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Magnetic Properties of $LaSn_3$ [†]

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The normal-state nuclear-magnetic-resonance (NMR) Knight shifts and spin-lattice relaxation times are reported for La^{139} and Sn^{119} in $LaSn_3$ from 1.6 to 300 °K. New susceptibility data on higher-purity samples are reported for 4.2–700 °K which allow a more accurate determination of the susceptibility χ than previously reported. Above 100 °K, χ is Curie-Weiss, but it increases by only 6% below 77 °K. The Sn^{119} relaxation time ($T_1T = 0.033$ sec °K) and isotropic Knight shift (+0.640%) are temperature independent, while the anisotropic Knight shift is strongly temperature dependent. The La^{139} Knight shift (+0.207% at 4.2 °K) and relaxation time ($T_1T = 1.25$ sec °K at 4.2 °K) have a temperature dependence more than an order of magnitude smaller than expected in the case of a strong exchange enhancement of the La d-spin susceptibility. Various partitions of the NMR and χ data are discussed using the customary approximations for transition metals. We find that the assumption of a dominant La d-orbital susceptibility which has the same temperature dependence as the La d-spin susceptibility gives the most reasonable results, although with the large number of assumptions involved the fit is not unique. Finally, we discuss the nature of this orbital susceptibility and point out that paramagnetic contributions exist which usually are neglected and which may have the observed magnitude and temperature dependence.

I. INTRODUCTION

Recently a number of interesting yet puzzling results have been reported for the LaX_3 intermetallic compounds, where X = Sn, In, Tl, and Pb. These compounds are superconducting with transition temperatures of 6.42, 4.05, 1.6, and 0.77 °K for Sn, Pb, Tl, and In, respectively.[1] Of these compounds the properties of $LaSn_3$ are perhaps the most unusual. The normal-state susceptibility is Curie-Weiss above 100 °K with an effective moment of about 1 Bohr magneton per $LaSn_3$ formula unit.[2] The existence of a large strongly temperature-dependent normal-state susceptibility χ, along with a relatively high superconducting transition temperature, makes the correlation of the magnetic and superconducting properties of this compound of particular interest. While properties such as the specific heat, susceptibility, and superconducting critical temperature of $LaSn_3$ have been studied, there is little information about the behavior of this compound on a microscopic level such as can be provided by NMR studies. In this paper we report studies of the La^{139} and Sn^{119} Knight shifts and spin-lattice relaxation times, and new susceptibility measurements. These quantities are partitioned using the customary methods for transition metals based on the assumption that either the La d-spin susceptibility or the La d-orbital susceptibility is dominant. We obtain a reasonable separation of the paramagnetic bulk susceptibility and La NMR contributions only in the case of a dominant La d-orbital susceptibility. Finally, we discuss the various contributions to the orbital susceptibility and point out that terms which have not previously been considered to be important may, in fact, dominate all other contributions in the LaX_3 compounds.

II. BULK MEASUREMENTS

Preparation of the $LaSn_3$ ingots and studies of the crystal structure and metallurgical properties of $LaSn_3$ have been described elsewhere.[3] Samples for the bulk measurements were spark-cut from these ingots and were about 10 g in mass.

In Fig. 1 we show the inverse bulk susceptibility versus temperature T for $LaSn_3$. The dashed line of Fig. 1 is the plot of χ^{-1} corrected only for the temperature-independent diamagnetic core contribution of -0.068×10^{-3} emu/mole while the solid line is χ^{-1} corrected for both the diamagnetic core and the paramagnetic impurity contributions. These results are for a sample of a lower-impurity content than previously reported, which has allowed the paramagnetic impurity contribution and hence χ to be determined with more accuracy at temperatures below 100 °K. As Fig. 1 indicates, χ follows a Curie-Weiss law above 100 °K with a paramagnetic Curie temperature $\Theta_p = -267$ °K and an effective moment of 1.0 Bohr magneton per $LaSn_3$ formula unit. At low temperatures, χ becomes nearly temperature independent, changing by only 6% between 77 and 4.2 °K. This temperature dependence suggests that $LaSn_3$ might be an antiferromagnet, but no magnetically ordered state has been observed by

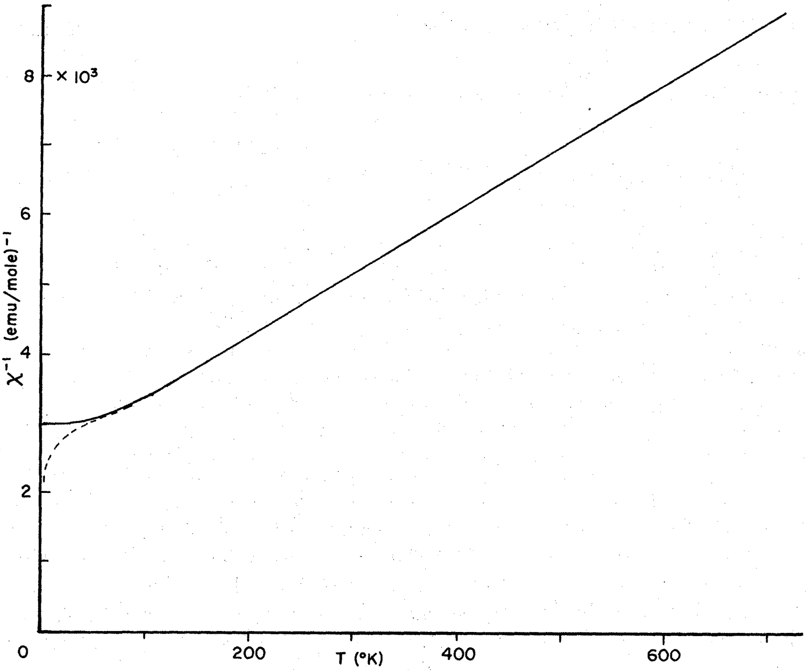

FIG. 1. Inverse bulk susceptibility (χ^{-1}) of $LaSn_3$ versus temperature. The dashed line is χ^{-1} corrected only for the diamagnetic core contributions. The solid line is χ^{-1} corrected for the paramagnetic impurity contributions as well.

neutron diffraction or Mössbauer measurements, or by the NMR measurements reported here. In addition to the temperature dependence, the magnitude of χ is also puzzling. The susceptibility extrapolated to $T = 0\,°K$, $\chi(0)$, is 3.3×10^{-4} emu/mole. This is 3.8 times larger than the spin susceptibility χ_0, that one would expect from the bare density of states $N(0) = 0.33$ state/eV atom (per spin direction), which has been calculated from the low-temperature specific-heat data using the model described by McMillan.[4] This model assumes that the electron-phonon interaction is the same for all band electrons at both the Sn and La states. If χ is assumed to be a conduction-electron spin susceptibility, then it must be strongly exchange enhanced, since $\chi(0)/\chi_0 = 3.8$. Indeed if χ results from a strongly exchange enhanced La d-spin susceptibility, the enhancement factor for the d-spin contribution might be considerably larger than 3.8 since $N^{\mathrm{La}}(0)$ is less than $N(0)$ as a result of the Sn s- and p-electron contributions to the density of states.

