Effect of pressure on Knight shifts in rare-earth singlet ground-state systems*

H. T. Weaver and J. E. Schirber
Sandia Laboratories, Albuquerque, New Mexico 87115
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Pressure effects on Knight shifts of rare-earth and pnictide nuclei, contained in intermetallic compounds, have been measured to 4 kbar as a function of temperature from 4 K to as high as 300 K. An attempt to separate the effects of crystal field and exchange was made. Even with the inclusion of exchange (via simple parameterization), the often used point-charge model is unable to account in a straightforward manner for the results. We attribute the behavior to conduction-electron effects.

Recently, independent experiments[1,2] have indicated a remarkable failure for the point-charge model (PCM) in describing crystal-field effects. Specifically, the magnitude of the crystal-field splitting (Δ) is observed (indirectly) to increase with increasing atomic volume (Ω), i.e., $d\Delta/d\Omega > 0$. This is in contradiction to qualitative PCM arguments in which $d\Delta/d\Omega < 0$. Unfortunately, the interpretation of the experiments, involving pressure effects on Knight shifts and susceptibilities, is complicated by the presence and unknown behavior of exchange.

In order to determine whether simple models for exchange can account for the apparent failure of PCM, we have extended our earlier studies of singlet ground-state systems,[1] in which only low-temperature rare-earth (RE) Knight shifts (K) were measured, to include the temperature dependence of the pressure derivatives ($d\ln K/dP$). From the temperature dependence, one can, in principle, distinguish between crystal-field and exchange effects.

Our work now includes measurements of $d\ln K/dP$ at 4 K for Pr, P, and As contained in PrP and PrAs and for Tm in TmP. The pressure derivatives for P and As in PrP and PrAs were also determined for temperatures up to 300 K and for Tm in TmP at 27 K. Our experimental techniques have been described previously.[1,3]

Previous experimental work has demonstrated that the Knight shifts exhibited by nuclei in the rare-earth intermetallics of interest here are proportional to the susceptibility of the compound.[4] Since the susceptibility essentially reflects the net electron spin of the RE, Knight shifts provide a measure of the f-electron-nuclear coupling. This interaction is particularly strong for the RE nucleus. Here the orbital hyperfine interaction provides direct coupling and very large Knight shifts are observed.[5] In contrast, hyperfine interactions with the nonmagnetic nuclei are relatively weak and the interaction mechanism is not well understood. Evidence exists[4] which indicates the conduction electrons are the medium through which coupling is established. For present purposes, we simply assume the Knight shifts for both RE and pnictide nuclei are proportional to the susceptibility and thereby expect to have a reasonable approximation to the analytical form of the hyperfine interaction.

The most straightforward NMR evidence for difficulty with PCM is provided by the RE resonance in PrP and TmP. As noted, the RE Knight shift is mainly produced by the orbital hyperfine interaction, and is given by[5,6]

$$K_{\mathrm{orb}} = A_{\mathrm{orb}}\chi\,, \tag{1}$$

where χ is the susceptibility and A_{orb} is the coupling constant which, apart from numerical constants, is given by $\langle r_f^{-3}\rangle$, where r_f is the f-electron radius. Since the f electrons are confined to radii much smaller than the atomic radius, small changes in atomic volume have no effect on A_{orb}. Thus, the observed pressure effects on RE NMR are due to changes in χ.

The susceptibility is given by

$$\chi = C_J f_J(\Delta, T)/[T - \theta f_J(\Delta, T)]\,, \tag{2}$$

where C_J is the Curie constant, Δ the crystal-field splitting of the lowest spin-orbit state defined by total angular momentum J, and θ is proportional to the Curie temperature for $\Delta = 0$. The function f_J, defined in Ref. 4, contains the crystal-field effects and exhibits the property

$$\lim_{\Delta/T\to 0} f_J = 1\,. \tag{3}$$

Due to the existence of a ground-state singlet for all three compounds under consideration,[7] the low-temperature limit gives $f_J \propto T/\Delta$ and, for both Tm and Pr compounds, we find

$$\chi(T = 4\ \mathrm{K}) \propto 1/\Delta\,. \tag{4}$$

The sign of the pressure derivative for χ or K_{orb}, as predicted by PCM, is evident from Eq. (4). Coulomb interactions give rise[7,8] to $\Delta \propto R^{-n}$,

