splitting quantity Δ in Fig. 1. Determinations on these splittings beyond the first excited state as well as on other compounds are therefore encouraged.

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Induced-Moment Systems: Paramagnetic Region of La_3Tl-Pr_3Tl

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Superconducting and magnetic properties in the La_3Tl-Pr_3Tl system are discussed. Superconductivity persists up to very high Pr concentrations, Pr^{3+} being in a crystal-field-singlet ground state. The Van Vleck susceptibility per Pr^{3+} ion at $T=0$ increases with increasing Pr concentration, indicating ferromagnetic exchange coupling between the Pr ions. At concentrations higher than 93-at.% Pr the system becomes ferromagnetic. No current theoretical model accounts for the observed magnetic behavior.

I. INTRODUCTION

It is well known that many rare-earth compounds with an even number of $4f$ electrons exhibit a crystal-field-singlet ground state. It has been shown by various authors using different models[1-4] that such materials exhibit Van Vleck paramagnetism if the exchange forces do not exceed a certain strength. On the other hand, if the exchange interaction exceeds a certain limit, we expect a

magnetic phase transition. This transition is driven by an instability in the singlet ground state, which in the presence of strong exchange is no longer the true ground state. The nature of such a transition is basically different from the usual magnetic ordering in a material with a magnetic ground state. This statement, of course, is only true as long as the crystal field splitting Δ between the singlet and the spontaneously admixed higher state is large compared to the ordering temperature T_0. Such systems not occurring too frequently have not been studied in detail yet, although theory has been predicting a variety of properties in such materials.[5] On the other hand, if we have a magnetically ordering material one might ask "What are the critera that we have a case $T_0/\Delta \ll 1$, with a singlet being the ground state?" In this paper, we would like to discuss this problem using the example of La_3Tl-Pr_3Tl, particularly all problems pertinent to the paramagnetic region. The properties of the ferromagnetic part of the phase diagram and some problems related to the nature of the ferromagnetic phase transition will be discussed in the following paper. An additional interesting problem occurs on the paramagnetic side. La_3Tl was found to be a strong-coupling superconductor with T_C close to 9 °K. We will discuss however the thermodynamics of superconductors with impurities in a singlet ground state only briefly here. An extended study of superconducting properties of La_3In-Pr_3In and La_3Tl-Pr_3Tl and some related phases will follow this work.[6]

II. EXPERIMENTAL PART

Preparation

La_3Tl and Pr_3Tl were prepared by direct fusion in an arc furnace. The existence of these phases has been first reported by Haschke, Nowotny, and Benesovsky.[7,8] Since the reaction is quite exothermic, about 0.5-wt% Tl excess had to be added in advance, in order to obtain proper stoichiometric melts. However, once the compound is formed no Tl will boil off anymore. Ternaries of the form $(La_{1-x}Pr_x)_3Tl$ were made by premelting first a homogeneous alloy button of $La_{1-x}Pr_x$ and then adding Tl in the second step. For La we used 99.99% pure rare-earth product material and Pr was zone-refined nuclear-grade material supplied by Lunex Co. of nominal 99.9*% purity. Tl was supplied by Asarco Co. and listed as 99.999% pure. X-ray analysis showed fcc structure even in the as-cast state, but magnetic analysis showed the presence of Pr_5Tl_3 and Pr_2Tl, too. Annealing of La_3Tl and Pr_3Tl, therefore, was necessary in order to obtain reproducible and sharp phase transitions. The samples were annealed for 72 h at 700 °C and cooled down to 400 °C at a rate of 50 °C/day. After completion of this work it was reported[9] that Pr_3Tl undergoes an order-disorder transformation at 750 °C with a remarkable change in lattice constant from 4.93 to 5.03 Å. Our lattice constants at 296 °K of 5.06 and 4.935 Å for La_3Tl and Pr_3Tl, respectively, suggest that our materials are in a well-ordered state.

Specific Heat and Susceptibility

A description of this equipment has been given in earlier papers.[10,11] For measurements on the ferromagnetic side we refer to the following paper.

