Supporting Information

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Temperature Induced Valence Phase Transition in Intermediate-Valent $YbPd_2Al_3$

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Single-crystal X-ray diffraction

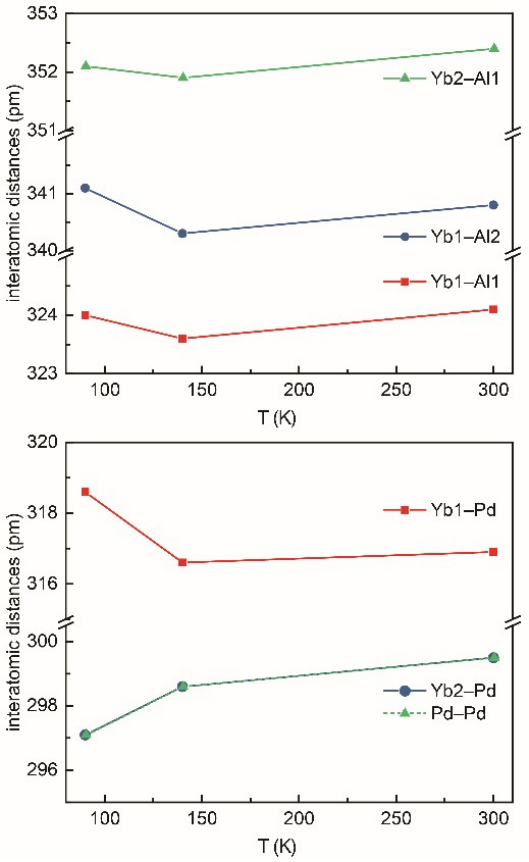

Figure S1. Temperature dependence of the interatomic Yb–Al, Yb–Pd and Pd–Pd distances obtained by single-crystal X-ray diffraction experiments at 90, 140 and 300 K.

Field-dependent heat capacity

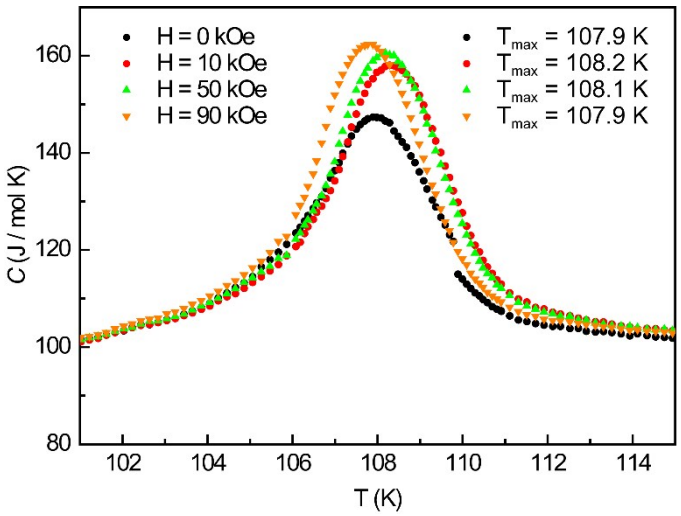

Figure S2. Heat capacity of $YbPd_2Al_3$ at different applied magnetic fields (H = 0, 10, 50, 90 kOe). The peak temperatures of the four different measurements are given.

