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Superconducting and Other Electronic Properties of La_3In, La_3Tl, and Some Related Phases

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The low-temperature specific heats of La_3In and La_3Tl were measured in the superconducting and the normal state, the latter being stabilized in a magnetic field of 90 kOe. From these data, the thermodynamic critical fields and other thermodynamic properties could be determined. High and strongly varying electronic densities of states near the Fermi level are derived from magnetic-susceptibility measurements and confirmed by strongly temperature-dependent Knight shifts on the In^{115} nuclei in La_3In and on the Tl^{203} and Tl^{205} nuclei in La_3Tl. All remarkable properties of La_3In and La_3Tl, suggest that these compounds belong to the class of strong-coupling superconductors and are closely related to the behavior of fcc La under pressure.

I. INTRODUCTION

Lanthanum is known to form a series of intermetallic compounds of the type La_3X and LaX'_3, both crystallizing in the Cu_3Au structure. X may stand for In or Tl and X' for Pd, In, Tl, Sn, and Pb. With the exception of $LaPd_3$ all these compounds exhibit superconductivity above 0.7 °K. In this paper we shall discuss essentially La_3In and La_3Tl. A superconducting transition at 10.4 °K in La_3In has been discovered first by Matthias *et al.*[1] Superconductivity in La_3Tl and some preliminary results on thermodynamic properties of this superconductor have been reported recently by Bucher *et al.*[2] They found a T_c of 8.95 °K and a specific-heat jump at T_c, $\Delta C/\gamma T_c$, appreciably above the maximum value of 1.84, given by the BCS theory in the extreme-strong-coupling limit. One of the aims of this paper is to study more, in detail, the strong-coupling behavior of these two compounds, La_3In and La_3Tl.

It is interesting to consider these two compounds in relationship to the properties of fcc La. This element is known to be an intermediate to strong-coupling superconductor with a relatively high electronic-specific-heat coefficient,[3] having a very large and positive pressure dependence of T_c.[4] It is tempting to interpret the compounds La_3In and La_3Tl as ordered solid solutions of In or Tl in fcc La. The substitution of the La atoms in 000 positions of the cubic unit cell by an element of a much smaller atomic radius leads to a strong contraction of the fcc lattice (see Table I) and might therefore generate effects similar to high pressure. La_3In and La_3Tl indeed exhibit a remarkable increase in the superconducting transition temperature over that of fcc La. We shall discuss also this point of view with respect to other electronic properties of these metals.

La_3In and La_3Tl show a number of remarkable properties. First, they are strong-coupling superconductors exhibiting all typical features of such materials, large T_c/Θ_D ratios, strongly enhanced specific-heat jumps at T_c, positive deviations of $H_c(T)$ from a parabolic law, a high ratio $2\Delta(0)/kT_c$ for the energy gap $2\Delta(0)$ as determined from specific heat at low temperatures, and so on. Second, La_3In and La_3Tl are ideal host superconductors for magnetic impurities. Many experiments with magnetic impurities, such as Gd and Ce in La_3In, have been performed[5-7] allowing to test theories for relatively large variations in both temperature and concentration. Third, it was recently found that Pr shows a crystal-field-singlet ground state in both La_3In[8] and La_3Tl.[2] The pair breaking due to such an impurity occurs via inelastic processes involving the off-diagonal matrix elements of the angular momentum operator $\tilde{J}$, $\langle \Phi_0 | \tilde{J} | \Phi_K \rangle$, where Φ_0 and Φ_K are the wave functions of the ground state and the excited crystal-field states, respectively.[9] In the course of investigating the thermodynamic properties for such superconductors, we felt it necessary to first determine the properties of the host materials.

After a description of the sample preparation in Sec. II A, we present in Sec. II B specific-heat data in the normal and the superconducting state of La_3In and La_3Tl, the former being measured in a magnetic field of 90 kOe in order to quench the supercon-

TABLE I. Superconducting transition temperature T_c, Debye temperature $\Theta_D(0)$, electronic specific heat γ, specific-heat jump $\Delta C/T_c$, thermodynamical critical field H_c $(T=0)$ and dH_c/dT at T_c, Ginzburg-Landau parameter κ^{GL}, the energy gap $2\Delta(0)/kT_c$ as determined from specific heat, magnetic susceptibility χ, Knight shift K, lattice constant a, and other parameters as derived from these quantities, for La_3In, La_3Tl, and $La_3In_{0.7}Ga_{0.3}$ in comparison with fcc La.

		fcc La	La_3In	La_3Tl	$La_3In_{0.7}Ga_{0.3}$
T_c	(°K)	6.06	9.54	8.86	9.25
γ	[mJ/g atom °K^2]	11.3	14.0 ± 0.8	12.4 ± 1.0	10.6 ± 1.0
$\Theta_D(0)$	(°K)	139	170 ± 10	163 ± 8	170 ± 10
$\Delta C/T_c$	[mJ/g atom °K^2]		41 ± 1	30 ± 1	27 ± 1
$\Delta C/\gamma T_c$			2.9 ± 0.2	2.4 ± 0.3	2.5 ± 0.3
H_c $(T=0)$	(Oe)		2270 ± 70	1900 ± 50	
dH_c/dT	(Oe/°K)		−512	−440	
K^{GL}			11.8		
$2\Delta(0)/kT_c$	(from C_{es} at $T \leq 0.4\ T_c$)		5.8	5.3	
$2\Delta(0)/kT_c$	(from $\Delta C/\gamma T_c$)		5.0 ± 0.4	4.6 ± 0.6	
$\chi(T=20\ °K)$	(10^{-6} emu/mole)		480	468	
$\gamma(T=300\ °K)$	(10^{-6} emu/mole)		318	318	
$K_{In,Tl}(T=14\ °K,\ 6.5\ °K)$	(%)		−0.155	−0.265	
$K_{In,Tl}(T=300\ °K)$	(%)		+0.058	+0.319	
a	(Å)	5.290	5.07	5.06	5.05
V_m	(cm^3/g atom)	22.30	19.63	19.51	19.40
M_m	(g/g atom)	138.91	132.89	155.28	129.51
$T_c/\Theta_D(0)$		0.0436	0.0561	0.0544	0.0544
$\lambda^{(MM)}$	(for $\mu^* = 0.1$)	0.85	0.98	0.96	0.96
$N_{BS}^{MM}(0)$	(eV^{-1})	1.29	1.50	1.34	1.34

ducting transition down to below 1.5 °K. From these two sets of measurements, thermodynamic properties of the superconductors were derived in a straightforward way. To allow the discussion of some type-II properties, we also measured $H_{c2}(T)$ in La_3In. In Sec. II C we give results for a certain number of ternary alloys of the form $La_3X_{1-y}X'_y$ and for the perovskites La_3XC, where X and X' may stand for Cd, Al, Ga, In, Tl, Sn, or Pb. In Sec. II D and II E we present experimental results from susceptibility measurements and NMR on Tl^{203}, Tl^{205}, and In^{115}. In Sec. III we shall discuss the experimental results on the basis of current theories.

