

## Low Temperature Heat Capacities of Pr-Containing $m212$ ( $m=1,2,3$ ) Cuprates

James C. Ho

*Department of Physics, Wichita State University, Wichita, Kansas, U.S.A.*

(Received December 1, 1997)

Low temperature calorimetric data for several Pr-containing  $m212$  ( $m=1,2,3$ ) cuprates are summarized in conjunction with the magnetic heat capacities associated with the anomalous Pr-ordering.

PACS. 65.40.+g – Heat capacities of solids.

PACS. 74.25.Ha – Magnetic properties.

### I. Introduction

Shortly after the discovery of superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , many isostructural compounds  $\text{RBa}_2\text{Cu}_3\text{O}_7$  were synthesized to have similar  $T_c$  values near 90 K, where R represents most of the rare earth elements. A notable exception occurs when  $R = \text{Pr}$ . The essentially insulating  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  remains normal to low temperatures, but exhibits an antiferromagnetic transition with an anomalously high Ndel temperature  $T_N(\text{Pr})$  of 17 K [1]. In comparison, other  $\text{RBa}_2\text{Cu}_3\text{O}_7$  compounds have a maximum  $T_N(\text{R})$  of 2.2 K in  $\text{GdBa}_2\text{Cu}_3\text{O}_7$ [2]. Not surprisingly, extensive research followed revealing a rather complicated magnetic behavior of Pr ions. Relevant to this paper are calorimetric studies, which yielded a broad heat capacity peak and less-than-expected entropy change below  $T_N(\text{Pr})$ . Furthermore, a large linear-term in heat capacity prevails above  $T_N(\text{Pr})$ , which is reminiscent to heavy-fermion systems. Questions being raised include, among others, the valence of Pr ions, dimensionality of the magnetic ordering, and hybridization between Pr-4f and O-2p $_{\pi}$  orbitals.

High-T, or related cuprates can be systematically categorized by a classification with four numbers, which represent the stoichiometric ratios among metallic elements located at different sites of the layered structures. Following this scheme,  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  would be written as  $\text{CuBa}_2\text{PrCu}_2\text{O}_7$ . The 1212C-type designation reflects one insulating CuO (chain), two spacing BaO, one separating Pr. and two normally conducting  $\text{CuO}_2$  layers per unit cell. Similarly,  $\text{PrBa}_2\text{Cu}_4\text{O}_8$  corresponds to 2212C  $\text{Cu}_2\text{Ba}_2\text{PrCu}_2\text{O}_8$ , which also has a  $T_N(\text{Pr})$  value of 17 K and anomalous low temperature heat capacities[3]. This paper summarizes calorimetric data for some additional 1212, 2212 and 3212 compounds as listed below:

[Tl - 1212]	TlSr <sub>2</sub> PrCu <sub>2</sub> O <sub>7</sub> Tl(Sr <sub>0.5</sub> Ba <sub>0.5</sub> ) <sub>2</sub> PrCu <sub>2</sub> O <sub>7</sub> TlBa <sub>2</sub> PrCu <sub>2</sub> O <sub>7</sub> TlBa <sub>2</sub> YCu <sub>2</sub> O <sub>7</sub> (for reference)
[Hg - 1212]	HgSr <sub>2</sub> PrCu <sub>2</sub> O <sub>7</sub>
[Pb/Cu - 1212]	(Pb <sub>0.6</sub> Cu <sub>0.4</sub> )Sr <sub>2</sub> PrCu <sub>2</sub> O <sub>7</sub>
[Bi - 2212]	Bi <sub>2</sub> Sr <sub>2</sub> PrCu <sub>2</sub> O <sub>8</sub>
[Pb/Cu - 2212]	(Pb <sub>0.5</sub> Cu <sub>0.5</sub> ) <sub>2</sub> (Ba <sub>0.5</sub> Sr <sub>0.5</sub> ) <sub>2</sub> PrCu <sub>2</sub> O <sub>8</sub> (Pb <sub>0.5</sub> Cu <sub>0.5</sub> ) <sub>2</sub> (Ba <sub>0.5</sub> Sr <sub>0.5</sub> ) <sub>2</sub> YCu <sub>2</sub> O <sub>8</sub> (for reference)
[Pb/Cu - 3212]	(Pb <sub>2/3</sub> Cu <sub>1/3</sub> ) <sub>3</sub> Sr <sub>2</sub> PrCu <sub>2</sub> O <sub>8</sub> (Pb <sub>2/3</sub> Cu <sub>1/3</sub> ) <sub>3</sub> (Ba <sub>1/2</sub> Sr <sub>1/2</sub> ) <sub>2</sub> PrCu <sub>2</sub> O <sub>8</sub> (Pb <sub>2/3</sub> Cu <sub>1/3</sub> ) <sub>3</sub> Ba <sub>2</sub> PrCu <sub>2</sub> O <sub>8</sub>