field dependent magnetization studies

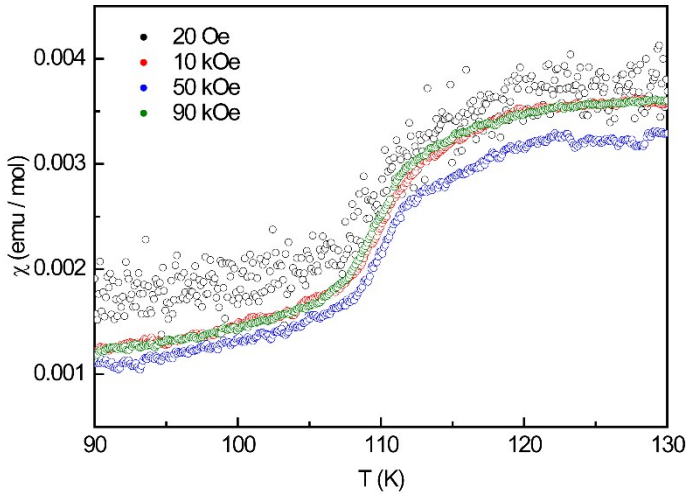

Figure S3. Temperature dependence of the magnetic susceptibility around the valence phase transition, measured at 20 Oe (black), 10 kOe (red), 50 kOe (blue) and 90 kOe (green).

