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# SUPERCONDUCTIVITY UNDER PRESSURE AND LOW TEMPERATURE SPECIFIC HEAT OF ThPr ALLOYS

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Measurements of superconducting transition temperature under pressure and low temperature specific heat are presented for ThPr alloys. At 18.2 kbar the normal- to superconducting-state phase boundary extends beyond 50 at.% Pr. This system is discussed in terms of a non-magnetic singlet ground state for the $Pr^{3+}$ ions due to crystal field splitting. A splitting scheme which varies with Pr concentration is proposed.

## 1. INTRODUCTION

BUCHER *et al.* have shown that when Pr is alloyed with Th, the effect of crystal field splitting in the f.c.c. alloy removes the degeneracy of the $J = 4$ configuration leaving nonmagnetic singlet ground state $Pr^{3+}$ ions, and superconductivity persists to high Pr concentration [1]. We have measured down to 0.1 K the superconducting transition temperatures $T_c$ of selected ThPr samples under hydrostatic pressures up to 18.2 kbar. We find with increasing pressure that while the $T_c$ of Th is dropping, superconductivity persists to increasingly higher Pr concentrations. We have also measured the low temperature (through $T_c$) specific heats $C$ of Th and two ThPr alloys in order to determine the jumps $\Delta C$ at $T_c$ as well as the electronic coefficients $\gamma$. We will discuss our results in terms of the cubic crystal field splitting scheme of Lea *et al.* [2], aided by qualitative comparison of the paramagnetic susceptibility versus temperature data of Bucher *et al.* [1] to the calculations of Buschow *et al.* [3].

## 2. EXPERIMENTAL

The samples were prepared by melting together lump Pr (Research Chemicals; 99.9% purity) and crystal bar Th [4] in an arc furnace. The small (about 50 mg) $T_c$ samples had slight boil-off during the several homogenizing melts; however, nominal compositions are used. The larger (about 2 g) specific heat samples had negligible boil-off. We note that Pr forms solid solution f.c.c. alloys with Th out to 90% Pr [5].

All $T_c$'s were measured inductively in either a zero pressure holder or Be–Cu pressure clamps suspended beneath the mixing chamber of a dilution refrigerator [6]. Transition widths were 20 mK or less. Pressure measurements less than 15 kbar were made in miniature clamps ($\frac{3}{16}''$ bore) with the $T_c$ of Th serving as the manometer; those at 18.2 kbar were made in a medium size clamp ($\frac{1}{4}''$ bore) using the $T_c$ of In as the manometer. The hydrostatic environment was provided by a 1 : 1 mixture of *n*-pentane and isoamyl alcohol. Four-lead d.c. resistance measurements of a calibrated germanium resistor and a carbon resistor (calibrated each run against marker $T_c$'s) gave temperatures above and below 0.6 K, respectively.

The specific heat measurements were made in a semi-adiabatic $He^3$ calorimeter utilizing a heat-pulse technique [7]. A calibrated germanium resistor in a three-wire configuration in an a.c. Wheatstone bridge, determined temperature.

## 3. RESULTS

In Fig. 1 we present our $T_c$ vs. Pr concentration results at 0 and 18.2 kbar (the lines simply tie the points together and represent the normal- to superconducting-state phase boundaries). The zero pressure data agree

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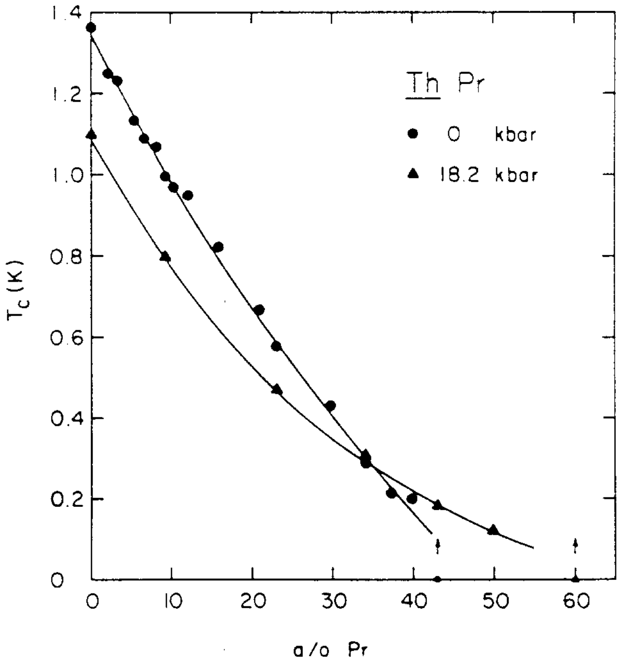

Fig. 1. Superconducting transition temperature versus atomic percent Pr for ThPr alloys at 0 and 18.2 kbar pressure. The arrows signify: no transition above the temperature indicated for that Pr concentration at the pressure shown by the symbol below.