They hold the common feature of having two CuO<sub>2</sub> planes across elemental Pr per unit cell. Otherwise, the 1, 2 or 3 insulating layers contain Hg, Tl, Bi, or Pb/Cu, while the invariably two spacing layers contain Ba or Sr. Without the constrain of the four numbers scheme, the 3212-type compounds could also be written as Pb<sub>2</sub>(Ba/Sr)<sub>2</sub>PrCu<sub>3</sub>O<sub>8</sub>. The inclusion of two Y-based compounds provides base lines for lattice heat capacities of the Pr-based materials.

Most details of sample preparation, structure determination and magnetic characterization, as well as the experimental aspect of calorimetric measurements can be found in several earlier publications on individual compound or system [4-8]. The four summarizing figures, Fig. 1 to Fig. 4 being presented here, all in the same format of C/T (0 to 1.2 J/mol K<sup>2</sup>) versus T (0 to 15 K), are mainly for the purpose of emphasizing phenomenologically the complex nature of Pr-ordering. Indeed, while broad heat capacity peaks prevail in most of the compounds, a clear trend in their shape or magnitude is obviously lacking. Part of this almost certainly reflects the difficulty in making these materials with high quality and phase purity. As far as Bi<sub>2</sub>Sr<sub>2</sub>PrCu<sub>2</sub>O<sub>8</sub> is concerned, the data in Fig. 3 without an apparent heat capacity peak were obtained from a polycrystalline sample. Single crystals of the same compound yielded the same results [9]. Its  $T_N(\text{Pr})$  must be then below 2 K. A systematic dependence of  $T_N(\text{Pr})$  on the bond length between Pr and oxygen in the adjacent Cu<sub>2</sub>O layers has been discussed in two cited references [4, 5]. Nevertheless, in comparison with the data of Y-based (Pb<sub>0.5</sub>Cu<sub>0.5</sub>)<sub>2</sub>(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)<sub>2</sub>YCu<sub>2</sub>O<sub>8</sub>, there are still extra heat capacity contribution directly or indirectly related to the Pr effect. Moreover, the heat capacities above  $T_N(\text{Pr})$  for each set of data in Fig. 1 through Fig. 4 appear to contain an unexpectedly large term linear with temperature (as identified by a linear fit to the experimental data in a C/T-T<sup>2</sup> plot) just as in the case of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. With its origin not yet understood, this term more or less dominates the non-lattice related heat capacity.