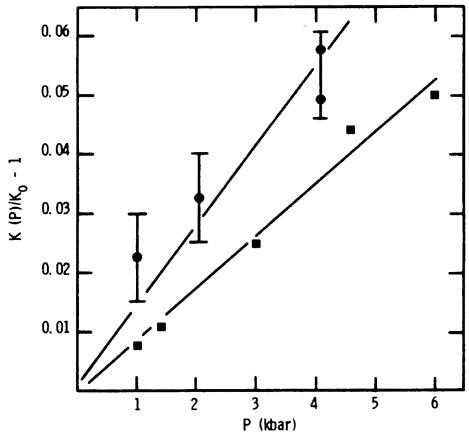

FIG. 1. Pressure dependence at 4 K of Knight shifts for ^{31}P (●) and ^{141}Pr (■) contained in PrP.

where R is the atomic radius and n is of order 5. Thus, decreasing R (raising the pressure) decreases χ or K. Figure 1 shows our results for PrP and is typical of the low-temperature data. Table I summarizes the derivatives taken at 4 K. This experiment shows $d\ln K/dP>0$, in contradiction to the PCM argument. Direct measurement of $d\ln\chi/dP$ by Guertin *et al.*[2] is in agreement with this conclusion.

A similar result is found from low-temperature NMR of P and As in PrP and PrAs. In general, the pnictide Knight shift can be written

$$K=K_0(1+\Gamma\chi)\,, \tag{5}$$

where K_0 is the shift due to Pauli paramagnetism and $K_0\Gamma$ is the coupling constant. For convenience we write Eq. (5) in a form which is directly comparable to the uniform polarization model,[4,9] but we use none of the constraints of the model in our analysis. Determination of pressure effects on crystal-field parameters from Eq. (5) is less straightforward than with the RE shift [Eq. (1)], since both K_0 and Γ are pressure sensitive. However, we usually find such quantities to exhibit pressure derivatives comparable in magnitude to the compressibility.[10] Should that be the case here, our measurements shown in Table I imply

TABLE I. Summary of low-temperature (T=4.02 K) pressure derivatives ($d\ln K/dP$) measured in units of %/kbar. The numbers in parentheses represent the error in the last quoted digit.

	RE	Pnictide
PrP	0.83(5)	1.6(2)
PrAs	0.47(4)	0.89(8)
TmP	0.48(4)	•••

$d\ln\chi/dP>0$, as was found from the RE data.

The effect of exchange can be parametrized in the following manner. Differentiating Eq. (5) yields

$$\frac{d\ln K}{dP}=\frac{d\ln K_0}{dP}+G(T,\theta)\left(\frac{d\ln\chi}{dP}+\frac{d\ln\Gamma}{dP}\right), \tag{6}$$

with

$$G(T,\theta)=C_J f_J\Gamma/[T+f_J(C_J\Gamma-\theta)]\,, \tag{7}$$

and using Eq. (2) we find[11]

$$\frac{d\ln\chi}{dP}=\frac{T\Delta}{T-\theta f_J}\frac{d\ln f_J}{d\Delta}\frac{d\ln\Delta}{dP}+\frac{f_J}{T-\theta f_J}\frac{d\theta}{dP}. \tag{8}$$

The unknown parameters are the pressure derivatives for θ, K_0, Γ, and Δ, where remaining quantities are taken from Refs. 4 and 9. However, the function $G(T,\theta)$ in Eq. (6) is within 10% of unity for $4\le T\le 300$ K. In essence, this reduces the number of parameters to three. If we assume PCM,[8,9] $d\ln\Delta/dP=\frac{5}{3}\kappa$, where κ is the compressibility. We further assume the pressure derivatives of θ, K_0, Γ, and Δ are independent of T. Thus, the experimental, low-temperature RE pressure derivative, when substituted into Eq. (8), determines[11] $d\theta/dP$. [Note that from the dis-

