Thermodynamic properties of superconductors containing impurities in a crystal-field singlet ground state

F. Heiniger*
Bell Laboratories, Murray Hill, New Jersey 07974
and University of Geneva, Switzerland

E. Bucher, J. P. Maita, and L. D. Longinotti
Bell Laboratories, Murray Hill, New Jersey 07974
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Experimental results on superconducting and magnetic properties of La_3In and La_3Tl containing magnetic impurities are presented and discussed. From magnetic susceptibility and low-temperature specific heat we conclude that Pr^{3+} substituted for La^{3+} in these compounds is in a crystal-field singlet ground state; this also explains the characteristic behavior of the superconducting transition temperature as a function of the Pr concentration. The upper critical field of $(La_{1-x}Pr_x)_3In$ is limited by the mean exchange field due to the Pr ions which are polarized in the external magnetic field. At Pr concentrations higher than $x = 0.90$ the system $(La_{1-x}Pr_x)_3In$ shows a transition to a self-polarized antiferromagnetic state at low temperatures.

I. INTRODUCTION

The intermetallic compounds La_3In and La_3Tl are ideal host metals for the investigation of the influence of rare-earth magnetic impurities on superconducting properties. These compounds have high transition temperatures and allow a partial or complete substitution of La by another rare-earth element, and the destruction of superconductivity by such impurities can be followed over a wide range of temperature and impurity concentration. Furthermore, the electronic properties of the pure La_3In and La_3Tl compounds were extensively studied recently by Heiniger *et al.*,[1] and it was found they belong to the class of strong-coupling superconductors showing large deviations from the BCS law of corresponding states. One of the aims of this work is to study how those thermodynamic properties, which are sensitive to strong-coupling behavior, are changed by the addition of magnetic impurities.

The influence of magnetic impurities like Gd and Ce on the properties of La_3In has been investigated by several authors.[2–5] However, very little is known about the influence of the crystalline electric field (CEF) on magnetic and superconducting properties of La_3In and La_3Tl containing non-S-state rare-earth impurities. In fact, the behavior of such alloys is expected to be very different, especially in those cases where the magnetic impurities have a singlet state as a ground state. The influence of such impurities on the critical temperature T_c of superconductors has been studied both experimentally[6,7] and theoretically,[8–10] and good agreement is found in general between experiment and theory.

Recent numerical calculations of the upper critical field and of the specific heat in superconductors containing crystalline-field-split impurities by Keller and Fulde[11] have been compared with experimental data for a few alloy systems like $(La_{1-x}Tm_x)Sn_3$ by Guertin *et al.*[12] and $(La_{1-x}Tb_x)Al_2$ by Pepperl *et al.*[7] In the former case a significant difference in $H_{c2}(T)$ is seen between $(La_{1-x}Gd_x)Sn_3$, where no CEF effects are expected, and $(La_{1-x}Tm_x)Sn_3$, where Tm has a nonmagnetic ground state.[6] However, it is not clear in this case how far mean-free-path effects (pure $LaSn_3$ is a type-I superconductor) and Sn precipitations are responsible for the differences between these alloys. The results for H_{c2} in $(La_{1-x}Tb_x)Al_2$ on the other hand do not show a behavior as expected from theory except at the highest Tb concentrations. This, however, could be explained as being due to the mean exchange field produced by the magnetic impurities which are polarized in the external magnetic field.[7] Our new results on H_{c2} in $(La_{1-x}Pr_x)_3In$ are a new test for that theory; they also have the further interest that they concern upper critical fields which are almost two orders of magnitude higher than those observed in $(La_{1-x}Tm_x)Sn_3$ and $(La_{1-x}Tb_x)Al_2$.

From the theory of superconductors containing magnetic impurities one also expects in such systems large deviations from the law of corresponding states in the specific-heat discontinuity ΔC at T_c. Impurities with a magnetic S ground state depress ΔC much more than T_c.[13,14] In the case of impurities with two singlet levels separated by the energy δ, characteristic maxima in ΔC are expected for $\delta \approx k_B T_{c0}$ (T_{c0} is the critical temperature of the pure superconductor), which disappear for a higher level separation.[11] Some related measurements have been published for $(La_{1-x}Pr_x)_3Tl$ by Bucher *et al.*[15] and for $(La_{1-x}Tb_x)Al_2$ by Happel and Hoenig.[16] In both cases $\Delta C/\Delta C_0$ (ΔC_0 is the specific-heat jump for the pure superconductor) versus T_c/T_{c0} is higher than expected from the Abrikosov-Gor'kov theory (AG)[13,14] for impurities with a magnetic S ground state, thus in qualitative agreement with the theory for superconductors containing singlet-ground-state impurities. A quantitative comparison of $\Delta C/\Delta C_0$ for $(La_{1-x}Pr_x)_3Tl$ with this theory, however, is difficult owing to the strong coupling enhancement of this quantity over the BCS value. For comparison we also give in this work the corresponding data for the $(La_{1-x}Pr_x)_3In$ system.

After a description of the sample preparation in Sec. IIA, we present in Sec. IIB specific-heat data for $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$ and deduce quantities like transition temperatures T_c, specific-heat discontinuities ΔC at T_c, electronic specific heats, Debye temperatures, and for pure Pr_3In the hyperfine field. Together with results of magnetic properties of $(La_{1-x}Pr_x)_3In$, given in Sec. IIC, it is possible to obtain from the normal-state specific heat some information about the CEF parameters in this system. In Sec. IID we also present experimental data on the upper critical field H_{c2} in the ternary system $(La_{1-x}Pr_x)_3In$. Section III finally is devoted to a detailed discussion of the new experimental data on the basis of recent theories.

II. EXPERIMENTAL RESULTS

A. Sample preparation

All samples prepared for this investigation were obtained by direct fusion in an argon arc furnace. As elements we used 99.999%-pure In and Tl from Asarco Co. and La from Rare Earth Products of a nominal purity of 99.99% with respect to other rare earths. Pr was zone-refined nuclear-grade material of 99.9% purity, supplied by Lunex Co. Details on the preparation and the x-ray analysis of the binary compounds La_3In and La_3Tl, and those of the ternary alloys $(La_{1-x}Pr_x)_3Tl$, can be found in earlier papers.[1,15] Alloys of the type $(La_{1-x}Pr_x)_3In$ were prepared in an analogous way. In a first step homogeneous $La_{1-x}Pr_x$ alloys were formed from the elements by arc melting, and In was then added in a second step. The weight of the ingots was checked after each melting process in order to detect losses by evaporation. A slight weight loss was noticed in the second step; this, however, could be compensated by an excess of about 1% In, which we added in advance. An annealing of the La-rich $(La_{1-x}Pr_x)_3In$ sample was not necessary; no other phases than that with the $L1_2$ structure could be detected in these alloys, and reproducible and sharp superconducting transitions were obtained in the as-cast state.

B. Specific heats in $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$

A large part of the data presented in this paper were obtained from low-temperature specific heats, measured in a heat-pulse calorimeter as described elsewhere.[17] Typical curves of the specific heat in superconducting alloys of the form $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$ have been shown in earlier papers,[1,15] and will not be reproduced here. Instead we summarize in Table I and Figs. 1 and 2 these data by the most important parameters obtained from an analysis of the measured specific heats.

For the superconducting transition temperatures T_c we find a similar behavior for both systems, $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$, except that the transition temperatures of the latter are throughout 0.4–0.5 °K lower. The behavior of T_c in these systems is typical for metals containing magnetic impurities in a crystal-field nonmagnetic ground state and will be discussed later. For comparison we also show in Fig. 3 the transition temperatures as a function of the Gd concentration in $La_{0.75-x}Gd_xIn_{0.25}$ and $La_{0.25-x}Gd_xSn_{0.75}$, where no CEF effects are expected. The results for $La_{0.75-x}Gd_xIn_{0.25}$ agree with published data[2] for low

TABLE I. Thermodynamic data for $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$.

