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Microscopic and Macroscopic Electronic Properties of the $AuCu_3$-Type Alloys: The $LaSn_3$-$LaIn_3$ Pseudobinary Alloy System*

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The bulk properties of the $LaSn_{3x}In_{3(1-x)}$ and similar alloy systems display a dramatic, somewhat oscillatory, dependence on the valence-electron concentration. For the $LaSn_{3x}In_{3(1-x)}$ alloy system we have studied the dependence on x of the magnetic susceptibility χ and the local electronic behavior at the La and Sn-In sites using the La^{139} and Sn^{119} nuclear-magnetic-resonance Knight shifts K and spin-lattice relaxation times T_1. These results are compared with those for the superconducting transition temperature T_c, the electronic-specific-heat coefficient γ, and the Debye temperature Θ_D. Using McMillan's strong-coupling model we have calculated from γ and T_c/Θ_D, the electron-phonon coupling parameter λ, the bare density of states $N(0)$, and the electron-phonon interaction strength V. For the NMR measurements, the Sn NMR properties follow the behavior of the bulk density of states at the Fermi energy, $N(0)$, considerably better than do the La NMR properties suggesting that the local electronic properties of the Sn-In sites play the dominant role in determining T_c. Analysis of the La NMR and χ behavior with x indicates the paramagnetic susceptibility of these alloys arises from the La d band with the La d-orbital contribution accounting for most of the large susceptibility for x near $LaSn_3$ and $LaIn_3$.

I. INTRODUCTION

The properties of the $LaSn_{3x}In_{3(1-x)}$ alloy system have been the subject of a number of studies in recent years.[1-7] This is a result of both the dramatic variation of the bulk properties of these alloys with the electron/atom ratio $\mathfrak{z}$ and the fact that the properties of this alloy system are representative of a number of similar alloy systems where the La site is occupied by a column-IIIb transition-metal atom and the Sn-In sites are occupied by column-IIIa and -IVa non-transition-metal atoms.[4] Most of these alloy systems form in the $AuCu_3$ crystal structure. The LaX_3 intermetallic compounds (X = Sn, In, Tl, Pb) became of interest originally because of the puzzling coexistence of a high superconducting transition temperature T_c with a large temperature-dependent paramagnetic susceptibility χ for several of these compounds, which was believed to result from a large exchange enhancement of the La d-spin susceptibility.[3] When these studies were extended to the alloys[4-7] it was found that the electronic-specific-heat coefficient γ and the thermopower S, as well as T_c and χ, showed a similar and somewhat oscillatory dependence on $\mathfrak{z}$. Havinga *et al.*[4] have shown that the variations with $\mathfrak{z}$ observed for the $LaSn_{3x}In_{3(1-x)}$ alloys are fairly typical of a large number of similar alloy systems.

Nuclear-magnetic-resonance (NMR) Knight-shift and spin-lattice relaxation-rate measurements made in the intermetallic compounds $LaSn_3$,[8-10] $LaIn_3$,[10,11] and $LaPb_3$[10] indicated that the LaX_3 compounds should be treated as transition-metal compounds in contrast to the conclusions of Havinga *et al.*[4] Most of the paramagnetic susceptibility of these compounds was interpreted as deriving from the La d bands with the d-orbital contribution to the paramagnetic susceptibility dominating the d-spin contribution in $LaIn_3$ and $LaSn_3$.[9,10]

In the present study we report the results of magnetic susceptibility and NMR measurements for the $LaSn_{3x}In_{3(1-x)}$ alloy series. From our results we find that the variation of the local properties with composition often differs considerably at the La and Sn sites. The local properties at the X site, as determined from the NMR measurements, appear to track the bare density of states at the Fermi energy $N(0)$, but this is not found to be the case for the local properties at the La site. On the other hand, in both $LaSn_3$ and $LaIn_3$ where the bulk susceptibility is large and paramagnetic, the La Knight shift correlates with the bulk susceptibility.[9,10] A comparison of the local electronic properties at the La and X sites suggests that the superconducting properties[4,5,7] of these materials derive primarily from the X-site electron states while for those compositions where the paramagnetic susceptibility is enhanced much above the bare density of states value, the dominant paramagnetic susceptibility contribution results from the La d-orbital term.

