Supplementary Material (ESI) for Chemical Communications

Refinement Details for Pd K-edge EXAFS data for Ba_2PdO_3, $Ba_{0.5}Sr_{1.5}PdO_3$ and $Ba_{0.5}Sr_{1.5}PdO_2F_2$.

All of the refinements were carried out using EXCURV98.[1] Although it was possible to use the literature XRD bond lengths[2] for Ba_2PdO_3 and just refine the Debye-Waller factors to give a very good fit, this is not a practible approach when refinement of the bond lengths is required (e.g. the mixed Sr-Ba compounds or the fluorinated materials) as the difference between the two Pd-O bond lengths in Ba_2PdO_3 is less than 0.02 Å. Therefore, the first Pd-O shell was always refined as a single distance. In all cases, the coordination number was fixed at 4, and this was verified by mapping the R factor against the coordination number and the Debye-Waller factor. This gave the best fit to around 3.5 in all cases. For the other shells, the appropriate values were used. In order to reduce the number of refined parameters the Debye-Waller factor for the Pd-Ba and Pd-Sr shells was constrained to have the same value. In the chain structures, only half of the Pd-Pd shell at *ca*. 4 Å is involved in multiple scattering through an intervening O atom, whereas in the sheet structure all of the Pd-Pd shells are involved in multiple scattering. Whilst the full cluster approach to multiple scattering is the best, in this case there are a larger number of shells, and it was decided to use the "units" version of multiple scattering within EXCURV98 to model the multiple scattering. For the chain structures this entails using a split Pd-O first shell but constraining the bond lengths and Debye-Waller factors to be identical for both pairs. Likewise, there are two Pd-Pd shells defined at *ca*. 4 Å, but both were constrained to have identical Debye-Waller factors. As the Pd-Pd shell involved in the multiple scattering has the greatest intensity in both the EXAFS and the FT this will dominate the spectrum. Using the reduced χ^2 approach a preference for two Pd-Pd shells was shown in the data for $Ba_{0.5}Sr_{1.5}PdO_3$ but not for $Ba_{0.5}Sr_{1.5}PdO_2F_2$. This is interpreted to indicate a change from a chain to a sheet structure.

The number of refined parameters was always kept below the number of independent points ($2\Delta r\Delta k/\pi$). The details of the refinements are given below, and the EXAFS and FTs are shown on the following page.

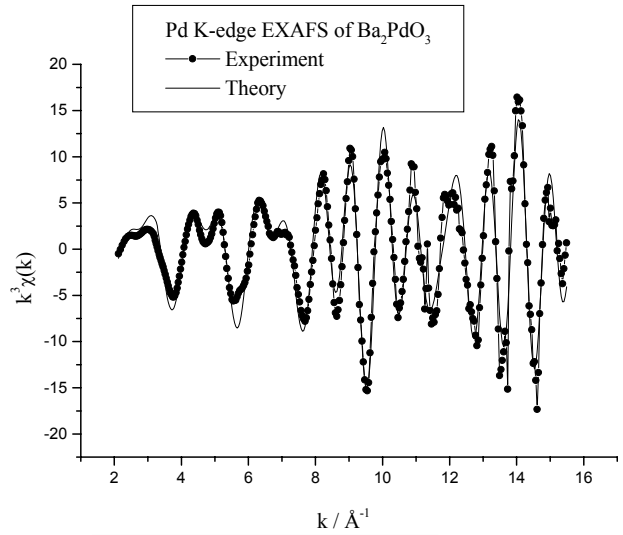
Refined EXAFS parameters for Ba_2PdO_3, $Ba_{0.5}Sr_{1.5}PdO_3$ and $Ba_{0.5}Sr_{1.5}PdO_2F_2$ [(a)]

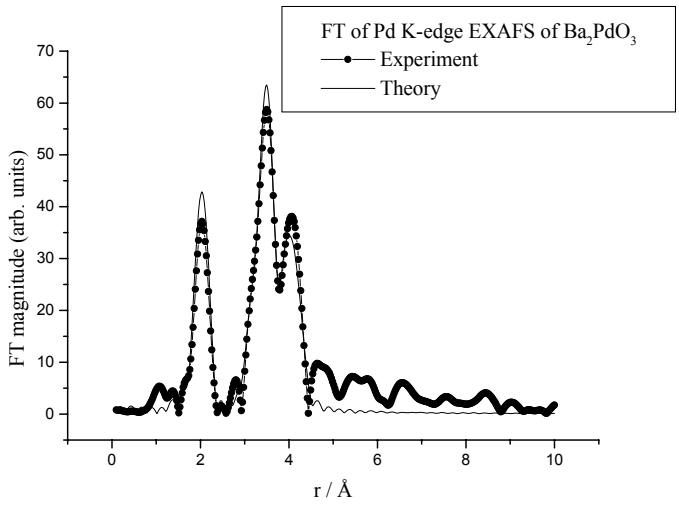
	Pd-O r[(d)] /Å	$2\sigma^{2}$ [(e)] /Å^2	Pd-Sr r /Å	Pd-Ba r /Å	$2\sigma^2$ /Å^2	Pd-Pd r /Å	$2\sigma^2$ /Å^2	E_f[(f)] /V	R[(g)]
Ba_2PdO_3[(b)] (XRD)	2 x 2.026 2 x 2.040			8 x 3.411		2 x 3.836 2 x 4.08			
Ba_2PdO_3[(c)]	4 x 2.057(6)	0.0044(10)		8 x 3.404(4)	0.0098(4)	2 x 3.981(25) 2 x 4.072(4)	0.0046(18)	-1.73(88)	32.5
$Ba_{0.5}Sr_{1.5}PdO_3$[(c)]	4 x 2.025(4)	0.0055(7)	6 x 3.285(4)	2 x 3.338(15)	0.0120(11)	2 x 3.916(23) 2 x 3.991(6)	0.0046(13)	2.48(82)	26.6
$Ba_{0.5}Sr_{1.5}PdO_2F_2$[(c)]	4 x 2.033(5)	0.0055(7)	6 x 3.375(13)	2 x 3.402(44)	0.0186(25)	4 x 4.085(4)	0.0070(5)	2.61(87)	30.8