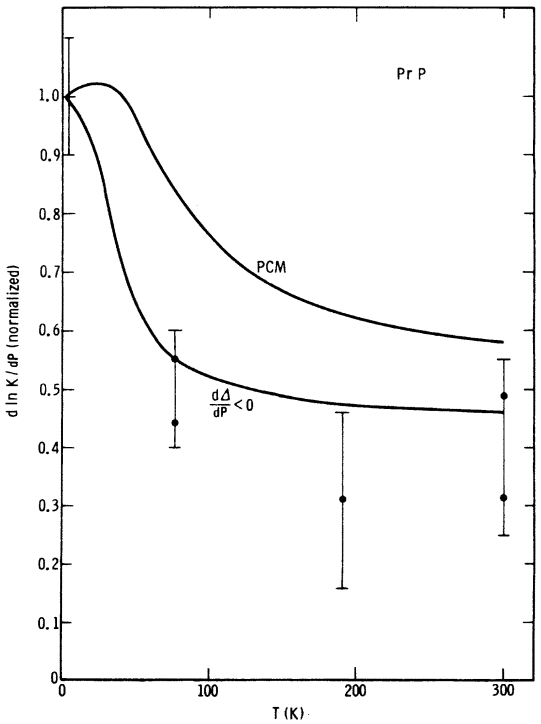

FIG. 2. Temperature dependence of Knight-shift pressure derivative of ^{31}P contained in PrP. The two curves represent results of a point-charge model (PCM) and a model using RE data as explained in the text.

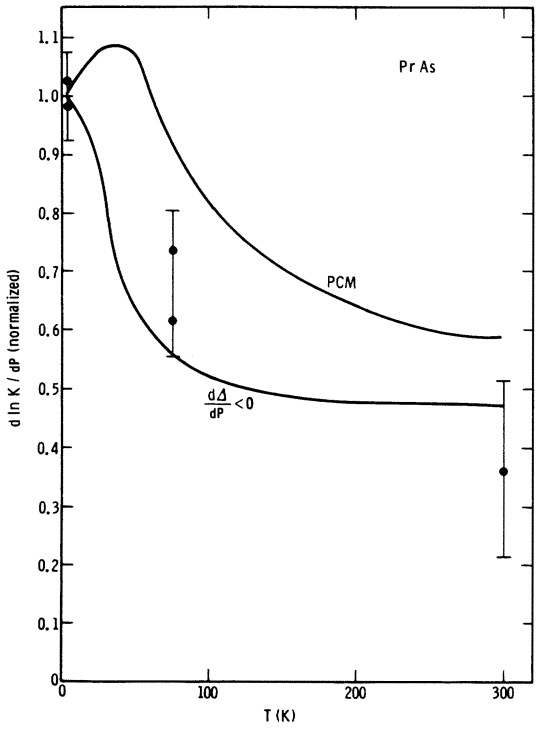

FIG. 3. Temperature dependence of Knight-shift pressure derivative of ^{75}As contained in PrAs. The two curves represent results of a point-charge model (PCM) and a model using RE data as explained in the text.

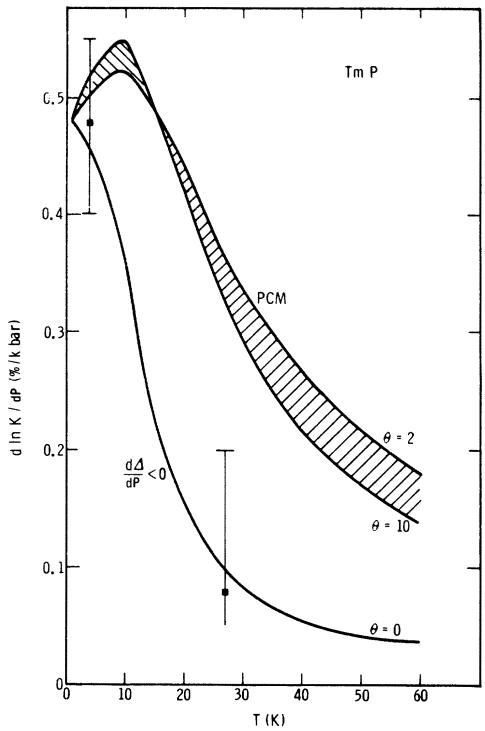

FIG. 4. Temperature dependence of Knight-shift pressure derivatives of ^{169}Tm contained in TmP. The curves are obtained from models explained in the text.