II. EXPERIMENTAL RESULTS

A. Sample Preparation

La_3In and La_3Tl are readily prepared in an argon arc furnace from the elements. In and Tl were 99.999%-pure ASARCO materials. La was supplied by Rare Earth Products and listed as 99.99% pure with respect to other rare earths. In the case of La_3Tl a slight weight loss corresponding to approximately 0.2-at.% Tl is noticed; this however could easily be compensated after the first fusion. Once the composition is established there is no longer a danger of further Tl loss. The phase diagrams of La-In and La-Tl have not as yet been fully established. Phase relations on the La-rich side of La-In and La-Tl, however, may be guessed from recent work of Griffin and Gschneidner[10] on analogous Pr systems. In the case of Pr_3Tl these authors found peritectic phase formation and an order-disorder transition at 750 °C involving a remarkable change in lattice constants. Following our arc-melting procedure, the samples were annealed for 4 weeks, first at 720 °C for one week and then cooled down to 300 °C at a rate of about 20 °C per day. Filings for x-ray measurements were taken from the annealed samples in a nitrogen atmosphere and immediately sealed in a glass capillary. Powder of La_3Tl and La_3In is extremely pyrophoric in air. Our lattice constants listed in Table I are somewhat smaller than previously published values,[11] but in excellent agreement with Ref. 1.

B. Thermodynamic Properties of La_3In and La_3Tl

In Table I we present a number of parameters describing superconducting and normal-state properties of La_3In and La_3Tl. They are compared as closely as possible with parameters for fcc La. Most of these parameters are based on specific-heat data for these materials. The new specific-heat data for La_3In and La_3Tl as obtained in zero magnetic field and in a field of 90 kOe are given in Fig. 1. Details about the zero-field and the high-field specific-heat measurements by a heat-pulse technique can be found elsewhere.[12] The most striking features of the specific-heat curves for La_3In and La_3Tl are the large and relatively sharp

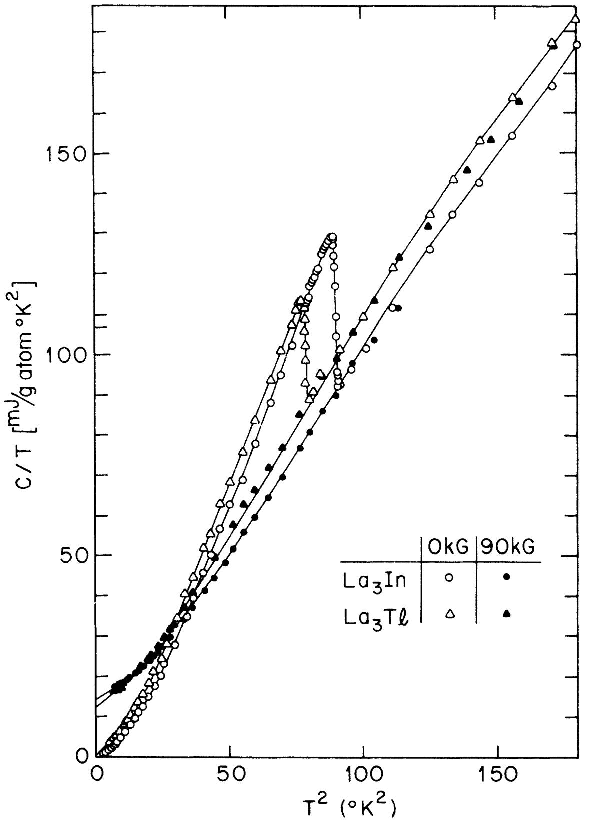

FIG. 1. Low-temperature specific heats for La_3In and La_3Tl in the normal and the superconducting state as measured in zero magnetic field and in a field of 90 kOe.

jumps at the transition temperatures. The widths of the calorimetric transitions are about 0.12 and 0.05 °K in La_3In and La_3Tl, respectively; other samples of La_3Tl showed even sharper transitions of about 0.03 °K. The transition temperatures T_c and the values of the specific-heat discontinuities at T_c, $\Delta C/T_c$, are given in Table I; the T_c's were determined by the midpoints of the specific-heat jumps. The normal-state data, the Debye temperature $\Theta_D(T)$, and the electronic-specific-heat coefficient γ could be obtained directly from the high-field specific heat. These data were fitted by a least-squares method to a polynomial $C_n = \gamma T + \alpha T^3 + \beta T^5 + \delta T^7 + \epsilon T^9$ for temperatures below 15 °K. In order to increase the precision of the parameters, and also to assure internal consistency, we further determined the entropy at $T > T_c$ from the specific-heat data in zero magnetic fields and determined the coefficients in the polynomial for C_n with the constraint to give the correct value for the entropy above T_c. Our lanthanum, however, contains about 70 ppm of magnetic impurities (as derived from susceptibility measurements) which give a magnetic contribution to the specific heat. A quantitative analysis shows that this should be negligible in C_n as well as in the total entropy at T_c. Another check of our least-squares fit is given by the analysis of the specific heat at $T < 0.4T_c$; by fitting the measured specific heat in the superconducting state to $C_s = \alpha T^3 + C_{es}$, where C_{es} is given by the BCS theory. However, allowing for a constant scaling factor for the energy-gap function $2\Delta(T)$, we obtained a coefficient α, which is in agreement with the former analysis. The analysis of the specific heat of these compounds is rather critical and has to be done very carefully, because of the rather-high T_c and the low and strongly varying Debye temperature $\Theta_D(T)$ (Fig. 2). For these reasons, it was important to have specific-heat data in high magnetic fields in order to obtain reliable normal-state parameters. With the normal-state specific heat C_n, smoothed out in this way, and with the usual assumption that the lattice part of the specific heat is the same in both the normal and the superconducting state, and furthermore is independent of an applied magnetic field, we determined the electronic specific heat in the superconducting state: $C_{es}(T) = C_s - (C_n - \gamma T)$. In Fig. 3 we report $\ln(C_{es}/\gamma T_c)$ as a function of T_c/T, together with the same function as given by the BCS theory. It is well known that $2\Delta(0)$, the energy gap at $T = 0$, of a real superconductor can be different from the BCS value of $3.52kT_c$. Assuming that the temperature dependence of the energy gap is given by the BCS theory (i.e., $\Delta(T)/\Delta^{BCS}(T) = \text{const}$), we determined $2\Delta(0)/kT_c$ for La_3In and La_3Tl from C_{es} at $T_c/T > 2.5$ (Table I); the corresponding specific heat in the superconducting state at $T_c/T > 2.5$ is approximated by the straight lines in Fig. 3. The ratios $2\Delta(0)/kT_c$ for these two compounds are considerably higher than the BCS ratio of 3.52. In Table I we also give the values for the jumps in the specific heats at T_c, $\Delta C/T_c$, and the ratios $\Delta C/\gamma T_c$ for a compar-

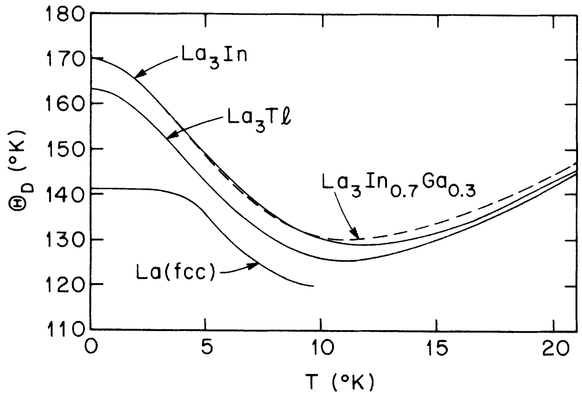

FIG. 2. Debye temperatures $\Theta_D(T)$ as a function of temperature. For comparison, $\Theta_D(T)$ of fcc La (from Ref. 3) is also reproduced.