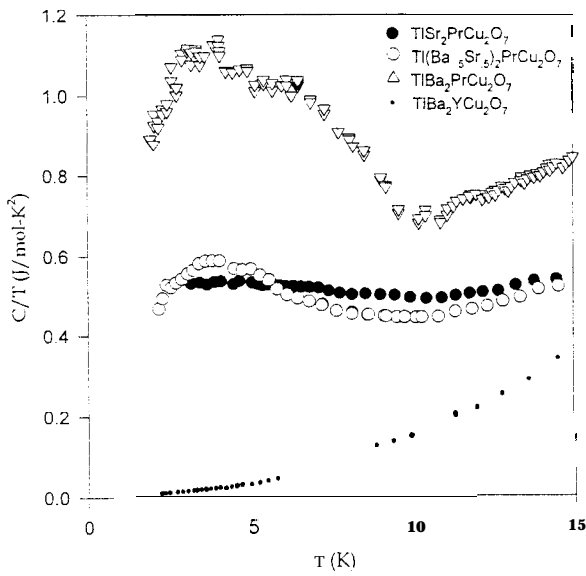


FIG. 1. Heat capacities of Pr-containing Tl-1212 compounds. The Y-compound provides the baseline for lattice contribution.

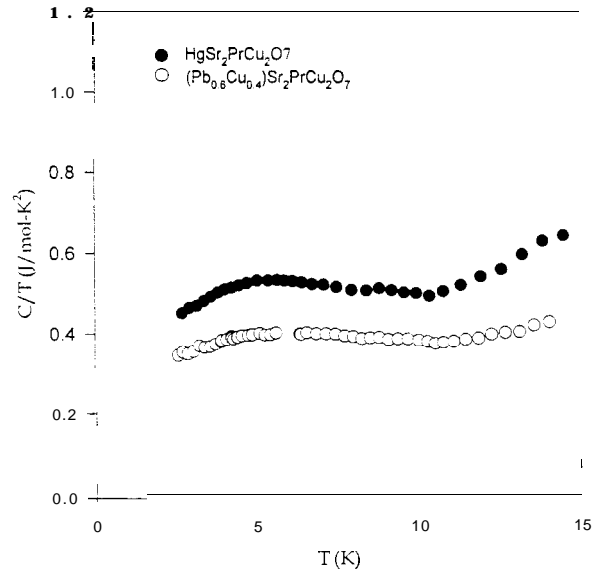
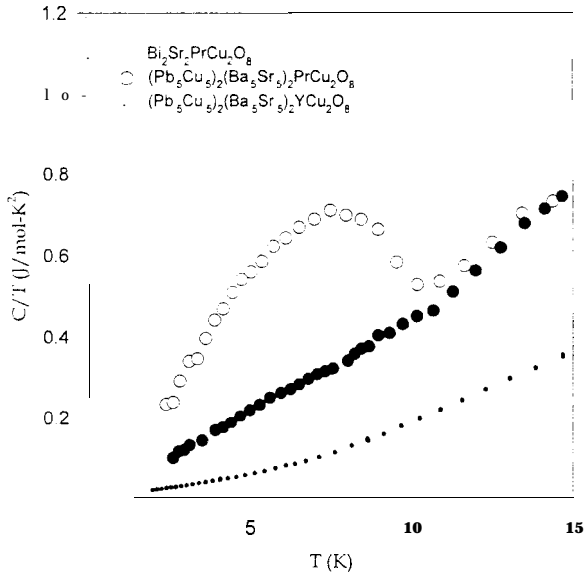


FIG. 2. Heat capacities of Pr-containing Hg-1212 and (Pb/Cu)-1212 compounds.



Heat capacities of Pr-containing Bi-2212 and (Pb/Cu)-2212 compounds. The Y-compound provides the baseline for lattice contribution.