cussion of Eq. (1) $d\ln K(\mathrm{RE})/dP = d\ln\chi/dP$.] Aside from scale factors, the temperature dependence of $d\ln K/dP$ is then determined by Eq. (6). The results of this model are plotted for PrP and PrAs in Figs. 2 and 3 and labeled PCM.

Our NMR data are also shown in Figs. 2 and 3. It is clear that this straightforward effort to patch up PCM with exchange is not sufficient to interpret the experiment. Also shown in each of these figures is a plot generated by setting $d\theta/dP = 0$ in Eq. (8). As noted earlier, this requires $d\ln\Delta/dP < 0$. The fact that rough agreement is obtained indicates internal consistency between low- and high-temperature measurements if $d\ln\Delta/dP < 0$.

Evidence for failure of PCM is also provided by the temperature dependence of the pressure derivative of the RE Knight shift in TmP. In this case only Eq. (8) is needed. The low-temperature experimental $d\ln K/dP$ $(= d\ln\chi/dP)$ is used to determine (i) $d\theta/dP$ with $d\ln\Delta/dP = \frac{5}{3}\kappa$ or (ii) $d\ln\Delta/dP$ with $d\theta/dP = 0$. The first condition is again denoted as PCM and the resulting curves are shown in Fig. 4. Although earlier work has shown[4] $\theta \approx 0$, we illustrate the effect of allowing θ values in the range $2 \leq \theta \leq 10$ K. Figure 4 shows PCM inadequate to account for the temperature dependence of the pressure derivative of the RE Knight shift, as was the case with the nonmagnetic nuclei in PrP and PrAs.

This result for TmP can be described somewhat differently using the 4- and 27-K pressure derivatives to determine $d\ln\Delta/dP$ and $d\theta/dP$ from Eq. (8). The error in this calculation is large due to the inaccuracy of the 27-K data. However, we find $d\ln\Delta/dP = (-0.48 \pm 0.43)\%/\mathrm{kbar}$ and $-0.07 \leq d\theta/dP \leq 0.07$ K/kbar. These numbers simply illustrate the conclusion drawn from Fig. 4; that is, $d\ln\Delta/dP < 0$.

Estimates of $d\theta/dP$ derived from recent EPR work[12,13] on Pr and Tm pnictides also support our conclusion that $d\ln\Delta/dP < 0$. Exchange constants, measured in various RE-pnictide compounds, are used to determine $\theta(a_0)$, where a_0 is the lattice constant of a given compound. Subsequent specification of the compressibility[2] of the material of interest yields[14] $d\theta/dP$. For TmP this yields $d\theta/dP = 0.034$ K/kbar, which is consistent with our estimated range of values.[15]

An alternative approach, supported now by the qualitative agreement between the NMR and EPR work, is to use the values of $d\theta/dP$ derived from EPR measurements[13] and the RE-NMR low-temperature values of $d\ln K/dP$ $(= d\ln\chi/dP)$ to deter-

mine $d\ln\Delta/dP$ from Eq. (8). For TmP, PrP, and PrAs we find $d\ln\Delta/dP$ is -0.26, -0.40, and -0.19 %/kbar, respectively. Significantly, all values are negative as we concluded earlier. In fact, the values of $d\theta/dP$ would have to be several factors larger than estimated to yield positive $d\ln\Delta/dP$.

As further support we note that thermal expansion measurements[16] for TmSb also suggest $d\ln\Delta/dP<0$ in that particular compound. Again, this involves a parameter determination, but the results are in good agreement with the pressure dependence of the TmSb susceptibility.[2] This work is particularly significant in that the RE-RE exchange is not directly involved in determination of $d\ln\Delta/dP$. Thus, the difficulty of sorting out the effect of exchange, which is something of a problem with NMR, is avoided.

