

*Title:*

**Crystal Structure, Superconductivity and  
Magnetism of the Quasi-2D Heavy Fermion  
Materials CeTIn<sub>5</sub> (T = Co, Rh, Ir)}**

*Author(s):*

E. G. Moshopoulou, J. L. Sarrao, P. G. Pagliuso,  
N. O. Moreno, J. D. Thompson, Z. Fisk and  
R. M. Ibberson

*Submitted to:*

<http://lib-www.lanl.gov/la-pubs/00796313.pdf>

**Crystal Structure, Superconductivity and Magnetism of the Quasi-2D Heavy Fermion Materials  
CeTIn<sub>5</sub> (T = Co, Rh, Ir)}**

E. G. Moshopoulou<sup>1</sup>, J. L. Sarrao<sup>2</sup>, P. G. Pagliuso<sup>2</sup>, N. O. Moreno<sup>2</sup>, J. D. Thompson<sup>2</sup>, Z. Fisk<sup>2,3</sup>, R. M. Ibberson<sup>4</sup>

<sup>1</sup>National Center for Scientific Research "Demokritos", Institute of Materials Science, 15310 Agia Paraskevi, Greece; evagelia@ims.demokritos.gr, tel.+30-1-6503320; fax +30-1-6519430

<sup>2</sup>Los Alamos National Laboratory, Los Alamos, NM 87545, USA

<sup>3</sup>National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL32306, USA

<sup>4</sup>ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11, 0QX, United Kingdom

**Abstract**

The crystal structure of the recently discovered heavy-fermion (HF) superconductor CeCoIn<sub>5</sub> ( $T_c = 2.3$  K) has been determined by high-resolution neutron powder diffraction. It is tetragonal (space group P4/mmm), with lattice parameters  $a = 4.61292(9)$  Å and  $c = 7.5513(2)$  Å at ambient conditions. Whereas CeCoIn<sub>5</sub> is isostructural with the HF antiferromagnet CeRhIn<sub>5</sub> and the HF superconductor CeIrIn<sub>5</sub>, its cell constants and its only variable positional parameter,  $z_{In2}$ , differ significantly from the corresponding ones of CeRhIn<sub>5</sub> and CeIrIn<sub>5</sub>. As a result, the distortions of the cuboctahedron [CeIn<sub>3</sub>], which is the key structural unit in all three materials, are different in CeCoIn<sub>5</sub> from the ones in CeRhIn<sub>5</sub> and CeIrIn<sub>5</sub>. The compounds CeCoIn<sub>5</sub> and CeIrIn<sub>5</sub>, which contain the most distorted (in one or another way) [CeIn<sub>3</sub>] cuboctahedra exhibit superconductivity at ambient pressure below 2.3 K and 0.4 K, respectively. On the other hand, CeRhIn<sub>5</sub>, in which [CeIn<sub>3</sub>] cuboctahedra are the less distorted, and the cubic HF CeIn<sub>3</sub> are antiferromagnets at ambient pressure with  $T_N = 3.8$  K and 10 K respectively; they become superconductors under pressure of 16 kbar and 25 kbar with  $T_c = 2.1$  and 0.2 K respectively.

Pacs 61.12.Ld, 71.27.+a, 72.15.Qm, 74.70.Tx

## 1. INTRODUCTION

A recent advance in the physics and chemistry of heavy fermion (HF) systems has been the discovery of the quasi-2D materials  $\text{CeTIn}_5$ , where  $T = \text{Co, Rh, Ir}$ . Collectively, these new systems enhance our knowledge of superconductivity, magnetism and HF behavior, and provide a suitable experimental environment to search for possible structure-property relationships in HF materials.