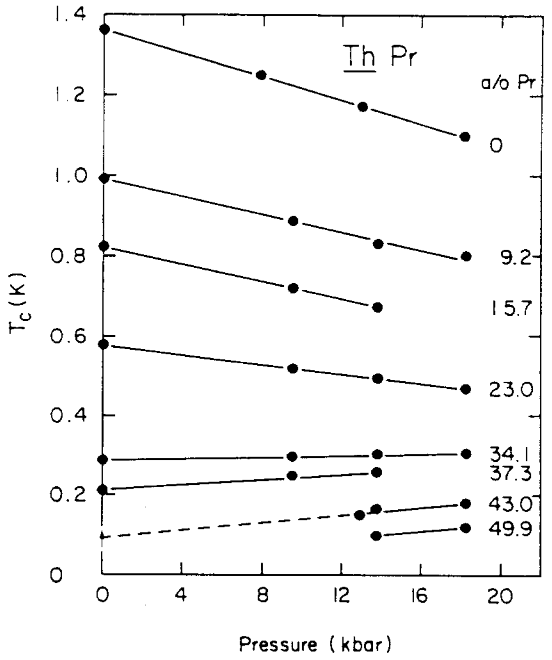

Fig. 2. Superconducting transition temperature versus pressure for ThPr alloys. The arrow signifies: no transition above 0.10 K for 43.0 at.% Pr at zero pressure, although an onset was seen.

with those of Bucher *et al.* [1] and merely extend the ranges of temperature and Pr concentration. The striking feature is found in our pressure data (see Fig. 2). Although the $T_c$'s of Th-rich alloys decrease with pressure, the $T_c$'s of alloys containing greater than 34 at.% (*a*/*o*) Pr actually increase with pressure. Referring back to Fig. 1, it is seen that the ThPr phase boundary extends to significantly higher Pr concentration with the application of rather modest pressure.

Our specific heat measurements are shown in Fig. 3. We have plotted the electronic contribution $C_e$ vs. temperature $T$ for pure Th and alloys containing 12.7 and 30.0 *a*/*o* Pr over ranges which include their superconducting transitions. The lattice contributions $\beta T^3$ have been subtracted off using the $\beta = 0.40$ mJ/mole-K$^4$ of pure Th. Although our assumption that $\beta$ remains unchanged to such large Pr concentration would seem presumptuous, we observe for the 30.0 *a*/*o* Pr alloy that the normal-state data show negligible deviation from proportionality to $T$ (due to a possible $\pm\ \Delta\beta T^3$) as $T$ doubles. For each set of points we have extrapolated both the normal- and superconducting-state data linearly through the transition; points in the transition have also been fitted linearly. The intersection of this latter line with the former two are taken to define the transition width $\Delta T_c$, and the midpoint of $\Delta T_c$ is called $T_c$. $\Delta C$ is found at $T_c$ as the difference between the extrapolated values for $C_e$ in the normal and the superconducting states. $\gamma$ is taken as the slope of the normal-state linear fit (which extends through the origin in each case). Listed below are $T_c$, $\Delta T_c$ and $\gamma$ for pure Th and the two ThPr alloys.

| *a*/*o* Pr | $T_c$(K) | $\Delta T_c$(K) | $\Delta C$(mJ/mole-K) | $\gamma$(mJ/mole-K$^2$) |
|---|---|---|---|---|
| 0 | 1.37 | 0.01 | 8.35 | 4.12 |
| 12.7 | 0.91 | 0.02 | 5.55 | 4.95 |
| 30.0 | 0.54 | 0.04 | 3.25 | 5.50 |

The inset of Fig. 3 is a plot of reduced specific heat jump $\Delta C/\Delta C_0$ vs. both (above) reduced superconducting transition temperature $T_c/T_{c0}$ and (below) reduced normal state electronic specific heat at $T_c$, $\gamma T_c/\gamma_0 T_{c0}$ (the subscript zero designates the value for pure Th). The straight line labelled BCS is the Law of Corresponding States predicted by Kaiser [8] for a system of "non-magnetic" paramagnetic ions a superconductor. The curved line labelled AG was derived by Abrikosov and Gor'kov [9] for a system of "magnetic" paramagnetic ions in a superconductor with the preferred ion spin-conduction electron spin orientation being parallel.