ac-susceptibility investigations

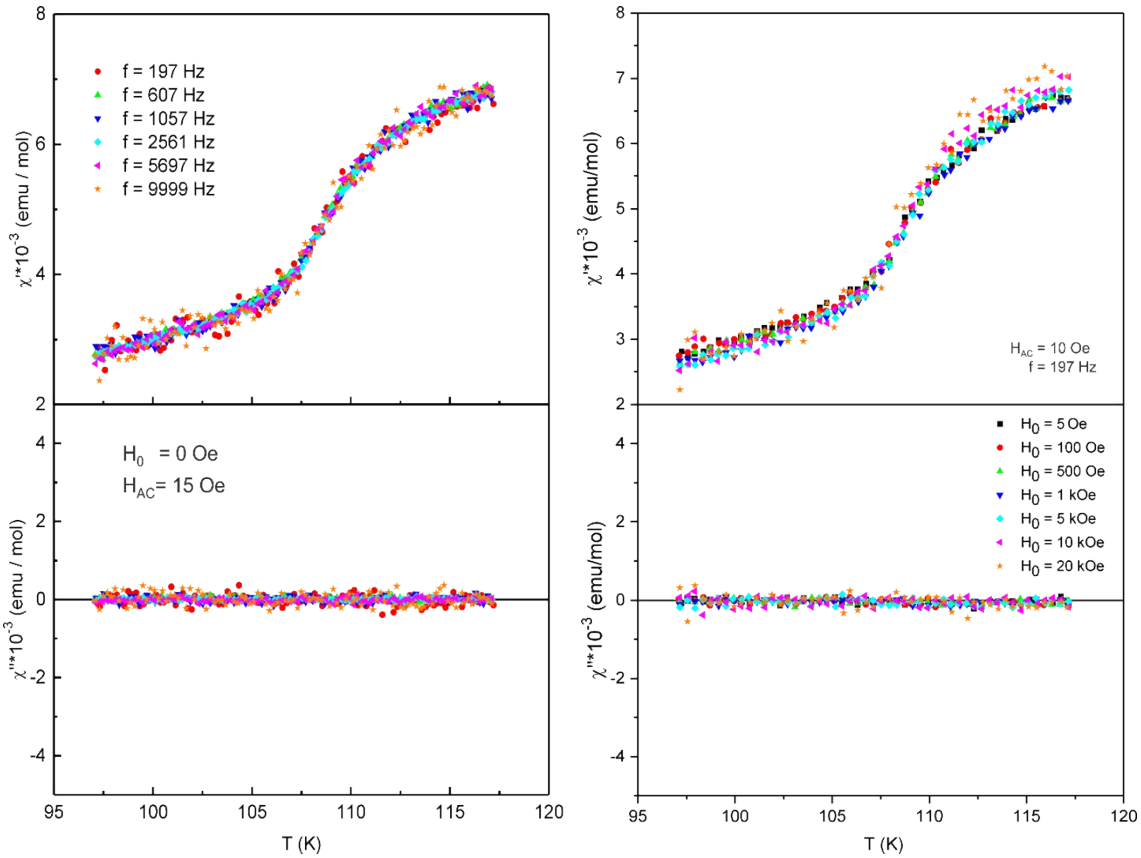

Figure S4. Magnetic properties of $YbPd_2Al_3$ (*ac*-MS susceptibility): (left) temperature dependence of the magnetic in-phase $\chi'(\omega,T)$ and out-of-phase $\chi''(\omega,T)$ susceptibilities measured after zero-field cooling with an internal magnetic field of H_{AC} = 15 Oe and a frequency range of 197 to 9999 Hz. (right) temperature dependence of the magnetic in-phase $\chi'(\omega,T)$ and out-of-phase $\chi''(\omega,T)$ susceptibilities measured after zero-field cooling with increasing temperature at applied external magnetic fields up to 20 kOe and a constant internal field of H_{AC} = 10 Oe and a constant frequency of f = 197 Hz.

dc-susceptibility investigations

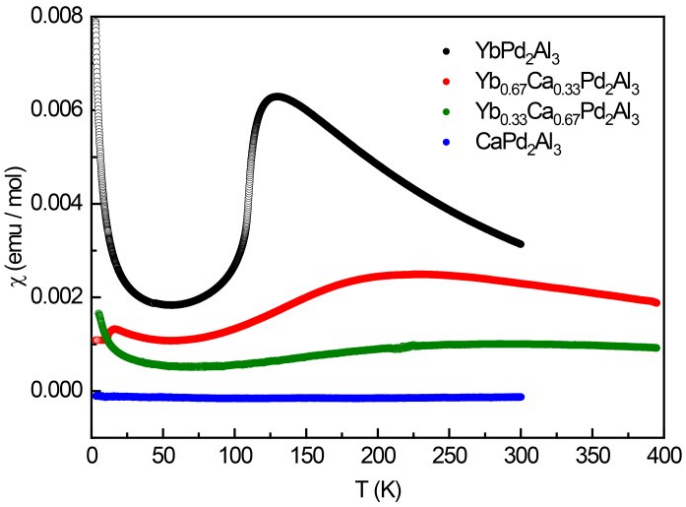

Figure S5. Comparison of the magnetic susceptibilities (χ) of $YbPd_2Al_3$ (black), $Yb_{0.33}Ca_{0.67}Pd_2Al_3$ (red), $Yb_{0.67}Ca_{0.33}Pd_2Al_3$ (green) and $CaPd_2Al_3$ (blue) measured at 10 kOe.

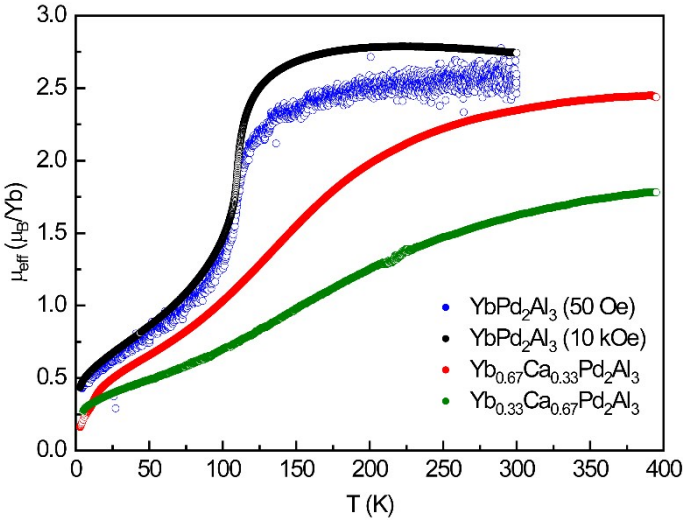

Figure S6. Temperature dependence of the effective magnetic moment per Yb atom of $YbPd_2Al_3$ (black and blue), $Yb_{0.33}Ca_{0.67}Pd_2Al_3$ (red), $Yb_{0.67}Ca_{0.33}Pd_2Al_3$ (green).