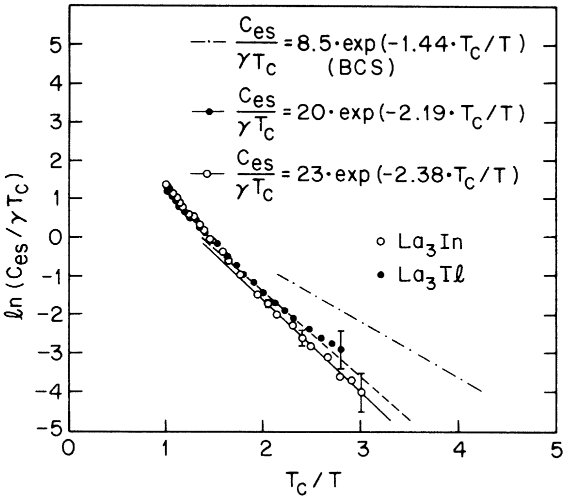

FIG. 3. Electronic specific heat in the superconducting state for La_3In and La_3Tl. Dash-dotted line, electronic specific heat as expected from BCS theory; full line and dotted line, fitted electronic specific heat at $T_c/T > 2.5$ for La_3In and La_3Tl, respectively.

ison with the value of 1.43 as obtained by the BCS theory. Our values of $\Delta C/\gamma T_c$ and $2\Delta(0)/kT_c$ for La_3Tl (as derived from $\Delta C/\gamma T_c$ fit empirical curves,[13] depending on a single parameter $x = (T_c/\Theta_D)$, very well. In contrast, both quantities $\Delta C/\gamma T_c$ and $2\Delta(0)/kT_c$ of La_3In exceed considerably values expected from such empirical plots.[13] The fact that two so closely related compounds fail to fit a universal dependence on $(T_c/\Theta_D)^2\ln(\Theta_D/T_c)$ only may strongly support arguments of Geilikman and Kresin[14] that individual phonon spectra inhibit a simple dependence of $\Delta C/\gamma T_c$ and $2\Delta(0)/kT_c$ on the single parameter $(T_c/\Theta_D)^2\ln(\Theta_D/T_c)$. Thus tunneling experiments for both materials would be most valuable in clarifying this point. In particular, La_3In exhibits values of $\Delta C/\gamma T_c$ and $2\Delta(0)/kT_c$, ranging among the largest values observed thus far.

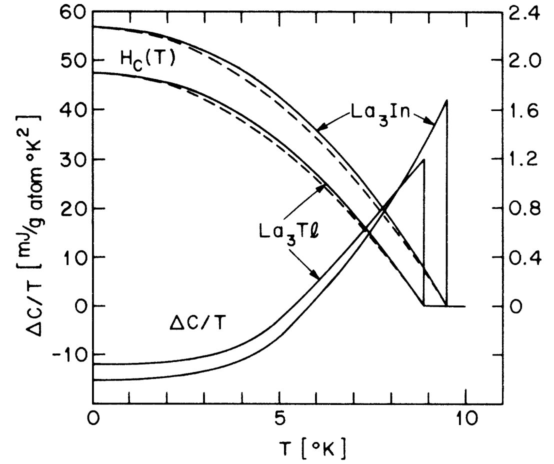

FIG. 4. Difference of measured specific heats in the superconducting and the normal state, $\Delta C/T = (C_s - C_n)/T$, and thermodynamical critical fields $H_c(T)$ obtained from $\Delta C/T$. Dashed line, $H_c^{(\mathrm{parab})} = H_c(0)[1-(T/T_c)^2]$.

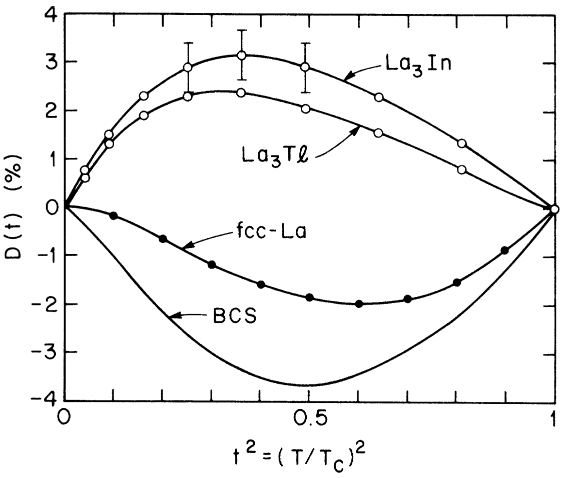

FIG. 5. Deviation function $D(t) = H_c/H_0 - (1-t^2)$ for La_3In and La_3Tl, compared with fcc La (from Ref. 3) and with the result from BCS theory, where $t = T/T_c$.

Knowing the specific heats C_s and C_n in the superconducting and the normal state, respectively, and assuming an unchanged lattice specific heat, we obtained the thermodynamic critical field in a straightforward way by numerical integration:

$$H_c(T)=\left(\frac{8\pi}{V_m}\int_T^{T_c}dT'\int_{T'}^{T_c}\frac{C_s(T'')-C_n(T'')}{T''}\,dT''\right)^{1/2}. \tag{1}$$

The volume per gram atom, V_m, was obtained from the lattice constants, determined by x-ray analysis, and is given in Table I. $H_c(T)$ for La_3In and La_3Tl is reported in Fig. 4. For both of these compounds $H_c(T)$ shows a positive deviation from a parabolic law, which is comparable with that observed in Pb and Hg (Fig. 5). We have also measured $H_{c2}(T)$ in La_3In and obtained results which are in good agreement with those of Jones *et al.*[6] From these results we can determine the Ginzburg-Landau $\kappa_1(t) = H_{c2}(t)/\sqrt{2}\,H_c(t)$ and $\kappa = \kappa_1(t=1)$, as given in Table I. These results however will be discussed in more detail in a forthcoming paper.[8]

C. Superconducting Properties of Ternaries La_3XC and $La_3X_{1-y}X'_y$

All experimental results on the ternary alloys and compounds are summarized in Table II. We observe that the substitution of In by other elements, such as Al, Ga, Cd, Sn, and Tl, leads only to a small reduction of T_c. In $La_3In_{0.7}Ga_{0.3}$ we measured the low-temperature specific heat (Fig. 6) and found an important decrease of the electronic

TABLE II. Superconducting transition temperatures T_c, electronic specific heats γ, Debye temperatures $\Theta_D(0)$, and lattice constants a of some ternary compounds and alloys derived from La_2X compounds.