## 4. DISCUSSION

To begin this discussion of our results, we reiterate the conclusion of Bucher *et al.*: in ThPr alloys crystal

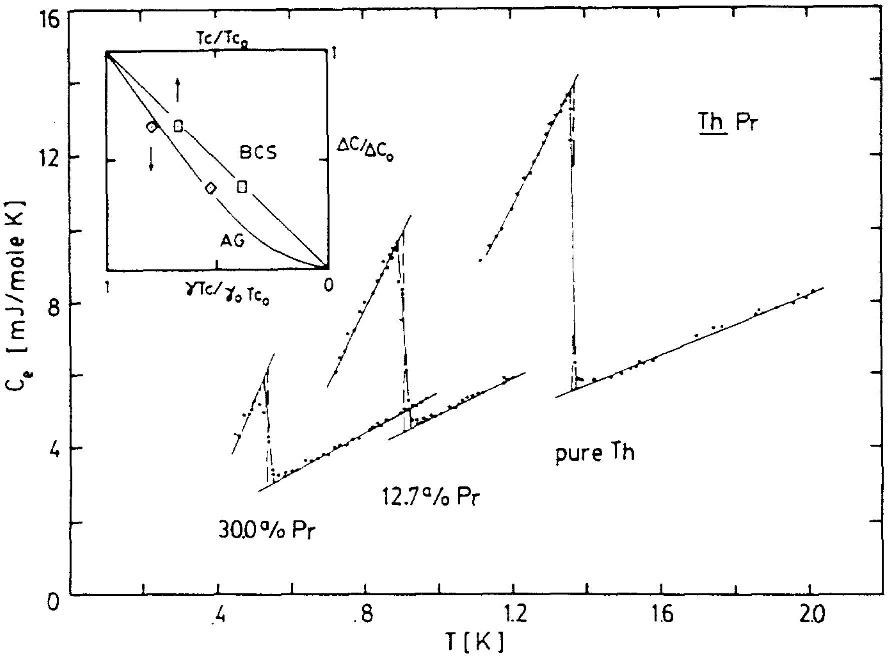

Fig. 3. Electronic specific heat vs. temperature for pure Th and two ThPr alloys. The inset shows: reduced specific heat jump at the superconducting transition versus (above) reduced superconducting transition temperature ($T_c$) and (below) reduced normal state electronic specific heat at $T_c$ (transition widths are included in the dimensions of the symbols).

