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LLNL-TR-657137

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July 15, 2014

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This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Summary of EXAFS results on Cd-doped $PuRhIn_5$

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(Dated: June 11, 2014)

Extended x-ray absorption fine-structure (EXAFS) data of a solid sample of $PuRhIn_5$ and a ∼2% Cd-doped $PuRhIn_5$ were obtained in fluorescence mode from the Pu L_{III}, and the Rh, In, and Cd K edges. Pu-edge results are consistent with the known structure $PuRhIn_5$ for both samples. Rh-edge results are also consistent with the nominal crystal structure, but indicate some Rh-In impurity phase in the Cd-doped sample. In-edge fits fit the nominal structure well, and are not as sensitive to the possible impurity. Cd-edge data were used to determine how much of the Cd resides on In(1) sites, and we find 48% ± 4% substitute for Cd onto the In(1) site, in contrast to the 20% one would expect by a random distribution of Cd onto both the In(1) and In(2) sites. This result is consistent with similar data on $CeCoIn_5$ doped with Cd reported previously.

I. INTRODUCTION

The crystal structure of $PuRhIn_5$ is shown in Fig. 1.

II. EXPERIMENTAL DETAILS

A Cd-doped sample and a control sample of $PuRhIn_5$ were prepared. The Cd concentration of between 1% and 2% was determined by **(microprobe???)** on samples that started from similar nominal Cd concentrations. X-ray diffraction... Magnetic susceptibility...

EXAFS data were collected at 30 K from the Pu L_{III} edge and at 50 K from the Rh, In, and Cd edges using a Si(220) ($\phi = 0°$) half-tuned double monochromator on BL 11-2 at the Stanford Synchrotron Radiation Light-

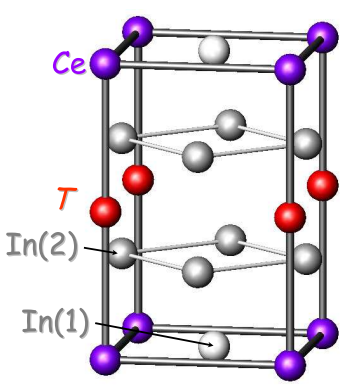

FIG. 1: (Color online) The tetragonal unit cell of the Ce-115s.

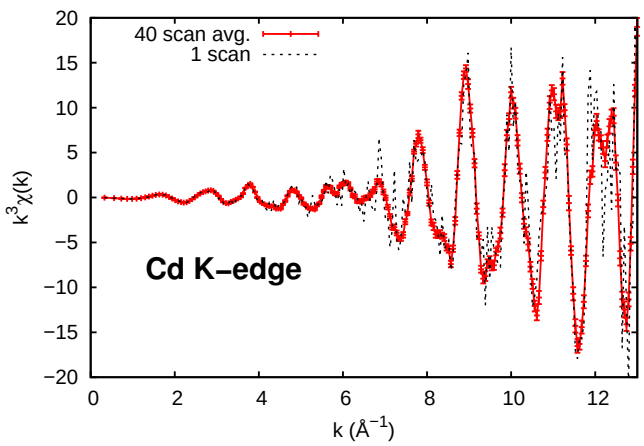

FIG. 2: (Color online) Cd K-edge EXAFS data at 50 K.

source. Data were collected in fluorescence mode on solid samples using a 100-element Ge dectector windowed on either the L_α line (for Pu L_{III} or the K_α line (the other edges), and corrected for dead time. The absorption data were reduced to the EXAFS $\chi(k)$ representation, transformed to r-space, and fit with calculated backscattering functions [1] using standard procedures [2–4]. In particular, a self-absorption correction was applied to these data [5], although the correction was only about 1% for the Cd data. Due to the low (∼2%) concentration of Cd, 7 hours of data collection were necessary at the Cd K edge to obtain high quality data (Fig. 2).