II. BULK MEASUREMENTS

Susceptibility measurements were carried out on this system from 1.4 to 800 K, prompted by the

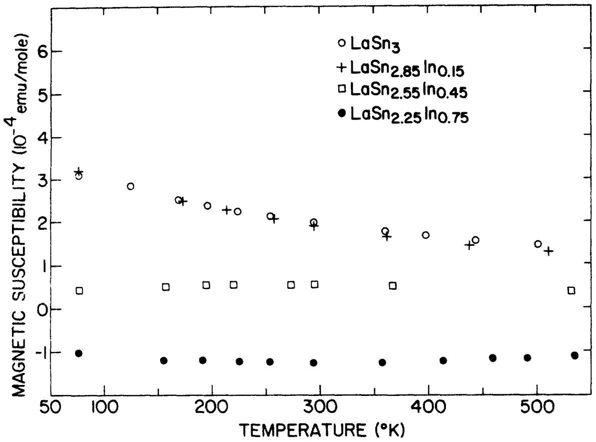

FIG. 1. Variation with temperature of the magnetic susceptibility in the $LaSn_{3x}In_{3(1-x)}$ alloys for $x=1$, 0.95, 0.85, and 0.75. The susceptibility has been corrected for the temperature-dependent core diamagnetism.

unusual susceptibilities of $LaSn_3$ and $LaIn_3$. The samples were about 10 g in size and were spark-cut from ingots whose preparation and physical properties are described elsewhere.[12] Mass-spectrographic analysis of a sample ($LaSn_3$) gave an impurity concentration of 500 ppm of various rare-earth impurities and 130 ppm of various transition-metal impurities (which come from the La used). These impurities give rise to a paramagnetic "tail" which is Curie-like ($\sim 1.5\times10^{-3}T^{-1}$ emu/mole) assuming that the intrinsic bulk susceptibility has little temperature dependence below 77 K, an assumption which is consistent with the NMR measurements. Because of the difficulty of determining the intrinsic low-temperature suscepbtility accurately, we will only discuss the data for $T \geq 77$ K. In Figs. 1 and 2 the susceptibilities are plotted for the Sn-rich and In-rich samples, respectively. The data are for the temperature range 77–550 K and have been corrected for the diamagnetic core contribution by interpolating the values calculated from the Landolt-Bornstein tables[13] for $LaSn_3$ ($\chi_D = -0.68\times10^{-4}$ emu/mole) and $LaIn_3$ ($\chi_D = -0.77\times10^{-4}$ emu/mole). Since the temperature variation of the susceptibility above 550 K was monotonic and quite small it has not been included in Figs. 1 and 2. From Figs. 1 and 2 it is clear that the temperature dependence, magnitude, and sign of the susceptibility depend strongly on composition. Near $LaSn_3$ ($x \simeq 1$), the susceptibility is paramagnetic and quite temperature dependent. As x decreases, χ decreases and becomes diamagnetic near $x = 0.75$. At $x = 0.1$ the susceptibility is diamagnetic and quite temperature dependent. Finally, at $LaIn_3$ ($x = 0$), χ is again similar to that observed for $LaSn_3$. To see the compositional dependence of χ, in Fig. 3 the susceptibility at 77 K, χ(77 K), is plotted as a function of x.

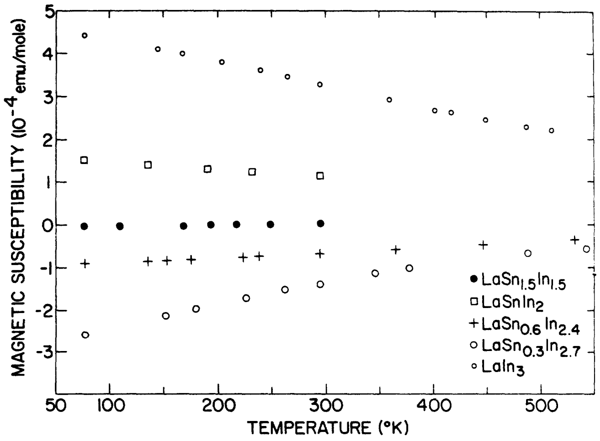

FIG. 2. Variation with temperature of the magnetic susceptibility in the $LaSn_{3x}In_{3(1-x)}$ alloys for $x=0.5$, 0.33, 0.20, 0.10, and 0. The susceptibility has been corrected for the temperature-independent core diamagnetism.

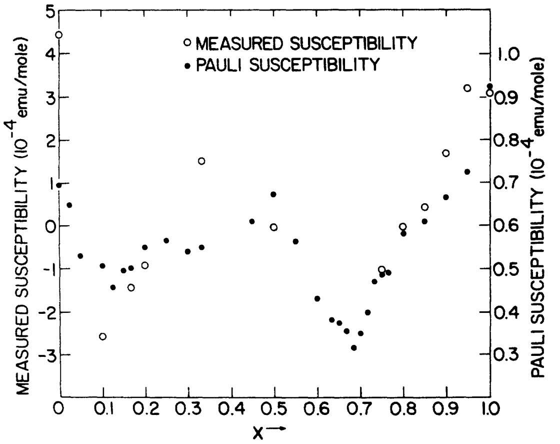

FIG. 3. Variation with composition of the susceptibility at 77 K, χ(77 K), corrected for the ion-core diamagnetism, and the variation of the unexchanged enhanced Pauli paramagnetic susceptibility χ_p, calculated from the bare density of states. Note the difference in scale of the two quantities.