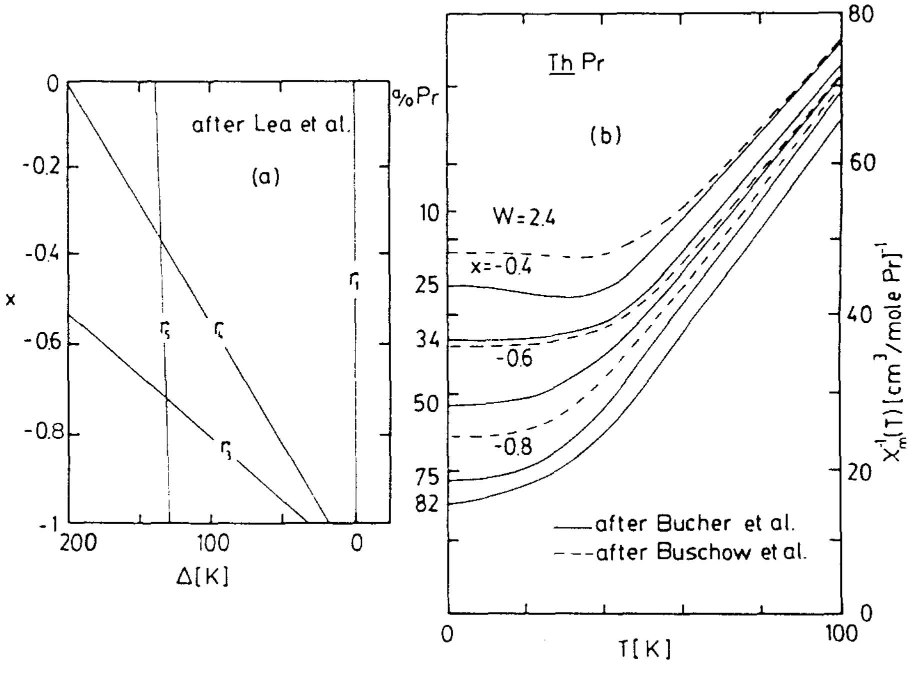

Fig. 4. (a) Energy (temperature) of excited states above ground state vs. LLW crystal field parameter x after [2]. (b) Inverse paramagnetic susceptibility of Pr vs. temperature from ThPr measurements of [1] (solid lines) and from calculations of [3] (dashed lines).

field splitting removes the degeneracy of the $J = 4$ configuration of the $Pr^{3+}$ ions and gives them a nonmagnetic, singlet ground state [1]. This allows superconductivity to persist to high Pr concentration even though at elevated temperatures ThPr alloys are strongly paramagnetic with essentially Curie–Weiss law behaviours and effective Pr moments appropriate to $J = 4$ [1]. In Fig. 4(b) we reproduce the smoothed ThPr paramagnetic susceptibility results of Bucher *et al.*, plotted as $\chi_m^{-1}(T)$ vs. $T$ (we show the data-fitting lines of their Fig. 3), for several Pr concentrations (we show also $\chi_m^{-1}(0)$ for 10*a/o* Pr taken from their Fig. 6) [1]. We feel that we can explain the different, but systematically changing, low temperature $T$ dependencies for the various alloys.

Buschow *et al.* [3] have taken the level scheme due to Lea, Leask and Wolf (hereafter LLW) [2] for a $J = 4$ ion in a cubic crystal field and they have calculated what amounts to normalized $\chi_m^{-1}(T)$ for selected x values in each quadrant of the W–x plane. W and x are the LLW crystal field parameters which describe the level schemes for the different Hund's rules $J$ values assumed by ions with integral occupation of $f$-electron shells. W is an energy scale factor, while x is a measure of the relative magnitudes of the fourth- and sixth-order crystalline potentials. The calculations of [3] for $\chi_m^{-1}(T)$ in the quadrant with $W > 0$ and $x \leqslant 0$ look remarkably similar to the experimental results of [1] if x is free to vary with Pr concentration. Our efforts to fit theory to experiment were aided by the chance coincidence that $\chi_m^{-1}(T)$ for $PrIn_3$ due to Lethuiller and Chaussy [10] is nearly identical (within a constant molecular field coefficient) to $\chi_m^{-1}(T)$ for the 34*a/o* Pr alloy of Bucher *et al.* [1]. In [10] the $PrIn_3$ data are best-fit by a choice of $W = 2.36$ and $x = -0.6$. We have assumed $W = 2.4$ (to more closely match $\chi_m^{-1}(0)$ for 34*a/o* Pr in Th with that for $PrIn_3$) and scaled the calculations of [3] for $x = -0.4$ and $-0.8$.

In Fig. 4(b) we show (dashed lines) the calculated inverse crystal field susceptibilities for $J = 4$ Pr ions in sites with cubic symmetry for $W = 2.4$ and $x = -0.4$, $-0.6$ and $-0.8$. We observe quite satisfactory agreement with the trends of the results for ThPr alloys (solid lines) and we conclude that x must become increasingly negative as the Pr concentration increases. We point out that for all x in the $W > 0$ and $x < 0$ quadrant of the LLW $J = 4$ W–x diagram the ground state is the nonmagnetic singlet $\Gamma_1$. Since the calculations of Buschow *et al.* for $W > 0$ and $x < 0$ yield $\chi_m^{-1}(0)$ values which vary linearly with x [1], we are able to match the $\chi_m^{-1}(0)$ axis of Fig. 4(b) with the x-axis of the aforementioned W–x diagram [2]. Our choice of $W = 2.4$ assigns an energy scale. Thus, we can propose in Fig. 4(a) a continuous level scheme for Pr ions in ThPr alloys from which the order and energy (temperature) separation of the excited states can be determined knowing only $\chi_m^{-1}(0)$. In the gap between Figs. 4(a) and (b), we have placed at $\chi_m^{-1}(0)$ the Pr concentrations of the ThPr alloys for which $\chi_m^{-1}(T)$ was measured.

