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Nuclear Magnetic Resonance in the LaX_3 Intermetallic Compounds*

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The La^{139} nuclear-magnetic-resonance (NMR) Knight shift and spin-lattice relaxation time (T_1) in $LaPb_3$ were measured from 1.5 to 300 °K. The isotropic and anisotropic Pb^{207} Knight shifts were measured at 1.5, 4.2, and 77 °K and T_1 was measured at 1.55 °K. Also presented are measurements of the La T_1 in $LaIn_3$ from 1.5 to 300 °K which are more complete than previously reported. These measurements are compared with previously reported measurements for $LaSn_3$. The La^{139} Knight shift (+0.010% at 4.2 °K) in $LaPb_3$ has a temperature dependence roughly five times that found in $LaSn_3$ and $LaIn_3$ even though the bulk susceptibility is considerably smaller. For $LaPb_3$, the La T_1T product is nearly temperature independent ($T_1T = 0.59$ sec °K at 4.2 °K) and is about half that found in $LaSn_3$. For $LaIn_3$, T_1T increases by 50% between 1.5 and 300 °K and has a temperature dependence similar to $LaSn_3$. The isotropic and anisotropic Pb Knight shifts ($K_{iso} = +0.70\%$ and $3K_{ax} = +0.43\%$ at 4.2 °K) are nearly temperature independent. The Pb relaxation time in $LaPb_3$ ($T_1T = 63 \times 10^{-4}$ sec °K) is about four times faster than in Pb metal, indicating a larger s-contact contribution than in Pb metal and a large negative Knight-shift component. The La NMR and bulk-susceptibility data are partitioned using the customary approximation for transition metals. We find the results for $LaIn_3$ and $LaSn_3$ are quite similar suggesting that in both these materials the La d-orbital susceptibility is much larger than the d-spin susceptibility and that exchange-enhancement effects are probably not important. For $LaPb_3$, d-orbital effects are less important than the d-spin contributions. In all three compounds the La d-spin contributions to the NMR properties and the bulk susceptibility are of similar magnitude.

I. INTRODUCTION

The LaX_3 intermetallic compounds (X = Sn, In, Pb, Tl, etc.) have been the subject of a number of recent experimental and theoretical studies which have attempted to determine their magnetic and superconducting properties.[1–5] Because of their interesting properties, band-structure calculations for some of these compounds have also received considerable attention.[6,7] In this paper we present the results of nuclear-magnetic-resonance (NMR) studies of these compounds which allow a comparison of the microscopic behavior of the band electrons at the La and X sites in different compounds and a determination of the various spin and orbital contributions to their NMR and bulk magnetic properties.

The most intriguing property of the LaX_3 intermetallic compounds is the coexistence of a fairly high superconducting transition temperature T_c and a large temperature-dependent paramagnetic susceptibility χ for some of these compounds. Several authors[8–10] have shown that for alloys of these compounds both T_c and χ vary radically with changing electron/atom (e/a) ratio and that maximum values of T_c and χ occur at nearly the same e/a ratios. For $LaSn_3$, $LaPb_3$, and $LaIn_3$ the superconducting transition temperatures are 6.45, 4.05, and 0.68 °K, respectively,[2,4] and the susceptibilities at 4.2 °K are 3.3

$\times 10^{-4}$, 1.1×10^{-4}, and 4.2×10^{-4} emu/mole, respectively.[3] These results for $LaSn_3$ and $LaIn_3$ are particularly interesting in that the paramagnetic susceptibility estimated from the bare density of states at the Fermi surface would indicate a spin-susceptibility contribution of less than 10^{-4} emu/mole. These large susceptibilities were originally thought to arise from an exchange-enhanced La d-spin susceptibility. This interpretation seemed reasonable as Toxen and Gambino were able to obtain a fit to the magnitude and temperature dependence of the bulk susceptibility of $LaIn_3$, assuming a parabolic La d band and a large d-spin exchange enhancement.[11] However, the NMR data for $LaIn_3$ appeared to be inconsistent with this assumption. The same difficulty with this model of a large exchange enhancement of the La d-spin susceptibility arises in $LaSn_3$. The results of Welsh *et al.*[12] (hereafter referred to as WTG) show that the assumption of a dominant La d-orbital paramagnetic susceptibility leads to a consistent partitioning of the s- and d-band contributions to the La NMR properties and the bulk susceptibility, as well as a reasonable result for the density of La d states at the Fermi energy.

In Sec. II, we present the experimental results for $LaPb_3$ and more complete spin-lattice-relaxation-rate data for $LaIn_3$ than previously reported.[13] In Sec. III, the La and Pb NMR properties are discussed, and the various spin and orbital contributions to the La NMR properties are determined for $LaPb_3$ and $LaIn_3$. Finally, we compare the results for $LaPb_3$ and $LaIn_3$ with the results for $LaSn_3$ and WTG.[12] We find that with the same assumptions employed in partitioning the spin and orbital contributions to the La NMR Knight shift, spin-lattice relaxation rate, and bulk susceptibility in $LaSn_3$, consistent results are also obtained for $LaPb_3$ and $LaIn_3$. This suggests that the large temperature-dependent susceptibility present in some of the LaX_3 compounds arises mainly from the La d-orbital contribution and not from an exchange-enhanced d-spin susceptibility. Instead, the La d-spin contributions to the magnetic properties of these three compounds appear to be similar.