The systems  $\text{CeTIn}_5$  exhibit fascinating and unexpected physical properties.  $\text{CeRhIn}_5$  is a HF antiferromagnet with electronic coefficient of specific heat  $\gamma \equiv C/T \geq 420 \text{ mJ}/(\text{molCe K}^2)$  and Néel temperature  $T_N = 3.8 \text{ K}$ . Application of hydrostatic pressure of about 16 kbar induces a first-order like transition from antiferromagnetic state to an unconventional superconducting state with  $T_c = 2.1 \text{ K}$  (ref. 1). This transition is not expected within widely accepted theoretical predictions and is markedly different from any previously reported for a HF material.  $\text{CeCoIn}_5$  is a HF superconductor at ambient pressure with Sommerfeld coefficient  $\gamma \approx 290 \text{ mJ}/(\text{molCe K}^2)$  at 2.4 K and critical temperature  $T_c = 2.3 \text{ K}$  which is the highest known  $T_c$  for a HF system (ref. 2).  $\text{CeIrIn}_5$  is also a HF superconductor at ambient pressure with  $\gamma \approx 750 \text{ mJ}/(\text{molCe K}^2)$  and a bulk superconducting transition temperature  $T_c = 0.4 \text{ K}$ . An intriguing feature of  $\text{CeIrIn}_5$  is that its resistivity drops to zero at  $T_0 = 1.2 \text{ K}$  without any obvious thermodynamic signature (ref. 3). Specific heat and thermal conductivity (ref. 4, 5) as well as NMR experiments (ref. 6, 7) showed that the pairing symmetry in the superconducting state of  $\text{CeCoIn}_5$  and  $\text{CeIrIn}_5$  is unconventional.

Single crystal neutron, x-ray and electron diffraction experiments on  $\text{CeRhIn}_5$  and  $\text{CeIrIn}_5$  (ref. 8) and conventional powder x-ray diffraction on  $\text{CeCoIn}_5$  (ref. 2, 9, 10) demonstrated that the compounds  $\text{CeTIn}_5$  adopt the tetragonal  $\text{HoCoGa}_5$ -type structure (s.g.  $P4/mmm$ ). The compounds are built by monolayers of face-sharing distorted cuboctahedra  $[\text{CeIn}_3]$  and monolayers of edge-sharing rectangular parallelepipeds  $[\text{TIn}_2]$ , stacked alternatively in the  $[001]$  direction. The key structural unit of the series is the distorted cuboctahedron  $[\text{CeIn}_3]$ . Such structural arrangement implies that  $\text{CeCoIn}_5$ ,  $\text{CeRhIn}_5$  and  $\text{CeIrIn}_5$  are quasi-2D variants of  $\text{CeIn}_3$ .  $\text{CeIn}_3$  is a cubic HF antiferromagnet in which superconductivity is induced by pressure of  $\approx 25 \text{ kbar}$  and below  $T_c = 200 \text{ mK}$  (ref. 11). Whether the reduced dimensionality is responsible for the significant increase of  $T_c$  in the materials  $\text{CeTIn}_5$  is an outstanding question, which, if answered, will have an important impact on the present understanding of the physics of superconductivity not only in the HF materials but also in the broader class of correlated electron systems.

Our current structural investigations of the materials  $\text{CeTIn}_5$  at both ambient and non-ambient conditions aim to determine accurately their detailed crystallographic parameters and reveal the structural aspects associated with the rich array of phases and phenomena described above. In this conference, we present the crystal structure of  $\text{CeCoIn}_5$  at ambient conditions and compare it with those of  $\text{CeRhIn}_5$ ,  $\text{CeIrIn}_5$  and  $\text{CeIn}_3$  reported earlier.

## 2. DATA COLLECTION AND ANALYSIS

Time-of-flight neutron powder diffraction data were collected at the High Resolution Powder Diffractometer (HRPD) at ISIS facility of Rutherford Appleton Laboratory. The data were collected in the backscattering detector bank with  $\Delta d/d$  resolution of  $\sim 4 \times 10^{-4}$ . This unprecedented resolution is effectively constant over the whole d-spacing range 0.75 to 2.35 Å where the data were collected. It allows a highly accurate determination of the crystal structure as well as detection of potential very subtle changes in symmetry.