	T_c (°K)	γ[mJ/g atom °K^2]	Θ_D(°K)	a (Å)
La_3AlC	<1.02			5.12
La_3GaC	<1.02			5.17
La_3InC	<1.02	5.9	203	5.19(5.14)[a]
La_3TlC	<1.02			5.20
La_3SnC	<1.02			5.18(5.13_3)[a]
La_3PbC	<1.02			5.20
$La_3In_{0.5}Tl_{0.5}$	8.90			5.06
$La_3In_{0.7}Al_{0.3}$	9.42			5.06
$La_3In_{0.7}Ga_{0.3}$	9.25	10.6	170	5.05
$La_3In_{0.8}Sn_{0.2}$	7.80			5.05
$La_3In_{0.9}Cd_{0.1}$	9.55			5.07

[a] From Ref. 17.

specific heat γ and the ratio $\Delta C/\gamma T_c$ (see Table II) with respect to pure La_3In. An analysis of the superconducting specific heat at the lowest temperatures was not possible because the sample contained about 5% of a normal phase. The strong decrease in γ is not too surprising since the long-range order is destroyed. The reason why T_c is not also strongly reduced in this alloy with respect to La_3In may lie in the strong-coupling behavior of these superconductors. They are probably situated in the strong-coupling region where T_c, as a function of the electron-phonon coupling constant λ, tends to saturate.[15,16] It seems, therefore, difficult to raise T_c much above the value of La_3In by increasing the electron-phonon coupling constant. La_3In has a T_c/Θ_D ratio, which is comparable with that of A15 compounds with the highest T_c values. Being in the region where T_c vs λ saturates, one might hope to raise T_c by stiffening the lattice of La_3In even if at the same time the coupling constant decreases somewhat (we assume that the relation $M\Theta_D^2\lambda = \text{const}$ does not hold in this case). Attempts to do this in going to the corresponding perovskite carbide La_3InC were unsuccessful. The carbon atom in the center of the unit cell of La_3In is detrimental to the electronic density of states (Table II), and T_c dropped to below 1.02 °K. It cannot be decided as yet if this change in T_c can be explained only by the reduction of the electronic density of states. On the other hand, the change in the electronic parameters cannot be due to the change in the lattice constants alone, and must be related to the strong interaction of the carbon atoms with the rare-earth-metal atoms.[17] Likewise, all other perovskite carbides failed to show superconductivity above 1 °K. It is interesting to note that many perovskite carbides La_3XC of La do exist, whereas the corresponding Cu_3Au phases La_3X do not form (except for X = In and Tl). This fact and also the striking difference in the electronic properties strongly support the idea that the rare-earth perovskite carbides are true ternary compounds which have little in common with their corresponding Cu_3Au phases.[17] Similar observations have been made in analogous compounds as, e.g., Pr_3Tl, which is ferromagnetic with a Curie temperature of $T_C = 11.3$ °K,[18] and Pr_3TlC, which is antiferromagnetic with a Néel temperature of $T_N = 5.1$ °K.[19] The lattice constants of our as-cast rare-earth perovskite carbides are slightly higher than previously published values[17] and, in part, have not yet been reported. These materials are even more reactive in air than La_3X and were x rayed by the same method as described in Sec. II A.

D. Magnetic Susceptibility

The magnetic susceptibilities of La_3In and La_3Tl as measured in a pendulum magnetometer[20] in the temperature range 10–370 °K are displayed in Fig. 7. In both cases we note a strongly increasing magnetic susceptibility $\chi(T)$ for decreasing temperatures. The results for the low-temperature side had to be corrected for magnetic impurities. At the lowest temperatures we assume that χ of pure La_3In and La_3Tl becomes temperature independent and that the impurity contribution to χ can be written in the form of a Curie law $\chi_i = C_i/T$. The latter, of course, is not true if impurities with orbit-

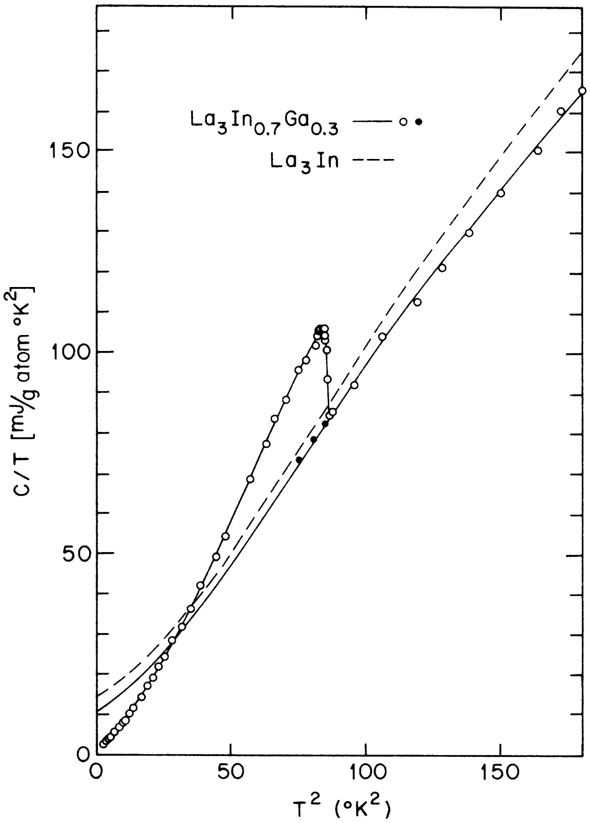

FIG. 6. Low-temperature specific heat for $La_3In_{0.7}Ga_{0.3}$.

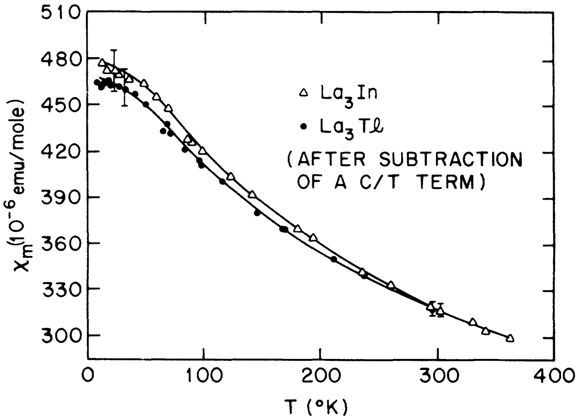

FIG. 7. Magnetic susceptibilities for La_3In and La_3Tl.

al moments are present and crystal-field effects have to be considered. Usually there is a whole spectrum of rare-earth impurities present, of which the contribution to the magnetic susceptibility is not known exactly. We shall neglect crystal-field effects and interpret the impurity contribution as that of a Gd impurity equivalent assuming $g_J = 2$ and $S=\frac{7}{2}$. In this way we estimated the impurity content to be equivalent to 75 and 67 ppm of Gd in La_3In and La_3Tl, respectively. These numbers were derived from a plot $\chi(T)T$ vs T in the range of 10-50 °K. The slope of this curve represents the magnetic susceptibility χ_0 of the pure compounds at low temperatures, and we obtain $\chi_0 = (480 \pm 15)$ and $(468 \pm 15) \times 10^{-6}$ emu/mole for La_3In and Ta_3Tl, respectively. After having subtracted from the measured susceptibility the impurity contribution $\chi_i = C_i/T$, as determined in this way, we obtained $\chi(T)$ as shown in Fig. 7. Below about 80 °K the accuracy of $\chi(T)$ is limited by this analysis, owing to unknown crystal-field effects on the impurities. The values above 100 °K, however, are much more reliable, since the impurity corrections become unimportant; indeed the results in this temperature range are very reproducible for various samples prepared from different La lots. Thus, the relatively strong temperature dependence of $\chi(T)$ must be considered as an intrinsic property of these two compounds.