Alloy system	x	$\Delta C/T_c$ (mJ/g-at. °K^2)	T_c (°K)	γ (mJ/g-at. °K^2)	Θ_0 (°K)	T_{ord} (°K)
$(La_{1-x}Pr_x)_3In$	0.00	41.0[a]	9.95 (9.54[a])	14.0[a]	170[a]	...
	0.05	30.0	7.92	...	...	...
	0.10	27.5	6.20	16.2[b]	...	...
	0.15	23.2	4.71	...	...	...
	0.20	18.6	3.20	18.1	161	...
	0.25	15.2	1.94	18.2	159	...
	1.00	...	...	24.3	160	T_N = 16.8 °K
$(La_{1-x}Pr_x)_3Tl$	0.00	31.5 (30.0[a])	9.1 (8.86[a])	12.4[a]	163[a]	...
	0.10	...	...	18.0 ± 2.0	...	...
	0.15	...	...	18.9 ± 1.5	...	...
	0.20	...	...	18.0 ± 1.0	...	...
	1.00	...	...	...	...	T_f = 11.3 °K[c]

[a]Reference 1. [b]Interpolated value. [c]Reference 27.

Gd concentrations. However, we were not able to reproduce the anomalies, found by Crow and Parks[2] in this system near the critical concentration and attributed by Bennemann[18] to spin correlations among the Gd impurities. Also, $T_c(x)$ for $La_{0.25-x}Gd_xSn_{0.75}$ follows rather well the predictions of the Abrikosov-Gor'kov model,[13] if the slope of $T_c(x)$ is adjusted for $x=0$ (Fig. 3), and no relevant anomalies could be affirmed by these results.[19]

In Table I and Figs. 1 and 2 we report the specific-heat jumps at T_c, $\Delta C/T_c$, for $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$. In both alloy series this quantity decreases strongly with increasing Pr concentrations for $x > 0.1$. At lower Pr concentrations, however, the two alloy systems behave differently, as was stated already in Ref. 15: While $\Delta C/T_c$ is almost constant in $(La_{1-x}Pr_x)_3Tl$ for $0 \leq x \leq 0.06$, this quantity drops monotonically with $d^2(\Delta C/T_c)/dx^2 > 0$ for all Pr concentrations in $(La_{1-x}Pr_x)_3In$. In fact one should rather compare the reduced specific-heat jumps $\Delta C/\gamma T$, where γ is the coefficient of the electronic specific heat. This coefficient is not easily determined in these alloys, but it seems that it increases in both alloy systems with x and stronger in the Tl alloys than in the In alloys. If we assume a linear increase of γ with x for $0 \leq x \leq 0.1$ in $(La_{1-x}Pr_x)_3Tl$, we find a similar behavior of $\Delta C/\gamma T_c$ vs x in both systems. Near the critical concentration $\Delta C/\gamma T_c$ drops well below

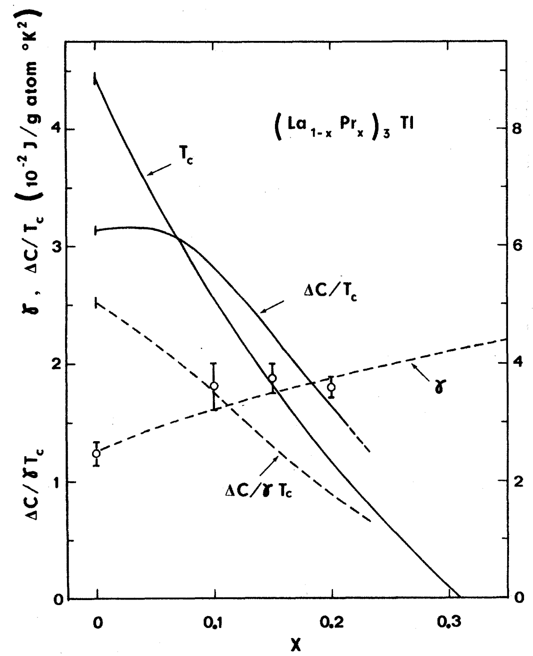

FIG. 2. Coefficient γ of the linear term in the specific heat and reduced specific-heat discontinuity $\Delta C/\gamma T_c$, for $(La_{1-x}Pr_x)_3Tl$. The curves for T_c and $\Delta C/T_c$ are from Ref. 15.

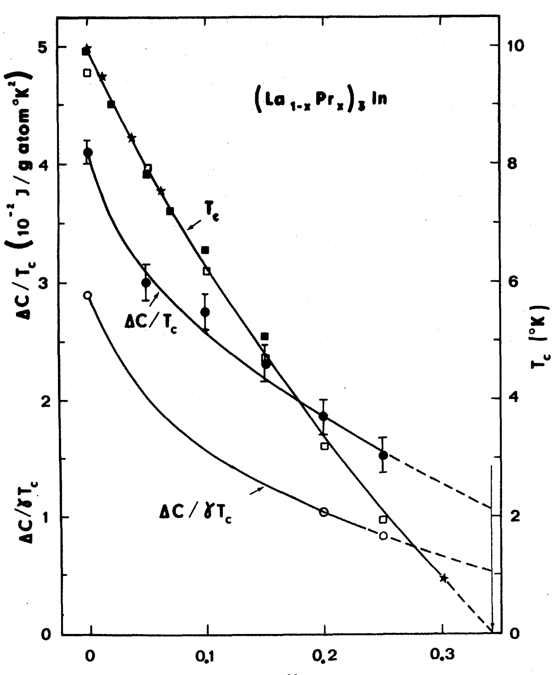

FIG. 1. Superconducting transition temperatures T_c and specific heat discontinuities ΔC at T_c in $(La_{1-x}Pr_x)_3In$ (○, ●, □: specific heat samples; ■: samples for H_{c2} measurements; ★: other samples).

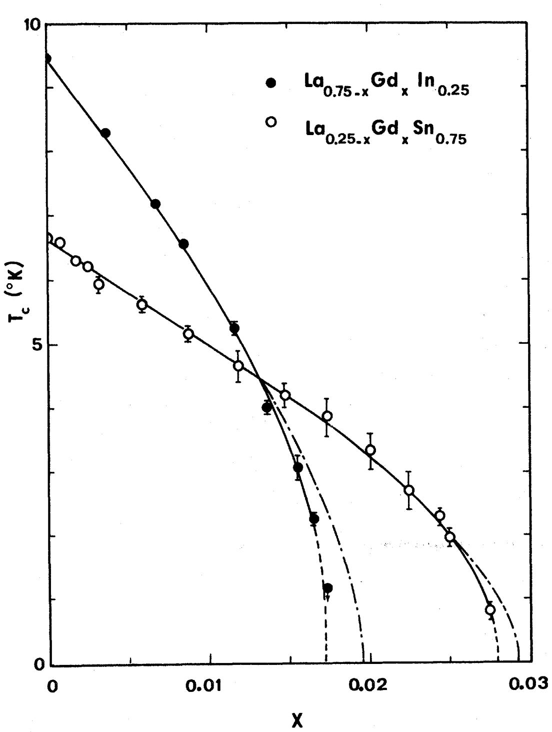

FIG. 3. Superconducting transition temperatures T_c in $La_{0.75-x}Gd_xIn_{0.25}$ and $La_{0.25-x}Gd_xSn_{0.75}$. Chain lines: $T_c(x)$ according to the AG theory (Ref. 13) adjusted at $x=0$.

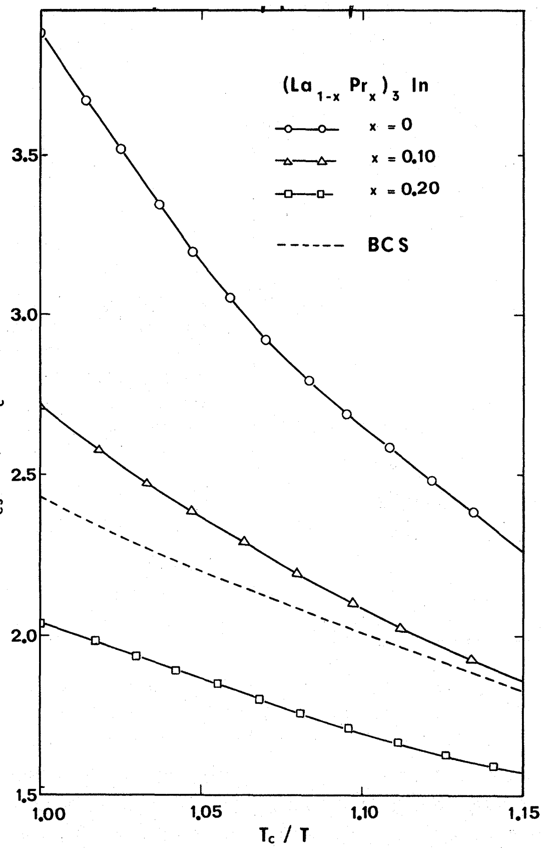

FIG. 4. Electronic specific heat in $(La_{1-x}Pr_x)_3In$ in the superconducting state near T_c. Broken line: the same quantity according to the BCS theory.

the value of 1.43 of the BCS law of corresponding states, but extrapolates to a finite value at the critical concentration. With respect to this parameter the singlet-ground-state systems thus show an intermediate behavior between BCS superconductors without magnetic impurities and gapless superconductors.