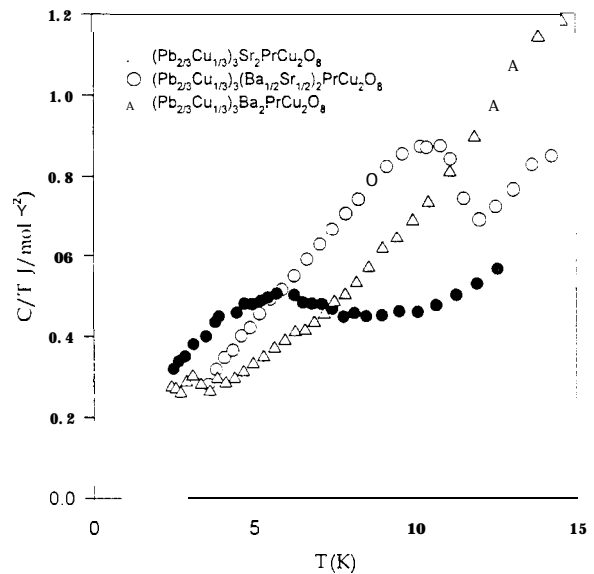


FIG. 4. Heat capacities of Pr-containing (Pb/Cu)-3212 compounds.

The calorimetric data are often used to derive the entropy,  $S = \int (C/T)dT$ . For the insulating compounds being considered, the magnetic component  $S_m$  would be normally the difference between the total entropy and the lattice contribution. Accordingly, in a  $C/T$  versus  $T$  plot, the integrated area between the measured values and those for a corresponding Y-base compound, if available, could provide a reasonable estimate of the magnetic entropy  $S_m$  associated with the Pr ordering. Ideally, it should be close to  $R \ln 3$  or  $R \ln 2$  for  $\text{Pr}^{3+}$  with a quasi-triplet ground state or  $\text{Pr}^{4+}$  with a double ground state, respectively, below  $T_N(\text{Pr})$  if short-range ordering persisting to higher temperatures is limited. Unfortunately, the presence of the large linear-term in heat capacity adds uncertainties in this regard. It is not clear whether this term should be taken into account in estimating the  $S_m$  directly associated with the Pr ordering. Just as questionable is its behavior below  $T_N(\text{Pr})$ . It has been noted that, at temperatures much lower than  $T_N(\text{Pr})$ , the total heat capacity can actually be less than the extrapolated linear-term alone [10].

In conclusion, low temperature calorimetry complements magnetic measurements and provides additional information on Pr-containing cuprates. Meanwhile, the thermodynamic approach reveals more of their complex bulk properties.

#### Acknowledgment

This note is based on earlier collaborations with the research groups of H. C. Ku, National Tsing Hua University, and Y. Y. Chen and Y. D. Yao, Academia. Sinica.

#### References

- [1] H. B. Rodousky, *J. Mater. Res.* 7, 1917 (1992) and references therein.
- [2] J. C. Ho, P. H. Hor, R. L. Meng, C. W. Chu, and C. Y. Huang, *Solid State Commun.* 67, 711 (1987).
- [3] H. D. Yang, J. Y. Lin, S. S. Weng, C. W. Lin, H. L. Tsay, Y. C. Chen, T. H. Meen, T. I. Hsu, and H. C. Ku, to be published.
- [4] C. C. Lai, T. J. Lee, H. K. Fun, H. C. Ku, and J. C. Ho, *Phys. Rev.* B50, 4092 (1994).
- [5] C. H. Chou, Y. Y. Hsu, J. H. Shieh, T. J. Lee, H. C. Ku, J. C. Ho, and D. H. Chen, *Phys. Rev.* B53, 6729 (1996).
- [6] H. C. Ku, C. C. Lai, J. H. Shieh, C. Y. Wu, and J. C. Ho, *Physica* B194-196, 213 (1994).
- [7] C. L. Yang, J. H. Shieh, Y. Y. Hsu, H. C. Ku, and J. C. Ho, *Phys. Rev.* B52, 10452 (1995).
- [8] J. H. Shieh, H. C. Ku, and J. C. Ho, *Phys. Rev.* B50, 3288 (1994).
- [9] T. I. Hsu. M. S. Thesis, National Tsing Hua University (1997).
- [10] J. C. Ho, C. Y. Wu, K. Kumar, M. K. Wu, W. Y. Guan, and Y. H. Xu, *Physica* C229, 351 (1994).