The fact that similar temperature dependences have been observed in the susceptibilities of Pd and Sc suggests that the magnetic properties of $LaSn_3$, Pd, and Sc may be similar. In Pd, χ_{Pd} follows a Curie-Weiss law above 800 °K with $\Theta_p \approx 50\,°K$ and with an enhancement of 6.2,[5] while in Sc, χ_{Sc} is Curie-Weiss above 100 °K with $\Theta_p \approx -1050\,°K$[6] and an enhancement of ~ 3.4.[7] The susceptibilities of Pd and Sc have been postulated to arise from the d-spin contributions of the relatively localized d electrons in these materials as a result of their atomic d^9 and d^1 configurations, respectively. For Pd this approach has been well substantiated by the results of bulk measurements and NMR studies, since the d-spin contributions clearly dominate all others.[8] For Sc the bulk measurements and NMR studies also appear to be consistent with this assumption.[7] The nonzero values for Θ_p in these two elements are then interpreted as evidence for spin correlations between the d electrons.[6] Indeed, the presence of spin correlations is consistent with the absence of superconductivity in Pd and Sc, which is otherwise somewhat puzzling since both metals have large electronic densities of states.

Because $LaSn_3$ has a Curie-Weiss susceptibility above 100 °K, it would be natural to assume that it is similar to Pd and Sc with d states arising from the La d^1 state and a nonzero Θ_p arising from spin correlations. However, $LaSn_3$ is a superconductor with $T_c = 6.5\,°K$. In fact it is a fairly strong coupling superconductor as one can see from two independent pieces of evidence. Using the McMillan strong-coupling model, one can estimate from the measured Debye temperature[1] of $\Theta_D \approx 200\,°K$ and the fact $T_c = 6.5\,°K$ that the BCS parameter has a value of $\lambda \equiv N(0)V \approx 0.81$, which is about the same as for Nb. Another indication of the strength of the coupling comes from the measured energy gap $2\Delta(0)/kT_c = 3.8$[9] which is larger than the BCS weak-coupling limit of 3.5. Thus, if $LaSn_3$ has an exchange enhanced susceptibility, then the fact that it is superconducting with a moderately strong electron-phonon coupling is puzzling.

Large contributions to the susceptibility can also result from the d-orbital terms in transition metals. In vanadium, for example, the orbital susceptibility has been found to be twice as large as the spin susceptibility.[10] The dominant paramagnetic orbital susceptibility is normally believed to be the Van Vleck susceptibility. This susceptibility is generally large at the center of the transition metal series and small at the ends, since it depends on the product of the number of d-band electrons and d-band holes. Then assuming that La has a $5d^1$ configuration in $LaSn_3$, this Van Vleck contribution to the orbital susceptibility might be expected to be small. However, as shown by Hebborn and coworkers,[11] other orbital susceptibility contributions exist. Grobman[12] has shown that these additional orbital terms can give important paramagnetic contributions in the alkali metals. These terms might be expected to be considerably larger in the transition metals, since their magnitudes depend upon the deviation of the conduction electron wave functions from free-electron behavior. Unfortunately, obtaining an estimate of the magnitude of these terms is quite difficult since a knowledge of the wave functions and their derivatives is required. As a result, estimates have only been made for the alkali metals. The question of the nature of the susceptibility in $LaSn_3$ will be discussed later in more detail.

III. NMR MEASUREMENTS

For the NMR measurements, powders of 40-μ-size particles were obtained by grinding the bulk materials and sieving the powder (325 mesh) to obtain a more uniform size. The powders were then annealed in tantalum crucibles at 450 to 600 °C for from 24 to 72 h. No deterioration of the powders was observed as long as they were kept under helium gas, although in a few minutes exposure to air sample deterioration was sufficient to render the La NMR signal unobservable.

Both continuous wave (cw) and pulsed NMR measurements were made on the La^{139} and Sn^{119} nuclei. The cw NMR measurements were made from 2–17 MHz using either a Varian cross-coil spectrometer or a marginal oscillator. The pulsed NMR measurements were carried out using a single-coil phase-coherent spectrometer. Signal averaging was accomplished with a boxcar integrator.

The crystal structure of $LaSn_3$ is that of Cu_3Au with the La atoms occupying sites of cubic symmetry while the Sn sites are axially symmetric. From the cw NMR measurements, the La^{139} line shape is found to be symmetric and nearly Gaussian. The peak-to-peak separation of the derivative of the La line ΔH_{pp} varies from 2.2 ± 0.1 Oe at 300 °K to 2.6 ± 0.1 Oe at 4.2 °K and is independent of the applied magnetic field from 3 to 15 kOe, indicating a lack of any second-order quadrupolar broadening. No temperature dependence of the La linewidth is observed from 1.6 to 4.2 °K, indicating that the La resonance is insensitive to the presence of the paramagnetic impurities which contribute to the bulk susceptibility. First-order quadrupolar wipeout apparently removes all but the $\frac{1}{2}$-$\frac{1}{2}$ transition from the central part of the cw line. This is verified by the free induction decay signal following a 90° pulse which is Gaussian except at the shortest times. The Gaussian decay corresponds to a linewidth of 2.6 ± 0.2 Oe at 4.2 °K in excellent agreement with the measured cw linewdith.

Measurements of the La^{139} Knight shift were made from 1.6 to 460 °K using the La^{139} NMR in an aqueous solution of $LaCl_3$ as a reference. The La^{139} Knight shift data taken at 8 MHz are plotted in Fig. 2 versus temperature. Also shown in Fig. 2 are data taken earlier on $LaSn_3$ by Borsa *et al.*[13] which agree with the data reported here within experimental error. No field dependence of the Knight shift was observed between 4 and 9 MHz. The La^{139} Knight shift is listed for several temperatures in Table I and varies from +0.237% at 460 °K to +0.207% at 1.6 °K. In Fig. 3 a plot of the La Knight shift versus the bulk susceptibility data (solid line) of Fig. 1 shows that K varies linearly with χ with a slope of $dK/d\chi = -1.72$ mole/emu. The fact that $dK/d\chi < 0$ generally indicates a d-core polarization contribution to the La Knight shift. The slope of the K-versus-χ curve gives an effective hyperfine field at the La site of $-\gamma_e \hbar N dK/2d\chi$ equal to -9.8×10^3 Oe/μ_B, where N is Avogadro's number. The data of Fig. 3 extrapolate to a value of $K(\chi = 0) = +0.263\%$. Neither the La Knight shift nor the linewidth data appears to be sensitive to the presence of the paramagnetic impurities which cause the low-temperature tail in the uncorrected bulk susceptibility of $LaSn_3$.