In Fig. 4 we show more in detail, for $(La_{1-x}Pr_x)_3In$, the electronic specific heat in the superconducting state, C_{es}, near T_c. Assuming that the lattice part of the specific heat is unchanged at the superconducting transition, we obtained this electronic specific-heat term C_{es} from the total specific heat in the superconducting state, C_s, and the normal-state specific heat C_n, measured in a magnetic field of $H = 10$ kOe: $C_{es} = C_s - C_n + \gamma T$. For comparison, Fig. 4 also shows this quantity as obtained from BCS theory.

The normal-state specific heats of the paramagnetic $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$ alloys at the lowest temperatures show a standard behavior, and the analysis was done in the same way as for the binaries La_3In and La_3Tl, described in Ref. 1. Magnetic contributions, however, had to be considered in these ternary alloys at higher temperatures ($T > 15$ °K), and in the case of the Pr-rich alloys, which order magnetically, even at the lowest temperatures. Results of the analysis of the normal-state specific heats are found in Table I and in Figs. 2 and 5–8. Owing to the low Debye temperature Θ_D, a reliable determination of the coefficient γ of the electronic specific heat was not possible without specific-heat data in a magnetic field to suppress superconductivity in $(La_{1-x}Pr_x)_3In$ for $x < 0.2$ and in $(La_{1-x}Pr_x)_3Tl$ for $x < 0.1$; T_c is too high in these cases to allow an extrapolation to $T = 0$. From alloys with a higher Pr content we observe in both alloy series a strong increase of the linear term in the specific heat. It is possible to explain this by an increase in the electronic density of states at the Fermi level by the addition of Pr to La_3In and La_3Tl, assuming that the Fermi level is shifted towards a peak in the electronic density of states[1] if the atomic volume is reduced. We cannot, however, exclude completely any magnetic contribution responsible for an increase in the linear term of the specific heat.

At temperatures $T > 15$ °K the magnetic contribution of the Pr atoms to the specific heat in paramagnetic $(La_{1-x}Pr_x)_3Tl$ becomes predominant and can be separated from the total specific heat. This was done for $(La_{1-x}Pr_x)_3Tl$ in an earlier paper.[15] For the $(La_{1-x}Pr_x)_3In$ system we subtracted the specific heat of La_3In from the measured specific heat neglecting the slight γ and $\Theta_D(T)$ variation vs x and obtained for the magnetic part of the specific heat the results given in Fig. 6. The agreement between the results for $x = 0.10$ and 0.15, normalized to 1 g-at. of Pr, seems to support this procedure for the analysis of the specific heat; the slight deviations for $x = 0.25$ might be explained by a corresponding decrease in

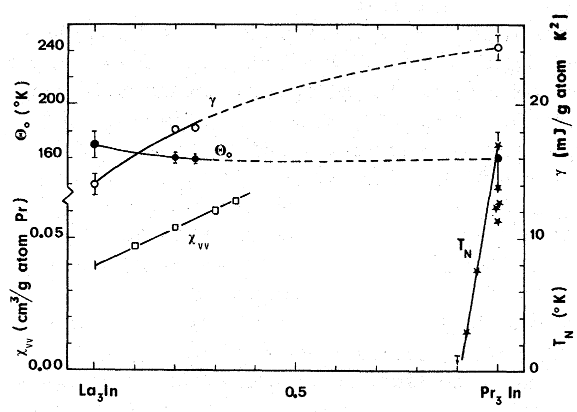

FIG. 5. Thermal and magnetic properties of $(La_{1-x}Pr_x)_3In$. γ: coefficient of the linear term in the specific heat; Θ_0: low-temperature Debye temperature; χ_{vv}: Van Vleck paramagnetic susceptibility; T_N: Néel temperatures.

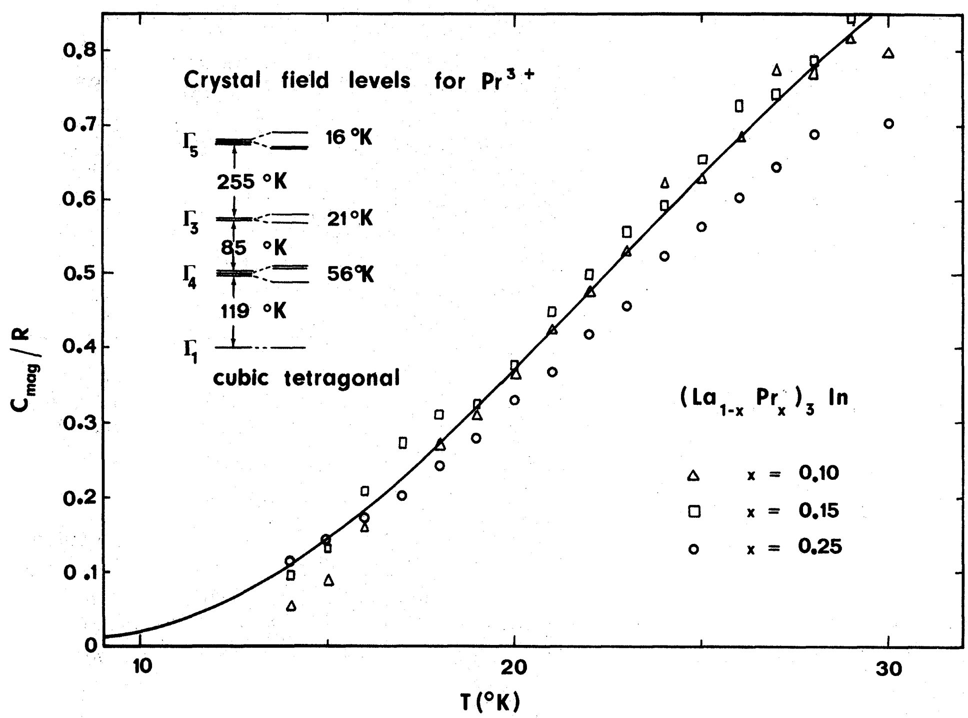

FIG. 6. Crystal-field specific heat in $(La_{1-x}Pr_x)_3In$ for $x = 0.10$, 0.15, and 0.25. Curve: specific heat as calculated from tetragonal level scheme in the insert.

the lattice specific heat with respect to La_3In. Figure 6 also shows the CEF splitting for Pr^{3+} giving the best fit to this Schottky specific heat, and which also explains the Van Vleck paramagnetic susceptibility, as will be discussed in Sec. III A.

In Fig. 7 we show the experimental specific heat between 1.5 and 22 °K for the binary compound Pr_3In, in comparison with the same quantity found in La_3In.[1] This figure shows that additional contributions are present in Pr_3In. At the lowest temperatures a hyperfine field at the ^{141}Pr nuclei is at the origin of a specific-heat contribution $C_{hf} = A/T^2$; at higher temperatures, up to the Néel point at 16.8 °K, another magnetic contribution to the specific heat is due to antiferromagnetic ordering. Assuming that we can neglect the latter contribution below 3 °K, we analyzed the measured specific heat between 1.5 and 3 °K by a least-squares fit to the expression $C/T = A/T^3 + \gamma + \alpha T^2$ (Fig. 8) and obtained for the coefficients $A = 64 \pm 3$ mJ °K/g-at., $\gamma = 24.3 \pm 1.0$ mJ/°K^2. g-at., and $\alpha = 0.51 \pm 0.20$ mJ/°K^4. g-at. The third term, $C_{ph} = \alpha T^3$, represents mainly the phonon part of the specific heat, and we obtain from α for the Debye temperature a value of $\Theta_D = 160 \pm 20$ °K. If one had to consider also a spin-wave contribution, one would obtain for Θ_D a somewhat higher value; a Debye temperature of 160 °K, which is comparable to that of La_3In and of ternary $(La_{1-x}Pr_x)_3In$ alloys, however, seems to be reasonable, and the spin-wave contribution to the specific heat in this temperature range cannot be important. In order to clarify this point, and to estimate the magnetic contribution also between 3 °K and the Néel point, elastic constants of Pr_3In should be determined. If we assume that the lattice part of the specific heat in Pr_3In below 17 °K is comparable to that in La_3In,[1] we obtain for the sum of the electronic and the lattice entropy of Pr_3In at 16.8 °K a value of $S_{el} + S_{ph} = 0.29R$ per g-at. Pr. We find in this way that the magnetic entropy per g-at. Pr at the Néel point $T_N = 16.8$ °K is of the order of $S_{mag} = 0.11R$ per g-at. Pr and much lower than the total entropy expected for Pr^{3+} with $J = 4$, $S/(\text{g-at. Pr}) = R \ln 9$