Single crystals of  $\text{CeCoIn}_5$  were ground into a fine powder and packed loosely in a flat plate holder; such sample geometry is the optimal one in order to reduce absorption effects. Local ISIS programs were used for the instrument control, data acquisition and corrections of the data from instrumental effects. The data analysis and structure refinements were carried out by GSAS (ref. 12). The initial structural model was the structure of  $\text{CeRhIn}_5$  (ref. 8), i.e. s.g.  $P4/mmm$ ,  $a = b = 4.656$  Å,  $c = 7.542$  Å and atomic coordinates: Ce at (0, 0, 0), Co at (0, 0, 1/2), In1 at (1/2, 1/2, 0) and In2 at (0, 1/2,  $z = 0.306$ ). The parameters varied in the refinement were the scale factor, ten background coefficients, four profile coefficients, the lattice constants, the positional parameter  $z_{\text{In2}}$ , nine thermal factors, three diffractometer constants and the preferred orientation, extinction and absorption coefficients. The detailed procedure for the data analysis and refinement of the structure as well as the values of all refined parameters will be reported in detail elsewhere. The Rietveld refinement fit is given in Fig. 1. The cell constants, the positional parameter and the main interatomic distances of  $\text{CeCoIn}_5$  are listed in Table 1 and compared with the corresponding ones of  $\text{CeRhIn}_5$ ,  $\text{CeIrIn}_5$  and  $\text{CeIn}_3$  obtained from references 8 and 13.

### 3. DISCUSSION

As can be seen in Table 1, in  $\text{CeCoIn}_5$  the interatomic distances Ce-In1 are smaller than the Ce-In2 ones. This means that the  $[\text{CeIn}_3]$  cuboctahedra in  $\text{CeCoIn}_5$  are distorted (compared with the cubic  $\text{CeIn}_3$ ) differently than the ones in  $\text{CeRhIn}_5$  and  $\text{CeIrIn}_5$ . In the former compound the chemical pressure induced on each  $[\text{CeIn}_3]$  by its two adjacent  $[\text{CoIn}_2]$  rectangular parallelepipeds, is lower than the chemical pressure due to its four adjacent  $[\text{CeIn}_3]$  cuboctahedra of the same layer. As a result, the  $[\text{CeIn}_3]$  cuboctahedra of  $\text{CeCoIn}_5$  are slightly elongated along the c axis, while they are dilated in the (a, b) plane in  $\text{CeRhIn}_5$  and  $\text{CeIrIn}_5$ .

Comparison of the structural parameters of  $\text{CeCoIn}_5$  given in Table 1, with the recently reported ones by Settai et al (ref. 10) reveal an important difference: the parameters reported in this reference, obtained from Rietveld analysis of conventional powder x-ray diffraction data, result in undistorted  $[\text{CeIn}_3]$  cuboctahedra. Better (but not complete) agreement exists between the results of the present study and the ones of Kalychak et al. (9) obtained again from conventional powder x-ray diffraction data but on arc-melted samples.

Finally, we point out that the  $[\text{CeIn}_3]$  cuboctahedra are more distorted (in one or another way) in the two superconducting compounds  $\text{CeCoIn}_5$  and  $\text{CeIrIn}_5$  than in the antiferromagnet  $\text{CeRhIn}_5$ . Possibly, the stronger distortions in  $\text{CeCoIn}_5$  and  $\text{CeIrIn}_5$  generate special features in their underlying electronic structure and magnetic fluctuation spectra, which are at the origin of superconductivity in these systems. Band structure calculations, as well as high resolution inelastic neutron scattering experiments, are necessary to address this issue. Undoubtedly, the structural trend just outlined suggests that some structural parameters of the  $\text{CeTiIn}_5$  and  $\text{CeIn}_3$  can be correlated with their physical properties [14]; however a more general and relevant structure-property relationship can be obtained only through comparison of the structural responses of the compounds  $\text{CeTiIn}_5$  and  $\text{CeIn}_3$  around their corresponding critical points.

*Acknowledgements:* E. G. M. acknowledges the support of the European Community, Access to Research Infrastructure Action of the Improving Human Potential Program. Work at Los Alamos National Laboratory was performed under the auspices of the US Department of Energy. Z.F. acknowledges partial support from U.S. National Science Foundation Grant No. DMR-9971348.