The data were fit using a model based on the nominal crystal structure of $PuRhIn_5$. The main focus of this work is to determine the site distribution of the Cd atoms, and as such, The Pu and Rh edge data are only used to check for sample purity, etc., since once cannot

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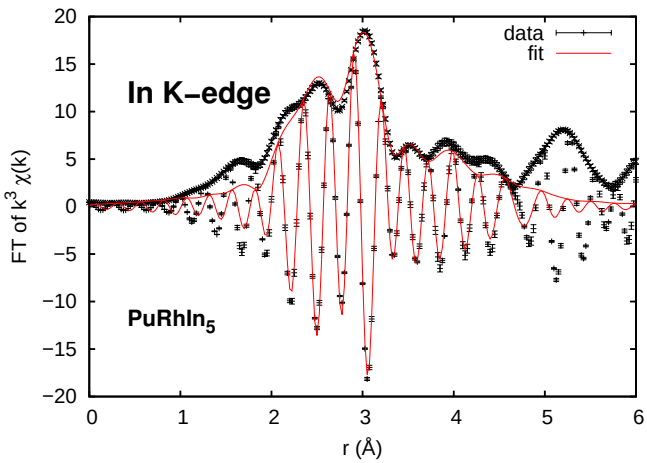

FIG. 3: (Color online) In K-edge EXAFS data (points) and fit (lines) in r-space after Fourier transform (FT) of the k-space data from 2.5-13.0 Å, Gaussian narrowed by 0.3 Å$^-$1. These data were fit between 1.9 and 5.1 Å to a model described in the text and more fully in Ref. 6. Error bars are determined from multiple scans and indicate reproducibility.

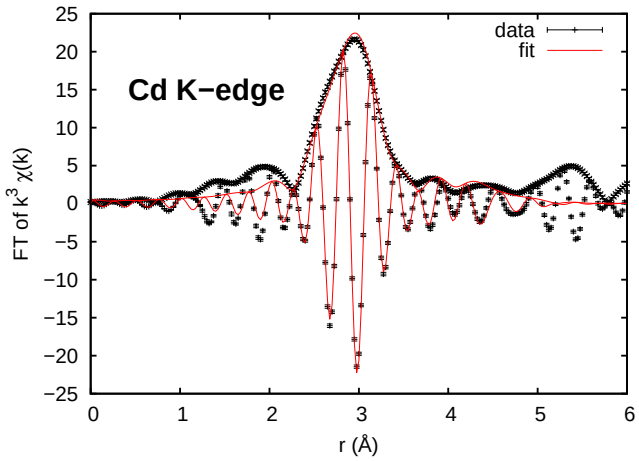

FIG. 4: (Color online) Cd K-edge EXAFS data (points) and fit (lines) in r-space, as described in Fig. 3. The resulting fit parameters are described in Table I.

differentiate between In and Cd as backscattering atoms. Instead, the most important data is that from the Cd edge, since different bond lengths are expected depending on whether the Cd sits on the In(1) or the In(2) site. The In edge data are used as a check for the heavily-constrained fitting model.

Although the differences in the local structure between the In(1) and In(2) sites are significant, even in the nominal crystal structure there are many distinct scattering paths, potentially generating more fit parameters than can be reasonably fit. We therefore employ a fit model that includes many constraints, as previously used on Cd-doped $CeCoIn_5$ [6]. Within this model, there are only three fit parameters that determine all the bond lengths, many of the Debye-Waller factors (σ^2s) are either constrained to similar scattering pairs or simply held fixed, and a single E_0 threshold shift is employed, as well as a single amplitude reduction factor S_0^2. In this way, the fit model can include 20 single scattering path up to 5 Å, including the Cd backscattering atoms, while only allowing 10 fit parameters to vary in the Cd K edge case. The data were fit in r-space between 1.9 and 5.1 Å after being Fourier transformed between 2.5 and 13.0 Å^{-1} (Gaussian narrowed by 0.3 Å^{-1}). The fit degrees of freedom were determined to be 13.4 [7].

III. RESULTS

The Pu L_{III}-edge EXAFS from both samples were found to be consistent with the nominal crystal structure, indicating that any potential impurity phases involving Pu are either insignificant or have a similar local structure to $PuRhIn_5$. This result is also consistent with the relatively large magnetic moment of 0.9 μ_{B}. Likewise, Rh edge data from $PuRhIn_5$ are consistent with the nominal crystal structure; however, a reduction in amplitude on such data from $PuRhIn_5$:Cd may indicate a Rh/In impurity phase, possible $RhIn_3$. From this amplitude reduction and comparing to FEFF [1] simulations on $PuRhIn_5$ and $RhIn_3$, we estimate a maximum $RhIn_3$ impurity of 15%. Such a reduction would cause only a maximum ∼7% error in the susceptibility, and so is likely insignificant for the present results.