E. NMR Results on La_3In and La_3Tl

In order to obtain some insight into the origin of the large temperature dependence of the magnetic susceptibility in La_3In and La_3Tl, we studied these two compounds by NMR techniques. Powders of these two compounds (60-μ size) were wrapped into Mo foils, sealed in quartz capsules under vacuum and annealed for 12 h at 450 °C. For the NMR experiments the powders were transferred into glass capsules and sealed under 200 torr of helium gas. NMR measurements were done with cw methods, using a Varian 16-B wide-line spectrometer, which was modified to work with a cross-coil system at low temperatures.[21] The magnetic field was calibrated for each measurement by determining the resonance frequency of the H^1 or D^2 resonance in water or heavy water using a transistorized Robinson spectrometer. In order to increase the signal-to-noise ratio, all measurements were done by accumulating the signal in a Technical Measurement Corp. type CAT-400 time-averaging computer connected to the output of the spectrometer. In this way, it was possible to observe the Tl^{205} and Tl^{203} resonances in La_3Tl from 6.5 to 300 °K and the In^{115} resonance in La_3In from 14 to 300 °K. Because of the small natural abundance of the isotope In^{113}, its resonance was only observable at low temperatures. In all these cases the line shape of the resonances is symmetric and nearly Gaussian. We used an aqueous solution of $InCl_3$ for In^{115} and the values of the Varian table for Tl^{203} and Tl^{205} as standard references for the Knight-shift measurements.

In La_3In the linewidth of the resonance of In^{115}, ΔH, taken as the peak-to-peak separation of the first-derivative curve, is about 6.5 Oe at room temperature (rt) and is independent of the applied magnetic field from 4 to 15 kOe. As expected for sites with cubic symmetry, we did not observe any quadrupolar effects on this resonance. At rt the Knight shift $K_{In} = +0.058\%$ is positive but very small compared to the value in pure indium, where $K_{iso} = +0.82\%$.[22] A strong temperature dependence of K_{In} in La_3In is found at lower temperatures where K_{In} becomes negative: $K_{In} = -0.155\%$ at 14 °K (Fig. 8). At rt no anisotropy and no field dependence of the Knight shift was observed from 5 to 15 kOe. At low temperatures the small increase of the linewidth ΔH_{In} is probably an impurity effect. The In^{113} resonance, observed only at 14 °K, has practically the same linewidth ΔH and the same Knight shift as the In^{115} resonance.

The Tl^{205} and Tl^{203} resonances in La_3Tl show a similar behavior as In^{115} in La_3In. No differences have been found in the linewidths and the Knight shifts between the two Tl isotopes. The linewidth at 10 MHz is 9 Oe at rt and 10.8 Oe at 6.5 °K. At rt the Knight shift $K_{Tl} = +0.319\%$ is positive but lower than the value for pure thallium, which is $K = +1.55\%$ at the same frequency at rt.[23] The temperature dependence of K_{Tl} in La_3Tl below rt is even stronger than K_{In} in La_3In (Fig. 8); K_{Tl} also becomes negative with a value of $K_{Tl} = -0.265\%$ at 6.5 °K.

In certain samples we also observed a La^{139} resonance with a Knight shift of about +0.203%, which was temperature independent and is assumed to belong to traces of La hydrides. On the other hand, we were not able to detect a resonance of La^{139} on

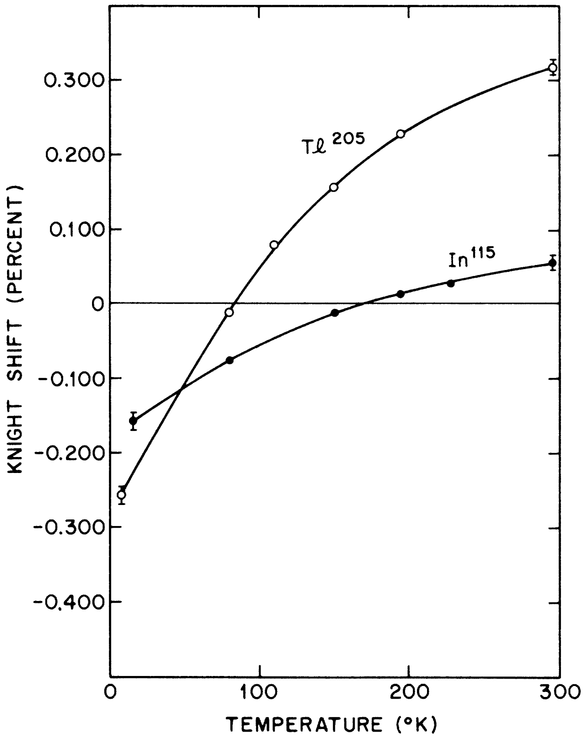

FIG. 8. Knight shifts for In^{115} and Tl^{205} in La_3In and La_3Tl, respectively.

the La sites of La_3In and La_3Tl; this is probably due to quadrupolar effects on these sites with tetragonal symmetry.[24]

Actually, we are also studying La_3In and La_3Tl with pulsed techniques in order to measure the spin-lattice relaxation time T_1 and the spin-spin relaxation time T_2 for the different resonances. The results of these investigations will be published in a forthcoming paper.[24]

III. DISCUSSION

A. Crystal Chemistry and Superconductivity

It is interesting to realize that the La compounds La_3X with the Cu_3Au structure seem to be less stable than the corresponding compounds of other light rare-earth elements. In fact, La_3In and La_3Tl are the only representatives of such La compounds, while these compounds of Ce, Pr, and Nd also are formed with Ga, Al, Sn, and Pb. Although it is possible to substitute limited amounts of these four elements for In and Tl in La_3In and La_3Tl, respectively, the pure binaries could not be obtained in this structure. The reason for this difference is not clear at present. It might be explained perhaps by atomic-size considerations. It should be kept in mind, however, that La_3In and La_3Tl exhibit an electron-phonon coupling strength as large as is found in A15-type high-temperature superconductors, which are known for their lattice instabilities. If such instabilities are the reason for the nonexistence of certain La compounds, one could then also understand why this anomalous behavior is not found among the ternary rare-earth perovskite carbides. They all have considerably smaller electron-phonon coupling constants than the pure Cu_3Au phases and therefore should be more stable than the binary compounds.