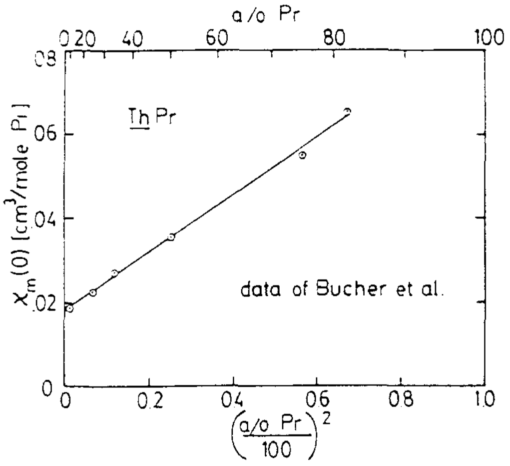

Fig. 5. Paramagnetic susceptibility of Pr at zero temperature in ThPr alloys after [1] vs. (above) at.% Pr and (below) atomic fraction Pr squared.

In concluding our discussion of the ThPr susceptibility results of Bucher *et al.* [1], we note an interesting systematic: $\chi_m(0)$ (taken from Fig. 6 of [1]) appears to be proportional to the Pr concentration squared (see Fig. 5). This, of course, facilitates the assignment of an x to a ThPr alloy for which $\chi_m(0)$ is not known.

We have a picture of the level scheme for the states available for $Pr^{3+}$ ions in ThPr alloys, once the $(2J + 1)$-fold degeneracy has been removed by crystal fields. This picture should be viewed as semi-quantitative. Nonetheless, it presents us with a system where the ground state ($\Gamma_1$) is a nonmagnetic singlet and the first excited state ($\Gamma_5$ for low Pr concentration or $\Gamma_4$ for high Pr concentration) is a magnetic triplet. Either magnetic state, however, is sufficiently elevated in energy [on the order of 100 K in the alloys which superconduct (see Fig. 4(a)] that at superconducting temperatures (the $T_c$ of Th is 1.37 K) its thermal population is negligible. The matter is simplified by the fact that only the $\Gamma_4$ triplet, and not the $\Gamma_5$ triplet or the $\Gamma_3$ doublet, is coupled by the exchange interaction to the $\Gamma_1$ singlet; i.e. $\langle\Gamma_1|J_z|\Gamma_j\rangle \neq 0$ for $j = 4$ only [11].

Keller and Fulde have derived the normal- to superconducting-state phase boundary for just such a two level $Pr^{3+}$ ion $\Gamma_1$–$\Gamma_4$ system [11]. They predict a family of curves which are parametrized by the ratio $\Delta/T_{c0}$; $\Delta$ is the energy (temperature) of the $\Gamma_1$–$\Gamma_4$ splitting [see Fig. 4(a)]. The data of Bucher *et al.* [1] for the f.c.c. system $La_{1-x}Pr_xPb_3$ are fitted very well using $\Delta/T_{c0} = 4.4$ [11]. Keller and Fulde have also stated that the