III. RESULTS AND DISCUSSION

All our experimental results on La_3Tl-Pr_3Tl are summarized in Table I. For convenience we also include data on the ferromagnetic side of La_3Tl-Pr_3Tl, although we will not discuss them further here.

a. Materials. No phase diagram around 25-at.% Tl has been worked out yet. Griffin and Gschneidner[9] only explored Pr-Tl up to 16-at.% Tl. From visual observation in the arc furnace as well as from the fact that La_3Tl and Pr_3Tl stick considerably to Ta, W, or Mo if melted in such crucibles, we consider a congruent melting behavior as highly unlikely. Nevertheless, the phase formation occurs easily. Even as-cast buttons only contain a weak trace of Pr_2Tl and Pr_5Tl_3, as tested magnetically. Our x-ray results on La_3Tl and Pr_3Tl are in disagreement with the data of Haschke *et al.*[7,8] According to Griffin and Gschneidner's results,[9] these authors may have measured disordered La_3Tl, or Pr_3Tl, or their higher lattice constants may be due to partial formation of perovskites (with C, N, in the center of the unit cell) which are known to increase the lattice constant of La_3Tl and Pr_3Tl considerably.[12] Our results on Pr_3Tl, however, agree in the first four figures with the ordered phase of Pr_3Tl given by Griffin and Gschneidner.[9]

b. Superconductivity. Some of the superconducting parameters of La_3Tl and $(La_{1-x}Pr_x)_3Tl$ are given in Table I. In Fig. 1 and also in Fig. 4 we plot the superconducting transition temperature T_s vs Pr concentration x. The specific-heat curves of La_3Tl and $(La_{0.85}Pr_{0.15})_3Tl$ as typical representatives of this series are shown in Fig. 2. Inserted is also an analysis of the specific heat jump $(1/\gamma)\Delta(C/T)_{T=T_s}$ as due to Swihart[13] for a magnetically undoped superconductor. Our value of 1.8 for La_3Tl is based on a electronic specific-heat value of $\gamma = 23.3$ mJ/ °K^2 mole.[13(a)] Since this number was very uncertain from a specific-heat analysis of the undoped La_3Tl, γ was obtained from samples containing 15-, 20-, and 25-at.% Pr and found to be constant. As we will discuss below,

TABLE I. Summary of experimental results on La_3Tl-Pr_3Tl.

Compound	T_s (°K)	$\Delta(C/T)$ $\left(\frac{mJ}{°K^2\ mole}\right)$	$\chi_{1.42°K}$ $\left(\frac{cm^3}{mole\ Pr}\right)$	T_C (° K)	a (at 296 °K) (Å)
La_3Tl	8.95	42			5.06
$(La_{0.972}Pr_{0.028})_3Tl$	7.70	42			
$(La_{0.97}Pr_{0.03})_3Tl$	7.55				
$(La_{0.95}Pr_{0.05})_3Tl$			0.051		
$(La_{0.94}Pr_{0.06})_3Tl$	6.51	41.7			
$(La_{0.902}Pr_{0.098})_3Tl$	5.25	37.2	0.053		
$(La_{0.858}Pr_{0.142})_3Tl$	3.92	31.1			
$(La_{0.85}Pr_{0.15})_3Tl$	3.68	28.0	0.056		
$(La_{0.802}Pr_{0.198})_3Tl$	2.40	22.4	0.058		
$(La_{0.75}Pr_{0.25})_3Tl$	1.24		0.061		
$(La_{0.70}Pr_{0.30})_3Tl$			0.064		
$(La_{0.60}Pr_{0.40})_3Tl$			0.073		
$(La_{0.50}Pr_{0.50})_3Tl$			0.0855		
$(La_{0.40}Pr_{0.60})_3Tl$			0.102[a]		
$(La_{0.35}Pr_{0.65})_3Tl$			0.117[a]		
$(La_{0.0606}Pr_{0.9394})_3Tl$				1.65[b]	
$(La_{0.0497}Pr_{0.9503})_3Tl$				3.4	
$(La_{0.04}Pr_{0.96})_3Tl$				3.95	
$(La_{0.038}Pr_{0.962})_3Tl$				4.90	
$(La_{0.0295}Pr_{0.9705})_3Tl$				6.6	
$(La_{0.02}Pr_{0.98})_3Tl$				7.9	
$(La_{0.0095}Pr_{9905})_3Tl$				9.6	
Pr_3Tl				11.0–11.3[b]	4.935

[a]Low-field limit of the slightly curved magnetization curves.