The superconducting T_c of La_3In and its pressure dependence were compared some time ago with the pressure dependence of T_c in fcc La by Smith and Luo.[4] In fact, the introduction of In into the fcc lattice of La by substitution causes a considerable lattice contraction, similar to that produced by high pressure. From their data, Smith and Luo conclude that the transition temperatures T_c of these superconductors follow essentially a linear function of the distance between La-La nearest neighbors. This behavior has been confirmed later for fcc La under even-higher pressures, producing volume changes $\Delta V/V$ of more than 23%.[25,26] Also, the new T_c of La_3Tl at zero pressure is in qualitative agreement with such a relation. According to its slightly lower lattice constant than that of La_3In, it should show a slightly higher T_c of about 9.7 °K instead of 8.9 °K. Compared with the over-all variations of T_c in fcc La under pressure, this is a minor deviation and could arise somehow from their important differences in the individual phonon spectrum and band-structure details. No explanation has been given up to now for the empirical relations between the pressure dependence of T_c in fcc La and the transition temperatures in La_3In and La_3Tl. However, there do exist different theories explaining the pressure dependence of T_c in fcc La.[27,28] We do not think that the empirical relations between the properties of fcc La, La_3In, La_3Tl, and other La compounds are fortuitous, and we assume that a correct analysis of the pressure dependence of T_c for fcc La should also explain the behavior of La_3In and La_3Tl. Garland and Bennemann[27] were able to estimate the pressure dependence of T_c for most of the transition metals, including fcc La, essentially on the basis of the McMillan formalism.[15] According to these authors the positive pressure dependence in fcc La is due to a low lattice Grüneisen constant and a high compressibility, with the consequence that the increase of the electron-phonon coupling constant caused by an increasing overlap of the d wave functions becomes predominate. The model of Ratto *et al.*,[28] developed in order to explain the superconducting behavior of La and Ce under pressure, makes quite different assumptions: a small $4f$ character of the conduction electrons in La at normal pressure is assumed to be removed at high pressure. From these two models one is expecting a different behavior of the electronic properties of fcc La under pressure. In the second model a diminishing $4f$ character should be accompanied by a decrease in the total electronic density of states, and one has to assume a positive electronic Grüneisen constant $\gamma_e^{(N)} = \partial \ln N(0)/\partial \ln V$. In their analysis, Garland and Bennemann,[24] however, estimate this parameter to be about -1. Considering the difficulties to measure electronic properties, such as the electronic specific heat or the magnetic susceptibility in fcc La as a function of pressure, it might be of interest to compare the theoretical models to La_3In and La_3Tl as substitutes for fcc La under pressure.

In their discussion of the pressure dependence of T_c in transition metals, Garland and Bennemann[27] use a generalized version of a relation of McMillan[15]:

$$T_c = (\langle \omega^2 \rangle^{1/2}/1.20)\, e^{-1/g} , \qquad (2)$$

where

$$g = \frac{0.96\lambda - (1 + 0.6\lambda)(\mu^* + \mu_{sp})}{1 + \lambda + \mu_{sp}} , \qquad (3)$$

$$\lambda = N(0)\langle I^2 \rangle / M \langle \omega^2 \rangle . \qquad (4)$$

$N(0)$ is the bare density of electronic states, $\langle I^2 \rangle$ stands for the averaged squares of the electron-ion matrix elements and $\langle \omega^2 \rangle$ for a weighted mean-square frequency. M is the atomic mass. The repulsive interactions are taken into account by μ^*, the screened Coulomb interaction, and μ_{sp}, measuring the effect of possible spin fluctuations on T_c. Assuming with Garland and Bennemann[27] for fcc La $\mu_{sp} \approx 0$ and the volume dependence of μ^* to be negligible, the pressure dependence of T_c becomes

$$\partial \ln T_c / \partial \ln V = -\bar{\gamma}_G + g^{-1} F(\lambda, \mu^*)(2\bar{\gamma}_G - \delta_\lambda) . \quad (5)$$

$\bar{\gamma}_G = -\partial \ln \langle \omega^2 \rangle^{1/2} / \partial \ln V$ is an effective Grüneisen constant which is not easily accessible. It may, however, be estimated from the room-temperature Grüneisen constant $\gamma_G = \alpha_V V_m / C_V^l \kappa$, where α is the cubic thermal expansion coefficient, V_m is the volume per gram atom, C_V^l is the lattice specific heat at constant volume, and κ is the compressibility. The function $F(\lambda, \mu^*)$, given by $F(\lambda, \mu^*) = 1/(1+\lambda) + \mu^*/[0.96\lambda - (1+0.6\lambda)\mu^*]$, is of the order of unity; δ_λ stands for $\delta_\lambda = -\partial \ln[N(0)\langle I^2 \rangle]/\partial \ln V$. In such a model the increase of T_c in fcc La under pressure can be explained by an important increase of $\langle I^2 \rangle$. In a tight-binding approximation for the d electrons, neglecting also dielectric screening, this increase is given by $\partial \ln \langle I^2 \rangle / \partial \ln V \cong -(\frac{2}{3}) q_0 a$ and is due to an increasing overlap of the d-electron wave functions.[27] The Slater coefficient q_0 can be estimated from atomic wave functions; a is the La nearest neighbor distance. Under these assumptions δ_λ becomes $\delta_\lambda = (\frac{2}{3}) q_0 a - \gamma_e^{(N)}$, where $\gamma_e^{(N)} = \partial \ln N(0)/\partial \ln V$ accounts for the decrease in the density of states due to band broadening under pressure and to possible Fermi-level shifting due to electron transfer. Considering also dielectric screening any change of $N(0)$ is at least partly compensated by an additional change in $\langle I^2 \rangle$ and μ^*, provided that[27] $N(0) \gtrsim 1$ state/eV atom; changes in $N(0)$ should therefore less affect γ and T_c than is expected from the form of Eq. (4). As was already mentioned, an estimate of the different physical parameters for fcc La lead to the conclusion that the large positive value of $\partial T_c / \partial p$ is essentially due to a large compressibility, responsible for a strong variation of $\langle I^2 \rangle$ with pressure, and a low Grüneisen constant γ_G.[27] Applying these results to La_3In and La_3Tl, one might expect that a larger electron-phonon coupling λ, due to a larger $\langle I^2 \rangle$, than in fcc La is responsible for the increase in T_c. On the other hand, the change in $\langle \omega^2 \rangle$ should be of less importance.

Unfortunately, the significant average values of $\langle \omega^2 \rangle$ or $\bar{\gamma}_G = -\partial \ln \langle \omega^2 \rangle^{1/2} / \partial \ln V$ are not available for La, La_3In, or La_3Tl and must be determined indirectly from other properties. For fcc La the Grüneisen parameter $\bar{\gamma}_G$ was estimated from room-temperature data to $\bar{\gamma}_G \cong 0.7$.[27] This value may be compared to $\gamma_G^{(\Theta_D)} = -\partial \ln \Theta_D / \partial \ln V \cong -V \Delta\Theta_D / \Theta_D \, \Delta V$ by using differences in Θ_D and V between fcc La and the La compounds, keeping in mind that these Grüneisen parameters need not to be equal, especially if Θ_D is measured at low temperatures where the shear-modes predominate. Grüneisen parameters $\gamma_G^{(\Theta_D)}$, as obtained in this way from $\Theta_D(0)$, are about 1.9 ± 0.6 and 1.4 ± 0.5 for La_3In and La_3Tl, respectively. The difference between La_3In and La_3Tl is due to the atomic-mass difference. Taking instead of $\Theta_D(0)$, the Debye temperatures $\Theta_D^{(M)}$ at the minimum of $\Theta_D(T)$ near 10 °K, the corresponding values $\gamma_G^{(M)} = -V \Delta\Theta_D^{(M)} / \Theta_D^{(M)} \Delta V$ might be more readily comparable to $\bar{\gamma}_G$; the values obtained in this way are 0.66 ± 0.03 and 0.41 ± 0.03. It is interesting to note that they are even lower than the value estimated from room-temperature data for fcc La and give some support to this value, which is rather low compared to those found in other transition metals.

This comparison may explain another anomaly found in these metals. It was noticed in several alloy systems of transition metals, that the electronic specific heats γ and the low-temperature Debye temperature $\Theta_D(0)$ tend to show opposite variations as a function of concentration.[29] Comparing fcc La with La_3In and La_3Tl, we note that both γ and $\Theta_D(0)$, increase between fcc La, La_3Tl, and La_3In. It seems evident to us that in these cases the normal increase of the Debye temperature due to the lattice contraction predominates the effect of the increase in the electronic density of states. The latter, however, may well be responsible for the anomalously low lattice Grüneisen parameter in these metals.