II. EXPERIMENTAL RESULTS

The preparation of the LaX_3 samples and studies of their crystal structure and metallurgical properties have been discussed elsewhere.[5] For the NMR measurements, 40-μ-size particles were obtained by grinding the bulk material and sieving the resulting powder (325 mesh). The powder was then annealed in a tantalum crucible at 450 °C for 72 h. Sample deterioration was prevented by storage of the samples under helium gas. The continuous-wave (cw) NMR measurements were carried out using either a Varian cross-coil spectrometer or a marginal oscillator. The pulsed NMR measurements were made using a single-coil phase-coherent spectrometer. Signal averaging was accomplished using either a boxcar integrator or a Fabritek model No. 1072 instrument computer with a 1-μsec/channel resolution.

In the Cu_3Au crystal structure of the LaX_3 intermetallic compounds, the La atoms occupy sites of cubic symmetry while the X sites have axial symmetry. The cw La^{139} line shape in $LaPb_3$ is symmetric with a peak-to-peak separation of the derivative of the La line which varies from 3.1 ± 0.1 Oe at 300 °K to 3.4 ± 0.1 Oe at liquid-helium temperatures. The field independence of the La linewidth indicates a lack of any second-order quadrupolar or paramagnetic impurity broadening. The La linewidth behavior is similar to that of $LaSn_3$ (2.6 Oe at 4.2 °K)[12] and $LaIn_3$ (7.0 Oe at 4.2 °K).[13] The calculated dipolar peak-to-peak linewidths for $LaSn_3$, $LaPb_3$, and $LaIn_3$ are 0.75, 0.60, and 3.1 Oe, respectively, for a Gaussian line shape.[14]

Measurements of the La^{139} Knight shift in $LaPb_3$ were made from 1.5 to 430 °K using the La^{139} NMR in an aqueous solution of $LaCl_3$ as a reference. In Fig. 1 the La^{139} Knight shift is shown as a function of temperature. In Table I the La Knight shift is listed for several temperatures. The temperature dependence of the La Knight shift in $LaPb_3$ varies from +0.208% at 430 °K to +0.002% at 1.5 °K, which is about five times the variation found in either $LaSn_3$ or $LaIn_3$. Since the paramagnetic part of the bulk susceptibility increases with decreasing temperature (see Sec. III), $dK/d\chi$ is negative. This generally indicates a d-core polarization contribution to the La Knight shift.

The Pb^{207} isotropic Knight shift K_{iso} and anisotropic Knight shift K_{ax} in $LaPb_3$ were measured at 77 °K and liquid-helium temperatures using the La NMR of the sample as a reference. The ratio of ν_{Pb} in $PbSO_4$ to ν_{La} in $LaCl_3$ was taken to be 1.4752. This value was obtained using 6.014 MHz in 10 kOe for ν_{La} and 9.0047 MHz in 10 kOe for the value of ν_{Pb} in Pb metal,[15] which has a Knight shift of 1.47% relative to $PbSO_4$.[16] Traces of the Pb NMR line were obtained by integrating the Pb spin echo following a 90°–180° pulse sequence. From a comparison of these traces with computer-generated resonance lines, we have determined the isotropic and anisotropic Pb Knight shifts listed in Table I.[17] A better fit to the Pb line shape is obtained assuming an intrinsic Gaussian line shape than with the assumption of a Lorentzian line shape. The full width of the

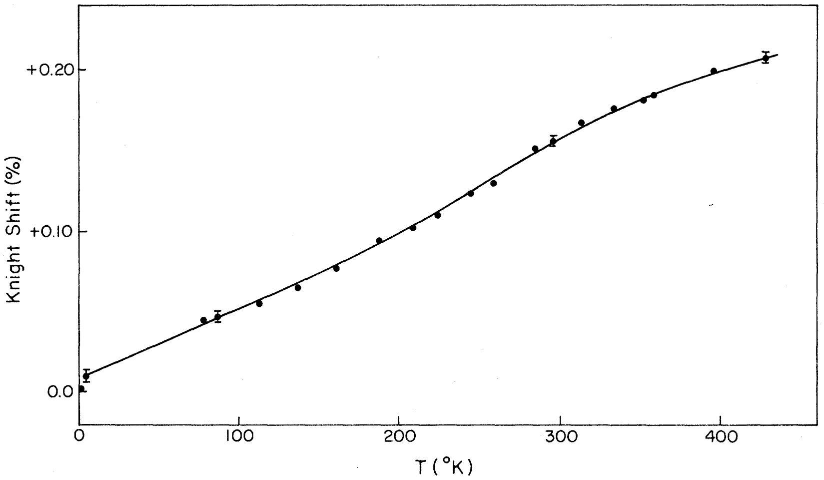

FIG. 1. La^{139} Knight shift at 7.5 MHz vs temperature in $LaPb_3$.