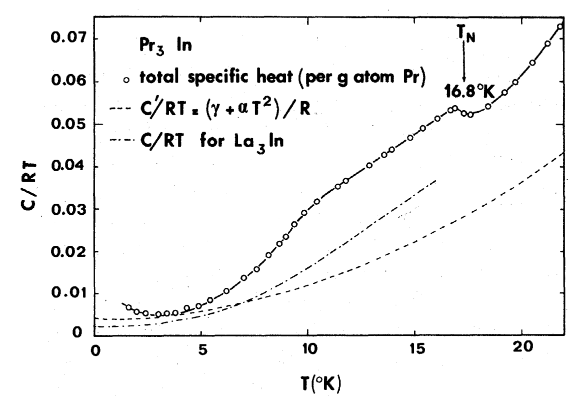

FIG. 7. Total specific heat of Pr_3In (line through open circles), in comparison with total specific heat of La_3In (dash-dot line), and the sum of the linear and the cubic terms of the specific heat in Pr_3In (dashed line).

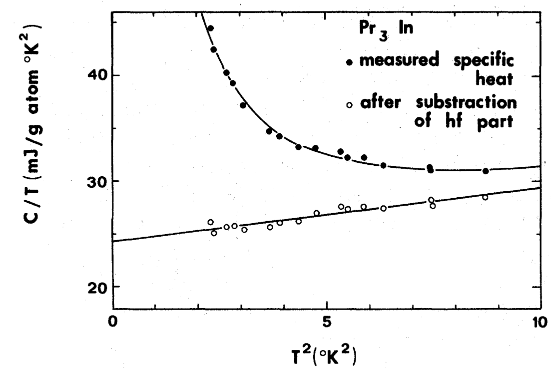

FIG. 8. Analysis of the low-temperature specific heat in Pr_3In.

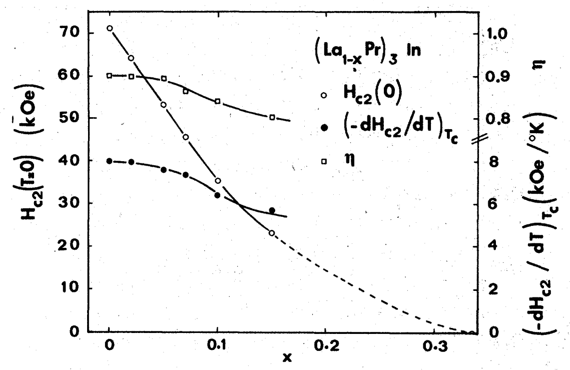

FIG. 10. Upper critical field $H_{c2}(T=0)$, slope $-dH_{c2}/dT$ at T_c, and ratio $\eta = H_{c2}(T=0)/T_c(-dH_{c2}/dT)_{T=T_c}$ for $(La_{1-x}Pr_x)_3In$ as a function of x.

$=2.2R$. This is typical behavior for an induced-moment system, as will be discussed later.

C. Magnetic properties of $(La_{1-x}Pr_x)_3In$

The magnetic susceptibility of $(La_{1-x}Pr_x)_3In$ was measured between 1.4 and 300 °K with a pendulum magnetometer[20] in fields up to 15 kOe. In these alloys, no magnetic ordering was detected for $x<0.35$; they show, however, a strong Van Vleck paramagnetic susceptibility χ_{VV}, characteristic for Pr atoms in a CEF nonmagnetic ground state. As in the $(La_{1-x}Pr_x)_3Tl$ system,[15] $\chi_{VV}(T=0)$ per g-at. Pr in $(La_{1-x}Pr_x)_3In$ increases monotonically with x (Fig. 5). The magnetization of Pr_3In and Pr-rich alloys of $(La_{1-x}Pr_x)_3In$ also was investigated in low fields (~10 Oe) by a mutual-induction method at 27 Hz.[21] It shows a Curie-Weiss type behavior down to ~17 °K and a sudden decrease with temperature below a critical temperature T_N. This behavior is typical for an antiferromagnetic ordering at the Néel temperature T_N. Figure 5 shows T_N as a function of x. An ordering temperature of 16.8 °K for pure Pr_3In seems reasonable compared to similar compounds, but is in contradiction with earlier findings of other authors, who report ferromagnetic ordering with Curie temperatures of 62 °K,[22] and 56.5 °K,[23] respectively. Suspecting that traces of a ferromagnetic phase could have been at the origin of the observed transition near 60 °K, we also investigated the neighboring Pr_2In phase and found it to be ferromagnetic with a Curie temperature of 70 °K.[21] It is important to notice that antiferromagnetic ordering with a low Néel temperature can be inhibited by strong magnetic fields and that such ordering temperatures should be determined in low or zero magnetic fields.

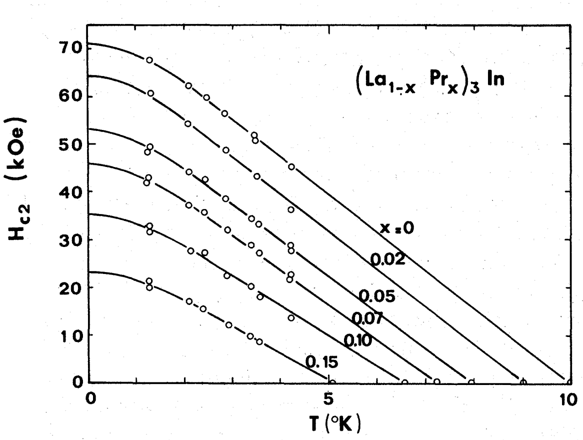

FIG. 9. Upper critical fields H_{c2} in $(La_{1-x}Pr_x)_3In$ for $x=0$, 0.02, 0.05, 0.07, 0.10, and 0.15.

D. Critical fields $H_{c2}(T)$ in $(La_{1-x}Pr_x)_3In$

Upper critical fields H_{c2} were measured by four-probe resistance measurements on slabs of 10 mm×1 mm×1 mm size in a transverse magnetic field, produced by a superconducting solenoid. The temperature of the samples, which were completely submerged in liquid helium, was obtained from the helium vapor pressure. The ac resistance (100 Hz) of the samples as a function of the applied field showed a well-defined onset at the field H_{c2}, which was independent of the applied current. The experimental results for $H_{c2}(x, T)$ are shown in Fig. 9; the curve for $x=0$ is in agreement with results obtained by Jones *et al.*[5] In Fig. 10 we also show the upper critical field $H_{c2}(0)$ at $T=0$, obtained from extrapolation, the slope $-dH_{c2}/dT$ at T_c, and the ratio $\eta = H_{c2}(0)/T_c(-dH_{c2}/dT)_{T=T_c}$ as a function of the Pr concentration.