The Sn^{119} NMR was observed between 1.6 and 300 °K and from 5 to 16 MHz. An aqueous solution of LiCl was used as a reference for the Sn^{119} Knight shift measurements with $\nu(Li^7Cl)/\nu(Sn^{119}Cl_2) = 1.04285$.[13] The analysis of the Sn line shape and Knight shift is complicated by anisotropic hyperfine interactions. However, the NMR data can be analyzed, as discussed by Borsa and Barnes,[14] in order to obtain the intrinsic linewidth, the isotropic Knight

TABLE I. Summary of La^{139} NMR data in $LaSn_3$. 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)	T_2(10^{-3} sec)	K^2T_1T/S
300	+0.228(2)	1.75(5)		0.69
205	+0.222(2)	1.61(4)		0.60
77	+0.207(2)	1.35(3)	0.70(5)	0.44
4.2	+0.207(2)	1.25(3)	2.25(5)	0.40
1.6	+0.207(2)	1.25(3)	2.63(5)	0.40

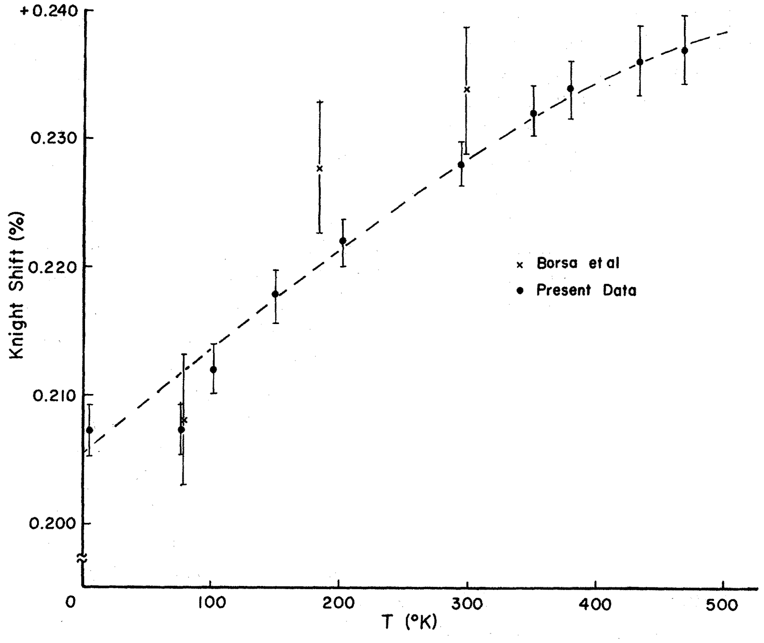

FIG. 2. La^{139} Knight shift in $LaSn_3$ versus temperature at 8MHz. The data by Borsa *et al.* are taken from Ref. 13.

shift K_{iso}, and the anisotropic Knight shift K_{ax}. The Sn Knight shifts are given for several temperatures in Table II. Comparison of the observed derivative line shape with curves calculated from equations given by Borsa and Barnes[14] shows the observed line shapes are nearly Gaussian. The intrinsic peak-to-peak separation of the derivative curve is 2.8 ± 0.2 Oe and is temperature independent but slightly field dependent. The isotropic Sn Knight shift $K_{iso} = +0.640\%$ is also temperature independent. The values of the intrinsic linewidth and K_{iso} are in good agreement with the 77–300 °K data of Borsa *et al.*[13]

For the anisotropic part of the Sn Knight shift, we find $3K_{ax} = +0.089\%$ at 77 °K and +0.110% at 1.6–4.2 °K. These values are sample independent. However, the value of K_{ax} we observe at 77 °K is 20% larger than the value observed by Borsa *et al.*[13]

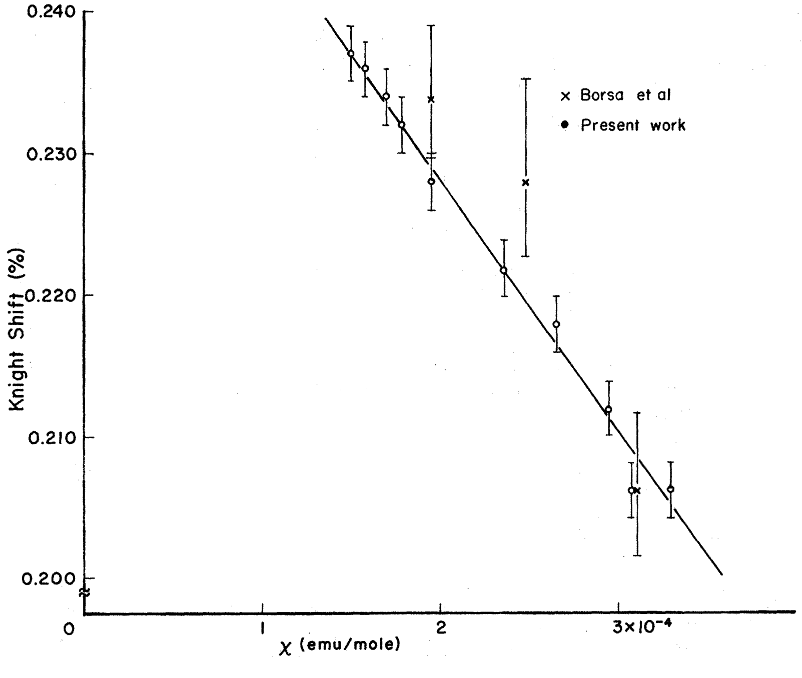

FIG. 3. La^{139} Knight shift in $LaSn_3$ versus the susceptibility corrected for core diamagnetism and paramagnetic impurity contributions.

The reason for this difference is not known. Of more importance is the fact that the value of $dK_{ax}/d\chi$ is not constant but is about twice as large for temperatures below 77 °K. Thus, K_{ax} does not vary linearly with the bulk susceptibility as does the La Knight shift. Hence the temperature dependence of K_{ax} may be unrelated to the bulk susceptibility and may instead arise from the effects of lattice vibrations on the Sn electronic structure, as was found to be the case in Cd.[15]

The La^{139} nuclear-spin-lattice relaxation time T_1 was measured on several samples as a function of temperature (see Fig. 4). The recovery of the transient signal was observed either following a 180°-90° pulse sequence, or with 90°-30° (which maximizes the quadrupolar 2τ spin echo) or 90°-90° pulse sequences following a train of 90° pulses of length T_1, which saturated the NMR signal. No field dependence of the relaxation time was observed between 6 and 9.5 MHz. The recovery of the echo over the two orders of magnitude observed was exponential. The product of T_1T varies from 1.25 sec °K at 1.6 °K to 1.75 sec °K at 300 °K. In Table I, the value of T_1T is listed for several temperatures and in Fig. 5 we plot the relaxation rate $R=(T_1T)^{-1}$ versus χ^2. The relaxation rate can be fitted by the straight line $R=R(\chi=0)+a\chi^2$ as shown by the dashed line of Fig. 5. The values of $R(\chi=0)$ and a obtained are 0.45 $(\text{sec °K})^{-1}$ and $a=3.3\times10^6$ $(\text{mole/emu})^2$.