Although our data are not adequate to supply detailed comments on the EPR work, it is clear that the higher temperature P and As results are consistent with the EPR and low-temperature RE-NMR work in suggesting qualitative disagreement with PCM in these particular compounds. As noted earlier, this conclusion contrasts with neutron scattering results[8] for series of RE pnictides, where PCM was found quite adequate.

One plausible explanation, which can account for the failure of PCM in the pressure experiments and for the success of PCM in neutron scattering, is that variations of atomic volume produce changes in the conduction-electron character. Specifically, the relative p- or d-electron character could be altered. This has been demonstrated dramatically[17] in previous pressure experiments. Such an effect can significantly affect the magnitude of the crystal field.[18] In fact, under proper conditions the conduction electrons can change the sign of the crystal field, i.e., invert the splitting pattern.[19] In contrast to pressure experiments where variations in the conduction-electron character are produced, experiments conducted on a series of RE compounds, particularly where rigid-band–type behavior is expected, are likely to reflect a constant electron character. For such a situation PCM will work with an effective charge value. Deviations from rigid-band behavior within a series of compounds, however, quite possibly could change electronic character in a manner which would be reflected in the crystal-field splitting. Here, PCM would fail. In this regard, it is interesting that not all the RE-pnictide neutron scattering data[8] can be fit by PCM. In particular, roughly the first half of the RE series is in agreement with PCM. These deviations from PCM are quite possibly a conduction-electron effect.

In summary, we have carried out pressure measurements of Knight shifts as functions of temperature for both RE and nonmagnetic nuclei in the singlet ground-state intermetallic compounds PrP, PrAs, and TmP. A simple, straightforward analysis using the point-charge model, including the effect of exchange, is unable to account for these data. From this and corroborating analyses of work on related systems, we have concluded a qualitative point-charge model failure. Although this conclusion is in part based upon our estimates for exchange effects, the weight of current evidence clearly does not support the model. A plausible explanation for such a failure is presented which suggests atomic-volume changes affect the conduction-electron character. This, in turn, alters the crystal field in the observed manner.

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[11]Using PCM and constraints listed in text we find $d\theta/dP$ is 0.47 and 0.37 K/kbar for PrP and PrAs, respectively. For TmP, values of 0.13 and 0.092 K/kbar are found for assumed θ of 2 and 10 K, respectively.

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[14]This procedure involves many uncertainties. First, the host exchange in the RE compounds is assumed to be represented by the magnetic behavior of a probe spin. Secondly, the compound-to-compound variabi-

lity may not be representative of volume changes alone. And, finally, there is some disagreement in the literature on the sign of θ for Pr compounds (compare Refs. 2 and 4 to Refs. 12 and 13). Of the several studies, only Ref. 13 measures $d\theta/dV$ with reasonable accuracy for the compounds of interest here. As a consequence, we use this work exclusively in discussion of the NMR.

[15]Our estimates of $d\theta/dP$ are consistent with the work of Sugawara *et al*. (Ref. 13) only if a failure of PCM is assumed. This is readily seen by comparing the value of $d\theta/dP$ listed in Ref. 11, where PCM is used, to results of Ref. 13. (From Ref. 13 we estimate $d\theta/dP$ = 0.083, 0.084, and 0.034 K/kbar for PrP, PrAs, and TmP, respectively.) The NMR estimates of $d\theta/dP$, using PCM, are factors of 3 to 5 larger than analogous EPR values.

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[19]Although an alteration of the conduction-electron character most likely changes the ratio of fourth-to-sixth–order crystal-field interaction, we strongly contrast this effect with the result of changing the ratio within PCM. Using the results and notation of Ref. 7, where x is a measure of the fourth-to-sixth–order interaction strength, we find $d \ln x/dP = \frac{2}{3}\kappa$ which leads to $d \ln \Delta/dP \sim \pm 0.1\ \kappa$, for Tm and Pr, respectively. Clearly, the magnitude of this effect is negligible, as well as being inconsistent with the observed pressure effects for Tm and Pr having the same sign.