III. DISCUSSION

A. Magnetic properties

Ternary alloys $(La_{1-x}Pr_x)_3In$ crystallize in the Cu_3Au ($L1_2$-type) structure; In atoms occupy the cubic sites, and La and Pr atoms are statistically distributed on the tetragonal sites. Pr atoms have

12 nearest and equidistant neighbors; four of them are In and eight are La or Pr. The point symmetry at a Pr position is tetragonal; the deviation from a situation with cubic symmetry is due to differences in the electronic structures of In and La or Pr. At low Pr concentrations the exchange interactions can be neglected, and the $J=4$ term of the Pr ion is split by a tetragonal crystalline electric field into two doublets and five singlets. It was shown recently, from inelastic neutron scattering measurements and also from specific-heat data, that the deviations from a CEF of cubic symmetry are weak in the isomorphous system $(La_{1-x}Pr_x)_3Tl$. Assuming that this is also true in $(La_{1-x}Pr_x)_3In$ and neglecting sixth-order crystal-field terms, one can obtain the CEF level scheme from our data, using theoretical results from Lea, Leask, and Wolf[24] for cubic symmetry. Neglecting deviations from cubic symmetry one expects, in order to explain the magnetic properties, the Γ_1 state to be lowest, followed by the Γ_4 state at an energy of Δ above the ground state. The level difference Δ can be obtained from the experimental low-temperature Van Vleck crystal-field susceptibility $\chi_{VV}(0)$ given by

$$\chi_{VV}(0)=2g_J^2\,\mu_B^2\,\alpha^2/\Delta\ , \tag{1}$$

with $\alpha=\langle\Gamma_1|\vec{J}|\Gamma_4\rangle=(\frac{20}{3})^{1/2}$. In the limit of $x\to 0$ we found experimentally $\chi_{VV}(0)=0.040$ cm^3/(g-at. Pr) (Fig. 5), which would lead to $\Delta/k_B=82$ °K. However, in order to explain the Schottky anomaly in the specific heat we would have to assume a Δ/k_B of about 119 °K. This discrepancy may be due in part to magnetic impurities other than Pr or to a self-polarizability of the singlet-state ion. The most obvious explanation, however, is given by the fact that slight deviations of the CEF from cubic symmetry influence differently $\chi_{VV}(0)$ and the Schottky specific heat. For a "weakly tetragonal" crystalline electric field the levels of Pr^{3+} are split as shown in Fig. 6. The specific-heat anomaly is determined in this case by the centers of gravity of the Pr levels and therefore insensitive to a tetragonal distortion. The Van Vleck susceptibility, on the other hand, is determined by the singlet state derived from the cubic Γ_4 triplet. It is therefore possible to explain the experimental data correctly by the level scheme, shown in Fig. 6, for tetragonal symmetry, from which we obtain the correct value for $\chi_{VV}(0)$ and a good fit to the experimental specific heat (Fig. 6).

In Fig. 5 we notice that the Van Vleck susceptibility per Pr atom is not constant but increases with increasing Pr concentration. Such a behavior was found already in the $(La_{1-x}Pr_x)_3Tl$ system and could be explained at least qualitatively by an increase of the exchange interaction which finally leads to ferromagnetism for overcritical exchange.[15] In the $(La_{1-x}Pr_x)_3In$ system, however, the effective exchange interaction between Pr ions leads to antiferromagnetism at high Pr concentrations, and one would expect, on the basis of a simple molecular-field model, rather a decrease of the low-field susceptibility as was found, e.g., in (Y-Tb)Sb by Cooper and Vogt.[25] On the other hand, no systematic variation of the Schottky specific heat was found as a function of x and no lowering of the Γ_4 CEF level can be invoked in order to explain this increase of the Van Vleck susceptibility with x. In a single-atom picture, both the increase of $\chi_{VV}(0)$ and the constancy of the Schottky anomaly could be explained by an increasing tetragonal distortion of the crystalline electric field. It is probable, however, that sign and magnitude of the effective exchange interaction between Pr ions depends critically on the concentration-dependent Pr nearest-neighbor configuration and on changes of the electronic structure with x. It is therefore possible that such effects are not only at the origin of the enhancement of $\chi_{VV}(0)$ in $(La_{1-x}Pr_x)_3In$, but also of the differences between Pr_3Tl (ferromagnetic[15]) and Pr_3In (antiferromagnetic) and of the deviations of the experimental Van Vleck susceptibility in $(La_{1-x}Pr_x)_3Tl$ from a behavior as expected from a molecular-field theory.[15]

At high concentrations of Pr, for $x>0.90$, $(La_{1-x}Pr_x)_3In$ shows a transition from the Van Vleck paramagnetic state to an antiferromagnetic state. The Néel temperature T_N increases monotonically with x from $T_N=0$ at the critical concentration $x_{cr}\cong 0.90$ to the value of $T_N=16.8$ °K at $x=1.0$. $(La_{1-x}Pr_x)_3In$ is one of the few alloy systems where the exchange interaction changes with composition from an undercritical value to an overcritical value. Magnetic properties of such systems depend mainly on two interactions: (a) the interaction of the rare-earth ions with their surrounding CEF and (b) the exchange interaction between the rare-earth ions via the conduction electrons. If the exchange interaction is weak enough, it is possible for non-Kramers ions (J integer) that the CEF produces a crystal-field singlet ground state, leading to a Van Vleck paramagnetism down to the lowest temperatures (undercritical exchange). This is the case for $(La_{1-x}Pr_x)_3In$ with $x\leq 0.90$. If the exchange interaction exceeds a certain value (critical exchange) the singlet ground state mixes spontaneously with higher-lying crystal-field states to produce a lower-lying polarized ground state. Magnetic ordering here does not occur through the usual process of alignment of permanent magnetic moments but rather through a polarization of the Pr $4f$ states by the exchange interaction.

A characteric behavior of induced-moment systems with low ordering temperatures is that little entropy change is caused by magnetic ordering. In fact, the total magnetic entropy for magnetic ions is $S_{mag} = R\ln(2J+1)$; however, if all excited levels in the paramagnetic state lie considerably higher than $k_B T_{ord}$, most of this entropy is given up by the system of magnetic ions upon cooling down to the ordering temperature T_{ord}. For Pr_3In we can estimate the magnetic entropy left at the Néel temperature $T_N = 16.8$ °K if we assume that the level scheme of Pr ions above T_N is the same as in La-rich $(La_{1-x}Pr_x)_3In$ alloys. Neglecting any many-body effects in the paramagnetic region we obtain for the entropy at T_N

$$S(T_N) = \int_0^{T_N} (C_{mag}/T)\, dT$$
$$\cong R\left(1 + \frac{\Delta}{k_B T_N}\right) e^{-\Delta/k_B T_N}, \qquad (2)$$

where Δ is the energy of the first excited level as measured from the ground-state level. For $\Delta/k_B = 82$ °K we obtain $S(T_N) = 0.045R$ or 1.5% of the total magnetic entropy for Pr^{3+} with $J=4$. This is about half of our estimation from the experimental specific heat. However, neither the analysis of the experimental specific heat is very reliable nor can the assumption of a level separation of $\Delta/k_B = 82$ °K obtained for dilute alloys be verified, and the agreement seems therefore satisfactory. In any case, these estimations show that one has to expect in such systems, where $\Delta/k_B T_{ord} \gg 1$, small specific-heat anomalies connected with magnetic ordering.

As another characteristic of induced-moment systems, magnetic ions usually show a reduced magnetic moment. Pr_3In being antiferromagnetic, it is not possible to determine the magnetic moments of the Pr ions by a simple measurement of the macroscopic spontaneous moment. No neutron-diffraction data exist for this compound up to now. An estimation of the magnetic moment of Pr in Pr_3In, however, can be obtained from its hyperfine specific heat. Neglecting quadrupole interactions, and for $k_B T \gg \mu_I H_{hf}$, this specific-heat contribution C_{hf} is given at high T by

$$C_{hf} = A/T^2$$
$$= cR\,\frac{I+1}{3I}\left(\frac{\mu_I H_{hf}}{k_B T}\right)^2, \qquad (3)$$

with $c = 0.75$ (concentration of ^{141}Pr in Pr_3In), $I = \frac{5}{2}$ (nuclear spin of ^{141}Pr), $\mu_I = 4.28\,\mu_N$ (nuclear magnetic moment of ^{141}Pr in nuclear magnetons μ_N), and H_{hf} is the hyperfine field. From $A = 64 \pm 3$ mJ °K/g-at. we obtain $H_{hf} = (0.92 \pm 0.02) \times 10^6$ Oe. This hyperfine field is related to the electronic magnetic moment $\langle \mu_z \rangle$ (z axis taken parallel to the mean magnetic moment) through the magnetic hyperfine constant a_J:

$$-\mu_I H_{hf} = a_J \langle J_z \rangle I_z ,$$
$$\langle \mu_z \rangle = g_J \mu_B \langle J_z \rangle = -g_J \mu_B g_N \mu_N H_{hf}/a_J . \qquad (4)$$

Assuming for Pr^{3+} a magnetic hyperfine-structure constant of $a_J/h = -1093$ MHz,[26] we find for the Pr^{3+} magnetic moments in Pr_3In a value of $\langle \mu_z \rangle \cong 0.90\,\mu_B$ or 28% of the full Pr^{3+} magnetic moment. It is interesting to compare this result to properties of Pr_3Tl and Pr-rich $(La_{1-x}Pr_x)_3Tl$ which were investigated recently by Andres *et al.*[27] From experiment and theory these authors find that the ferromagnetically ordered Pr^{3+} magnetic moment and the Curie temperature T_f are increasing functions of the overcritical exchange interaction. Although a direct comparison of the antiferromagnetic Pr_3In to these ferromagnetic alloys is not possible we notice that with respect to Pr_3Tl the 50% higher ordering temperature in Pr_3In is accompanied by a 29% increase in the induced magnetic moment. In order to see if there exist fundamental differences between the exchange-induced ferromagnet Pr_3Tl and the exchange-induced antiferromagnet Pr_3In one should measure the Pr^{3+} magnetic moment also in the tenary $(La_{1-x}Pr_x)_3In$ as a function of x and thus as a function of T_N.