Pb line at half-maximum intensity is 10 ± 2 Oe. Both K_{iso} and K_{ax} appear to be nearly temperature independent from 1.5 to 77 °K with the values $K_{iso} = +0.72\%$ and $3K_{ax} = +0.43\%$ at 1.5 °K. The isotropic Pb Knight shift in $LaPb_3$ is about one-half of the metallic Pb Knight shift of +1.47%.[16]

The La^{139} nuclear-spin-lattice relaxation time T_1 was measured at several temperatures from 1.5 to 295 °K. The recovery of the spin echo was observed following either a 180°-90°-30° pulse sequence, or with a 90°-30° pulse sequence following a train of 90° pulses of length T_1 which saturated the NMR signal. The recovery of the echo was exponential over the nearly two orders of magnitude observed. The same T_1 values were obtained at 4.3 and 8.5 MHz indicating no field or frequency dependence of T_1. The product of $T_1 T$ is nearly temperature independent in contrast to the temperature dependence of $T_1 T$ found in $LaSn_3$[12] and $LaIn_3$. For $LaPb_3$, the values of $T_1 T$ are listed in Table I and vary from 0.64 sec °K at 295 °K to 0.59 sec°K at 1.6 °K. Also listed in Table I are the values of the Korringa product $K^2 T_1 T/S$.[18] The fact that the Korringa product is much less than unity is indicative of a large d-core polarization contribution.[19] For $LaIn_3$ the temperature dependence of $T_1 T$ differs considerably from that found in $LaPb_3$, but is quite similar to that of $LaSn_3$ as shown in Fig. 2. For both $LaSn_3$ and $LaIn_3$, T_1T increases by roughly 50% as the temperature increases from 1.5 to 295 °K and has a magnitude of from 2 to 3 times that of $LaPb_3$. The La Knight shift, spin-lattice relaxation time, and Korringa product are given at 4.2 °K for $LaSn_3$ in Table II. In contrast to the values of the Korringa product for $LaPb_3$ and $LaSn_3$, the Korringa product for $LaIn_3$ is greater than unity.

The Pb^{207} nuclear-spin-lattice relaxation time was measured at 1.55 °K following a 180°-90°-180° pulse sequence. The recovery of the Pb echo was exponential with a relaxation time of $T_1 = 4.1 \pm 0.2 \times 10^{-3}$ sec so that $T_1T = 63 \times 10^{-4}$ sec °K. Measurements at 4.3 and 8.5 MHz gave the same result within experimental error indicating no field dependence of the relaxation time. An exponential recovery may appear surprising in view of the large value of the anisotropic Pb Knight shift, but as discussed in Sec. III the very short value of T_1 implies the existence of isotropic-Pb-Knight-shift contributions much larger than the anisotropic Knight shift. A comparison of the value of T_1T for Pb in $LaPb_3$ with the value of $T_1T = 253 \times 10^{-4}$ sec °K for Pb metal[20] shows that the Pb relaxation rate is nearly four times faster in $LaPb_3$. Thus both the Pb Knight shift and spin-lattice relaxation rate in $LaPb_3$ differ considerably from their values in Pb metal.

III. DISCUSSION

In order to discuss the data for the LaX_3 compounds we follow the customary scheme employed with transition metals for partitioning the bulk susceptibility, Knight shift, and spin-lattice re-

TABLE I. Summary of the NMR data for $LaPb_3$. Numbers in parentheses indicate the estimated uncertainties in the preceding digit. The quantity S is given by $S = (\hbar/4\pi k_B)\ (\gamma_e/\gamma_n)^2$.

	T(°K)	K(%)	T_1T(sec °K)	K^2T_1T/S
La^{139}	296	+0.156(3)	0.64(3)	1.18×10^{-1}
	77	+0.045(3)	0.60(2)	9.2×10^{-3}
	4.2	+0.010(3)	0.59(2)	4.5×10^{-4}
	1.55	+0.002(3)	0.59(2)	2×10^{-5}

	T(°K)	K_{iso}(%)	$3K_{ax}$(%)	T_1T(sec °K)	K^2T_1T/S
	77	+0.68(3)	+0.45(4)	...	...
Pb^{207}	4.2	+0.70(1)	+0.43(2)	...	...
	1.55	+0.72(1)	+0.43(2)	63×10^{-4}	0.056

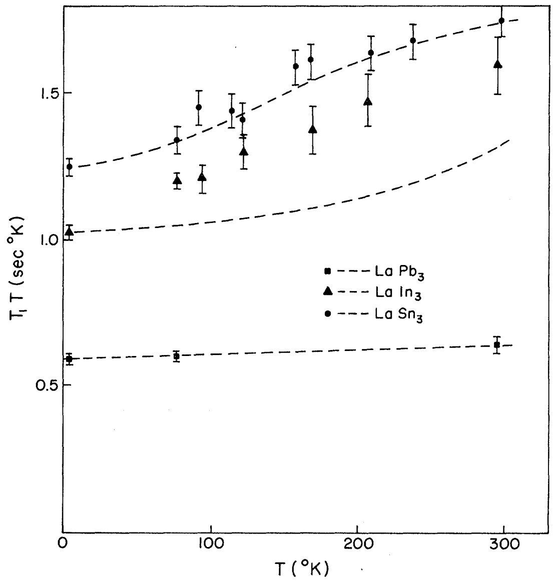

FIG. 2. La^{139} spin-lattice relaxation time for LaPb$_3$, LaIn$_3$, and LaSn$_3$ plotted as T_1T vs temperature. The dashed lines are determined by partitioning the NMR and χ data as described in the text with the assumption that F_d is temperature independent. The data for LaSn$_3$ are taken from Ref. 12.