From the specific-heat measurements[4,5,7] one can determine both γ and the Debye temperature Θ_D. McMillan[14] has derived a relationship between T_c and the electron-phonon parameter λ which is

$$T_c = \frac{\Theta_D}{1.45}\exp\left(-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right), \qquad (1)$$

where μ^* is the Coulomb pseudopotential. Taking $\mu^* = 0.13$, a value found by McMillan[14] to be typical for transition metals, we have calculated λ. Using the relation between γ, λ, and $N(0)$ of

$$\gamma = \tfrac{2}{3}\pi^2 k_B^2 N(0)(1+\lambda) \qquad (2)$$

we have calculated $N(0)$. Since $\lambda = N(0)V$, where V is the BCS electron-phonon interaction strength, we can calculate V from $N(0)$ and λ. In Fig. 4 we have plotted T_c, $N(0)$, and V (normalized to its maximum value of 3.13 eV) as a function of composition.[7] Even though the $LaSn_{3x}In_{3(1-x)}$ system is single phase, its physical properties vary greatly. Over the entire composition range T_c follows the somewhat oscillatory variation of $N(0)$. However, in the region $x = 1.0-0.75$, where T_c and $N(0)$ vary rapidly, V is nearly constant, while at $x = 0.68$, V has a marked maximum but T_c is minimum.

III. NUCLEAR-MAGNETIC-RESONANCE MEASUREMENTS

A. Knight Shifts

Powders of 40-μ-size particles were prepared by grinding the bulk materials and sieving the powder (325 mesh). These powders were then annealed in tantalum crucibles at 450–600 °C for 24–72 h. No sample deterioration was observed over a 2 month period if the powders were kept under helium gas; over the same period no change was observed in the NMR properties. From the NMR measurements no evidence exists that these alloys have any second phase. Both the La^{139} and Sn^{119} linewidths were about 20% larger at 4.2 than at 300 K. While the linewidths are independent of magnetic field near $x = 0$ and 1, for intermediate composition the linewidths become much broader and field dependent as a result of inhomogeneous Knight-shift broadening.

The La^{139} Knight shift was measured at 300, 77, 4.2, and 1.6 K using the La resonance in an aqueous solution of $LaCl_3$ as a reference. The La Knight shift displays an oscillatory dependence on x similar to that observed for the bulk properties as shown in Fig. 5 where the La Knight shift at 4.2 and 300 K is plotted versus x. However, a comparison of the composition dependence of $\Delta K = K_{300} - K_{4.2}$ with the composition dependence of the magnitude of the Knight shift and bulk paramagnetic susceptibility shows that these quantities do not correlate very well. This indicates that the various contributions to the La Knight shift have a complicated dependence upon the In/Sn ratio. A study of the La Knight shift at intermediate temperatures shows that in the alloys the Knight shift has the same monotonic behavior with temperature found in $LaSn_3$ and $LaIn_3$. While the magnitude of the temperature dependence of the Knight shift for the alloys is often similar to that observed for $LaSn_3$ and $LaIn_3$, the temperature dependence of the susceptibility can be quite different both in sign and magnitude from that observed for $LaSn_3$ and $LaIn_3$ as a result of temperature-dependent diamagnetic contributions. Perhaps the most interesting feature of the La

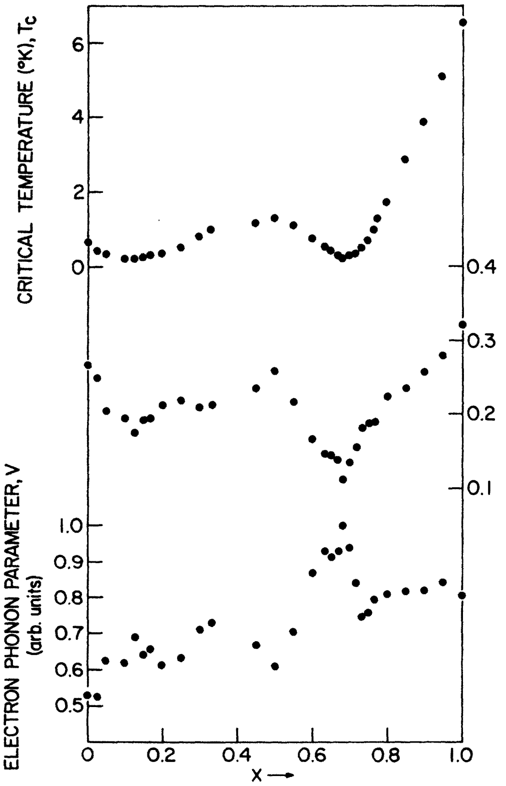

FIG. 4. The variation with composition of the superconducting transition temperature, the bare density of states, and the electron-phonon interaction strength in the $LaSn_{3x}In_{3(1-x)}$ alloys. The data are taken from Ref. 7.