[b]Reference 27.

Pr in this concentration and temperature range will not introduce any additional specific heat in our case. It is obvious from $T_s/\Theta_D(0) \approx 7\times10^{-2}$ that La_3Tl is a strong-coupling superconductor. Its specific-heat jump corresponds about to the maximum value of 1.84 given by the BCS theory in the extreme strong-coupling limit.[13–15] Usually in strong-coupling superconductors, enhanced values of $\Delta(0,0)/kT_s$ are mostly responsible for the enhanced specific-heat jump.[16] As has been shown previously,[17] the concentration dependence $T_s(x)$ is characteristic of Pr^{3+} being in a singlet ground state. Our results are in perfect agreement with calculations given by Fulde *et al.*[18] and Keller and Fulde.[19] The destruction of Cooper pairs occurs via virtual inelastic processes involving the higher crystal field states and the off-diagonal moments $\langle\varphi_0|\tilde{J}|\varphi_k\rangle$, where φ_0 and φ_k are the wave functions of the singlet and the higher levels forming off-diagonal matrix elements of the angular-momentum operator $\tilde{J}$. In Fig. 1 we demonstrate this pairbreaking effect by plotting also the reduced specific-heat peak $\Delta(C/T)_{T=T_s}$ vs x. Except for the lowest concentrations of x there is a gradual drop of $\Delta(C/T)_{T=T_s}$ with increasing x. This drop arises from normal states in the superconducting energy gap, due to inequivalent scattering amplitudes of the two components of the Cooper pairs. At the critical concentration x_0 for which T_s vanishes, we extrapolate a finite specific-heat jump. The situation in superconductors with singlet ground-state impurities is thus unlike a superconducting system containing localized spins. dT_s/dx is about an order of magnitude smaller in our case, there are no spin-flip processes, and there is probably no gapless region. Nevertheless, our $(La_{1-x}Pr_x)_3Tl$ system presents an interesting intermediate case between a pure and gapless superconductor. The introduction of Pr does not introduce additional (e.g., crystal field) entropy (since $T_s \ll \Delta$) and, therefore, the thermodynamic functions of such a state can be measured without worrying about magnetic contributions arising from localized spins. This is directly seen in Fig. 2. The specific heats between La_3Tl and $(La_{0.85}Pr_{0.15})Tl$ differ by less than 2% at the transition temperature of La_3Tl. At higher temperature, the difference is due, of course, to the crystal field specific heat of Pr in La_3Tl. It should be emphasized that the isoelectronic system $(La_{1-x}Pr_x)_3In$ behaves identically, except that $\Delta(C/T)_{T=T_s}$ is not constant at low concentrations x. Instead $\Delta(C/T)_{T=T_s}$ drops monotonically, with $d^2\Delta \times (C/T)_{T=T_s}/dy^2 > 0$. The reason for this different behavior is not clear yet and will be discussed in a forthcoming paper dealing in more detail with thermodynamic properties of superconductors with singlet impurities.[6]