laxation rate into the s-contact hyperfine contribution[18] and the core polarization[19] and orbital[21] hyperfine contributions from the p and d bands within the tight-binding model. As discussed in WTG,[12] this approach appears to be reasonable for LaSn$_3$ and allows a consistent partitioning of the NMR and susceptibility data. In terms of the various paramagnetic susceptibility contributions χ_i, the Knight-shift terms are given by

$$K_i = (\mu_B N)^{-1} H_{\rm hfs}^{(i)} \chi_i \qquad (1)$$

and the spin-lattice relaxation rates are given by

$$R_i = (T_1 T)_i^{-1} = (4\pi/\hbar)(\gamma_n \hbar)^2 k_B \,[H_{\rm hfs}^{(i)} N_i(0)]^2 F_i \qquad (2)$$

for noninteracting electrons.[22] The quantities $H_{\rm hfs}^{(i)}$ are the appropriate hyperfine fields (in Oe/μ_B), the $N_i(0)$ are the s-, p-, or d-electron density of states at the Fermi energy (per spin direction), and the F_i are the inhibition factors for the p and d contributions resulting from the orbital degeneracy at the Fermi energy.[19,21,22] In the presence of conduction-electron exchange enhancement, the spin (but not the orbital) contributions to the relaxation rate can be written as[22]

$$R_i = S^{-1} K_i^2 \, Q(\alpha_i) F_i \; , \qquad (3)$$

where $S = (\hbar/4\pi k_B)(\gamma_e/\gamma_n)^2$ and the quantities $Q(\alpha_i)$ reflect the wave-vector dependence of the exchange-enhanced susceptibilities. The conduction-electron exchange enhancement is given by $(1-\alpha_i)^{-1}$, and for free-electron metals with spherical bands, $Q(\alpha_i) \approx 1 - \alpha_i$ for small α_i.[22] Within the approximations expressed by Eqs. (1)–(3), we will first discuss the partitioning of the LaPb$_3$ data, then the LaIn$_3$ data, and finally compare these results with those obtained for LaSn$_3$ in WTG.[12]

A. LaPb$_3$

The temperature dependence of the bulk susceptibility of LaPb$_3$ from Toxen and Gambino[3] is shown by the broken line in Fig. 3 after correction for the estimated core diamagnetic contribution of -0.98×10^{-4} emu/mole. Because this correction is comparable to the resulting paramagnetic part of the bulk susceptibility, the uncertainty in the magnitude of χ shown in Fig. 3 is fairly large. The sharp increase of χ at low temperatures (4.3×10^{-4} emu/mole at 4.2 °K) results from the presence of paramagnetic impurities. The solid line in Fig. 3 shows the bulk susceptibility corrected for the estimated paramagnetic impurity contribution which is approximated by a Curie-law term of magnitude $2.3\times10^{-3}/T$ emu/mole. With this correction the bulk susceptibility is no longer a monotonically increasing function of decreasing temperature. This situation occurs in a number of the alloys of the LaX_3 compounds[9] and is thought to result from the diamagnetic contributions of pockets of very-low-effective-mass electrons or holes having a strong temperature-dependent density of states at the Fermi energy. That such a situation may exist in LaPb$_3$ is not surprising as a very small increase in the e/a ratio by the addition of a few percent of ThPb$_3$ has been shown to result in a large diamagnetic susceptibility.[9] Thus the temperature dependence of the susceptibility of LaPb$_3$ apparently results from a combination of temperature-dependent paramagnetic and diamagnetic contributions. (An alternative explanation involving the possibility of magnetic ordering around 100 °K would appear to be very unlikely in view of the smooth variation of the La Knight shift in this temperature range, the nearly temperature-independent value of the La T_1T, and the relatively high superconducting transition temperature.)

An estimate of the magnitude of the paramagnetic susceptibility χ_p in LaPb$_3$ at 0 °K can be made by noting that in both LaSn$_3$ and LaIn$_3$ the

TABLE II. Summary of the La^{139} NMR data in LaSn$_3$ (from WTG Ref. 12) and LaIn$_3$ (Ref. 13).

	K(%)	$dK/d\chi$(mole/emu)	T_1T(sec °K)	K^2T_1T/S
LaSn$_3$	+0.228	−1.72	1.25	0.40
LaIn$_3$	+0.402	+3.15	1.05	1.28

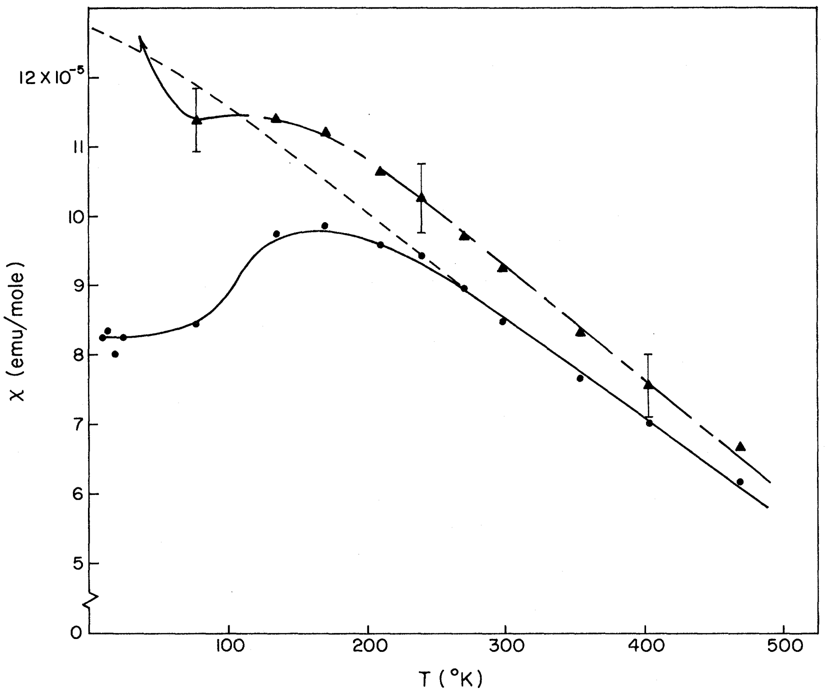

FIG. 3. Bulk susceptibility of $LaPb_3$ vs temperature (from Ref. 3). The triangles are data corrected only for the diamagnetic core contributions. The circles are data corrected for the paramagnetic impurity contributions as well. The dashed line is the estimated paramagnetic contribution χ_p to the bulk susceptibility.