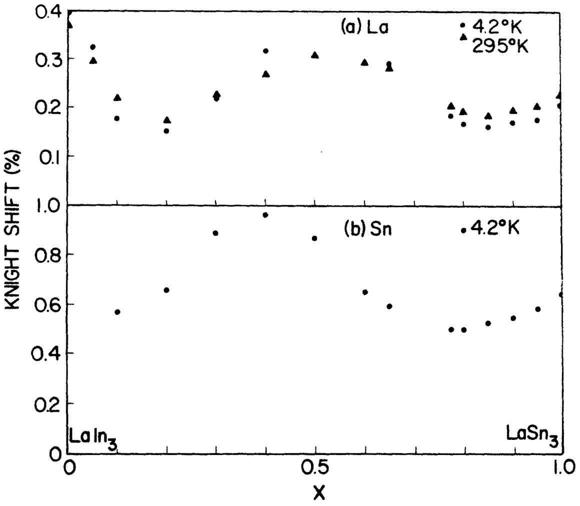

FIG. 5. Knight shifts in the $LaSn_{3x}In_{3(1-x)}$ alloys vs x at 8 MHz: (a) La^{139} Knight shift; (b) Sn^{119} Knight shift.

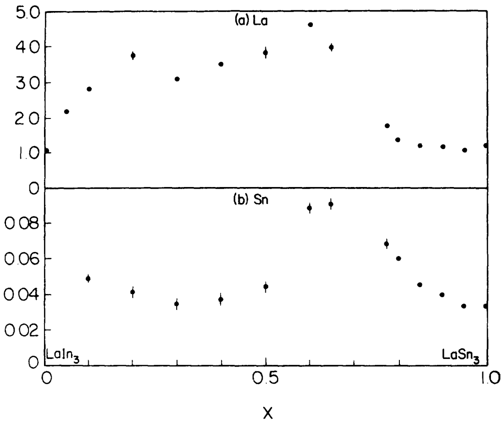

FIG. 6. Spin-lattice relaxation time in the $LaSn_{3x}In_{3(1-x)}$ alloys vs x at liquid-helium temperatures and 8 MHz: (a) La^{139} T_1T; (b) Sn^{119} T_1T.

Knight-shift data of Fig. 5 is that both K and ΔK are relatively independent of composition near $LaSn_3$ while K and ΔK vary rapidly with composition near $LaIn_3$. This behavior is to be contrasted with the rapid variation of the bulk susceptibility with composition found near both $LaSn_3$ and $LaIn_3$.

The Sn^{119} Knight shift was measured at 1.6 and 4.2 K for $x \geq 0.10$, using the Li^7 resonance in an aqueous solution of LiCl as a reference with $\nu_{Li^7}/\nu_{Sn^{119}} = 1.04285$. The isotropic Sn Knight shift is plotted versus x in Fig. 5. No temperature dependence was observed between 1.6 and 4.2 K. The anisotropic Sn Knight shift is small except in $LaSn_3$. The Sn Knight shift has a composition dependence not unlike that of the La Knight shift for $x \geq 0.50$, with a minimum near $x = 0.75$ and a maximum near $x = 0.40$ and at $LaSn_3$.

B. Spin-Lattice Relaxation Times

The La^{139} spin-lattice relaxation time T_1 was measured at liquid-helium temperatures following saturation of the NMR signal by a train of 90° pulses of duration about T_1. When necessary, signal enhancement was achieved either using a boxcar integrator or a Fabritek-1072 instrument computer with 1-μsec-per-channel resolution. Exponential recovery of the La spin echo was observed in all alloys. These data at 8 MHz are plotted in Fig. 6 as T_1T vs x. The value of T_1T was found to be independent of temperature from 1.6 to 4.2 K for all alloys and no field dependence of T_1T was observed. The La T_1T data display a somewhat oscillatory behavior with composition similar to that of the La Knight shift, although near $LaSn_3$ T_1T is practically constant. Both T_1T and the Knight shift vary dramatically with the substitution of Sn for In in $LaIn_3$. Between $x = 0.2$ and 0.65, T_1T is much longer than in $LaSn_3$ and roughly independent of x although the local peak in T_1T at $x = 0.20$ does coincide with a local minima for the La Knight shift.