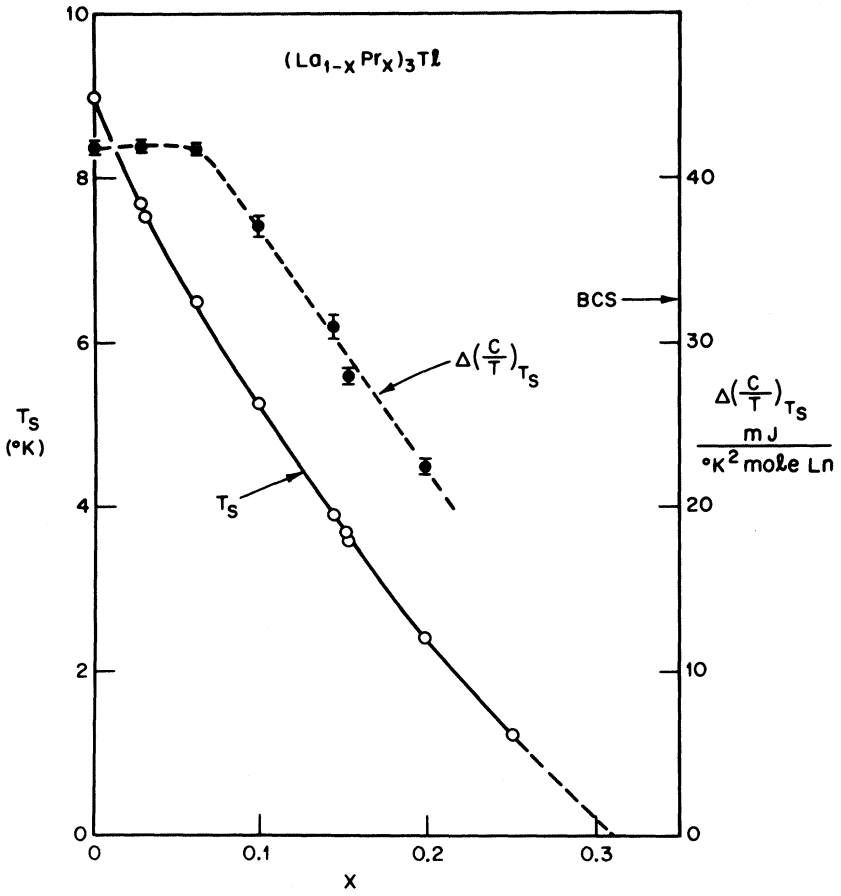

FIG. 1. Superconducting transition temperatures T_s and specific-heat jumps $\Delta(C/T)$ at T_s in $(La_{1-x}Pr_x)_3Tl$ vs concentration x. Ln stands for the sum of La and Pr concentration.

c. Magnetic properties. In Fig. 3 the unit cell of ordered Pr_3Tl is shown. The Pr ion has 12 nearest and equidistant neighbors, four of which are Tl and eight are Pr. The point symmetry is, strictly speaking, tetragonal. The $J=4$ term is split in this symmetry into two doublets and five singlets, as shown in Fig. 3 in which weak tetragonality is assumed. Neglecting sixth-order crystal field terms we write for the crystal field Hamiltonian $\mathcal{H}_{CF}$:

$$\mathcal{H}_{CF} = B_4(\Omega_4^0 + 5\Omega_4^4) + B_2\Omega_2^0 + C_4(3\Omega_4^0 - 35\Omega_4^4) \quad . \qquad (1)$$

B_4 is given by (3), $B_2 = (\langle r^2\rangle/R^3)\alpha_J\,\delta Z$, $C_4 = -\frac{1}{16}(\langle r^4\rangle/R^5)\beta_J\,\delta Z$; the Ω_i^k are the crystal-field operators α_J, β_J the Stevens factors. R is the Pr-ligand distance and δZ is the point-charge difference between Pr and Tl.[20] The tetragonal splitting pattern in Fig. 3 was obtained by neglecting the C_4 term using $B_2\Omega_2^0$ as a perturbation of the wave functions of cubic fcc Pr (with the same lattice constant as Pr_3Tl). For the discussion of the magnetic data, however, we will make the following simplifying assumptions:

(i) The tetragonality is neglected and we consider the point symmetry of Pr in the first approximation as octahedral with a coordination $z=12$. In a point-charge picture this means that we assign Pr^{3+} and also La^{3+} in the dilute case $(La_{1-x}Pr_x)_3Tl$, as well as the Tl ion, the same charge strength. Recent inelastic neutron scattering in Pr_3Tl[21] showed indeed that the tetragonal splitting of the Γ_4 triplet is small compared to the Γ_1-Γ_4 distance. An analysis of the excess specific heat of $(La_{1-x}Pr_x)_3Tl$ over La_3Tl analyzed as

$$\Delta C = x\,3R(\Delta/T)^2 e^{-\Delta/kT} \quad , \qquad (2)$$

leads to Δ values of 78 ± 10 °K for values of x between 0.03 and 0.25. The specific heat at low temperature is not very sensitive to the tetragonal distortion of the Γ_4, however an upper limit of 20 °K for the splitting $42B_2$ may be evaluated. (See Fig. 3.) The given splitting of 78 °K, of course, means the distance of the singlet to the center of gravity of the two higher levels. From recent inelastic neutron scattering measurements in $(Pr_{0.88}La_{0.12})_3Tl$ the splitting was determined as 79 °K,[22] thus in excellent agreement with our specific-heat values on the more dilute side. A somewhat less convincing argument is that in many metallic compounds such as PrS, PrSe, PrTe,[23]