The value of the Sn^{119} nuclear-spin-lattice relaxation time is listed in Table II for several temperatures. The value of T_1T we obtain is 0.033 sec °K, independent of temperature. The recovery of the Sn echo following a 180°-90°-180° pulse sequence is exponential. This indicates that if the Sn relaxation rate is anisotropic, the anisotropy is small compared to the average relaxation rate. This is not surprising since the direct s-contact hyperfine interaction, which is isotropic, is expected to be the dominant hyperfine interaction at the Sn site as it is in β-Sn,[16] and the anisotropic Knight shift, which results from non-s-contact hyperfine interactions, is always less than 20% of the isotropic Knight shift.

TABLE II. Summary of Sn^{119} NMR data in $LaSn_3$. 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_{ax}(%)	K_{iso}(%)	T_1T (sec °K)	K^2T_1T/S
300	+0.010(7)[a]	+0.640(5)		
77	+0.070(5)[a] +0.089(5)	+0.640(5)	0.035(2)	0.76
4.2	+0.110(5)	+0.640(5)	0.033(1)	0.72
1.6	+0.110(5)	+0.640(5)	0.033(1)	0.72

[a] Reference 13.

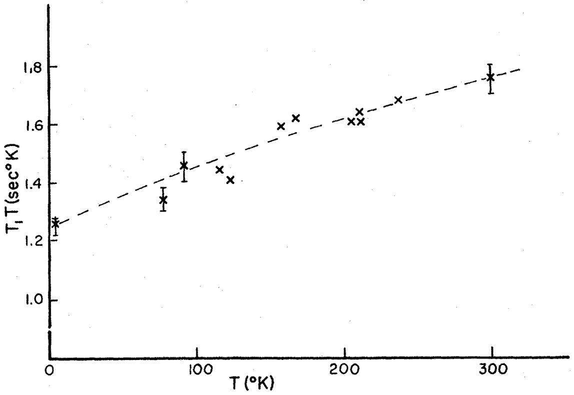

FIG. 4. The La^{139} relaxation time T_1 plotted as T_1T versus temperature at 8.5 MHz.

The phase memory times T_2 of the La^{139} and Sn^{119} spin echoes have been measured at low temperatures. The La T_2 values are summarized in Table I along with the Knight shift and T_1 data. The observed La spin-echo phase decay is Gaussian $[\exp(-t^2/2T_2^2)]$ following a 90°-30° or 90°-90° pulse sequence except for very short times and is slightly sample dependent (~ 20%). The Sn spin-echo phase decay is nonexponential and, depending upon the experimental conditions, varies from 250 to 600 μsec at 4.2 °K.

IV. DISCUSSION

For the discussion of the data we have presented on $LaSn_3$, we follow the customary scheme for partitioning the bulk susceptibility, Knight shifts, and spin-lattice relaxation rates into the spin and orbital contributions from the s, p, and d bands within the tight-binding model. Thus, we make the simplifying assumption that the spin and orbital contributions from each band are identifiable and that any cross terms or interference effects which result from effects such as s-d hybridization may be handled in a linearized fashion within the tight-binding approximation. In the LaX_3 compounds this approximation may be justified. Not only are the La atoms far apart (4.77 Å compared to 3.75 Å in La metal),[3] but each La atom is surrounded by 12 Sn nearest neighbors. In addition, the Sn $3d$ and $4d$ orbitals lie far below the Fermi surface and the Sn $5d$ orbitals have energies many eV too high. As a result, one might expect the La d-band electrons to be fairly localized. Preliminary band structure calculations[17] tend to support this picture in that the La d bands and the Sn s-p bands are considerably narrower in $LaSn_3$ than in the respective metals.

In terms of the various paramagnetic susceptibility contributions χ_i, the Knight shifts are given by

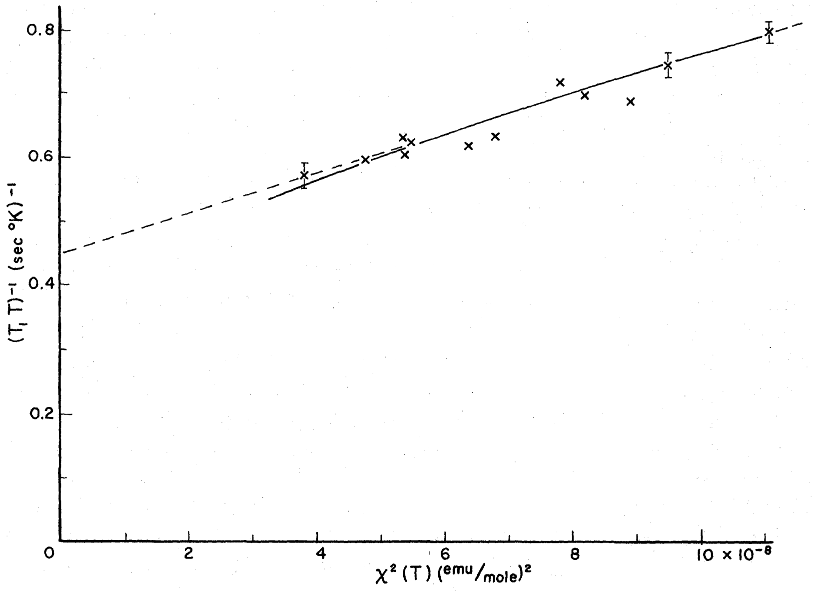

FIG. 5. The La^{139} relaxation rate $R=(T_1T)^{-1}$ versus the susceptibility squared. The solid line fit results assuming s-d mixing (see text or Appendix A). The dashed line fit results assuming a dominant La d-orbital susceptibility (see text or Appendix B). The solid line fit results from a partitioning of the La NMR data only and does not give the correct values of the bulk susceptibility.