The Sn^{119} spin-lattice relaxation time was measured at liquid-helium temperatures following a 180°-90°-180° pulse sequence for alloys from $x = 0.10$–1.0. Exponential recovery of the Sn signal was observed in all alloys. As with the La relaxation time, no field dependence or temperature dependence of T_1T was observed. The Sn T_1T data from 1.6 to 4.2 K are plotted versus x in Fig. 6. For the low-In concentration alloys the initial decrease of the Sn Knight shift is reflected in the increase of the Sn T_1T value. The value of T_1T has a maximum near $x = 0.65$ and then decreases with decreasing x to a minimum at $x = 0.30$ where T_1T has a value similar to the value of T_1T in $LaSn_3$. Finally, for small values of x, T_1T increases slowly with decreasing x.

IV. DISCUSSION

A. Bulk Properties

Because tin is tetravalent and indium is trivalent, the replacement of a tin atom by an indium atom in the $LaSn_{3x}In_{3(1-x)}$ system decreases the number of valence electrons by one. Hence in an electronlike conduction band decreasing x should decrease the density of states, whereas in a holelike band this should increase the density of states. As we see from Fig. 4, $N(0)$ is not a monotonic function of x (or electron concentration) but rather passes through maxima and minima. To explain this result one would have to have both types of bands. From the fact that similar behavior for $N(0)$ is observed in many of the $AuCu_3$ type alloys[4] the observed minima in $N(0)$ are thought to result from contact of the Fermi surface with Brillouin-zone boundaries. Maxima area of contact would correspond to relative minima in $N(0)$. However, Grobman[15] has shown that the picture of a nearly-free-electron sphere expanding through Brillouin-zone boundaries as x changes proposed by Havinga *et al.*[4] cannot account for the oscillations in $N(0)$ observed experimentally. This is in accord with the complexity of the calculated band structures for $LaSn_3$[16,17] and $LaIn_3$[17] which indicates a nearly-free-electron picture is inappropriate and the NMR measurements which show the changes with x in the local electronic properties of the La and Sn-In sites differ considerably.

As Eq. (1) indicates, if we assume that Θ_D and μ^* do not vary too much, the variations in T_c are largely due to variations in $\lambda = N(0)V$. As Fig. 4 indicates, the variations in T_c correlate well with the variations in $N(0)$. This is not the case for V. Over the range $x = 0.76$–1.0, where T_c is changing by a factor of 6.5, V is nearly constant so that λ is proportional to $N(0)$. If, for example, there were strong exchange interactions between the conduction electrons which would affect T_c, one would expect to see strong variations in V. For $x < 0.76$ there are some variations in V: a pronounced maximum at $x = 0.68$ where T_c is minimum, and a decrease in V with decreasing x. But in general the variations in V are much smaller than those of $N(0)$. Thus we can make the general observation that in this pseudobinary system, the complex variation of T_c is related in a simple way to the density of states.

As Figs. 1 and 2 indicate, the susceptibilities are temperature dependent and can be paramagnetic, diamagnetic, or nearly zero depending on x. This results from the varying importance of the Pauli paramagnetism χ_p, the Landau diamagnetism $\chi_{\rm LD}$, and the paramagnetic orbital contribution $\chi_{\rm orb}$. $\chi_{\rm orb}$ of course can contain many terms,[18] the most familiar of which is the Van Vleck paramagnetism. The Pauli paramagnetism is simply related to the density of states $N(E)$. If $N(E)$ varies sufficiently rapidly with energy, i.e., if $N(E)$ varies significantly in a range of energy $\Delta E \sim kT$, then χ_p (and $\chi_{\rm LD}$) will be temperature dependent.

If one considers $N(E)$ to be made up of contributions from the s, p, and d bands then $\chi_p + \chi_{\rm LD}$ will have s, p, and d contributions. One can further consider the contributions to the susceptibility to come from the La sites or the Sn-In sites. The studies of the bulk susceptibility and the NMR Knight shift and spin-lattice relaxation time in $\rm LaSn_3$[9] and $\rm LaIn_3$[10,11] suggested that $\chi_{\rm orb}$ was larger than χ_p and had the same temperature dependence as χ_p. Therefore, at low temperatures one might expect that $\chi_{\rm orb}$ is roughly proportional to the local density of states at the La site.

