Pair-distribution function analysis of the structural valence transition in $Cp^*_2Yb(4,4'\text{-}Me_2\text{-bipy})$

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Abstract. The $Cp^*_2Yb(L)$ class of compounds, where Cp^*=pentamethylcyclopentadienyl = C_5Me_5 and L is either a 1,4-diazabutadiene or bipy = 2,2′-bipyridine related ligand, have provided excellent analogies to the Kondo state on the nanoscale. $Cp^*_2Yb(4,4'\text{-}Me_2\text{-bipy})$ furthers this analogy by demonstrating a valence transition as the sample is cooled below 200 K. Here, pair-distribution function (PDF) analysis of x-ray powder diffraction data demonstrate that the $Cp^*_2Yb(4,4'\text{-}Me_2\text{-bipy})$ molecule is virtually unchanged through the valence transition. However, the molecule's stacking arrangement is altered through the valence transition.

In 1989, Neumann and Fulde [1] conjectured that a molecular analogue to the Kondo effect occurs in certain Ce- and Yb-based organometallic molecules. The theory of such effects (see Ref. [2] and references therein) indicates the traditional role of many-body interactions in Kondo systems is reduced to, essentially, including specific configuration interactions (CIs) to the single-electron theory using, for instance, the Complete Active Space Self-Consistent Field (CASSCF) approach. According to such methods, intermediate valence (IV) occurs in the ground state when open and closed shell singlet configurations mix, thereby lowering the combined open-shell singlet state below the triplet state [2]. For example, CASSCF calculations in $Cp^*_2Yb(bipy)$ indicate that the open-shell $f^{13}_{\uparrow}\pi^{*1}_{\downarrow}$ configuration interacts with, primarily, the closed-shell $f^{14}_{\uparrow,\downarrow}\pi^{*0}$ configuration to form an open-shell singlet below the triplet configuration [2], where Cp^* = pentamethylcyclopentadienyl = C_5Me_5, Me = methyl = CH_3, and bipy = 2,2′-bipyridine = $(C_5H_4N)_2$. This result is in contrast to lower-order calculations from Density Functional Theory (DFT) that indicate a triplet $f^{13}_{\uparrow}\pi^{*1}_{\uparrow}$ in the ground state in $Cp^*_2Yb(bipy)$ [2]. The IV ground state in the CASSCF calculation has an f-hole occupancy of about $n_f = 0.8$, consistent with Yb $L_{\rm III}$-edge x-ray absorption near-edge structure (XANES) experiments [2, 3]. In analogy to the Kondo effect, the singlet interactions are made possible both by symmetry and the more extended nature of the f-orbital in Yb and the π^* orbital in the aromatic bipy ligand, which plays the role of a quantum-confined metallic band in an intermetallic nanoparticle [4, 5]. The Kondo analogy has also worked very well for guiding many other aspects of the research

[2, 6]. These studies therefore have broad implications for fields such as solid-state physics, materials science, and organometallic chemistry, and may have future implications for nanoscale devices, which have spurred recent interest in understanding the Kondo effect on the nanoscale.

The Me-substituted $Cp^*_2Yb(bipy)$ complexes demonstrate one of the more dramatic differences between bulk and nanoscale Kondo behavior in that the first excited state need not be a triplet. However, the $Cp^*_2Yb(4,4'\text{-}Me_2\text{-bipy})$ molecule (Fig. 1) also undergoes a first-order +10% valence transition when cooling below 200 K [3, 7]. Here, we address the low temperature structure of the molecule using the pair-distribution function (PDF) technique to determine whether the molecule is isomorphic through the transition, in analogy to the isomorphic valence transition in $YbInCu_4$ [8] and the α-γ transition in elemental cerium [9, 10].

Synthesis details for the $Cp^*_2Yb(4,4'\text{-}Me_2\text{-bipy})$ complex are reported in Ref. [7]. In preparation for the x-ray scattering experiments, the air-sensitive single crystals were powdered in an inert atmosphere glove box. The finely powdered sample was packed into a 5 mm diameter hole in a 1 mm thick aluminum plate, and then sealed between aluminized mylar windows. The sample was then shipped to the Advanced Photon Source (APS) at Argonne National Laboratory in a nitrogen-filled jar. The sample was removed from the jar and then placed into a displex just prior to measurement at the 6ID-D beamline of MuCAT. Measurements were made at many temperatures between 50 K and 300 K. X-ray powder-diffraction data were collected using the rapid acquisition pair distribution function method [11]. The experiments were conducted using synchrotron x-rays with a wavelength of 0.12634 Å using a circular image plate camera (Mar345) 345 mm in diameter. The camera was mounted orthogonally to the beam path with a sample-to-detector distance of 240.464 mm. Other details of data collection and analysis are as described previously [12]. The corrected total scattering structure function, $S(Q)$, was obtained using standard corrections [13] with the program PDFGETX2 [14]. Finally, the PDF was obtained by Fourier transformation of $S(Q)$ according to $G(r) = \frac{2}{\pi}\int_0^{Q\mathrm{max}} Q[S(Q)-1]\sin(Qr)dQ$, where Q is the magnitude of the scattering vector. A $Q_{\mathrm{max}} = 15.0$ Å^{-1} was used. Fig. 2 shows $G(r)$ for several selected temperatures. Fits are performed using the PDFGUI analysis package [15].