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

and the spin-lattice relaxation rates are given by

$$R_i = (T_1T)_i^{-1} = (4\pi/\hbar)\, (\gamma_n\hbar)^2 k_B \,[H_{\rm hfs}^{(i)} N_i(0)]^2 F_i \qquad (2)$$

for noninteracting electrons.[18] 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 surface (per spin direction), the F_i are the inhibition factors for the p or d contributions ($F_s=1$) arising from their orbital degeneracy at the Fermi surface, and N is Avogadro's number. In the presence of electron-electron interactions giving rise to an exchange enhancement, it is more convenient to rewrite the relaxation rates from the spin contributions using the Korringa product K^2T_1T/S, modified for the effects of exchange enhancement and orbital degeneracy.[18] From Eqs. (1) and (2) the spin contributions (but not the orbital contributions) to the relaxation rate become

$$R_i = S^{-1}\, (\mu_B N)^{-2}\, (\chi_i H_{\rm hfs}^{(i)})^2\, Q(\alpha_i) F_i = S^{-1}\, K_i^2\, Q(\alpha_i) F_i \,, \qquad (3)$$

where $S=(\hbar/4\pi k_B)\,(\gamma_e/\gamma_n)^2$. The quantities $Q(\alpha_i)$ are correction factors which reflect the wave-vector dependence of the exchange enhanced susceptibility. For a free-electron metal and spherical bands, $Q(\alpha_i)\approx 1-\alpha_i$ for small α_i where the conduction-electron exchange enhancement is $(1-\alpha_i)^{-1}$.[18]

Since the total bulk susceptibility is the sum of the contributions from both the La and Sn sites, $\chi_{\rm La}+\chi_{\rm Sn}$, we must consider the partitioning of the NMR data at the Sn site as well as the La site. The important contributions to $K_{\rm iso}$ and R at the Sn site are expected to be the s- and p-spin contributions and possibly the p-orbital contribution. Dickson[16] determined that the direct s-contact hyperfine interaction is dominant in β-Sn and that all other contributions to the isotropic Knight shift in β-Sn are small and sum to zero. The values of the Sn^{119} Knight shift and spin-lattice relaxation time from Table II in LaSn$_3$ of $K_{\rm iso}=+0.640\%$ and $T_1T=0.033$ sec °K at 4.2 °K are not greatly different from the values for β-Sn of $K_{\rm iso}=+0.72\%$ and $T_1T=0.048$ reported by Dickson. However, the fact that in LaSn$_3$ the Korringa product is 0.72 at 4.2 °K as compared with 1.35 in β-Sn indicates some change in the character of the conduction electrons at the Sn site. If in LaSn$_3$ the s-contact hyperfine interaction at the Sn site is assumed to be dominant, then the sum of all other Knight shifts K' is small but negative. If $Q(\alpha_s)$ at the Sn site is allowed to vary between 0.75 (the value in β-Sn) and 1.00, then the Sn Knight shift and T_1 contributions may be partitioned using Eqs. (1)–(3) to give $K_s=+0.77\%$ and $K'=-0.13\%$ if $Q(\alpha_s)=1.00$ or $K_s=+0.88\%$ and $K'=-0.24\%$ for $Q(\alpha_s)=0.75$.

Several interesting features emerge from this partitioning of the Sn^{119} NMR results. The density of the s states at the Fermi surface $N_s^{\rm Sn}(0)$ has increased by 7–22% from that of β-Sn since the value of K_s scales with $N_s^{\rm Sn}(0)$ assuming the Sn s-contact hyperfine field is unchanged. Thus, the total density of states at the Sn site may be slightly larger than in β-Sn. Since the bare density of states is estimated to be 1.32 states/eV unit cell in LaSn$_3$, and $N^{\rm Sn}(0)=0.23$ states/eV atom in β-Sn, the density of states at the La site should be about $N_d(0)\approx N^{\rm La}(0)\approx 0.6$ to 0.7 states/eV atom. Also, a small but important negative contribution to the temperature-independent isotropic Sn Knight shift exists. This Knight shift probably results either from the p-core polarization hyperfine interaction or from transferred hyperfine effects from the La site. The expected d-electron localization and the temperature independence of K' would indicate that K' results from a p-core polarization contribution. Since $K'/K_s \sim 20\%$ and the inhibition factor F_i for non-s-electrons is less than 1, it is reasonable to assume that K' has little effect on the relaxation rate. The most important point to note is that the isotropic Sn Knight shift, relaxation rate, Korringa product, and intrinsic linewidth show no correlation with the temperature-dependent bulk susceptibility within experimental error. Thus, the Sn NMR data are consistent with the assertion that the conduction electrons associated with the Sn site do not contribute to the temperature-dependent bulk susceptibility.

We now discuss the manner in which the La NMR data and the temperature-dependent susceptibility may be partitioned. We will neglect both the effects of the La p-electron contributions which are normally small and the effect of spin-orbit coupling. The important paramagnetic terms to be considered are the s- and d-spin terms, χ_s and χ_d, and the d-orbital term, χ_{orb}. If we take a model of LaSn$_3$ similar to that of Sc metal and assume that χ_d is dominant, then clearly χ_d must be strongly exchange enhanced with an enhancement factor which may be as large as 8. This is very surprising in a high-T_c material. However, as discussed previously, one might expect the La d-band electrons to be fairly localized which is consistent with the observed susceptibility. Hence one might describe the situation as follows: The temperature-dependent bulk susceptibility arises from the states associated with the La atoms, whereas the superconductivity is due primarily to those states associated with the Sn sites.

The La hyperfine fields have been estimated from the results of free-atom calculations allowing for a reduction factor in each case of 0.75 for the value of the hyperfine field in a metal. The estimated value for the direct s-contact hyperfine field is $H_{\mathrm{hfs}}^{(s)} = 2.1\times 10^6$ Oe/μ_B.[19] In order to estimate the d-band hyperfine fields, we take a La^{2+} ($5d^1$) configuration. The d-orbital hyperfine field (appropriate for the Van Vleck term but not necessarily for the other terms discussed by Hebborn *et al.*[11]) can be estimated from the tabulated value of $\langle r^{-3}\rangle$[20] to be $H_{\mathrm{hfs}}^{(\mathrm{orb})} = 2\mu_B \langle r^{-3}\rangle \frac{3}{4} = 2.4\times 10^5$ Oe. [Note that for the La ($5d^3$) configuration which may be more appropriate for La metal, $H_{\mathrm{hfs}}^{(\mathrm{orb})}$ has decreased to 1.35×10^5 Oe.] It should be noted that the value of $\langle r^{-3}\rangle$ used for the orbital Knight shift involves an average over the excitations from all occupied states of the d band, while the value of $\langle r^{-3}\rangle$ used for the orbital relaxation rate involves an average over d states only at the Fermi surface. This difference will be neglected. The value for the d-core polarization hyperfine field is estimated to be $H_{\mathrm{hfs}}^{(d)} = -3.5\times 10^5$ Oe/μ_B.[21] This value is consistent with the expected increase of $H_{\mathrm{hfs}}^{(d)}$ in going from Sc to La as well as the observed La relaxation rates in dhcp La metal.[22]

The simplest way to partition the results at the La site if the d-spin susceptibility is dominant is an independent band approximation in which the temperature dependence of the susceptibility results from χ_d. This is clearly ruled out by the value of $dK/d\chi$ obtained from the data shown in Fig. 3. Using the above estimate for $H_{\mathrm{hfs}}^{(d)}$, one obtains $K_d = -2.05\%$ at 4.2 °K and $dK/d\chi = -63$ mole/emu in this approximation, as opposed to the measured values of $K = +0.207\%$ at 4.2 °K and $dK/d\chi = -1.72$ mole/emu. Thus, the independent-band approximation is clearly inappropriate for LaSn$_3$ in this case.