B. Superconducting properties

Superconducting properties of the binary compounds La_3In and La_3Tl have been discussed in two recent papers by Bucher *et al.*[15] and Heiniger *et al.*[1] Large T_c/Θ_D ratios, strongly enhanced specific-heat jumps at T_c, positive deviations of $H_c(T)$ from a parabolic law, and other thermodynamic properties suggest that these compounds belong to the class of strong-coupling superconductors. Another indication of strong coupling in La_3In is given by the temperature dependence of H_{c2}, as has been pointed out already by Jones *et al.*[5] $H_{c2}(T)$ in La_3In increases almost linearly with decreasing temperature down to about 2 °K (Fig. 9) and does not fit the weak-coupling theory of Werthamer *et al.*,[28] but can be understood qualitatively on the basis of recent calculations for strong-coupling superconductors by Rainer and Bergmann.[29] Our interest in this section is to see how these properties vary if magnetic impurities with a singlet ground state are introduced.

Experimental results on H_{c2} of high-field superconductors are commonly analyzed on the basis of the theory of Fulde and Maki[30] and of Werthamer *et al.*,[28] which permits a quantitative comparison with the data. This theory takes into account both the orbital and the paramagnetic effect of the external field as well as the scattering by nonmagnetic and magnetic impurities and by the spin-orbit interaction. Also, this theory has been extended by Fischer[31] in order to take into account the mean exchange field and possible compensation effects due to magnetic impurities aligned by an external magnetic field or by the exchange interaction. In the case of non-S-state magnetic ions one also has to consider the influence of the crystalline electric field. Theoretical[8-11] and experimental[6,7,12,16] investigations in recent years have shown that CEF can strongly influence the behavior of T_c vs the concentration of non-Kramers ions, and, to a lesser extent, the behavior of H_{c2} and the specific heat in the superconducting state.

Owing to inelastic scattering processes, magnetic impurities with a singlet ground state also exert a pair-breaking effect on the Cooper pairs, and it was shown by Fulde *et al.*[9] that the effect of such processes can be of the same order of magnitude as that of elastic scattering processes by impurities with a magnetic ground state, even in cases where the energy separation Δ of the first excited state from the ground state is considerably larger than k_BT. The physical reason why the dependence of T_c upon the impurity concentration strongly depends on the CEF level scheme can be understood from an approximate relation for the superconducting transition temperature T_c, valid in the dirty limit for not too high concentrations of magnetic impurities:

$$\ln\left(\frac{1}{t_c}\right) = \psi\left(\frac{1}{2} + \frac{\rho(c, t_c)}{2t_c}\right) - \psi(\tfrac{1}{2}) , \qquad (5)$$

where $\psi(z)$ is the digamma function, $t_c = T_c/T_{c0}$, and where the pair-breaking parameter $\rho(c, t_c)$ for zero magnetic field is given by the relation

$$\rho(c, t_c) = \lambda_m = \frac{2}{\pi k_B T_{c0}}\, c\, N(0)\, \langle \mathcal{J}^2 \rangle (g_J - 1)^2 f\left(\frac{\delta_i}{t_c T_{c0}}\right) . \qquad (6)$$

The quantities c, g_J, and $N(0)$ are, respectively, the impurity concentration, the Landé factor of the impurities, and the electronic density of states at the Fermi level, for one spin direction. $\langle \mathcal{J}^2 \rangle$ stands for a mean-square value of the q-dependent exchange interaction, as defined by Fischer.[31] $f(\delta_i/t_c T_{c0})$ is a function which was introduced by Keller and Fulde[10] to take into account the CEF splitting of magnetic impurities. In the absence of CEF effects, the $2J+1$ states of magnetic impurities are degenerate, and this function becomes $f(\delta_i/t_c T_{c0}) = (\frac{1}{4}\pi)J(J+1)$. One thus recovers the result of the AG theory[13]; the pair-breaking parameter $\rho(c, t_c)$ is proportional to c and independent of t_c, and it leads to the well-known behavior of $T_c(c)$ as shown in Fig. 11. In the case of Pr^{3+} in $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$, CEF effects have to be considered. Here only the first excited state (Fig. 6) is connected to the ground state by a nonvanishing matrix element of the angular momentum operator $\tilde{J}$, and one obtains

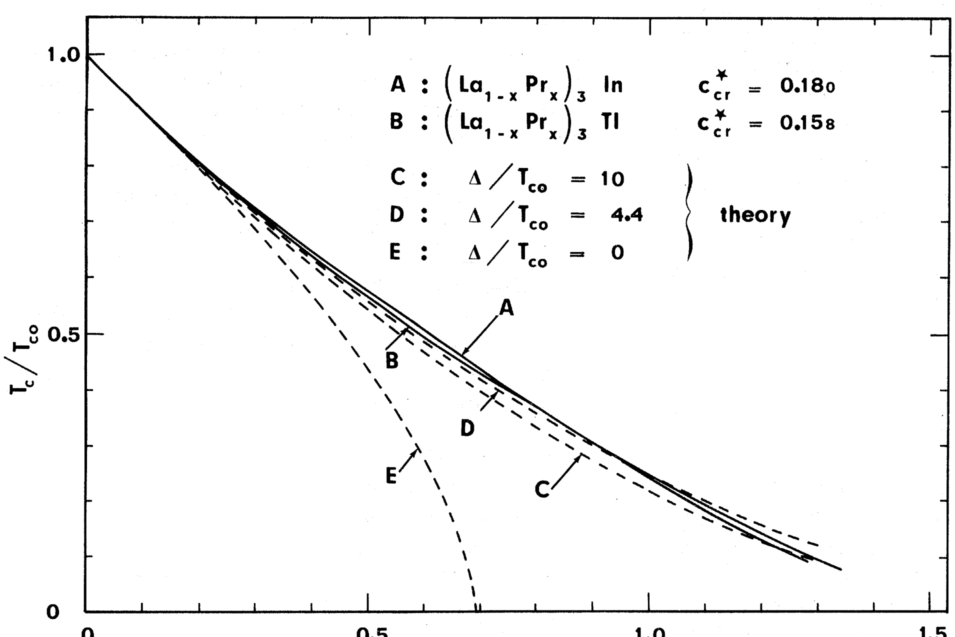

FIG. 11. Superconducting transition temperatures of $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$ in normalized units, compared to theoretical curves for alloys containing magnetic impurities with two singlet levels of energy separation Δ.

$$f(\delta_i/t_c T_{c0}) = \tfrac{1}{8}\pi |\langle 0|\tilde{J}|1\rangle|^2 y(\Delta/2k_B t_c T_{c0}),$$

where Δ measures again the energy separation of the first excited state from the ground-state level, and $y(x)$ is a monotonically decreasing function of x with $y(0)=2$ and $y(\infty)=0$, plotted in Fig. 4 of the paper of Fulde *et al.*[9] The pair-breaking parameter $\rho(c,t)$ therefore decreases with decreasing temperature, and higher impurity concentrations are needed at lower temperatures for a given T_c depression. As already mentioned, these relations are valid only for not too high concentrations, where $t_c \approx 1$; for higher concentrations, the correct dynamical frequency-dependent interaction between conduction electrons and magnetic impurities has to be taken into account and cannot be replaced by an effective temperature-dependent interaction, as was done in the above relations. The resulting equations are more complicated and have to be resolved numerically.[10]