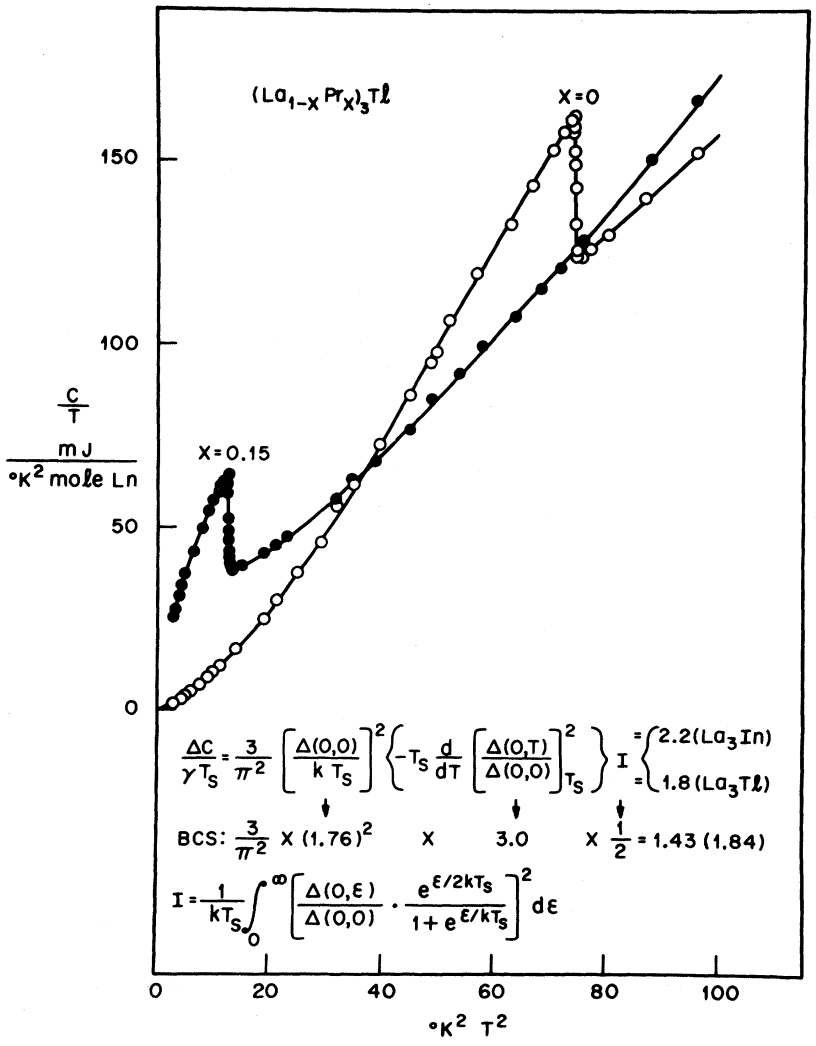

FIG. 2. Specific heat of La_3Tl and $(La_{0.85}Pr_{0.15})_3Tl$ below 10° K with analysis of superconducting specific-heat jump. Ln stands for the sum of La and Pr concentration.

and particularly in the anti-isomorphous $PrTl_3$[24] structure, the crystal-field levels can be quantitatively calculated assuming a point charge equal to the valence of the ligand (− 2 for Se and Te and +3 for Tl).

(ii) Crystal fields arising from second nearest neighbors are neglected. Because of the $1/R^5$ (and $1/R^7$) dependence their contribution without screening would amount to 17% for B_4 only.

(iii) The influence of the 4*f* contraction between La and Pr on the crystal field splitting in the $(La_{1-x}Pr_x)_3Tl$ series is neglected.