La Knight shift scales with the bulk susceptibility. In both compounds the value of $dK/d\chi$ given in Table II is constant and very small. While in these systems the temperature dependence of the paramagnetic susceptibility can be determined unambiguously, this is not the case in $LaPb_3$. In Fig. 4 a plot of the La Knight shift versus the bulk susceptibility corrected for both the core diamagnetic and paramagnetic impurity contributions suggests that for the higher temperatures (> 250 °K), $dK/d\chi$ may be nearly constant. If we assume that $dK/d\chi_p$ is constant with the high-temperature value, the extrapolated value of χ_p at 1.5 °K would be about 1.3×10^{-4} emu/mole. This compares reasonably well with the value of $\chi_p = 1.0\times10^{-4}$ emu/mole determined from the estimated bare density of states at the Fermi energy of 0.39 states/eV atom spin (obtained from specific-heat measurements[4] after correction for the electron-phonon enhancement[23]). As a result, any enhancement of χ_p above the bare-density-of-states value in $LaPb_3$ is probably small, unlike the cases of $LaSn_3$ and $LaIn_3$.

The assumption that $dK/d\chi_p$ is constant implies that the temperature dependence of the diamagnetic contribution is important only below 250 °K

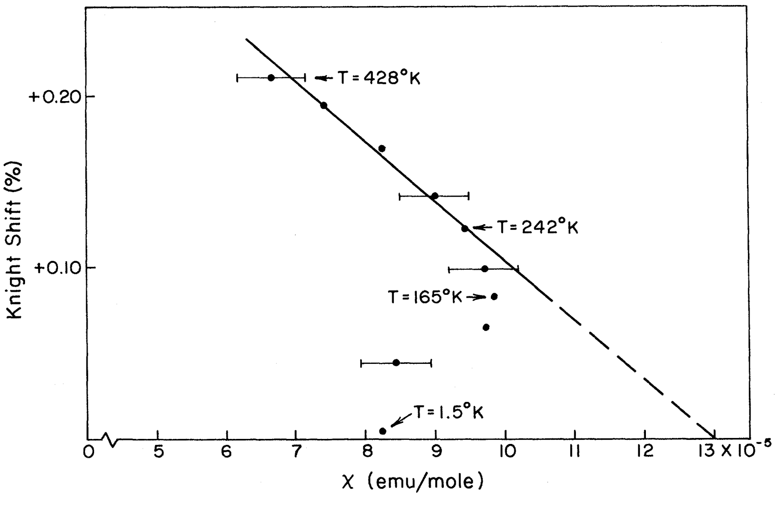

FIG. 4. La^{139} Knight shift in $LaPb_3$ vs χ corrected for both the diamagnetic core and paramagnetic impurity contributions.

and leads to the temperature dependence of χ_p shown by the dashed line in Fig. 3. From the high-temperature value of $dK/d\chi = 35$ mole/emu, the effective La d-core polarization hyperfine field of $-\gamma_e \hbar N dK/2d\chi$ can be estimated to be -2.0×10^5 Oe/μ_B assuming all the temperature dependence of χ_p results from the La d band. This value is within a factor of 2 of the value of -3.5×10^5 Oe/μ_B used in WTG for the d-core polarization hyperfine field which was determined from a free-atom spin-unrestricted Hartree-Fock calculation of Mallow and Freeman.[24]

