_0 in the nonmagnetic compound could have a large contribution from conduction electrons which are not affected by the s-f exchange mechanism. Both of these observations apply to all of the rare-earth intermetallic compounds and need not be restricted to the platanides, etc. However, aluminum and phosphorus spin-lattice relaxation time T_1 measurements in LaAl$_2$[91] and ThP[92] indicate that the experimental Korringa products K^2T_1T are in good agreement with the predicted independent electron value. This indicates, with some reservations, that there is probably only one major Knight-shift contribution to K_0 in these compounds, and it is this Knight-shift contribution which is enhanced by the s-f exchange process. It seems reasonable, therefore, that the Knight shifts K_0 used in the analysis of the XN, XP, XAs, XSb, XBi, XAl$_2$, and XAl$_3$ NMR data are correct. However, until the question concerning the correct value of K_0 in Eq. (3.5) is resolved for each compound, definitive statements regarding the constancy of the s-f exchange energy cannot be made.

Since a comparison of s-f exchange energies involves not only the model which is chosen to analyze the data, but also a reinterpretation of the Knight-shift data in order to determine the correct K_0, a more meaningful comparison of the data is afforded by the hyperfine field per unit spin H^{hf}. The total hyperfine field H^{hf} [Eq. (3.3)] is simply related to the slope $\partial K/\partial\chi$. Table VIII lists the various hyperfine fields for the intermetallic compounds given in Table VII. As can be seen from Table VIII, the signs of all the hyperfine fields H^{hf} are the same. This result is due to the empirical fact that, as previously mentioned, for all of the various rare-earth intermetallic compounds, $\partial K/\partial\chi>0$ for $g_J<1$ and $\partial K/\partial\chi<0$ for $g_J>1$. The ratios of the hyperfine fields H^{hf} for the rare-earth Group-VA compounds are essentially the same as those of the $3s$, $4s$, $5s$, and $6s$ atomic hyperfine fields (see Sec. IV), again indicating that the K_0 used is correct. Perhaps more important, it is to be noted that the order of magnitude differences between the rare-earth Group-VA (or aluminum), and the platinum (or tin) compounds for the s-f exchange energies are not reflected in the magnitudes of the total hyperfine field H^{hf}. The measured hyperfine fields listed in Table VIII have the same sign and are about an order of magnitude larger than found in rare-earth insulators such as

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[92] M. Kuznietz (to be published).

XF_3.[26,27] This result is strongly indicative of the role that the conduction electrons play in the Knight shift. However, the fact that the platinum and tin hyperfine fields are of the same order of magnitude as the phosphides and aluminides is also somewhat surprising, in view of the expectedly[49] large platinum 6*s* atomic hyperfine interaction.

It is interesting to remark here about the recent results[93–98] and interpretations of Knight-shift measurements in uranium intermetallic compounds which, from an experimental viewpoint, do not differ substantially from the rare earths. Currently, it is believed that the uranium 5*f* electrons are localized[98] and do not form conduction bands, as previously supposed.[93] Thus, for uranium $g_J<1$ and again, experimentally, $\partial K/\partial\chi>0$ for all of the uranium intermetallic compounds studied to date. Furthermore, some of the nonmagnetic isomorphs of the uranium intermetallic compounds, such as ThC,[98] have $K_0<0$, while others, such as Th_3P_4,[95] give $K_0>0$. Even though the Knight shifts K_0 may have opposite signs, for all of the compounds studied $\partial K/\partial\chi>0$. It thus appears that the contribution to K_0 from the conduction electrons interacting with the *f* electrons cannot be simply determined by measuring the Knight shift of the nonmagnetic isomorph. Finally, the measured hyperfine fields H^{hf} in all of the uranium compounds are *also* of the order of -50 kOe.[98]

VII. SUMMARY

The NMR data presented in this paper have shown that NMR techniques can provide detailed information concerning the 4*f* electronic susceptibilities $\chi_f(T)$. For most cases, the agreement between the Knight shift and susceptibility-derived parameters for crystal-field splittings, etc., was good. For those cases where there was serious disagreement, it was concluded that the limited temperature range for which most of the susceptibility data were taken accounted for this difference.

Knight-shift data in the samarium and europium Group-VA compounds were shown to provide a measurement of $\langle \mathbf{S}(T)\rangle$ and not $\langle \mathbf{J}(T)\rangle$. Thus, the magnetic interaction between the Group-VA nucleus and the rare-earth ion is spin- and not magnetization-dependent. Other consequences of Knight-shift measurement in these particular intermetallic compounds are the measurements of the energies of the first excited states for the Sm^{3+} and Eu^{3+} ions.

Thus, Knight-shift measurements of a nonmagnetic site in a paramagnetic rare-earth compound have been shown to provide detailed information about the rare-earth ion. Some of this information, in intermetallic compounds, is difficult to obtain by other conventional experimental techniques, such as optical spectroscopy, etc.

Unfortunately, the Knight-shift data presented in this paper did not provide any new insight regarding the origins of the hyperfine fields. However, the measurements did show that the hyperfine fields per unit spin for the nonmagnetic sites in various rare-earth intermetallic compounds are essentially equal. No explanation for this phenomenon was advanced.

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