Following Hutchings's article[20] the expressions for B_4 and B_6 for octahedral symmetry with coordination $z=12$ can easily be calculated and are

$$B_4 = -\tfrac{7}{32}(Ze^2/R^5)\langle r^4\rangle \beta_J \ , \tag{3}$$

$$B_6 = -\tfrac{39}{256}(Ze^2/R^7)\langle r^6\rangle \gamma_J \ , \tag{4}$$

where Z is the number of point-charge units of the nearest neighbors and R is the Pr-ligand distance. The other symbols have their usual meanings. (See Ref. 25.) B_4 and B_6 both change sign when going from the sixfold to the 12-fold coordination. Comparing with Lea, Leask, and Wolf's paper, [25] one has to expect a singlet ground state for a *positive* point charge of the ligand in the fcc lattice, with the same sequence of crystal field levels as given by Lea, Leask, and Wolf.[25] In the cubic approximation assuming a splitting Δ between Γ_1 and Γ_4 the low-temperature Van Vleck crystal field susceptibility $\chi_{vv}(0)$ is given as

$$\chi_{vv}(0) = (2g_J^2\mu_B^2\alpha^2/\Delta) \ , \tag{5}$$

with $\alpha = \langle\Gamma_1|J_i|\Gamma_4\rangle = (\frac{20}{3})^{1/2}$. For the single-Pr-impurity limit we extrapolate $\chi_{vv}(0) \approx 0.048$ cm^3/mole, which would lead to $\Delta = 68$ °K, compared to 78 °K as determined from specific heat. We will refer to this susceptibility as the pure crystal field susceptibility χ_{CF} of a Pr^{3+} ion. The dis-

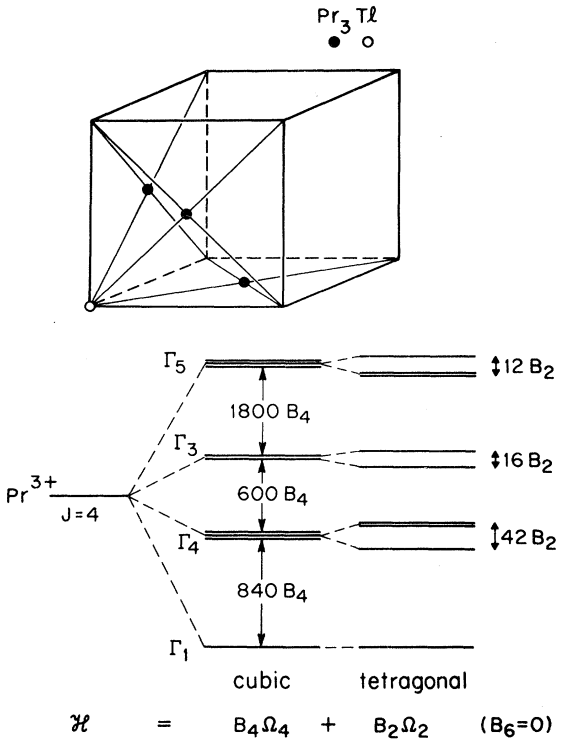

FIG. 3. Unit cell and crystal-field levels in cubic and weakly tetragonal case for Pr_3Tl.

crepancy may be due in part to the weak tetragonality and also to magnetic impurities. A further explanation may be the recently predicted self-polarizability of a singlet ion.[26] As can be seen in Fig. 4, this Van Vleck susceptibility *per* Pr^{3+} *ion* is not constant, but increases monotonically with increasing Pr concentration x. Eventually, for $x = 0.93$, a spontaneous moment appears at very low temperature, leading to a ferromagnetic region for $0.93 \leq x \leq 1.0$. Van Vleck susceptibilities were measured only up to 65-at.% Pr. Above this concentration, the magnetization curves show a very strong curvature down to the lowest fields, at 1.30 °K, presumably due to naturally occurring statistical concentration fluctuations. It is tempting to try a simple molecular-field (MF) approach. In this approximation we find for the susceptibility[1-3]:

$$1/\chi_{MF} = 1/\chi_{CF} - 2Kzx/g_J^2\mu_B^2 \quad . \tag{6}$$

χ_{MF} and χ_{CF} are the molecular-field and crystal field susceptibility, respectively, K the exchange interaction strength, $z = 12$ the coordination, and zx the average number of Pr nearest neighbors. For very low concentrations,