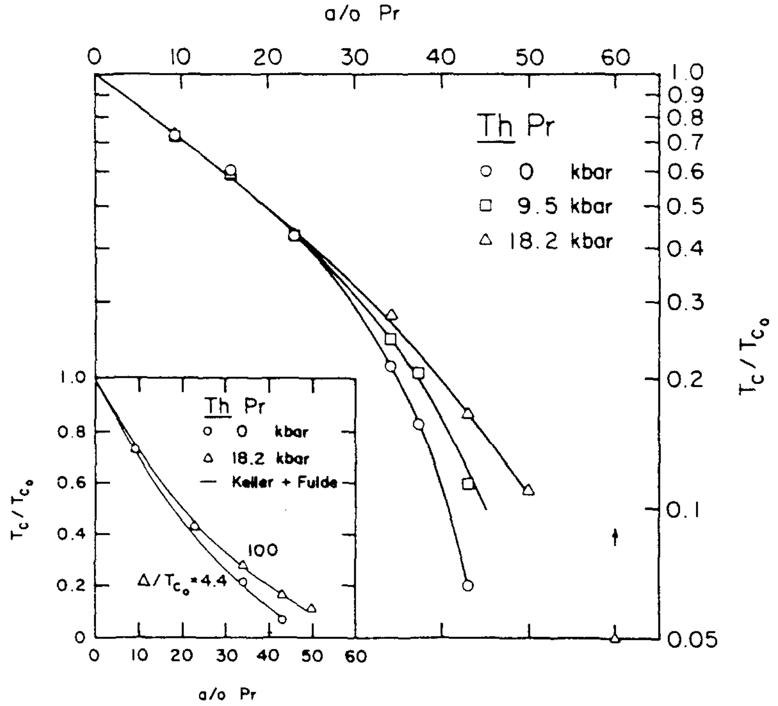

Fig. 6. Logarithm of reduced superconducting transition temperature ($T_c/T_{c0}$) vs. at.% (*a/o*) Pr for ThPr alloys at 0, 9.5 and 18.2 kbar pressure. The inset shows: $T_c/T_{c0}$ vs. *a/o* Pr at 0 and 18.2 kbar with theoretical curves for $\Delta/T_{c0} = 4.4$ and 100 after [11].

reduced superconducting transition temperature $T_c/T_{c0}$ as a function of $(\tau_n T_{c0})^{-1}$ (their normalized variable which is proportional to Pr concentration) does not depend very sensitively on details of the level scheme as long as the ground state is nonmagnetic and the energy separation is sufficiently large, that is $\Delta/T_{c0} \geqslant 4$ [11]. We show in the inset of Fig. 6 our reduced $T_c$ results at 18.2 kbar as well as our zero pressure data for only those samples measured at 18.2 kbar. Having multiplied the $(\tau_n T_{c0})^{-1}$ of Keller and Fulde [11] by 33, we show too their predictions for both $\Delta/T_{c0} = 4.4$ and 100. This we do in order to illustrate that the derived functional form for the phase boundary is not unreasonable even though the change in $\Delta$ required to follow its evolution with pressure is. General agreement for the f.c.c. system ThPr is as much as should be expected. Not only is $\Delta$ changing as a function of Pr concentration; but, unlike with other studies of the superconductivity of Pr alloy systems where $Pr^{3+}$ ions replace $La^{3+}$ ions at a rare earth site in compounds, here they replace the actinide $Th^{4+}$ ions to *very* high concentration in solid solution.

Setting aside for the moment considerations of theory, we focus on systematics in our $T_c$ measurements. In Fig. 6 we plot the logarithm of $T_c/T_{c0}$ vs. Pr concentration at 0, 9.5, 18.2 kbar (again zero pressure data are shown only for samples measured under pressure too). The lines represent the smoothed phase boundaries at the different pressures. It is striking that for Pr concentrations less than 23 *a/o* the phase boundary remains essentially unchanged, while for Pr concentrations greater than 23 *a/o* the "tail" sweeps up with increasing pressure. The implication is clear: with measurements to low temperatures on high Pr concentration alloys at sufficiently high pressures one will be able to extrapolate to a $T_c$ for *f.c.c.* Pr – it will be about 10 mK ($T_{c0}$, that of Th, levels off around 0.65 K over 70 kbar) [12]. To explain the low/high Pr concentration stationary/sweeping with pressure phase boundary, we suggest that the Pr ions in a ThPr alloy are squeezed to less negative LLW parameter x. The effect on superconductivity should be greater at higher Pr concentrations where $\Delta$ is initially less.