X-ray Photoelectron Spectroscopy (XPS)

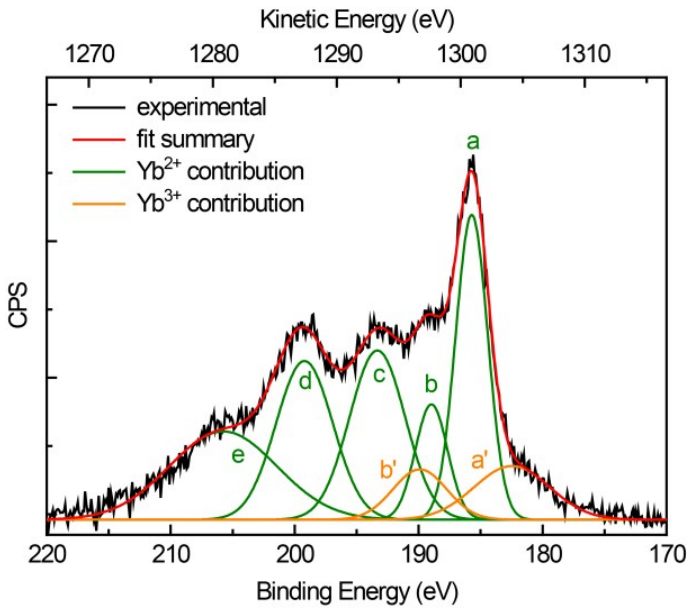

Figure S7. Fit of the X-ray photoemission spectra of the Yb 4*d* lines of $Yb_{0.67}Ca_{0.33}Pd_2Al_3$. The sum is depicted in red. (CPS = counts per second, linear scale).

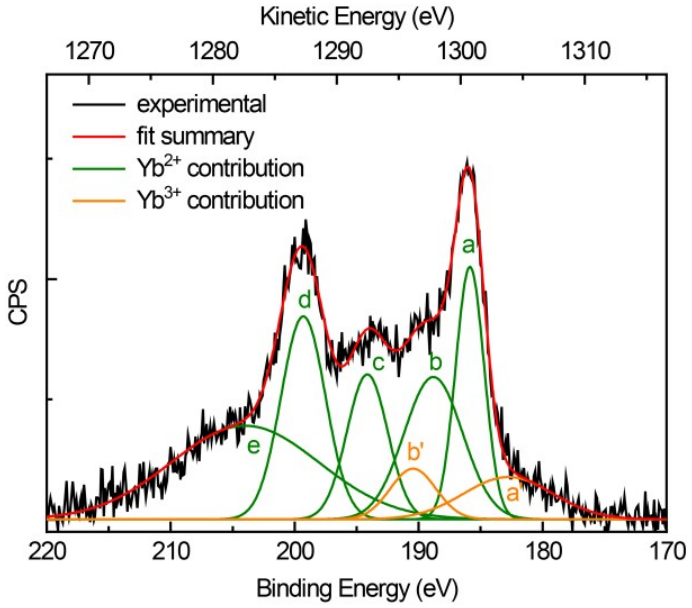

Figure S8. Fit of the X-ray photoemission spectra of the Yb 4*d* lines of $Yb_{0.33}Ca_{0.67}Pd_2Al_3$. The sum is depicted in red. (CPS = counts per second, linear scale).

Table S1. Temperature dependent lattice parameters of $YbPd_2Al_3$, space group *P6/mmm*, $Z = 3$, determined by temperature dependent powder X-ray diffraction. The standard deviations are within ±0.05 pm.