As was already stated, the electronic properties strongly vary between fcc La and La_3In or La_3Tl. In fact γ, the coefficient of the electronic specific heat, increases from 11.3 to 14.0 and 12.1 mJ/g atom K^2, respectively, this in spite of the "dilution" with non-d-metals. The enhancement of γ is even much higher, if it is assumed that only La-d-states contribute to the electronic density of states. In this case one has to compare γ of fcc La with values of 18.7 and 16.1 mJ/(g atom La)K^2 for La_3In and La_3Tl, respectively. Without anticipating the reason of the increase of $\gamma \sim N(0)(1+\lambda)$, which can be due to a rise of the bare density of states $N(0)$, of the electron-phonon coupling constant λ, or of both, such an increase of γ is in agreement with other measurements in pure La. Andres[30] observed in fcc La at low temperatures in the normal state a negative thermal expansion coefficient, which is rather unusual for a nonmagnetic material with a fcc structure. Such an effect could have been explained by assuming that some shear modes decrease their frequency with decreasing volume. The Debye temperatures $\Theta_D(T)$, however, are found to be higher in La_3In and in La_3Tl than in fcc La in the whole temperature range which was investigated. This seems to exclude such an effect and to support the supposition of Andres, that the anomalous behavior of the thermal expansion is an electronic effect.[30] With this assumption an electronic Grüneisen constant $\gamma_e = -1.2$ was deduced. γ_e(at $T=0$) is defined as

$$\gamma_e = 3aV_m/\kappa\gamma \ , \tag{6}$$

where a is the coefficient of the first term in the expression for the linear thermal expansion $\alpha = aT + bT^3$ at low temperatures. From thermodynamical considerations, using also data for the superconducting state, γ_e is estimated to $\gamma_e \cong -2$ in the liquid-helium temperature range.[30] A negative electronic Grüneisen constant does not necessarily mean that the electronic specific heat γ is increasing with decreasing volume. Due to a electron transfer between different bands, a positive or negative term $\Delta\gamma_e$ can drastically affect the electronic Grüneisen constant $\gamma_e = \partial \ln\gamma/\partial \ln V + \Delta\gamma_e$.[31] According to our data one can assume, however, that the negative sign of γ_e must be due to the inverse variation of γ with V. On the other hand, the results also give some support to results of Takata and Oshida,[32] who deduced from the pressure dependence of the critical field in pure La (with the hcp structure, however) a negative volume dependence of the electronic specific heat γ of $\partial \ln \gamma/\partial \ln V = -1.9 \pm 1.4$.[32]

In order to obtain more detailed information, we analyzed the data for La_3In and La_3Tl using McMillan's formulas: $T_c = 0.69\ \Theta_D(0) e^{-1/g}$ with $g = [\lambda - \mu^* \times (1+0.62\lambda)]/1.04(1+\lambda)$ derived for superconductors with the bcc structure, however. Using for μ^* a value of 0.1, we find for the electron-phonon coupling constant $\lambda^{(MM)}$ and for the bare density of states $N_{BS}^{(MM)}(0)$ the values given in Table I. We note that the enhancement of the electronic specific heat γ is indeed partially due to an increase in the bare density of states. On the other hand, one also finds an enhancement of the electron-phonon coupling constant, produced probably by an increase of both $N_{BS}(0)$ and $\langle I^2 \rangle$. It is difficult, however, to isolate the contribution of the change in the electronic density of states because of connected screening effects.

It would be rather speculative to try to draw more information from the parameters obtained by the latter analysis. Recently, another explicit formula for T_c of strong-coupling superconductors was given by Hertel[16]; it differs from McMillian's expression in the limit of strong coupling and is in good agreement with the experiment data for Pb and Hg. Comparing our data with this formula, although it was derived for an Einstein-type phonon spectrum, we would obtain for λ of La_3In and La_3Tl values, which are about 50% higher than those from McMillan's formula. It is not possible from existent data to decide which one of these two theoretical relations are closer to reality for describing the behavior of fcc La, La_3In, and La_3Tl. It is possible, however, that the influence of the lattice contraction on λ through $\langle I^2 \rangle$ and $N(0)$ to explain the volume dependence of T_c in these superconductors on the basis of the McMillan theory has been underestimated. To answer this question, an independent determination of the important parameters (e.g., from tunneling experiments) is necessary. In any case, an important conclusion about the upper limit of T_c may be drawn from these data. Both authors[15,16] give an expression for T_c^{Max} which can be reached for a given class of materials; these formulas, however, are based on the relation $M\Theta_D^2 \lambda = \text{const}$. We recognize that in the cases of fcc La, La_3In, and La_3Tl this is not verified and conclude that higher T_c's cannot be excluded in metals where pressure effects or strong variations of lattice constants are involved.

B. Magnetic Susceptibility and NMR Results

The striking features of the experimental results on La_3In and La_3Tl are the strong temperature dependence of the magnetic susceptibilities and of the Knight shifts K_{In} and K_{Tl}, and also the change in sign of K_{In} and K_{Tl}. The behavior of the Knight shifts confirms that the strong variation with temperature of the magnetic susceptibilities is an intrinsic effect and not due to magnetic impurities. No band-structure calculations are available for these compounds, and we therefore compare our results with a simple band model. We assume that near the Fermi level a wide free-electron-like band, formed principally from La-6s wave functions, overlaps a narrow d band, formed mainly from La-5d wave functions hybridized with In-5p or with Tl-6p wave functions. It cannot be decided as yet if the In-5s and the Tl-6s electrons participate in forming the s conduction band. According to calculated atomic energy spectra of In and La the In-5s states lie about 5.4 eV below the In-5p states and 3.9 eV below the La-5d states[33] and may therefore lie below the conduction band; for similar reasons the same may be true for the Tl-6s states in La_3Tl. The total susceptibility $\chi(T)$ of La_3X can now be separated into