From room temperature to just above the transition, the changes in the PDF data from temperature to temperature are small, consistent with thermally-induced variations. At the transition, a clearly resolved change occurs, as illustrated in Fig. 2, where in the 10 K above the transition the data overlap well (Fig. 2a), yet in the next 10 K (Fig. 2b), the changes in the local structure are easily discernible, especially starting at about 9 Å. However, below 9 Å, the local structure is nearly unaffected. Note that the intermolecular Yb-Yb distance is about 9 Å in these crystals, while the longest intramolecular distances are about 11 Å and the shortest intermolecular distances ar about 4 Å. We can therefore conclude simply from these data and with no fitting that the main structural change occurs in the molecular stacking.

Two questions remain unanswered: (1) can we resolve an actual change in the molecule's morphology, and (2) what is the change in the packing arrangement? To answer these questions,

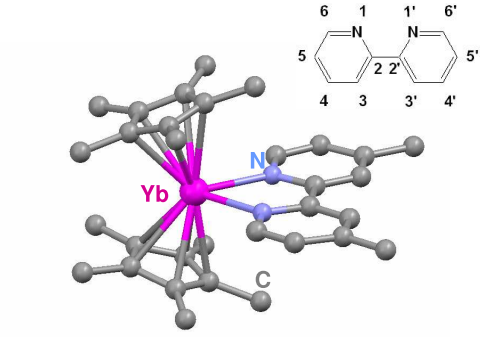

Figure 1. The $Cp^*_2Yb(4,4'\text{-}Me_2\text{-bipy})$ molecule and the position numbering scheme for bipyridine. The $Cp^*_2Yb(4,4'\text{-}Me_2\text{-bipy})$ molecule crystallizes into the $P2_1/c$ space group above 200 K.

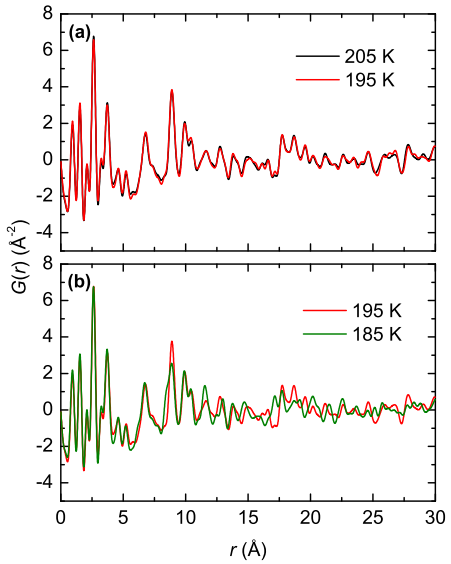

Figure 2. The PDF at two temperatures 10 K apart (a) above and (b) through the transition.

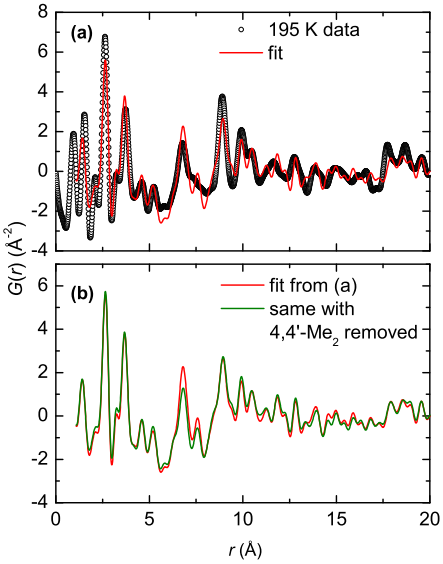

Figure 3. (a) Data and fit to the single crystal structure. (b) Fit from (a) with and without the 4,4′-Me_2 removed.

a detailed fit should be performed. Unfortunately, attempts to fit structural models to the low temperature data, even including a wide variety of constraints, did not produce satisfactory results. It is possible to fit the high-temperature-phase data to the nominal crystal structure [7] by only allowing a single mean-squared displacement parameter u^2 for each atomic species, the three lattice parameters, a scale factor, and a damping factor to vary. Such a fit is shown in Fig. 3a. Clearly, the high-temperature-phase data represent the structure from the much more accurate single-crystal diffraction results well.

Fortunately, we can demonstrate the sensitivity of the data (if not the fit) to possible changes in the molecule's morphology through the transition using these fit results. A relatively small change in the morphology, at least as far as the x-ray scattering is concerned, would be to eliminate a C atom from the molecule. In Fig. 3b, the effect of removing the Me carbons at the 4,4′ sites on the bipy is illustrated by taking the fit result shown in Fig. 3a and simply deleting these Me groups. The $G(r)$ is nearly unaffected, except at the Yb-Me distance of about 7 Å. This example, of course, illustrates the change from two carbon atoms; in any case, there is no change observed on this scale below 9 Å in the data spanning the phase transition (Fig. 2b). Consequently, we conclude that the molecule's morphology is unaffected by the valence transition. Changes in the bond lengths due to the change in valence can be observed in these data, but are more accurately presented in fits to extended x-ray absorption fine-structure (EXAFS) data described elsewhere [3].