Fits to the In K-edge data (Fig. 3 indicate the fitting model is reasonably accurate, giving a fraction f of In on the In(1) site of 25% ± 7%, compared to the nominal crystal structure value of 20% In on the In(1) site.

The main result of this work stems from the fits to the Cd K data, shown in Fig. 4. The fit parameters are summarized in Table I. In particular, these fits indicate $f = 48\% \pm 5\%$, very much like that found previously in Cd-doped $CeCoIn_5$ [6].

Acknowledgments

Supported by the U.S. Department of Energy (DOE) under Contract No. DE-AC02-05CH11231 (Lawrence Berkeley National Laboratory) and further supported by the U.S. DOE (Los Alamos). X-ray absorption data were collected at the Stanford Synchrotron Radiation Lightsource, a national user facility operated by Stanford University on behalf of the DOE, Office of Basic Energy Sciences.

TABLE I: Fit results from Cd.43 Fit range is between 1.90 and 5.10 Å.The k^3-weighted data are transformed between 2.50-13.00 Å^{-1} and are Gaussian narrowed by 0.30 Å.$^{-1}$ Fit assumes 2 at% Cd concentration.

		023b1G	
	N	σ^2(Å^2)	R(Å)
Cd1_Pu_3.2673.f7	1.92	0.0004(18)	3.32(2)
Cd1_In_3.2796.f7	3.76	0.0007(8)	3.18(1)
Cd1_Cd2_3.2796.f7	0.08	0.00069	3.180
Cd1_In_4.6207.f7	1.88	0.01000	4.695
Cd1_Cd1_4.6207.f7	0.04	0.01000	4.695
Cd1_Rh_4.9588.f7	3.84	0.011(8)	4.989
Cd2_Rh_2.7027.f7	1.04	0.008(3)	2.82(2)
Cd2_In_2.8051.f7	0.51	0.01000	3.149
Cd2_Cd2_2.8051.f7	0.01	0.01000	3.149
Cd2_In_3.2673.f7	2.04	0.00069	3.320
Cd2_Cd2_3.2673.f7	0.04	0.00069	3.320
Cd2_Pu_3.2796.f7	1.04	0.00040	3.180
Cd2_In_3.2796.f7	1.02	0.00069	3.180
Cd2_Cd1_3.2796.f7	0.02	0.00069	3.180
Cd2_In_4.3063.f7	2.04	0.003(2)	4.573
Cd2_Cd2_4.3063.f7	0.04	0.00316	4.573
Cd2_In_4.6207.f7	2.04	0.01000	4.695
Cd2_Cd2_4.6207.f7	0.04	0.01000	4.695
Cd2_In_4.6552.f7	0.51	0.01000	4.302
Cd2_Cd2_4.6552.f7	0.01	0.01000	4.302
ΔE_0		-8.9(33)	
S_0^2		1.000	
f		0.480(46)	
R(%)		13.60	

[1] A. L. Ankudinov and J. J. Rehr, Phys. Rev. B **56**, R1712 (1997).

[2] T. M. Hayes and J. B. Boyce, *Extended x-ray absorption fine-structure spectroscopy* (Academic, New York, 1982), vol. 37, p. 173.

[3] G. G. Li, F. Bridges, and C. H. Booth, Phys. Rev. B **52**, 6332 (1995).

[4] *RSXAP Analysis Package*, http://lise.lbl.gov/RSXAP/.

[5] C. H. Booth, M. D. Walter, M. Daniel, W. W. Lukens, and R. A. Andersen, Phys. Rev. Lett. **95**, 267202 (2005).

[6] C. H. Booth, E. D. Bauer, A. D. Bianchi, F. Ronning, J. D. Thompson, J. L. Sarrao, J. Y. Cho, J. Y. Chan, C. Capan, and Z. Fisk, Phys. Rev. B **79**, 144519 (2009).

[7] E. Stern, P. Livins, and Z. Zhang, Phys. Rev B **43**, 8850 (1991).