From the magnitude and near temperature independence of the La relaxation rate, it is clear that the nearly zero La Knight shift observed at liquid-helium temperatures is a result of a fortuitous cancellation of negative and positive Knight-shift contributions. From the negative value of $dK/d\chi$, we assume that the temperature dependence of the La Knight shift is dominated by the temperature dependence of the d-core polarization contribution.[22] Since the La relaxation rate is nearly temperature independent, the dominant contribution to the relaxation rate must be associated with a positive Knight-shift contribution, i.e., either the s-contact or d-orbital Knight shifts (K_s or K_{orb}). Estimates of the orbital hyperfine field from the $\langle r^{-3}\rangle$ values of Freeman and Watson[25] suggest that $H_{\text{hfs}}^{(\text{orb})} = 2\mu_B \times \langle r^{-3}\rangle$ is between 1.35×10^5 and 2.4×10^5 Oe depending on whether the La($5d^3$) or La^{2+}($5d^1$) configuration is assumed. These values assume a reduction factor of 0.75 in order to account for the expansion of the d orbitals in going from the free-atom to the metallic environment. (The values of $H_{\text{hfs}}^{(\text{orb})}$ obtained from WTG in partitioning LaSn$_3$ range from 0.5×10^5 to 0.95×10^5 Oe.[12]) These theoretical values of $H_{\text{hfs}}^{(\text{orb})}$ indicate that $H_{\text{hfs}}^{(\text{orb})}$ is less than $H_{\text{hfs}}^{(d)}$. From Eq. (2), one would then expect the orbital contribution to the relaxation rate to be smaller than the d-core polarization contribution. Thus the s-contact interaction appears to be the dominant relaxation mechanism. If the La d-orbital effects are neglected entirely, the Knight shift and spin-lattice relaxation rate can be partitioned between the temperature-independent s-contact and temperature-dependent d-core polarization contributions using Eqs. (1) and (2) neglecting any exchange-enhancement effects ($\alpha_d = 0$). The results of this partitioning at 4.2 °K are listed in Table III for $\alpha_d = 0$ and $F_d = 0.2$ (fivefold orbital degeneracy). Taking the temperature dependence of the d-core polarization contribution to the La Knight shift from Fig. 1, the temperature dependence of T_1T calculated from Eqs. (1) and (2) is shown by the dashed line in Fig. 2 (assuming F_d is temperature independent). From Eq. (1), at 1.5 °K the value of $K_d = -0.435\%$ indicates a La d-spin contribution to the paramagnetic susceptibility of about 7×10^{-5} emu/mole (using $H_{\text{hfs}}^{(d)} = -3.5\times10^5$ Oe/μ_B) so that about half of the spin susceptibility is associated with the La d band. The remaining spin susceptibility arises from the La s and p bands and the Pb s and p bands. The assumption of any sizable d-orbital contribution to the Knight shift requires a larger d-core polarization contribution and hence a more temperature-dependent relaxation rate than observed (as long as all exchange-enhancement effects are neglected). For the same reason any s-d hybridization leading to a temperature dependence of the s-contact contribution to the La Knight shift and relaxation rate must be small. The value of the $K_s = +0.435\%$ agrees well with the estimated extrapolated value of K_s for $\chi \to 0$ of $+0.4\%$ although this agreement may be fortuitous considering the uncertainty of the absolute magnitude of the paramagnetic susceptibility term and the value of $dK/d\chi_p$.

Within the partitioning scheme for LaPb$_3$ discussed above and the approximations involved in determining a value for $dK/d\chi_p$, this quantity should give the value of the d-core polarization hyperfine field. While the estimated value of $H_{\text{hfs}}^{(d)}$ from $dK/d\chi$ is within a factor of 2 of the value obtained from the free-atom calculation, this difference may be real. Since the d-core polarization contribution to the La spin-lattice relaxation rate is consistent with the estimate of $H_{\text{hfs}}^{(d)} = -3.5\times10^5$ Oe/μ_B, the difference could result from a small temperature-dependent orbital Knight shift if a small temperature-dependent exchange enhancement of the La d-spin susceptibility exists. For a value of the enhancement parameter $\alpha_d = 0.30$ and an orbital Knight shift of $K_{\text{orb}} = +0.100\%$ at 4.2 °K, the agreement with the relaxation-rate data of Fig. 2 is maintained with the assumption that K_{orb} is roughly proportional to χ. This fit indicates an orbital susceptibility 70% the size of the d-spin susceptibility. The resulting values for the spin and orbital contributions to the NMR properties and bulk susceptibility are given in Table III. These two cases (i.e., $\alpha_d = 0$ and $\alpha_d = 0.3$) set reasonable limits to the various NMR and χ contributions in LaPb$_3$.

From the value of $K^2T_1T/S = 0.056$ in Table I for the Pb NMR it is clear that the conduction-electron contributions to the Pb NMR properties in LaPb$_3$ are different than in Pb metal where $K^2T_1T/S = 0.93$. The size of the isotropic Knight-shift contributions can be estimated from the magnitude of the relaxation rate which is nearly four times faster than in Pb metal.[20] This indicates that if the s-contact interaction is dominant in LaPb$_3$ as it is in Pb metal, then the value of K_s is about 2.5% and a large negative contribu-

TABLE III. Results of partitioning the bulk susceptibility and La NMR data at 4.2 °K for $LaPb_3$, $LaIn_3$, and $LaSn_3$ assuming no exchange enhancement of the La d-spin susceptibility. The quantities are defined in the text. The value of $H_{hfs}^{(orb)} = 0.95\times10^5$ was used in partitioning the $LaSn_3$ data and the results for $LaSn_3$ were taken from Ref. 12.

		K(%)	$R=(T_1T)^{-1}$(sec °K)$^{-1}$	χ(10^{-4} emu/mole)
$LaPb_3$ $F_d=0.2$	$\alpha_d=0$	K_s = +0.435	R_s = 1.43	χ_s = 0.12
		K_d = −0.425	R_d = 0.27	χ_d = 0.66
		K_{orb} = 0	R_{orb} = 0	χ_{orb} = 0
	$\alpha_d=0.3$	K_s = +0.435	R_s = 1.43	χ_s = 0.12
		K_d = −0.525	R_d = 0.27	χ_d = 0.83
		K_{orb} = +0.100	$R_{orb}\approx 0$	χ_{orb} = 0.58
$LaIn_3$ $F_d=0.3$		K_s = +0.263	R_s = 0.53	χ_s = 0.07
		K_d = −0.428	R_d = 0.42	χ_d = 0.68
		K_{orb} = +0.568	R_{orb} = < 0.03	χ_{orb} = 3.32
$LaSn_3$ $F_d=0.2$		K_s = +0.263	R_s = 0.44	χ_s = 0.07
		K_d = −0.480	R_d = 0.35	χ_d = 0.76
		K_{orb} = +0.423	R_{orb} = < 0.02	χ_{orb} = 2.48

tion to the Pb Knight shift exists of about −1.8%. The existence of such a large negative Knight-shift term is puzzling. As pointed out by Tterlikkis *et al.*,[26] who calculated the Pb Knight shift and relaxation rate for Pb metal, relativistic contributions from the Pb p electrons can give negative Knight-shift contributions although these effects should be small compared to the s-contact Knight shift. It is also possible that negative contributions could arise from p- or d-core polarization hyperfine interactions,[19] transferred hyperfine effects,[25] or the higher-order spin-orbit interaction terms discussed by Tterlikklis *et al.*[26] Finally, we note that one would expect the anisotropic hyperfine interactions would have little effect on the relaxation rate because of the large ratio of $K_s/3K_{ax}\approx 5$. Consequently, the Pb spin-lattice relaxation should be nearly isotropic and governed by a single relaxation time.