Supporting the low/high Pr concentration distinction is a further systematic. Huber [13] has observed that the initial rate of change of $T_c$ as a function of pressure $dT_c/dp|_{p=0}$ for ThY alloys varies linearly with Y concentration. This linearly holds out to the disappearance of superconductivity at 70 *a/o* Y even though $dT_c/dp|_{p=0}$ crosses from negative to positive and the alloys change from one closed-packed phase (f.c.c.) to another (h.c.p.). The linear fit for ThY alloys of [13] is plotted in Fig. 7 along with $dT_c/dp|_{p=0}$ for ThPr alloys (the slopes of the straight lines in Fig. 2) vs. Pr

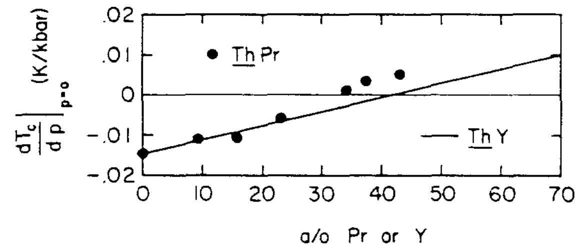

Fig. 7. Initial rate of change of superconducting transition temperature as a function of pressure vs. at.% Pr or Y for ThPr (points, this work) and ThY (line, after [13]) alloys.

concentration. Y is, after all, a nonmagnetic trivalent rare earth. At low Pr concentration the ThPr alloys respond to pressure like ThY alloys; at high Pr concentration their $T_c$'s are increasing with pressure more rapidly than expected.

We resume now our efforts to compare theory and experiment, and turn to look at our ThPr specific heat measurements. Normally, a plot of $\Delta C/\Delta C_0$ vs. $T_c/T_{c0}$ along with the detailed shape of the phase boundary would characterize the magnetic nature of paramagnetic solute ions in a metallic superconductor [14]. Distinctive curves are predicted and observed. Whether solute ion localized electron states are strongly mixed with the conduction electron states or the solute ion is non-Kramers with a nonmagnetic ground state and $\Delta/T_c$ is very large, alloys containing paramagnetic ions which are "nonmagnetic" at superconducting temperatures should obey the BCS Law of Corresponding States. In the context of alloys this is stated $\Delta C/\Delta C_0 = T_c/T_{c0}$, but with the assumption that the conduction electron $\gamma$ is unchanging. Superconductivity is usually suppressed while the alloys are still dilute and the descriptive coefficients of the solvent metal are only slightly altered. ThPr alloys follow $\Delta C/\Delta C_0 = T_c/T_{c0}$ (see Fig. 3 inset); however, the specific heat $\gamma$ is significantly altered. Stated correctly, the BCS Law of Corresponding States is $\Delta C/\gamma T_c$ = constant or $\Delta C/\Delta C_0 = \gamma T_c/\gamma_0 T_{c0}$. Our ThPr data deviate from the latter equality (again see Fig. 3 inset), but so do data for ThY and ThLa alloys of similar concentrations [15]. As functions of Rare Earths concentration, $\gamma$ and $\Delta C/\gamma T_c$ increase and decrease, respectively, not much more rapid for ThPr alloys than for ThY and ThLa alloys, and the scatter is large. Thus, as with our consideration of the phase boundary, comparison with theory is difficult. The problem, simply put, is that 30*a/o* is not dilute.

## 5. CONCLUSIONS

Our interpretation of the ThPr system is that the $Pr^{3+}$ ions have their $J = 4$ configuration degeneracy removed by a cubic crystal field. The ground state is the non-magnetic singlet $\Gamma_1$ and the first excited state is a magnetic triplet, $\Gamma_5$ at low Pr concentration or $\Gamma_4$ at high Pr concentration. The splitting energy (temperature) $\Delta$ between $\Gamma_5$ and $\Gamma_1$ is always large; that between $\Gamma_4$ and $\Gamma_1$ becomes less with increasing Pr concentration. This is a consequence of our hypothesis (based on the temperature dependencies of the paramagnetic susceptibilities given in [1]) that the LLW parameter x becomes more negative with increasing Pr concentration. We propose furthermore that x for a given alloy becomes less negative as pressure is applied. In effect, the Pr concentrations in the gap between Figs. 4(a) and (b) move upward. Measurements of the susceptibilities of ThPr alloys under pressure are needed; we would expect the zero temperature limits $\chi_m(0)$ to decrease. Specific heat should be measured on an f.c.c. alloy of maximal Pr concentration (where $\Delta$ would be least) to look for a Schottky anomaly which could determine $\Delta$.

Also, neutron scattering measurements would be useful; and certainly $T_c$'s must be measured at still greater pressures to test our prediction that extrapolation can be made to superconductivity for *f.c.c.* Pr.

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