## REFERENCES

1. H. Hegger, C. Petrovic, E. G. Moshopoulou, M. F. Hundley, J. L. Sarrao, Z. Fisk, J. D. Thompson, *Phys. Rev. Lett.* **84**, 4986 (2000).
2. C. Petrovic, P. G. Pagliuso, M. F. Hundley, R. Movshovich, J. L. Sarrao, J. D. Thompson, Z. Fisk, *J. Phys.: Condens. Matter* **13**, L337 (2001).
3. C. Petrovic, R. Movshovich, M. Jaime, P. G. Pagliuso, M. F. Hundley, J. L. Sarrao, Z. Fisk, J. D. Thompson, *Europhys. Lett.* **53**, 354 (2001).
4. R. Movshovich, M. Jaime, J. D. Thompson, C. Petrovic, Z. Fisk, P. G. Pagliuso, J. L. Sarrao, *Phys. Rev. Lett.* **86**, 5152 (2001).
5. K. Izawa, H. Yamaguchi, Yuji Matsuda, H. Shishido, R. Settai, Y. Onuki, *Phys. Rev. Lett.* **87**, 057002-1 (2001).
6. N. J. Curro, B. Simovic, P. C. Hammel, P. G. Pagliuso, G. B. Martins, J. L. Sarrao, J. D. Thompson, cond-mat/0105175
7. G. Q. Zheng, K. Tanabe, T. Mito, S. Kawasaki, Y. Kitaoka, D. Aoki, Y. Haga, Y. Onuki, *Phys. Rev. Lett.* **86**, 4664 (2001).
8. E. G. Moshopoulou, Z. Fisk, J. L. Sarrao, J. D. Thompson, *J. Sol. State Chem.* **158**, 25 (2001).
9. Y. M. Kalychak, V. I. Zareba, V. M. Baranyak, V. A. Bruskov, P. Y. Zavalii, *Russian Metallurgy* **1**, 213 (1989).
10. R. Settai, H. Shishido, S. Ikeda, Y. Murakawa, M. Nakashima, D. Aoki, Y. Haga, H. Harima, Y. Onuki, *J. Phys.: Condens. Matter* **13**, L627 (2001).
11. N. D. Mathur, F. M. Grosche, S. R. Julian, I. R. Walker, D. M. Freye, R. K. Haselwimmer, G. G. Lonzarich, *Nature* **394**, 39 (1998).
12. A.C. Larson and R.B. Von Dreele, "General Structure Analysis System (GSAS)", Los Alamos National Laboratory Report LAUR 86-748 (2000).
13. Jon Lawrence, *Phys. Rev. B* **20**, 3770 (1979).
14. P.G. Pagliuso, R. Movshovich, A.D. Bianchi, M. Nicklas, N.O. Moreno, J.D. Thompson, M.F. Hundley, J.L. Sarrao, Z. Fisk, cond-mat/0107266.

## CAPTIONS

Table 1: Select Structural and Refinement parameters for CeIn<sub>3</sub>, CeCoIn<sub>5</sub>, CeRhIn<sub>5</sub>, CeIrIn<sub>5</sub>

Fig. 1: Rietveld Refinement fit of CeCoIn<sub>5</sub>

Table 1

	CeIn <sub>3</sub>	CeCoIn <sub>5</sub>	CeRhIn <sub>5</sub>	CeIrIn <sub>5</sub>
$a(\text{\AA})$	4.689(2)	4.61292(9)	4.656 (2)	4.674(1)
$c(\text{\AA})$		7.5513(2)	7.542(1)	7.501(5)
$z_{\text{In}2}$		0.3094(3)	0.3059(2)	0.3052(2)
Ce-In1 $\times$ 4 ( $\text{\AA}$ )	3.3156(6)	3.26183(6)	3.292(2)	3.3050(7)
Ce-In2 $\times$ 8 ( $\text{\AA}$ )		3.283(1)	3.2775(7)	3.272(1)
T-In $\times$ 8 ( $\text{\AA}$ )		2.7187(9)	2.7500(9)	2.7560(7)
$R$		0.0572	0.056	0.051
$R_w$		0.0669	0.1152	0.082
$\chi^2$		1.133	1.674	1.552

Fig. 1