$$\chi_{MF} \approx \chi_{CF}[1 + (2Kz\,\chi_{CF}/g_J^2\,\mu_B^2)x] \tag{7}$$

χ_{CF} is thus obtained by extrapolating the measured low-temperature susceptibility to $x = 0$, yielding $\chi_{CF} = 0.048$ cm^3/mole. On the other hand, it is evident that χ_{MF} diverges for

$$Kzx = (\Delta/4\alpha^2) \quad . \tag{8}$$

Expression (6) provides a self-consistent test of molecular-field theory for the $(La_{1-x}Pr_x)_3Tl$ phase diagram. Adjusting χ_{CF} and Kz from the low-temperature paramagnetic susceptibilities in the concentration range between $0 \leq x \leq 0.30$, one extrapolates the dotted curve in Fig. 4, which should diverge for $x = 0.93$. Unfortunately, the prediction of ferromagnetism fails, since even extrapolation to $x = 1.0$ still yields a finite exchange enhanced Van Vleck susceptibility. For the unphysical region $x \gtrsim 1.12$ only, would one expect a spontaneous moment. On the other hand, the experimental value of $x_{crit} = 0.93$ could be used to determine Kz. This procedure leads to the dashed curve; values far too high on the paramagnetic side for $\chi_{MF}(x)$. It is thus obvious that the molecular-field theory fails to analyze the whole phase diagram. Statistical concentration fluctuations will certainly introduce complications. However, the discrepancies also occur on the dilute side, where the clustering problem should be less serious and the MF theory fails in this region too. In a limited concentration region, parameters can be adjusted but the numbers are probably not very meaningful. Likewise, MF theory also fails in the ferromagnetic regime as shown in Paper II, which follows.[27] Our results are also at variance with a recent analysis of the $Y_{1-x}Tb_xSb$[28] which seems to be a better system to fit the MF theory. But even there a deficiency of the MF theory is obvious, yielding too low ordering temperatures in the antiferromagnetic region. A number of improvements over the MF model have been undertaken, including dynamic effects, i.e., crystal-field excitons with a certain temperature-dependent dispersion relation.[3,5,29] Various modifications of the molecular-field theory lead to a substantial increase in critical exchange for induced magnetic ordering,[4] which would make the discrepancy even worse in the paramagnetic regime. In contrast, in the ferromagnetic regime, e.g., in the T_C-moment relationship, the modifications lead to an improvement over the molecular-field theory.[27] The theoretical situation is, therefore, quite confusing and our understanding of a phase diagram with an induced moment system, such as La_3Tl-Pr_3Tl presented in Fig. 4, is only qualitative. It clearly has to await more theoretical efforts in this complex many-body problem.

IV. CONCLUSIONS

(a) The La_3Tl-Pr_3Tl system presents an interesting model case for the study of an induced mo-