Although the molecule has the same morphology in the high and low temperature phases, it is possible, if not likely, that the change in packing produces a different crystal symmetry than $P2_1/c$. A likely alternative is a *Pbca* structure, such as occurs for $Cp^*_2Yb(bipy)$, $Cp^*_2Yb(5,5'\text{-}Me_2\text{-bipy})$, and others [3]. As mentioned above, fits using the *Pbca* structure are inconclusive. Attempts to fit these data using Rietveld refinement also failed to produce a unique answer, since the data can be fit using either space group if enough parameters are allowed to vary.

The molecule itself is therefore isomorphic through the valence transition, but based on the changes in packing, the most likely conclusion regarding the crystal structure is that it is not isomorphic through the transition. It remains unclear whether the valence transition is driven

by the Kondo effect or not. As the low-temperature structure may well be in the *Pbca* space group, the change in structure could be driven by steric effects. The observed valence transition would then be an indication that intermolecular, Van der Waals interactions are important in these molecules, although we note that CASSCF calculations on isolated molecules obtain an n_f that is generally well within 10% of the measured values. The changing intermolecular interaction could, in any case, have an effect on the overall π^* charge density, and so the change in valence could be a manifestation of a charge-density induced change to the f-orbital coupling. This scenario would be very similar to one suggested for $YbInCu_4$, except that in that case the change in density is thought to be due to a sharp band edge near the Fermi level [16].

Another possibility is that intermolecular effects are insignificant, and the valence transition is somehow analogous to that which occurs in the α-γ transition in cerium [9, 10]. Of course, even here, there remains a controversy regarding the basic physics underlying the volume collapes in elemental cerium. The two general possibilities at present are the so-called Kondo Volume Collapse model (KVM) [17], and the Mott transition model [18]. With regard to the role of the Kondo effect, the KVM achieves a volume change by exploiting nonlinearities in the pressure/volume relationship in the Kondo impurity model [17]. Although the possibility of a Mott transition exists in cerium, it is unlikely that there is some local equivalent possiblity in $Cp^*_2Yb(4,4'\text{-}Me_2\text{-bipy})$ given the observed IV in both the high temperature and the low temperature phases. Therefore, CI-induced IV behavior appears to play an important role in generating the valence transition in $Cp^*_2Yb(4,4'\text{-}Me_2\text{-bipy})$, either through structural-induced changes in charge density or through a KVM-like mechanism.

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References

[1] Neumann C S and Fulde P 1989 *Z. Phys. B* **74** 277
[2] Booth C H, Walter M D, Kazhdan D, Hu Y J, Lukens W W, Bauer E D, Maron L, Eisenstein O and Andersen R A 2009 *J. Am. Chem. Soc.* **131** 6480
[3] Booth C H *et al.* Intermediate-valence tautomerism in decamethylytterbocene complexes of methyl-substituted bipyridines (*Preprint* `http://lise.lbl.gov/chbooth/papers/Me_bipy.pdf`)
[4] Thimm W B, Kroha J and von Delft J 1999 *Phys. Rev. Lett.* **82** 2143
[5] Schlottmann P 2002 *Phys. Rev. B* **65** 024420
[6] Booth C H, Walter M D, Daniel M, Lukens W W and Andersen R A 2005 *Phys. Rev. Lett.* **95** 267202
[7] Walter M D, Berg D J and Andersen R A 2006 *Organometallics* **25** 3228
[8] Felner I and Nowik I 1986 *Phys. Rev. B* **33** 617
[9] Lawrence J M, Riseborough R S and Parks R D 1981 *Rep. Prog. Phys.* **44** 1
[10] McMahan A K, Huscroft C, Scalettar R T and Pollock E L 1998 *J. Comput.-Aid. Mater. Des.* **5** 131
[11] Chupas P J, Qiu X, Hanson J C, Lee P L, Grey C P and Billinge S J L 2003 *J. Appl. Crystallogr.* **36** 1342
[12] Lin H, Božin E S, Billinge S J L, Androulakis J, Malliakas C D, Lin C H and Kanatzidis M G 2009 *Phys. Rev. B* **80** 045204
[13] Egami T and S J L Billinge 2003 *Underneath the Bragg peaks: Structural analysis of complex materials* (Amsterdam: Pergamon)
[14] Qiu X, Thompson J W and Billinge S J L 2004 *J. Appl. Crystallogr.* **37** 678
[15] Farrow C L, Juhás P, Liu J W, Bryndin D, Božin E S, Bloch J, Proffen T and Billinge S J L 2007 *J. Phys.: Condens. Matter* **19** 335219
[16] Figueroa E, Lawrence J M, Sarrao J L, Fisk Z, Hundley M F and Thompson J D 1998 *Solid State Commun.* **106** 347
[17] Allen J W and Martin R M 1982 *Phys. Rev. Lett.* **49** 1106
[18] Johansson B 1974 *Phil. Mag.* **30** 469

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