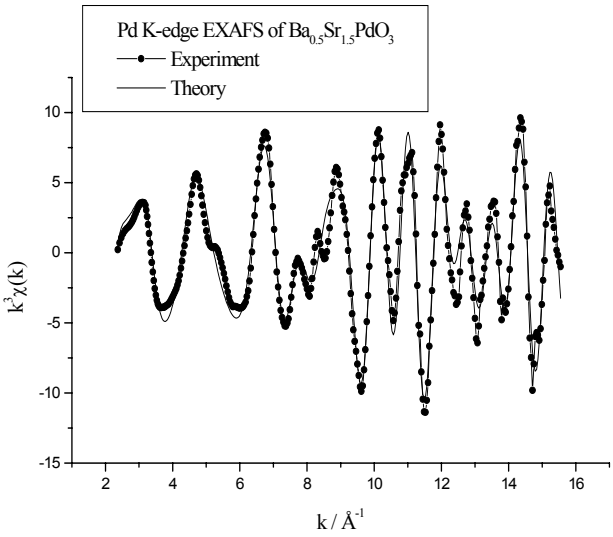
[(a)] Standard deviation in parentheses; [(b)] ref. 2; [(c)] this work; [(d)] given as *occupation number x distance*, the estimated systematic errors in EXAFS bond lengths are ± 1 % for well-defined co-ordination shells;[(e)] $2\sigma^2$ is the Debye-Waller factor; [(f)] E_f is a single refined parameter to reflect differences in the theoretical and experimental Fermi levels;

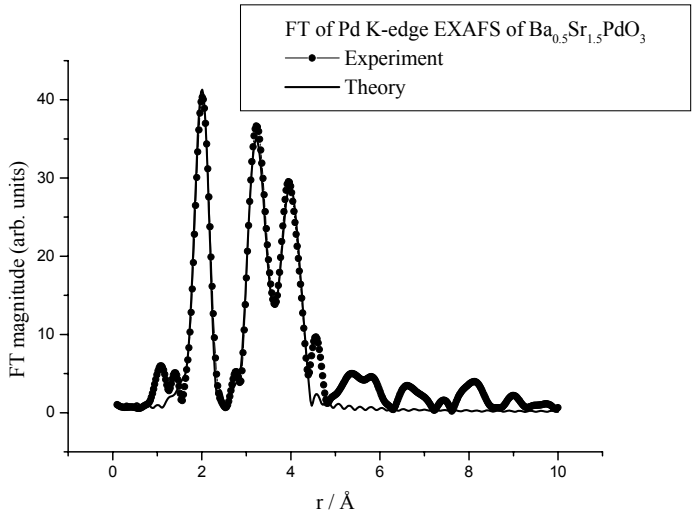
[(g)] $R = \left[\int \left| \chi^T - \chi^E \right| k^3 dk \Big/ \int \left| \chi^E \right| k^3 dk \right] x100\% \cdot$

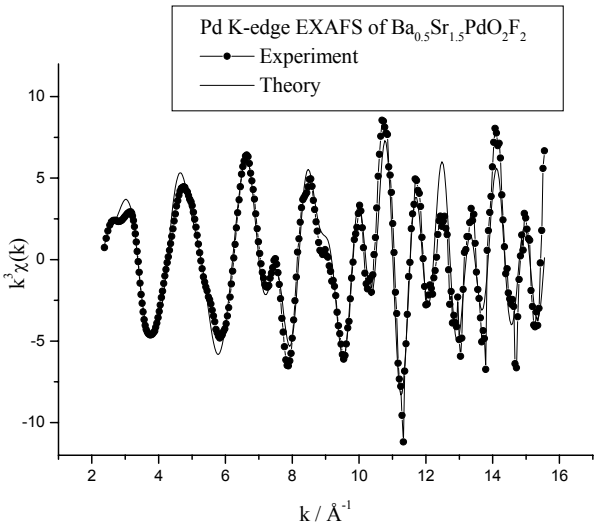
[1] EXCURV98 N. Binsted, EXCURV98, CCLRC Daresbury Laboratory Computer Program, (1998).
[2] Y. Laligant, A. LeBail, G. Ferey, M. Hervieu, B. Raveau, A. Wilkinson and A.K. Cheetham, *Eur. J. Solid State Inorg. Chem.,* 1998, **25**, 237