In Fig. 11, we have plotted the experimental transition temperatures $T_c(c)/T_{c0}$ for $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$ as a function of c/c^*_{cr}, where the critical concentrations are defined by $c^*_{cr} = (-dt_c/dc)_{c=0}$. In this way they can easily be compared to theoretical results. We reproduce in Fig. 11 such results for magnetic impurities having two singlet states with an energy difference Δ lowest and no other levels contributing to the function $f(\delta_i/t_c T_{c0})$; these results should apply directly to our systems. There is little variation of theroetical curves for $\Delta/k_BT_{c0}=10$ and $\Delta/k_BT_{c0}=4.4$, and a reasonable agreement is found with experimental curves for $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$, where we found $\Delta/k_BT_{c0}=8.3$ and 8.8, respectively. The AG result[13] ($\Delta/k_BT_{c0}=0$), on the other hand, shows a completely different behavior (curve E of Fig. 11) and is applicable to superconductors with S-state magnetic impurities like $La_{0.75-x}Gd_xIn_{0.25}$ and $La_{0.25-x}Gd_xSn_{0.75}$ (Fig. 3).

From the critical concentration c^*_{cr} we can evaluate the exchange interaction constant $\langle \mathcal{J}^2\rangle$,[10]

$$c^*_{cr} = \frac{2k_B T_{c0}}{\pi N(0)\langle \mathcal{J}^2\rangle (g_J-1)^2 f(\delta_i/T_{c0})} . \tag{7}$$

We use for $N(0)$ the values of $N(0)=1.50$ and $1.34\ eV^{-1}$ for La_3In and La_3Tl, respectively, as given in a previous paper,[1] and find for $|\langle \mathcal{J}\rangle| = \langle \mathcal{J}^2\rangle^{1/2}$ values of 0.19 and 0.21 eV for $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$, respectively. Recently, Jones *et al.*[5] reported for the exchange constant in $(La_{1-x}Ce_x)_3In$ a value of $|\mathcal{J}|=0.2$ eV. This value, however, was obtained from the mean exchange field produced by aligned Ce magnetic moments and therefore rather concerns $|\mathcal{J}(q=0)|$ of the q-dependent exchange interaction. As was discussed by Fischer[31] $|\mathcal{J}(q=0)|$ is expected to be higher than the appropriate mean value $|\langle \mathcal{J}\rangle|$ determining the initial slope of $T_c(c)$, and the agreement between these values therefore seems rather accidental. From a recent calculation of the upper critical field for strong-coupling superconductors by Rainer *et al.*,[32] one has to conclude that an exchange field is much less effective in depressing H_{c2} in strong-coupling than in weak-coupling superconductors. It is therefore possible that the exchange field and the exchange constant, determined by an analysis of $H_{c2}(x,T)$ for $(La_{1-x}Ce_x)_3In$[5] on the basis of a weak-coupling theory,[28,31] are somewhat underestimated.

The behavior of the upper critical field H_{c2} of a superconductor containing magnetic impurities in a singlet ground state has been calculated numerically by Keller and Fulde.[11] In reduced units the upper critical field $h_{c2}(t) = H_{c2}(T)/T_{c0}(-dH_{c2}/dT)_{T=T_c}$ as a function of $t=T/T_{c0}$ is found to increase more rapidly with decreasing t for singlet-ground-state impurities than for impurities with a magnetic ground state discussed by Fulde and Maki.[30] This again can be understood from relation (5), where the pair-breaking parameter now becomes $\rho(c,t_c)=\lambda_m+\lambda_h$, with $\lambda_h=(v_F^2 e\tau/3\pi T_{c0})H$; τ is the transport mean free time. Equation (5) determines the superconducting–normal-state phase boundary given by $T_c(c,H)$ or by the inverse function $H_{c2}(c,T)$. From the general form of this equation and of that for $\rho(c,t_c)$ we notice that the introduction of magnetic impurities has the same effect on the s-n phase boundary as the application of a magnetic field. In particular, the addition of a certain amount of S-state magnetic impurities, for which λ_m is temperature independent, causes a temperature-independent shift of the phase boundary to lower fields determined by $\Delta\lambda_h = -\Delta\lambda_m$.[30] On the other hand it was shown above that the pair-breaking parameter λ_m for CEF-split impurities decreases with decreasing temperature. Therefore, the shift of the phase boundary to lower fields by a certain amount of such impurities is expected to be smaller at lower temperatures than near T_{c0}. This formalism, although strictly valid only for low impurity concentrations and near T_{c0}, thus explains qualitatively the behavior of $H_{c2}(c,T)$ in superconductors containing CEF-split impurities.[11]

The results of Keller and Fulde,[11] however, cannot be compared directly to our $(La_{1-x}Pr_x)_3In$ data for at least two reasons: As was mentioned already above, the temperature dependence of the upper critical field in La_3In, and therefore also in dilute $(La_{1-x}Pr_x)_3In$, cannot be explained by a weak-coupling theory. Second, the theory of Keller and Fulde[11] does not take into account any spin-polarization effects which were found to be important in the analogous systems $(La_{1-x}Gd_x)_3In$[3]

and $(La_{1-x}Ce_x)_3In$[5]; at present, no theory exists which takes into account such effects in strong-coupling superconductors. For these reasons, the following discussion can only be qualitative.

In the following estimation we show that the effect of the mean exchange field $H_{\mathcal{J}}$ is not negligible in high-field superconductors containing singlet-ground-state impurities. In the case of $(La_{1-x}Pr_x)_3In$ the mean exchange field is given by

$$H_{\mathcal{J}} = \frac{c\mathcal{J}_0\langle \tilde{S}\rangle}{-g\mu_B} = H\,\frac{c\mathcal{J}_0\,|\langle 0|\tilde{J}|1\rangle|^2 g_J(g_J-1)}{g\Delta}\,. \qquad (8)$$

Using for the exchange parameter, instead of $\mathcal{J}_0 = \mathcal{J}(q=0)$, the value obtained from dT_c/dc at $c=0$, $|\langle\mathcal{J}\rangle| = 0.19$ eV, we find an exchange field $|H_{\mathcal{J}}| \cong 38$ kOe for $x = \frac{4}{3}c \cong 0.12$ at $H_{c2}(T=0)$. This is probably an underestimation because $|\mathcal{J}_0| > |\langle\mathcal{J}\rangle|$, as discussed by Fischer.[31] On the other hand this exchange field is not negligible with respect to the Clogston limit, $H_{p0} = 18.4\,T_c$ kOe/°K = 175 kOe for La_3In. Although the Maki parameter $\alpha = \sqrt{2}H^*_{c2}/H_{p0}$ (H^*_{c2} is the upper critical field from orbital effects) is relatively small in La_3In,[5] and although the effect of the exchange field might be less pronounced in strong-coupling superconductors[32] than expected from weak-coupling theories,[28,31] it will either increase or decrease the upper critical field at low temperatures, depending on whether $\mathcal{J}_0 > 0$ or $\mathcal{J}_0 < 0$, respectively. From the fact that we find rather a decrease in the slope of the reduced upper critical field, dh_{c2}/dt, with increasing impurity concentration at given t, despite an opposite contribution expected from CEF effects, we conclude that the exchange interaction constant $\mathcal{J}_0$ is negative in $(La_{1-x}Pr_x)_3In$.

In conclusion, we realize that CEF effects on the uppercritical field of high-field superconductors are expected to be small in general compared to other effects. There is, however, a qualitative difference in the behavior at low temperatures of superconductors containing magnetic impurities in a singlet ground state with respect to that of superconductors containing impurities with a magnetic ground state. Whereas in the latter the impurity spin polarization is strongly temperature dependent and, therefore, may produce nonmonotonic (reentrant) critical-field curves, as found in $(La_{1-x}Gd_x)_3In$ by Crow *et al.*,[3] it is temperature independent in the former, for undercritical exchange, the mean exchange field is proportional to the applied magnetic field, and a standard behavior is expected for the critical-field curves.