Assuming that χ_d is dominant, a better approach would be to assume the existence of s-d hybridization as has been postulated for Sc.[23] The s-spin susceptibility will then be of the form $\chi_s = \chi_s^0 + \xi\chi_d(T)$ where ξ is the s-d mixing parameter and both χ_s and ξ are assumed to be temperature independent. Then K_s and R_s will also have temperature-dependent contributions because of their dependence on χ_s. The details of this partitioning are discussed in Appendix A and the results are shown in Fig. 6(a) where K_s and K_d are plotted versus χ. Clearly a cancellation of the large temperature-dependent values of K_s and K_d is needed in order to account for the measured value of $dK/d\chi$. That such a large cancellation would be present over the observed temperature range seems unlikely. A more serious difficulty with this approach is the very large magnitude of the calculated s- and d-spin relaxation rates. For instance, the s-contact contribution at 4.2 °K is $R_s = 22.0$ (sec °K)$^{-1}$ assuming $Q(\alpha_s) = 1$ and the d-core polarization contribution is $R_d = 4.5Q(\alpha_d)$ (sec °K)$^{-1}$ if $F_d = 0.2$. The measured rate is $R = 0.79$ (sec °K)$^{-1}$, a factor of 30 smaller. Within the extreme tight-binding approximation there should be no interference between the s- and d-spin relaxation rates since the La site has cubic symmetry.[24] Because of the fairly localized nature of the La d electrons, violations of the tight-binding formulation for the relaxation rates of this magnitude seem improbable. Thus the assumption that the origin of the temperature-dependent susceptibility appears to be unlikely if the estimates of the La hyperfine fields are approximately correct.

It should be noted that a similar difficulty arises in partitioning the NMR[25] and susceptibility[2] data for LaIn$_3$ which has an even larger temperature-dependent (non-Curie-Weiss) susceptibility than LaSn$_3$. The value of $dK/d\chi$ for the La site is about the same as in LaSn$_3$ but it is positive. The La spin-lattice relaxation rate is also of a similar

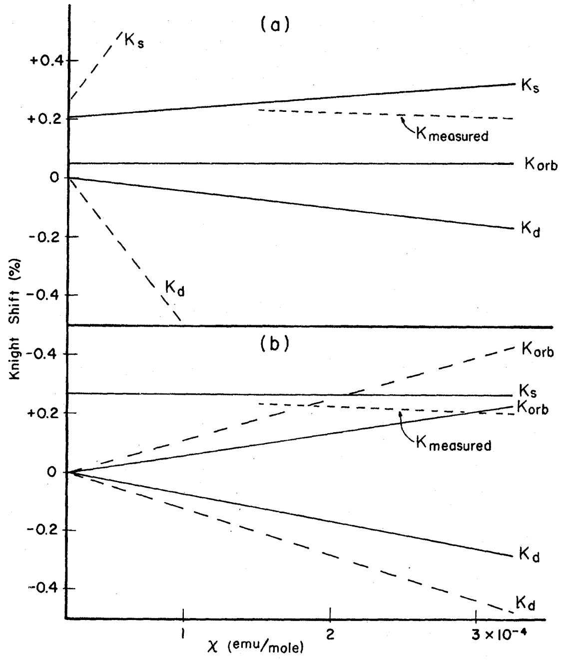

FIG. 6. Partitions of the La^{139} Knight shift into the s- and d-spin and d-orbital contributions as a function of the bulk susceptibility assuming (a) s-d mixing (see text or Appendix A) and (b) a dominant d-orbital susceptibility (see text or Appendix B). The dashed and solid lines represent different separations.

magnitude. Since it is reasonable to assume that the properties of La in $LaIn_3$ are not unlike those in $LaSn_3$, any fortuitous cancellation of the s- and d-spin contributions to the La Knight shift and relaxation rate is most unlikely. This difficulty, which results from the assumption of a strongly exchange enhanced La d-spin susceptibility, indicates that either the customary partitioning scheme (which gives reasonable results for materials like Sc metal) must be inapplicable or else the La d-spin susceptibility is not the dominant contribution. We consider now the possibility of a large d-orbital susceptibility.

A consistent fit to the NMR data and the bulk susceptibility within the customary partitioning scheme can be obtained even neglecting any s-d mixing if one assumes that the La d-orbital susceptibility is dominant. This assumption is not unreasonable as it is known that orbital susceptibilities can be large in transition metals. In the case of vanadium, for example, it is estimated that the orbital susceptibility is 2.07×10^{-4} emu/mole.[10] However, the La d-spin susceptibility is not small and as a result it must have the same temperature dependence as χ_{orb} in order that $dK/d\chi$ be constant. (This point will be discussed later.) The total temperature-dependent susceptibility is then $\chi_d+\chi_{orb}$. The s-spin susceptibility and hence K_s and R_s will be assumed to be temperature independent. The details of this partitioning are described in Appendix B. Two different partitionings are discussed which allow estimates of the upper and lower limits for the values of the various parameters to be made. The smallest value for χ_{orb}/χ_d of 2.9 results from the assumption that there is no exchange enhancement of χ_d and that there is a fivefold degeneracy of the d bands at the Fermi surface. The largest value for χ_{orb}/χ_d of 6.2 results from determining a minimum value for χ_d from estimates of the La d-band contribution to the bare density of states assuming no exchange enhancement. In Fig. 6(b) the results for the various contributions to the La Knight shift are presented. In Fig. 5, the dashed line is the result for the La relaxation rate for both partitionings. The results for the susceptibility and the La NMR contributions at 4.2 °K are summarized in Table III.

Let us now discuss the point raised earlier about the temperature dependence of the orbital susceptibility of the La d band, χ_{orb}. The spin susceptibility neglecting exchange enhancement is of the form

$$\chi_{spin}=C\int\frac{\partial f}{\partial E}N(E)\,dE, \tag{4}$$

TABLE III. Results of partitioning the bulk susceptibility and La NMR data at 4.2 °K assuming the La d-band orbital susceptibility χ_{orb} is larger than the spin susceptibility χ_d, where both terms have the same temperature dependence. The quantities are defined in the text.