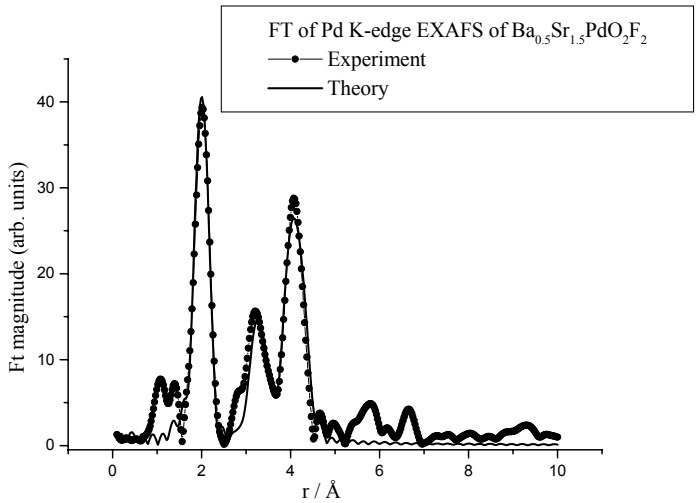












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$Ba_2PdO_2F_2$

a = 4.13979(32)Å; *b* = 4.13979(32)Å; *c* = 14.04595(134)Å
α = 90.0000(0)°; β = 90.0000(0)°; γ = 90.0000(0)°

HISTOGRAM	R_p	R_{wp}	R_{exp}	GOF	R_{BRAGG}
1	4.48	5.80	3.86	2.25	2.45

ATOMS	x	y	z	B_{iso}	N
Ba	0.0000(0)	0.0000(0)	0.3652(1)	1.83(6)	1.000
Pd	0.0000(0)	0.0000(0)	0.0000(0)	1.24(7)	0.500
O	0.0000(0)	0.5000(0)	0.0000(0)	1.00(0)	1.000
F	0.0000(0)	0.5000(0)	0.2500(0)	1.00(0)	1.000

ATOM1	ATOM2	DISTANCE	ERROR
Ba	Ba	4.1398	0.0003
Ba	Ba	3.7879	0.0004
Ba	Ba	4.3629	0.0004

ATOM1	ATOM2	DISTANCE	ERROR
Ba	Pd	3.4865	0.0003

ATOM1	ATOM2	DISTANCE	ERROR
Ba	O	2.8056	0.0002

ATOM1	ATOM2	DISTANCE	ERROR
Ba	F	2.6270	0.0002

ATOM1	ATOM2	DISTANCE	ERROR
Pd	O	2.0699	0.0002

ATOM1	ATOM2	DISTANCE	ERROR
Pd	F	4.0762	0.0004

ATOM1	ATOM2	DISTANCE	ERROR
O	O	2.9273	0.0002

ATOM1	ATOM2	DISTANCE	ERROR
O	F	3.5115	0.0003

$Ba_{0.5}Sr_{1.5}PdO_2F_2$

a = 4.07008(55) Å *b* = 4.07008(55) Å *c* = 13.10725(264) Å
α = 90.0000(0)˚ β = 90.0000(0)˚ γ = 90.0000(0)˚

HISTOGRAM	Rp	Rwp	Rexp	GOF	R_{BRAGG}
1	5.88	7.66	5.20	2.17	1.56

ATOM	x	y	z	B_{iso}	N
Ba	0.0000(0)	0.0000(0)	0.3627(1)	1.65(9)	0.250
Sr	0.0000(0)	0.0000(0)	0.3627(1)	1.65(9)	0.750
Pd	0.0000(0)	0.0000(0)	0.0000(0)	2.85(10)	0.500
O	0.0000(0)	0.5000(0)	0.0000(0)	1.00(0)	1.000
F	0.0000(0)	0.5000(0)	0.2500(0)	1.00(0)	1.000

ATOM1	ATOM2	DISTANCE	ERROR
Ba/Sr	Ba/Sr	4.0701	0.0005
Ba/Sr	Ba/Sr	3.5995	0.0007
Ba/Sr	Ba/Sr	4.1243	0.0006

ATOM1	ATOM2	DISTANCE	ERROR
Ba/Sr	PD	3.3944	0.0005

ATOM1	ATOM2	DISTANCE	ERROR
Ba/Sr	O	2.7167	0.0004

ATOM1	ATOM2	DISTANCE	ERROR
Ba/Sr	F	2.5146	0.0004

ATOM1	ATOM2	DISTANCE	ERROR
PD	O	2.0350	0.0003

ATOM1	ATOM2	DISTANCE	ERROR
PD	F	3.8573	0.0007

ATOM1	ATOM2	DISTANCE	ERROR
O	O	2.8780	0.0004

ATOM1	ATOM2	DISTANCE	ERROR
O	F	3.2768	0.0007
O	F	4.3612	0.0007

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