B. $LaIn_3$

The problems that arise in attempting to partition the $LaIn_3$ NMR and susceptibility data within the framework of Eqs. (1)–(3) are similar to the problems discussed in WTG[12] that arise for the partitioning of the $LaSn_3$ data. In both compounds the bulk susceptibility is much larger than that calculated from the bare density of states at the Fermi energy. While χ was originally thought to arise from a strongly exchange-enhanced La d-spin susceptibility, it was not found possible to partition the data for $LaSn_3$ within the tight-binding model even assuming a strong hybridization of the s and d bands. A consistent partitioning of the NMR and χ results was obtained only if the La d-orbital susceptibility was assumed to be dominant. As discussed in WTG, the tight-binding model for $LaSn_3$ would be expected to give at least qualitatively correct results. As is evident from Table II and Fig. 3, the NMR results for $LaIn_3$ are similar to those for $LaSn_3$, the main differences being a different sign for the small values of $dK/d\chi$ and some difference in the Korringa product. In addition, the bulk susceptibilities are similar although in $LaIn_3$ χ is not well approximated by a Curie-Weiss law while in $LaSn_3$ χ is Curie-Weiss above 100 °K.[3,12] It is not surprising then that the $LaIn_3$ results cannot be partitioned on the basis of a strongly exchange-enhanced La d-spin susceptibility as had been proposed earlier.[11] The assumption that the La d-orbital susceptibility is larger than the La d-spin susceptibility does lead to a consistent partitioning of the La Knight shift, spin-lattice relaxation rate, and the bulk susceptibility. Following the approach discussed in WTG[12] for the partitioning of $LaSn_3$, the La Knight shift is assumed to be of the form

$$K=K_s+(H_{hfs}^{(d)}/\mu_B N)\,\chi_d+(H_{hfs}^{(orb)}/\mu_B N)\,\chi_{orb}\ . \qquad (4)$$

We assume K_s is temperature independent and hence neglect any s-d admixture effects. With this assumption χ_d and χ_{orb} must have the same temperature dependence in order that $dK/d\chi$ be constant. Obtaining K_s from the extrapolation of the La Knight shift to its value for $\chi\to0$ and taking $H_{hfs}^{(orb)}$ as the parameter to be varied, the $LaIn_3$ data have been partitioned as shown in Fig. 5(a) where the various K_i are plotted versus the bulk susceptibility. The parameters used and the resulting values of these La Knight-shift, spin-lattice relaxation-rate, and susceptibility contributions at 4.2 °K are given in Table III. For comparison, the results for $LaSn_3$ with the same value of $H_{hfs}^{(orb)}$ are shown in Fig. 5(b) and the resulting NMR and susceptibility contributions at 4.2 °K are given in Table III. While the $LaSn_3$ data can be partitioned for $H_{hfs}^{(orb)}$ values from 0.5×10^5 to 0.95×10^5 Oe,[12] the latter value has been used for the results shown in Fig. 5 and Table III. This choice of $H_{\rm hfs}^{(\rm orb)}$ results in orbital inhibition factors of $F_d = 0.3$ for $\rm LaIn_3$ and $F_d = 0.2$ for $\rm LaSn_3$. The value of $F_d = 0.3$ corresponds to the d states at the Fermi surface having either t_{2g} or mostly e_g symmetry and $F_d = 0.2$ corresponds to a uniform occupation of the d states.[19,21] The nonrelativistic band-structure calculations by Gray and Meisel[6] for $\rm LaSn_3$ and the relativistic APW band-structure calculations by Freeman and Koelling[7] for $\rm LaIn_3$ and $\rm LaSn_3$ both indicate that one of the e_g states has a lower energy than the t_{2g} states and would be expected to be occupied at a lower e/a ratio. For $\rm LaSn_3$ the result that $F_d = 0.2$ is not unreasonable, since the e/a ratio is larger in $\rm LaSn_3$ than in $\rm LaIn_3$. Another interesting feature of the spin-lattice-relaxation data is the variation of the La relaxation rate with the bulk susceptibility. Whereas in $\rm LaSn_3$ $R = a + b\chi^2$,[12] this is not the case in $\rm LaIn_3$ as is shown by the dashed lines though the T_1T data of Fig. 2. Instead, the relaxation rate in $\rm LaIn_3$ rises too sharply with increasing χ at low temperature. This increase in R could easily result from small s-d admixture effects giving a smaller value of K_s (~0.225% at 300 °K) at higher temperatures, or from a more uniform d-state occupation ($F_d \to 0.2$) at higher temperatures.