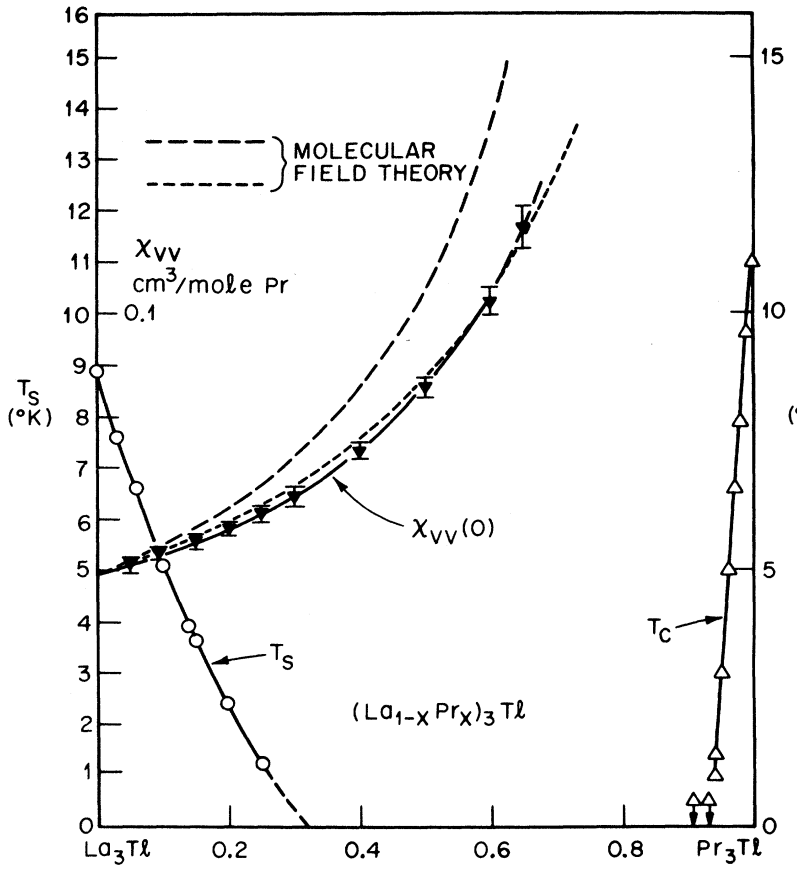

FIG. 4. Magnetic and superconducting phase diagram of La_3Tl-Pr_3Tl with molecular-field-theory analysis. Dotted curve: adjusted in the dilute paramagnetic region; dashed curve: adjusted at the critical concentration.

ment system in the range where the ordering temperature is small compared to the crystal field splitting.

(b) It is shown in various consistent ways that Pr_3Tl is an exchange-induced ferromagnet: (i) The drop dT_s/dx of the superconducting transition temperature T_s in $(La_{1-x}$-$Pr_x)_3Tl$ is characteristic of Pr being in a singlet ground state; (ii) at low temperature Van Vleck paramagnetism is observed up to very high Pr concentrations x; (iii) the introduction of La as "magnetic holes" causes a sharp characteristic linear drop in the Curie temperature T_C, leading to a finite threshold value of x for which T_C vanishes; (iv) the specific-heat anomaly at the magnetic transition is strongly reduced or may not even be perceptible. (See following paper.[27])

(c) At the present stage, no theoretical model accounts for the magnetic properties of the phase diagram of an exchange-induced moment system.

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Induced-Moment Ferromagnetism in Pr_3Tl

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It is shown that the intermetallic compound Pr_3Tl is a case of an induced-moment ferromagnet in which the nonmagnetic singlet ground state of Pr^{3+} is spontaneously polarized below 11 °K due to slightly overcritical exchange interactions. By substituting only 7 at.% of La for Pr, both the ordered moment m_0 (at 0 °K) and the Curie temperature T_C are reduced to zero, in contrast to the usual behavior of local-moment systems. The observed ratios of m_0/T_C for different La concentrations are compared with theoretical expectations. Specific-heat and resistivity anomalies at the transition are shown to be much reduced from what one would expect in an ordinary ferromagnet.

I. INTRODUCTION

The magnetic behavior of rare-earth intermetallic compounds and alloys depends mainly on two interactions: (a) the exchange interaction between the conduction electrons and the rare-earth ions and (b) the interaction of the rare-earth ion with its surrounding crystal field. If the resulting magnetic interaction between the rare-earth ions (via conduction electrons) is larger than the crystal field interaction, the latter is usually neglected at first and then reintroduced to explain the magnetic anisotropies in the ordered state. Examples of this case are the heavy-rare-earth metals from Gd to Tm. This paper deals with an example of the opposite situation, where the magnetic exchange interaction between the ions is smaller than the crystal field interaction. In this case one must first find the crystal field splitting of the lowest multiplet of the rare-earth ion and then consider the effect of magnetic exchange interactions on the crystal field levels. Of particular interest is the case of a crystal-field-singlet ground state, which can be realized in non-Kramers rare-earth ions (even J). Since such a ground state has no magnetic moment, it takes a finite critical magnitude of magnetic exchange interaction between neighboring ions in order to introduce a magnetically ordered ground state. If the exchange interaction is undercritical, the singlet ground state remains the stable state down to zero degrees, one then has Van Vleck paramagnetism and no magnetic order. For overcritical exchange, the singlet state mixes spontaneously with higher-lying crystal-field states to produce an energetically lower-lying polarized ground state. The ground-state moment m_0 must be determined self-consistently; it disappears at some finite ordering temperature T_C. In such an exchange-induced ferromagnet both m_0 and T_C are expected to go to zero continuously as the exchange interaction approaches the critical value (see Sec. III). The main purpose of this paper is to experimentally investigate this behavior in the