Let us now examine χ(77 K) and χ_p quantitatively, where χ_p is determined from $N(0)$ and hence excludes any exchange enhancement. First, note the differences in scale in Fig. 3. χ_p is positive and varies from 0.3×10^{-4} to 0.92×10^{-4} emu/mole, whereas χ(77 K) changes sign and varies from 4.5×10^{-4} to -2.6×10^{-4} emu/mole. Clearly at compositions near $x = 0$, 0.33, and 1, where χ(77 K) is positive and considerably larger than χ_p, $\chi_{\rm orb}$ is large. At compositions near $x = 0.1$ and 0.75, where χ(77 K) is quite diamagnetic, $\chi_{\rm LD}$ must dominate which means the presence of low effective mass carriers. It is quite interesting that near these compositions $N(0)$ is a minimum. This minimizes the Fermi surface area and hence minimizes the density of states. In addition, one would expect small pockets of carriers which would have low effective masses, and hence large $\chi_{\rm LD}$. The two effects together would minimize χ_p and $\chi_{\rm orb}$ and maximize $\chi_{\rm LD}$, which is just the situation to produce a net diamagnetism. In fact that is what is observed.

B. Nuclear-Magnetic-Resonance Results

In order to discuss the NMR results for the $\rm LaSn_{3x}In_{3(1-x)}$ alloys we use the customary approach for transition metals which has been reviewed in articles by Narath[19] and Jaccarino.[20] The $\rm LaX_3$ compounds and the alloys reported on here are treated as transition-metal compounds so that the Knight shift and spin-lattice relaxation rate can be partitioned into the spin and orbital contributions from the s, p, and d bands. In the independent band approximation, the Knight shift and spin-lattice relaxation rate are the sum of the individual band Knight-shift and relaxation-rate components. The Knight-shift components are related to the paramagnetic susceptibility components χ_i, by[19,20]

$$K_i = (\mu_B N)^{-1} H_{\rm hfs}^{(i)} \chi_i \,. \tag{3}$$

The relaxation-rate components are given by[19–22]

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

for noninteracting electrons (no spin-exchange enhancement) within the tight-binding approximation. 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 ($F_s = 1$).

Before discussing the NMR results for the $\rm LaSn_{3x}In_{3(1-x)}$ alloys we briefly review some of the most important features of the partitioning schemes[9,10] for $\rm LaIn_3$, $\rm LaSn_3$, and $\rm LaPb_3$ which are relevant to this study. The results obtained in partitioning the NMR and χ data for $\rm LaSn_3$ and $\rm LaIn_3$ suggest that the s-contact, d-core polarization, and d-orbital hyperfine interactions give substantial contributions to the La Knight shift while only the s-contact and d-core polarization hyperfine interactions give substantial contributions to the La spin-lattice relaxation rate. The paramagnetic susceptibility for $\rm LaIn_3$ and $\rm LaSn_3$ is several times larger than the Pauli susceptibility calculated from $N(0)$ and can only be accounted for by either an exchange enhancement of the La d-spin susceptibility of the order of or greater than 10 (which is larger than that of palladium[23]), or a large temperature-dependent La d-orbital susceptibility. With a value of $H_{\rm hfs}^{(d)}$ of the order of -3.5×10^5 Oe/μ_B determined from the value calculated for the $\rm La^{++}$ ion by Mallow and Freeman,[24] a consistent partitioning of the bulk susceptibility and La NMR properties can be obtained only if the La d-orbital susceptibility is the dominant contribution. For the bulk susceptibility to arise from an exchange enhancement of the La d-spin susceptibility would require that the La d-core polarization hyperfine field is less than 10% of the value given above and

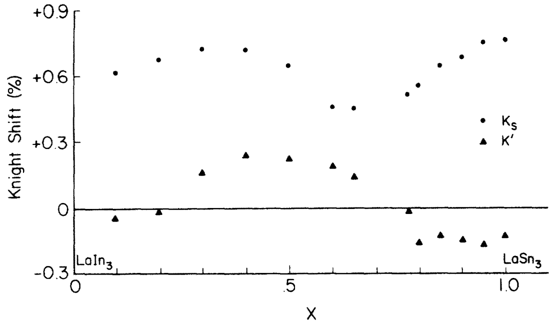

FIG. 7. The Sn Knight-shift components K_s and K' in the LaSn$_{3x}$In$_{3(1-x)}$ alloys vs x at liquid-helium temperatures.

gives rise to the unsatisfactory situation of the coexistence of a large La d-spin-exchange enhancement and a high superconducting transition temperature in LaSn$_3$.

It is difficult to partition the NMR and susceptibility results for the alloys of LaIn$_3$ and LaSn$_3$ in any quantitative way because of the importance of the temperature-dependent Landau diamagnetic susceptibility contributions to the bulk susceptibility. For this reason only the qualitative features of the NMR results will be discussed for these alloys. Based on the results obtained for the LaX_3 compounds[9,10] electron-electron interactions are not of great importance. Then the Korringa product,[19,20,25] K^2T_1T/S, where $S=(\hbar/4\pi k_B)(\gamma_e/\gamma_n)^2$, can be used as a guide to indicate the importance of the various spin and orbital contributions to the NMR properties. If only the s-contact interaction is considered, the Korringa product would be unity. However, when p- or d-band effects are included the Korringa product will be greater than or less than unity depending on the relative importance of the orbital and core-polarization hyperfine interactions.[19,20] The values of the Korringa product for both the La and Sn sites at 4.2 K are listed in Table I. In addition we assume that the hyperfine fields do not vary radically as the e/a ratio is varied.