The results given in Fig. 5 and Table III should be considered to be only approximate because of the neglect of possible s-d admixture effects, spin-orbit coupling, and exchange-enhancement effects.[22] Also, with the approximations given in Eq. (4), the $\rm LaIn_3$ data can be partitioned for values of $H_{\rm hfs}^{(\rm orb)}$ larger than the value chosen here if F_d is closer to its maximum value of 0.5, which would be the case if only e_g states were filled.[19,21] It is particularly interesting to find that the NMR data and the bulk susceptibility of $\rm LaSn_3$ and $\rm LaIn_3$ are similar and that the same partitioning scheme gives consistent results, because these compounds do have different e/a ratios and studies of the bulk properties[8–10,27] and NMR properties[28] of the alloy system $\rm LaSn_{3(1-x)}In_{3x}$ show that the behavior of these properties varies radically with increasing e/a ratio. The main differences between the NMR properties of $\rm LaSn_3$ and $\rm LaIn_3$ result from the fact that in $\rm LaSn_3$ the d-core polarization contribution to the La Knight shift is slightly larger than the d-orbital contribution giving a negative value of $dK/d\chi$ and a value of the Korringa product less than unity, while in $\rm LaIn_3$ the reverse situation holds. Reference to Table III shows that the other NMR and susceptibility contributions are similar.

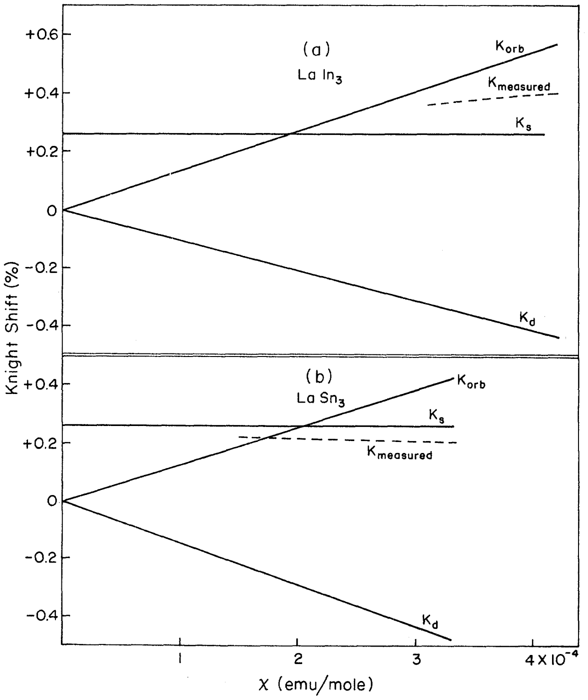

FIG. 5. Comparison of the estimated $\rm La^{139}$ Knight-shift components for $\rm LaIn_3$ and $\rm LaSn_3$ vs χ assuming $H_{\rm hfs}^{(\rm orb)} = 0.95 \times 10^5$ Oe. The results for $\rm LaSn_3$ are taken from Ref. 12.

C. Comparison of $\rm LaSn_3$, $\rm LaIn_3$, and $\rm LaPb_3$

A comparison of the results presented here for $\rm LaPb_3$, $\rm LaSn_3$, and $\rm LaIn_3$ suggests that in many respects these intermetallic compounds are quite similar. Reference to Table III shows that the estimated values of K_d and R_d are nearly the same and the d-spin contribution to the bulk susceptibility is similar in each compound. In view of the large differences in the superconducting transition temperatures of these compounds the role of the La d band appears to be of less importance than that of the nontransition-metal element in determining the superconducting properties. In $\rm LaSn_3$ and $\rm LaIn_3$ we find that the largest paramagnetic contribution to the bulk susceptibility results from the d-orbital susceptibility. This is consistent with the very small values of $dK/d\chi$ found in $\rm LaSn_3$ which arise from the near cancellation of the d-core polarization and d-orbital contributions. However, in $\rm LaPb_3$ the magnitude of the d-orbital susceptibility is small and the total paramagnetic susceptibility is close to the value calculated from the bare density of states. Of particular interest is the fact that the estimated value of $dK/d\chi$ is much larger for $\rm LaPb_3$ which provides a lower limit for $H_{\rm hfs}^{(d)}$ which is within a factor of 2 of the value expected from the free-atom value of $H_{\rm hfs}^{(d)}$.

An important consequence of the partitioning scheme for $\rm LaSn_3$ and $\rm LaIn_3$ is the assumption involved in Eq. (4) that the temperature dependence of χ_d and $\chi_{\rm orb}$ is the same. Only with this assumption can the magnetic properties of LaSn$_3$ and LaIn$_3$ be partitioned consistently within the tight-binding model[19,21,22] and the estimated value of the d-core polarization hyperfine field. Such a result would be quite unusual for a Van Vleck orbital susceptibility. In addition, the magnitude of $\chi_{\rm orb}$ is larger than the value ($\lesssim 10^{-4}$ emu/mole) expected for a Van Vleck susceptibility near the beginning of a transition-metal series. This problem was discussed in WTG[12] where it was pointed out that the calculations of Hebborn *et al.*[29] show that orbital susceptibilities involve several terms which are quite complex and depend on the derivative of the wave functions at the Fermi surface. Grobman[30] has shown at least one of these terms (χ_2 of Hebborn *et al.*[29]) other than the Van Vleck term can be paramagnetic. This term can also have the same temperature dependence as the density of states and hence χ_d (if $\alpha_d = 0$) under certain conditions. The numerical evaluation of the full orbital susceptibility calculated by Hebborn *et al.*[29] awaits a much better knowledge of the conduction-electron wave functions than is available at present.

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