Another property which is sensitive to the type of magnetic impurities is the discontinuity of the specific heat at the transition temperature $\Delta C = (C_s - C_n)_{T=T_c}$. In the absence of magnetic impurities this specific-heat jump is calculated from the BCS theory to be $\Delta C = 1.43\,\gamma T_c$, thus proportional to the critical temperature T_c. If magnetic impurities are introduced one expects deviations from this law of corresponding states, as shown in Fig. 12 for two special cases. The curve denoted by AG shows the case where CEF effects can be neglected: ΔC decreases more rapidly to zero than the BCS curve.[14] We also show, as an example, numerical results from Keller and Fulde[11] for the two-singlet case $\Delta/k_BT_{c0} = 1$, where two singlets lie lowest with an energy difference $\Delta = k_BT_{c0}$ and where no other levels contribute to exchange scattering. Marked deviations from the AG behavior and from the BCS law of corresponding states are found in this case; for higher Δ/k_BT_{c0} ratios these deviations from the BCS curve, however, seem to decrease, as is shown in Ref. 11. Comparing these theoretical expectations with our data for $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$ we come to the conclusion that again other than CEF effects are prevailing. At low Pr concentrations experimental ΔC's are considerably higher than given by the theoretical curves; in particular these quantities are enhanced by factors of 2.0 and 1.7 for La_3In and La_3Tl, respectively, over the BCS value as a consequence of their strong-coupling behavior. For higher x, however, ΔC falls below the theoretical curves,

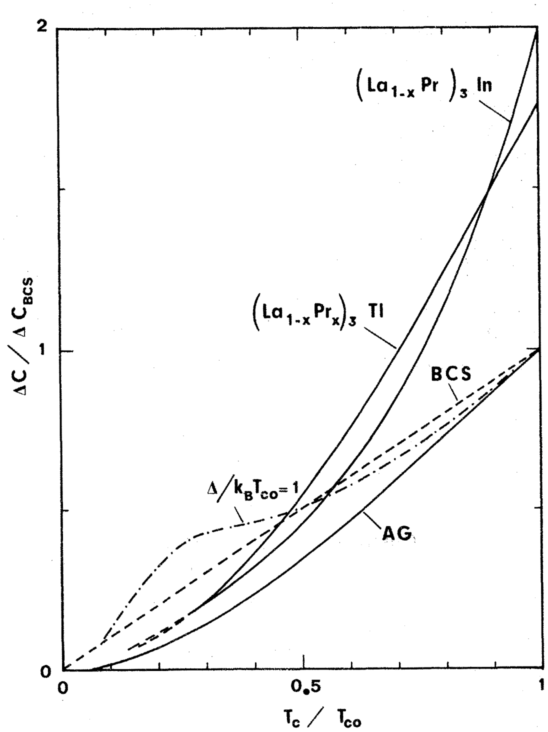

FIG. 12. Normalized specific-heat discontinuities at T_c, $\Delta C/1.43\gamma T_c$, in comparison with corresponding curves for the BCS weak-coupling case, for the AG case, and for the two-singlet case with $\Delta/k_BT_c = 1$.

but remains above the AG curve. It was shown recently that in strong-coupling superconductors quantities like ΔC critically depend on the phonon spectra, if the phonon frequencies are measured with respect to T_c, and that the depression of T_c influences in a complicated way $\Delta C/T_c$.[29] We therefore believe that the dependence of $\Delta C/T_c$ in $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$ on the Pr concentration is essentially determined by strong-coupling effects and not by the crystalline electric field.

IV. CONCLUSIONS

(a) $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$ show a transition from a Van Vleck paramagnetic state at low Pr concentration to an ordered induced-moment state at high Pr concentrations.

(b) In Pr_3In the induced magnetic order is antiferromagnetic with a Néel temperature of $T_N = 16.8\ °K$, compared to Pr_3Tl showing an induced ferromagnetism below the Curie temperature of $T_f = 11.3\ °K$.

(c) The CEF level schemes of Pr^{3+} in La-rich $(La_{1-x}Pr_x)_3In$ and $(La_{1-x}Pr_x)_3Tl$, as determined from magnetic susceptibility, low-temperature specific heat, and in $(La_{1-x}Pr_x)_3Tl$ from neutron data, also explain the characteristic behavior of the superconducting transition temperature $T_c(x)$; from dT_c/dx at $x=0$ the exchange constants are estimated to be $\langle \mathcal{J} \rangle = -0.19$ and -0.21 eV for Pr in La_3In and La_3Tl, respectively.

(d) In high-field superconductors, CEF effects on the upper critical field H_{c2} may be overcompensated by spin-polarization effects as was found in $(La_{1-x}Pr_x)_3In$; on the other hand the superconducting specific heat of such systems is found to be more sensitive to strong-coupling effects than to CEF effects.

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*Present address: Département de Physique de la Matière Condensée, University of Geneva, Switzerland.

[1]F. Heiniger, E. Bucher, J. P. Maita, and P. Descouts, Phys. Rev. B 8, 3194 (1973).

[2]J. E. Crow and R. D. Parks, Phys. Lett. 21, 378 (1966).

[3]J. E. Crow, R. P. Guertin, and R. D. Parks, Phys. Rev. Lett. 19, 77 (1967).

[4]M. B. Maple, J. G. Huber, and K. S. Kim, Solid State Commun. 8, 981 (1970).

[5]H. Jones, Ø. Fischer, G. Bongi, and A. Treyvaud, Solid State Commun. 10, 927 (1972).

[6]E. Bucher, K. Andres, J. P. Maita, and G. W. Hull, Jr., Helv. Phys. Acta 41, 723 (1968).

[7]G. Pepperl, E. Umlauf, A. Meyer, and J. Keller, report (unpublished).

[8]P. Fulde and H. E. Hoenig, Solid State Commun. 8, 341 (1970).

[9]P. Fulde, L. L. Hirst, and A. Luther, Z. Phys. 230, 155 (1970).

[10]J. Keller and P. Fulde, J. Low Temp. Phys. 4, 289 (1971).

[11]J. Keller and P. Fulde, J. Low Temp. Phys. 12, 63 (1973).

[12]R. P. Guertin, J. E. Crow, A. R. Sweedler, and S. Foner, Solid State Commun. 13, 25 (1973).

[13]A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. 39, 1781 (1960) [Sov. Phys.-JETP 12, 1243 (1961)].

[14]S. Skalski, O. Betbeder-Matibet, and P. R. Weiss, Phys. Rev. 136, A1500 (1964).

[15]E. Bucher, J. P. Maita, and A. S. Cooper, Phys. Rev. B 6, 2709 (1972).

[16]H. Happel and H. E. Hoenig, Solid State Commun. 13, 1641 (1973).

[17]J. P. Maita and E. Bucher, Phys. Rev. Lett. 29, 931 (1972).

[18]K. H. Bennemann, Phys. Rev. Lett. 17, 438 (1966). This work, however, is criticized by J. Keller and R. Benda [J. Low Temp. Phys. 2, 141 (1970)].

[19]A. M. Toxen, R. J. Gambino, and P. Kwok, Bull. Am. Phys. Soc. 13, 427 (1968).

[20]R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. 103, 572 (1956).

[21]K. Andres and G. W. Hull, Jr. (unpublished).

[22]W. E. Wallace, *Rare Earth Intermetallics* (Academic, New York, 1973), Chap. 5, p. 69; R. D. Hutchens, W. E. Wallace, R. S. Craig, and V. U. S. Rao (unpublished).

[23]B. Staliński, A. Czopnik, N. Iliew, and T. Mydlarz, Phys. Status Solidi A 19, K161 (1973).

[24]K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids 23, 1381 (1962).

[25]B. R. Cooper and O. Vogt, J. Phys. (Paris) 32, Cl-958 (1971).

[26]B. Bleaney, Quantum Electronics, Proceedings of Third International Congress, 1, Paris, 1964 (unpublished).

[27]K. Andres, E. Bucher, S. Darack, and J. P. Maita, Phys. Rev. B 6, 2716 (1972).

[28]N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. 147, 295 (1966).

[29]D. Rainer and G. Bergmann, J. Low Temp. Phys. 14, 501 (1974).

[30]P. Fulde and K. Maki, Phys. Rev. 141, 275 (1966).

[31]Ø. H. Fischer, Helv. Phys. Acta 45, 329 (1972).

[32]D. Rainer, G. Bergmann, and U. Eckhardt, Phys. Rev. B 8, 5324 (1973).