The dependence of the spin-lattice relaxation-rate components R_i on $N_i(0)$ in Eq. (4) suggest that $R^{1/2}$ may be used to estimate the variation of the local density of states of the La and Sn sites with the e/a ratio. For the La site the estimate will be of necessity rather crude since R depends about equally on both the s and d density of states at 4.2 K in LaIn$_3$[10] and LaSn$_3$.[9] For the Sn site this estimate is expected to be a reasonably good one since the relaxation rate and Knight shift are similar to the values determined for β-Sn, where only the s-contact hyperfine interaction is important.[26] Writing the Sn Knight shift as $K=K_s+K'$, then K_s can be determined by requiring that $K_s^2T_1T/S=1$. The term K' denotes all contributions to the Sn Knight shift apart from the s-contact contribution. Both K_s and K' have been determined at 4.2 K and are plotted in Fig. 7. For all compositions K' is less than one-third of K_s. From Eq. (4) it is clear that the orbital reduction factor F_i will further reduce the contribution of K' to the Sn relaxation rate. We estimate that less than 10% of the Sn relaxation rate arises from the hyperfine interactions which give rise to K'. The ratio $R^{1/2}/N(0)$ at 4.2 °K of the T_1-determined local density of states to the bare density of states of Fig. (4) is listed for the La and Sn sites in Table I.

Within the framework discussed above there are several features of the NMR results which should be stressed. Although there is a rough similarity to the behavior of the La and Sn NMR as the composition is varied, there are a number of important and in some cases dramatic differences. These differences are perhaps most pronounced for[27] $0.75<x\leq 1.00$, where the bulk properties shown in Fig. 4 change rapidly and the variation of the local electronic properties at the La and Sn sites with x differs considerably. The small variation of the Korringa product for both the La and Sn sites listed in Table I indicates that the relative importance of the various spin and orbital contributions to the NMR properties is not changing very much. Since the La Korringa product is substantially less than unity, the d-core-polarization term is apparently quite important throughout this composition range. While both the La T_1 and Knight shift show little variation, the Sn Knight shift decreases considerably and the Sn T_1 increases by a factor of 2 from $x=1.0$ to 0.775.

TABLE I. La^{139} and Sn^{119} Korringa products and $R^{1/2}/N(0)$ ratios for the LaSn$_3$In$_{3(1-x)}$ alloys at 4.2 °K, where $R=(T_1T)^{-1}$ is in (sec K)$^{-1}$, $N(0)$ is in states/eV atom spin, and $S=(\hbar/4\pi k_B)(\gamma_e/\gamma_n)^2$.

X		0.0	0.05	0.10	0.20	0.30	0.40	0.50	0.60	0.65	0.75	0.80	0.85	0.90	0.95	1.00
K^2T_1T/S	La	1.28	1.74	0.64	0.64	1.10	2.70	2.80	3.00	2.50	0.48	0.30	0.25	0.26	0.27	0.40
	Sn			0.84	0.95	1.50	1.80	1.81	2.00	1.70	1.90	0.80	0.65	0.61	0.61	0.72
$R^{1/2}/N(0)$	La	3.55	3.30	3.05	2.65	2.70	2.27	1.95	2.83	3.45	3.67	3.77	3.85	3.50	3.37	2.76
	Sn			22.5	22.5	25.5	22.5	18.3	20.2	22.5	19.2	18.8	20.0	19.4	19.6	17.1

Both the ratio $R^{1/2}/N(0)$ and K' for the Sn site are nearly constant while at the La site $R^{1/2}/N(0)$ shows a considerably larger variation. These results suggest that the rapid variation with x of $N(0)$ and hence T_c (since V is nearly constant for $0.75 \leq x \leq 1.00$) result primarily from changes of the local electronic properties at the Sn sites. Thus the superconducting properties of these alloys appear to be determined primarily by the local properties of the Sn and In sites for $0.75 \leq x \leq 1.00$.

The fact that $dK/d\chi$ for the La Knight shift in $LaSn_3$ is constant[9] and the isotropic Sn Knight shift is temperature independent for all x, indicates that the paramagnetic susceptibility derives from the local electronic properties at the La site. Since little change occurs in the La NMR properties for $0.75 \leq x \leq 1.00$, this suggests that the sharp decrease in χ with decreasing x results primarily from a rapidly increasing diamagnetic contribution.