$$\chi(T)=\chi_{\rm dia}+\chi_{\rm spin}(T)+\chi_{\rm orb}\,, \tag{7}$$

where $\chi_{\rm dia}$, $\chi_{\rm spin}$, and $\chi_{\rm orb}$ are, respectively, the diamagnetic susceptibility due to the ion cores, the spin susceptibility which in our band model is the sum of the spin susceptibilities χ_s and $\chi_{pd}(T)$ of the s band and the narrow pd band, and the orbital contributions to the magnetic susceptibility (the Van Vleck and Landau-Peierls term). Only the term $\chi_{pd}(T)$ is expected to show an important temperature dependence. The diamagnetic term $\chi_{\rm dia}$ can be estimated[34]: $\chi_{\rm dia}\cong-77\times10^{-6}$ emu/mole for La_3In and $\chi_{\rm dia}\cong-94\times10^{-6}$ emu/mole for La_3Tl. A first estimate for the spin susceptibilities $\chi_{\rm spin}$ $(T=0)$ can be obtained from the coefficients of the electronic specific heats γ. Correcting for the electron-phonon enhancement of the specific heat by using the electron-phonon coupling constants $\lambda^{(MM)}$ of Table I, but neglecting a possible exchange enhancement, the relation is $\chi_{\rm spin}=3(\mu_B/\pi k)^2[\gamma/(1+\lambda^{(MM)})]$, and we find for La_3In $\chi_{\rm spin}\cong390\times10^{-6}$ emu/mole and for La_3Tl $\chi_{\rm spin}\cong350\times10^{-6}$ emu/mole. Assuming one free electron per atom in the s band, $\chi_s\cong30\times10^{-6}$ emu/mole in both cases, and we obtain for La_3In $\chi_{pd}(T=0)\cong360\times10^{-6}$ emu/mole and for La_3Tl $\chi_{pd}(T=0)\cong320\times10^{-6}$ emu/mole. On the other hand, we can compare these results with the measured susceptibilities and estimate the orbital contributions to the susceptibilities: $\chi_{\rm orb}\cong167\times10^{-6}$ emu/mole in La_3In and $\chi_{\rm orb}\cong212\times10^{-6}$ emu/mole in La_3Tl or 56×10^{-6} emu/gatom La and 71×10^{-6} emu/gatom La, respectively, for these two compounds. These values are even reduced if one has to consider an exchange enhancement of the spin susceptibilities; therefore they represent an upper limit for the orbital contributions. On the other hand, we recognize that the exchange enhancement cannot be very important and is not responsible for the strong variation of about 50% in $\chi_{pd}(T)$ between room temperature and $T=0$. We have to assume that a sharp peak in the density of states of the pd band lies near the Fermi level. It is possible that this peak is also present in pure fcc La, and that its position with respect to the Fermi level is volume dependent; this could explain sensitive volume dependence of the electronic density of states and partly the increasing coupling strength with decreasing volume. Finally, it is interesting to note that with respect also to their magnetic properties, La_3In and La_3Tl behave very similarly.

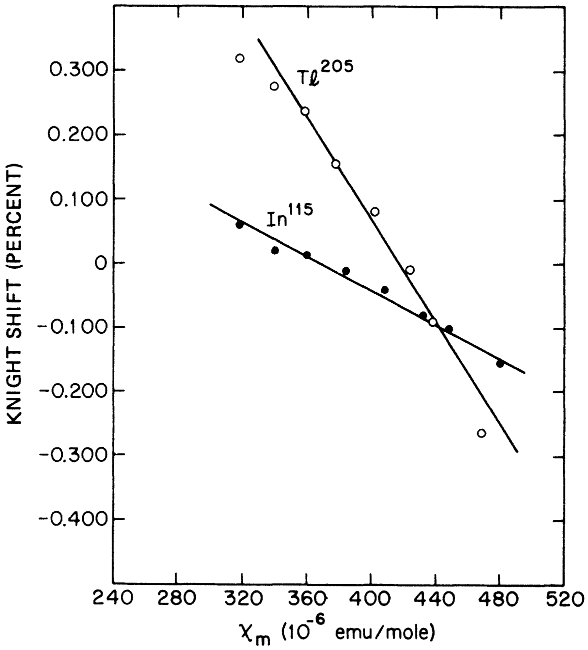

FIG. 9. In^{115} Knight shift vs χ for La_3In, and Tl^{205} Knight shift vs χ for La_3Tl.

For the Knight shifts $K_{\rm In}$ and $K_{\rm Tl}$, we may assume that they are composed by a positive s contact term $K^{(s)}$, a negative core polarization term $K^{(cp)}$ from the pd band and another positive term $K^{(VV)}$ due to the orbital contributions to the susceptibility. These different terms may be represented by

$$K^{(i)}=(N\mu_B)^{-1}H_{\rm hf}^{(i)}\chi^{(i)}\,,$$

where N and μ_B are the Avogadro number and the Bohr magneton, respectively, $\chi^{(i)}$ are the corresponding molar susceptibilities, and $H_{\rm hf}^{(i)}$ are appropriate hyperfine fields given in the units Oe/μ_B. From such relations we expect that the total Knight shift is a linear function of the total susceptibility at different temperatures if only one term $\chi^{(i)}$ depends on temperature. Supposing in our band model that only $\chi_{pd}(T)$ is temperature dependent, we can determine the corresponding hyperfine field $H_{\rm hf}^{(cp)}$ directly from the slope $dK/d\chi$ of $K(\chi)$. In Fig. 9, K vs χ is reported for La_3In and La_3Tl, and we obtain for $dK/d\chi$ -13.2 mole/emu and -39.7 mole/emu, respectively. As is expected generally for core-polarization hyperfine fields, they are found to be negative, and we obtain $H_{\rm hf}^{(cp)}\cong-0.74\times10^5$ Oe/μ_B and $H_{\rm hf}^{(cp)}\cong-2.2\times10^5$ Oe/μ_B at the In and the Tl sites of La_3In and La_3Tl, respectively. This hyperfine interaction is due to the hybridized *pd* states via a polarization of inner *s* shells which then give a contribution to the Knight shift by the contact interaction. Due to its higher atomic number, Tl is expected to show a larger core-polarization hyperfine field $H_{\mathrm{hf}}^{(cp)}$. Nothing quantitative can be said, however, about these hyperfine fields without careful band-structure calculations for these compounds. From our estimates for $H_{\mathrm{hf}}^{(cp)}$ and χ_{pd} $(T=0)$, we may also evaluate the corresponding contribution to the Knight shift $K^{(cp)}$ $(T=0)$: $K_{\mathrm{In}}^{(cp)} \cong -0.48\%$, $K_{\mathrm{Tl}}^{(cp)} \cong -1.27\%$. Since different parts of the Fermi surface do not contribute in the same way to the susceptibility and the Knight shift, these results are only correct as far as the temperature dependence of these properties is the same everywhere on the Fermi surface. Otherwise, a better description may be given by assuming that the *pd* band is constituted by a *d* band from essentially La-5*d* states overlapped by a *p* band from In-5*p* or Tl-6*p* states, respectively. The structure in the density of states in these bands may be different and therefore also the temperature dependence of $\chi_p(T)$ and $\chi_d(T)$. In the case of the In and Tl resonances one would therefore expect that the Knight shift $K^{(cp)}=K^{(p)}+K^{(d)}$ reflect rather the temperature dependence of $\chi_p(T)$ and not that of the total *pd*-band susceptibility $\chi_{pd}(T)=\chi_p(T)+\chi_d(T)$. This may explain the slight deviations of $K(\chi)$ from a straight line in Fig. 9. However, in order to be able to do the analysis in this way we need more information, e.g., about nuclear relaxation rates as a function of temperature.[24]

IV. CONCLUSIONS

(a) The compounds La_3In and La_3Tl are strong-coupling superconductors and exhibit many properties in common with fcc La under pressure.

(b) Perovskite carbides Ln_3XC have properties which are drastically different from those of the corresponding Ln_3X phases; in particular, they appear to be more stable and nonsuperconducting above 1 °K.

(c) Both compounds La_3In and La_3Tl are characterized by large electronic-specific-heat values and by almost-identical and strongly-temperature-dependent magnetic susceptibilities, suggesting that the electronic band structures of these compounds are quite alike and that the Fermi level is situated near a pronounced peak in the density of states.

(d) The strong temperature dependence of the spin susceptibility in La_3In and La_3Tl is strongly reflected in the Knight shifts of the non-*d* components In and Tl; in order to understand the relative importance of *p* and *d* electrons on the different properties, band-structure calculations are needed.

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