	$K(\%)$	$R=(T_1T)^{-1}$ (sec °K)$^{-1}$	χ (10^{-4} emu/mole)
		(a)	
$H_{hfs}^{(orb)}=0.95\times10^5$ Oe	$K_s^0=+0.263$	$R_s=$ 0.44	$\chi_s=0.07$
$F_d=0.2$	$K_d=-0.480$	$R_d=$ 0.35	$\chi_d=0.76$
	$K_{orb}=+0.423$	$R_{orb}=<0.02$	$\chi_{orb}=2.48$
		(b)	
$H_{hfs}^{(orb)}=0.45\times10^5$ Oe			
$F_d=0.55$	$K_s^0=+0.263$	$R_s=$ 0.44	$\chi_s=0.07$
	$K_d=-0.284$	$R_d=$ 0.35	$\chi_d=0.45$
	$K_{orb}=+0.227$	$R_{orb}=<0.02$	$\chi_{orb}=2.79$

where f is the Fermi function, $N(E)$ is the density of states, and C is a constant. The orbital susceptibility of spinless Block electrons for a crystal with a center of inversion was derived by Hebborn *et al.*[11] The result is written as the sum of four terms. Quoting Hebborn *et al.*, "The first part of χ, (the 'Landau-Peierls' term) is the analogue of the free-electron diamagnetism, χ_4 is the analogue of the atomic diamagnetism including the Van Vleck paramagnetism, whilst the other terms in χ are mixed terms which seem to have no simple interpretation and whose importance in practice has not yet been ascertained." The Van Vleck term can be written in the form

$$\chi_{vv} = \int G(E) f(E) N(E)\, dE, \tag{5}$$

where $G(E)$ is a function of energy involving derivatives of the electronic wave functions. It is clear that Eqs. (4) and (5) would not have the same temperature dependence except through the most exceptional of circumstances, since Eq. (4) contains $\partial f/\partial E$ and hence is dominated by states within kT of the Fermi surface, whereas Eq. (5) contains $f(E)$ and hence is contributed to by all occupied states. On the other hand, χ_2, which is one of the "other terms in χ," has the form

$$\chi_2 = \int g(E)\, \frac{\partial f}{\partial E}\, N(E)\, dE, \tag{6}$$

where $g(E)$ is a complicated function of energy involving wave functions and their derivatives. It is clear that if $g(E)$ is a slowly varying function of energy compared to $N(E)$, then Eq. (6) will have the same temperature dependence as Eq. (4). Thus, we feel that orbital susceptibility terms other than the Van Vleck term may well have to be considered in the analysis of the magnetic properties of the transition metals. In particular, it is possible that the orbital susceptibility χ_2 may account for the results which we report in this paper. Certainly it will be of considerable interest to have estimates of these terms for the LaX_3 compounds.

The partitioning of the NMR and susceptibility data presented above based on the assumption of a dominant temperature-dependent orbital susceptibility appears to give a reasonable picture of $LaSn_3$. However, a large number of assumptions are involved in partitioning these data and the neglect of spin-orbit coupling and s-d hybridization effects may not be justified. While the neglect of s-d hybridization effects is probably not too serious (see Appendix B), it is difficult to estimate what effect spin-orbit coupling will have on these results. The most important point that we wish to make here is that it is possible to obtain a consistent partitioning of the NMR and χ data with the assumption of a dominant χ_{orb}, but not in the case of a strongly exchange enhanced χ_d, unless either the tight-binding model breaks down completely or the estimated d-core polarization hyperfine interaction is much too large, a situation which is unlikely considering the relative localization of the La d electrons.

V. CONCLUSIONS

In this paper we present the results of a study of the magnetic properties of $LaSn_3$. The La^{139} and Sn^{119} Knight shifts and relaxation rates from 1.6 to 300 °K are reported along with new bulk susceptibility results. The normal-state magnetic properties are studied by partitioning these quantities into their various spin and orbital contributions using the customary methods employed for transition metals. From the NMR measurements we have concluded that the temperature-dependent susceptibility arises from the La d band. The resemblance of the bulk susceptibility of $LaSn_3$ to that of Sc suggests that it might arise from a strongly exchange enhanced La d-spin susceptibility. One difficulty with the assumption of a strongly exchange enhanced La d-spin susceptibility is the existence of strong spin-spin interactions which might be expected to lower T_c far below the observed value of 6.45 °K or destroy superconductivity completely, as is alleged in the case in Sc- and Pd-type systems. The coexistence of strong d-spin interactions with a high T_c would only be possible if the La d electrons were relatively localized (see Sec. IV) and responsible for the magnetic properties while the superconducting properties were determined by the properties of the Sn sites. However, we find that with this assumption it is not possible to partition that susceptibility and the La NMR data within the tight-binding approximation, even allowing for s-d hybridization. For only if strong interference effects occur between the s and d contributions to the La spin-lattice relaxation rate, indicating a complete breakdown of the tight-binding approximation, would it be possible to account for either the very small magnitude or the temperature dependence of the La relaxation rate. In view of the expected localization of the La d electrons, the tight-binding model would be expected to be a reasonable approximation.

More reasonable results were obtained with the assumption that the temperature-dependent bulk susceptibility derives mainly from the La d-orbital contributions. In this case, the La d-spin and d-orbital contributions to the susceptibility must have the same temperature dependence. With this assumption, we obtain reasonable limits for the various contributions to the La NMR Knight shift and spin-lattice relaxation rates and the bulk susceptibility, even though we neglect s-d mixing.

It is interesting to speculate upon the existence of a temperature-dependent orbital susceptibility of this type. The Van Vleck orbital susceptibility is expected to be small for $LaSn_3$ and would not be expected to have the same temperature dependence as the spin susceptibility. However, it is possible that the additional orbital susceptibility contribution discussed by Hebborn *et al.*[11] (namely χ_2) could give rise to a large orbital susceptibility in $LaSn_3$. This term can be paramagnetic and can scale with the density of states at the Fermi surface. Estimates of this contribution in the alkali metals show that it is appreciable and that it depends on the deviation of the conduction-electron wave function from plane-wave behavior, which indicates that it may be much more important in transition metals. Unfortunately, the calculation of this contribution requires detailed information of the wave functions and their derivatives at the Fermi surface which is not available for $LaSn_3$ at this time.