Another interesting feature of this alloy system which is evident both from the bulk and NMR properties is an apparent change in the character of the conduction electrons for $0.65 \leq x \leq 0.75$. Both the La and Sn Korringa products change dramatically and the Sn and La T_1's become much longer, which indicates that the density of states at both sites decreases substantially. This is consistent with the conclusions of Grobman[6] that a substantial change in the conduction electron states occurs near $x = 0.70$ based on his thermopower results. For $0.40 \leq x \leq 0.65$ the La Korringa product is much larger than unity which suggests that the d-core polarization contribution is much less important for this composition range than for the Sn-rich alloys. Also the ratio $R^{1/2}/N(0)$ at the Sn site varies much less than for the La site for $0.40 \leq x \leq 0.65$, which indicates that as for the Sn rich alloys the local properties at the La site are not strongly affected by the variation of $N(0)$.

For the In-rich alloys the most dramatic feature is the rapid variation of the bulk and NMR properties for $x \leq 0.10$. In contrast to the behavior of the La NMR for the Sn-rich alloys, in this composition range the changes in the bulk properties are strongly reflected in the changes of the La NMR properties and the La Korringa product and suggest there is a substantial change in the character of the conduction electron states at the La site. The decrease in the La T_1, the increase in the Knight shift and Korringa product, and change in the sign of the temperature dependence of the Knight shift are consistent with an increase in both $N_s(0)$ and $N_d(0)$ at the La site and a rapid increase in the importance of the d-orbital contribution as x decreases.

V. CONCLUSIONS

From the results of this and earlier studies[1-7] of the properties of the $LaSn_{3x}In_{3(1-x)}$ alloys it is clear that there is in somewhat oscillatory variation of the density of states at the Fermi energy as the composition is varied. The existence of minima and maxima in T_c are due largely to similar changes in the density of states which passes through maxima and minima as electronlike and holelike bands are emptied. In particular, over the range $1 > x > 0.75$, where the electron-phonon interaction strength V is nearly constant but T_c changes by a factor of 6.5, the coupling parameter χ is proportional to $N(0)$ and the drop in T_c is related in a simple way to the corresponding decrease in $N(0)$. However, the difference between T_c in $LaSn_3$ and $LaIn_3$ does not appear to be just a result of the difference in $N(0)$. Since $V \propto \langle \mathscr{I}^2 \rangle / \langle \omega^2 \rangle$, where $\mathscr{I}$ is the electronic matrix element and ω is the phonon frequency, the main difference in T_c for the endpoints of the alloy system results from either an increase in $\mathscr{I}$, or some softening of the phonon modes as x increases from 0 to 1.

From the NMR results, the local density of states at the Sn site appears to track the bulk density of states more closely than at the La site suggesting that the variation of $N(0)$ and T_c with x results primarily from the changes of the electronic states at the Sn site. However, both the Sn and La NMR properties change substantially near $x = 0.70$ where T_c has a sharp minimum and V has a sharp maximum, which is in agreement with the results of the transport property measurements of Grobman.[6] For the very In-rich alloys, the rapid variation of the La NMR properties as x decreases to zero is consistent with rapidly increasing La d-band contributions to the La NMR properties and the bulk susceptibility.

There are several important conclusions that can be drawn from the general behavior of La and Sn NMR properties of the $LaSn_{3x}In_{3(1-x)}$ alloy system which should be applicable to a number of the other $AuCu_3$ alloy systems discussed by Havinga *et al.*[4] Their results indicate that the Sn-In sites play a negligible role in determining the paramagnetic contribution to the bulk susceptibility. One expects that the size of the paramagnetic susceptibility for other $AuCu_3$ alloys will depend on whether the Au site is occupied by La or Y, or by a nontransition-metal atom. Thus contrary to the conclusions of Havinga *et al.*[4] that these alloys are basically nontransition-metal alloys, our NMR results are consistent with the assumption that these materials are transition-metal alloys. This is in agreement with the conclusions of Grobman[6] and the results of the band-structure calculations[16,17] on $LaSn_3$ and $LaIn_3$.

Another important point can be made for the $LaSn_{3x}In_{3(1-x)}$ alloys which one suspects is true of the $AuCu_3$ alloys in general. For large composition ranges the NMR properties of the La and Sn sites show little correlation. This is particularly true for $0.40 \le x \le 0.65$. We have concluded that the La conduction electron states play only a minor role in determining the superconducting properties of these alloys. For the other $AuCu_3$ alloys, the atom in the Au site can be expected to only weakly affect the superconducting properties. This is in agreement with the results of Havinga *et al.*[4] who observed that T_c has about the same composition dependence and magnitude if the Au site is occupied by Ca as if it is occupied by La or Y.

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