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APPENDIX A

In this section we present the details of partitioning the bulk susceptibility and La NMR results with the assumption that the La d-spin susceptibility dominates all other susceptibility contributions along with the assumption of a significant mixing of the s and d bands. The resulting s-spin susceptibility can be written in the form

$$\chi_s = \chi_s^0 + \xi\, \chi_d, \tag{A1}$$

where ξ is the s-d mixing parameter and both χ_s^0 and ξ are assumed to be temperature independent. The total temperature-dependent susceptibility will then be $\chi(T) = (1+\xi)\chi_d$. The La Knight shift is then given by

$$\begin{aligned} K &= K_0 + K_s(T) - K_d(T), \\ K &= K_0 + (H_{\text{hfs}}^{(s)}/\mu_B N)\xi\, \chi_d + (H_{\text{hfs}}^{(d)}/\mu_B N)\chi_d\,, \qquad \text{(A2)} \\ K &= K^0 + 378\xi\, \chi_d - 63\chi_d\,, \end{aligned}$$

using the hyperfine field estimates discussed in the text and with the susceptibility given in emu/mole. The orbital contribution and any temperature-independent s-contact contribution to the Knight shift are combined in the temperature-independent term K_0. From the data presented in Figs. 1–3 and Eq. (1), we find $K_0 = +0.263\%$ and $\xi = 0.16$. The results for the variation of K_s and K_d versus χ are plotted in Fig. 6(a). At 4.2 °K we find $K_s = +1.70\%$ and $K_d = -1.76\%$. The resulting relaxation rates calculated from Eq. (3) are $R_s = 22.0$ (sec °K)$^{-1}$ for $Q(\alpha_s) = 1$ and $R_d = 4.5Q(\alpha_d)$ (sec °K)$^{-1}$ if $F_d = 0.2$ at 4.2 °K.

It is interesting to note that it is possible to partition just the La NMR results consistently within the extreme tight-binding approximation assuming s-d hybridization. Writing the various Knight shift contributions as $K_s = K_s^0 + \eta\,\chi$, $K_d = -(\eta + dK/d\chi)\chi$, and $K_{\text{orb}} = \text{const}$, and taking $Q(\alpha_s) = 1$ and $F_d = 0.2$, a fit is obtained which is shown by the solid lines of Figs. 5 and 6(a) using the values $\eta = 3.55$ mole/emu and $K_s' = +0.210\%$. The only important contribution to the relaxation rate is R_s. This fit, however, is inconsistent with the assumption of an exchange enhanced χ_d unless the value of $H_{\text{hfs}}^{(d)}$ is reduced by a factor of 10, which seems quite unlikely in view of the relatively localized nature of the La d electrons.

APPENDIX B

In this section we present the results of partitioning the bulk susceptibility and La NMR results with the assumption that the La d-orbital susceptibility dominates the d-spin susceptibility. We neglect s-d hybridization effects, spin-orbit coupling, and any exchange enhancement of the La d-spin susceptibility. Since χ_d is not small, it must have the same temperature dependence as χ_{orb} in order that $dK/d\chi$ be constant. The total temperature-dependent susceptibility is then $\chi_d + \chi_{\text{orb}}$ and all s-spin contributions are assumed to be temperature independent. The La Knight shift is given by

$$K = K_s + (H_{\text{hfs}}^{(d)}/\mu_B N)\chi_d + (H_{\text{hfs}}^{(\text{orb})}/\mu_B N)\chi_{\text{orb}}\,, \tag{B1}$$

where K_s is found to be $+0.263\%$ from the extrapolated value of K at $\chi(T) = 0$. This gives a value of R_s from Eqs. (1) and (3) of 0.52 (sec °K)$^{-1}$ which is very close to the value obtained from the data presented in Fig. 5 of $R_s = 0.45$ (sec °K)$^{-1}$ when R is extrapolated to $\chi(T) = 0$. This confirms the identification of K and R at $\chi(T) = 0$ as resulting from the s-contact interaction. Then if we assume no exchange enhancement of the La d-spin susceptibility and take the minimum value of 0.2 for F_d the value of K_d at 4.2 °K consistent with $R_d = R - R_s = 0.35$ (sec °K)$^{-1}$, is $K_d = -0.480\%$. The Knight shift and susceptibility can then be partitioned by varying $H_{\text{hfs}}^{(\text{orb})}$, which determines the ratio of χ_{orb}/χ_d. This leads to the partitioning shown in Fig. 6(b) as the dashed lines where the Knight shifts are plotted versus χ. The values obtained at 4.2 °K are given in Table III(a). The ratio of χ_{orb}/χ_d obtained is 2.9 and we find $H_{\text{hfs}}^{(\text{orb})} = 0.95 \times 10^5$ Oe which is 40% of the estimated value. This partitioning gives a reasonable upper limit to the value of $H_{\text{hfs}}^{(\text{orb})}$ and the magnitudes of K_{orb} and K_d for the assumptions given above.

However the value obtained for the density of d states at the Fermi surface is $N_d(0) = \chi/(2N\mu_B^2)$ or 1.3 states/eV atom at 4.2 °K using the value listed in Table III(a) and assuming no exchange enhancement. From the partitioning of the Sn NMR data we estimated that $N_d(0) \cong 0.7$ states/eV atom at 4.2 °K. This assumes the electron-phonon interaction is the same for the Sn and La sites in $LaSn_3$. If either the McMillan determination[4] overestimates the mass enhancement (as may be the case for La metal[26]) or the mass enhancement is less at the La site than at the Sn site, a value of 1.3 states/eV atom need not be unreasonable for $N_d(0)$. The value of 0.7 states/eV atom for $N_d(0)$ in the absence of exchange enhancement gives $\chi_d = 0.45\times 10^{-4}$ emu/mole. Fitting these values to Eq. (B1) gives the results for the Knight shifts plotted as the solid line in Fig. 6(b) and the values of various quantities at 4.2 °K listed in Table III(b). Note that the value of $H_{\rm hfs}^{(\rm orb)}$ which results is $H_{\rm hfs}^{(\rm orb)} = 0.45\times 10^5$ Oe or about 20% of the value estimated from the free-atom $La^{2+}(5d^1)$ configuration. The small value of $H_{\rm hfs}^{(\rm orb)}$ could reflect a difference in the orbital hyperfine fields appropriate for the Van Vleck term and other orbital terms. The d-spin relaxation rate then requires a reduction factor $F_d = 0.55$, whereas the maximum value of F_d in the tight-binding approximation is 0.50. Thus, this partitioning represents a reasonable lower limit on the value of $H_{\rm hfs}^{(\rm orb)}$ and the magnitudes of $K_{\rm orb}$ and K_d, within the stated approximations. Since the t_{2g} d levels are expected to have the lowest energy,[17] the value of F_d would be expected to be about 0.3[18] which would favor values close to those indicated in Table III(a) and in Fig. 6(b) by the dashed lines. This suggests that some exchange enhancement of χ_d exists but that it is small ($<\sim 2$). The inclusion of s-d mixing as in Appendix A will lead to decreased values of $\chi_{\rm orb}/\chi_d$ in each case. However, s-d mixing must be relatively unimportant or else fairly large enhancements of χ_d are required.

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