T (K)	*a* (pm)	*c* (pm)	*V* (nm^3)
10	928.08	422.95	0.3155
20	927.96	422.94	0.3154
30	927.94	422.68	0.3152
40	927.69	422.61	0.3150
50	927.70	422.61	0.3150
60	927.86	422.72	0.3152
70	928.14	422.63	0.3153
80	928.23	422.35	0.3152
90	927.99	422.15	0.3148
95	928.03	421.92	0.3147
100	927.94	421.48	0.3143
105	927.97	420.75	0.3138
110	927.99	420.43	0.3136
115	927.98	420.34	0.3135
120	928.06	420.20	0.3134
125	928.03	420.15	0.3134
130	928.15	420.13	0.3134
140	928.20	420.10	0.3134
150	928.23	420.05	0.3134
160	928.40	419.99	0.3135
170	928.49	419.99	0.3136
180	928.56	420.10	0.3137
190	928.68	420.13	0.3138
200	928.74	420.22	0.3139
210	928.84	420.21	0.3140
220	929.06	420.26	0.3141
230	929.16	420.29	0.3142
240	929.36	420.30	0.3144
250	929.43	420.35	0.3145
260	929.55	420.38	0.3146
270	929.52	420.37	0.3145
280	929.61	420.43	0.3146
290	929.57	420.49	0.3147
300	929.64	420.43	0.3147

Table S2. Depository number, lattice parameters *a* and *c* (pm) and the 2*d* and 1*a* site occupancies of the four independent single-crystals from the solid solutions $Yb_{1-x}Ca_xPd_2Al_3$, with the refined compositions of $Yb_{0.68(1)}Ca_{0.32(1)}Pd_2Al_3$ and $Yb_{0.34(1)}Ca_{0.66(1)}Pd_2Al_3$.

CCDC-No.	*a* (pm)	*c* (pm)	Yb1:Ca1 (2*d*)	Yb2:Ca2 (1*a*)
$Yb_{0.68(1)}Ca_{0.32(1)}Pd_2Al_3$				
1875396	930.98(7)	421.40(3)	0.79(1):0.21(1)	0.46(1):0.54(1)
1892597	931.21(7)	421.35(3)	0.80(1):0.20(1)	0.45(1):0.55(1)
1892594	931.10(8)	421.08(3)	0.80(1):0.20(1)	0.46(1):0.54(1)
1892598	931.22(12)	420.90(5)	0.80(1):0.20(1)	0.46(1):0.54(1)
$Yb_{0.34(1)}Ca_{0.66(1)}Pd_2Al_3$				
1868849	933.53(7)	422.66(3)	0.44(1):0.56(1)	0.15(1):0.85(1)
1910744	933.76(7)	422.76(3)	0.44(1):0.56(1)	0.16(1):0.84(1)
1895369	933.21(7)	422.76(3)	0.44(1):0.56(1)	0.16(1):0.84(1)
1895370	933.30(8)	422.76(3)	0.44(1):0.56(1)	0.15(1):0.85(1)

Table S3. Crystal data and structure refinement for $YbPd_2Al_3$ (*P6/mmm*, *Z* = 3), measured at 90, 140 and 300 K.

Compound		$YbPd_2Al_3$	$YbPd_2Al_3$	$YbPd_2Al_3$
Temperature, K		90	140	300
Formula weight, g mol^{-1}			466.8	
Unit cell dimensions, pm			Table 1	
Calculated density, g cm^{-3}		7.38	7.43	7.40
Crystal size, µm^3			25 × 75 × 120	
Absorption correction			numerical	
Absorption coefficient, mm^{-1}		31.0	31.2	31.0
F(000), *e*			603	
θ range for data collection, deg		2.5-33.2	2.5-3.2	2.5-33.7
Range in *hkl*		±14; ±14; ±6	±14; ±14; ±6	–10, +15; ±15; ±6
Total no. of reflections		4589	5089	4478
Independent reflections / R_{int}		283 / 0.031	282 / 0.0401	332 / 0.0282
Reflections with $I > 3\sigma(I)$ / R_σ		276 / 0.0045	277 / 0.0041	324 / 0.0042
Data / parameters		283 / 17	282 / 17	332 / 17
Goodness–of–fit		1.53	1.81	1.62
Final *R* indices [$I > 3\sigma(I)$]	*R* =	0.0157	0.0166	0.0166
	w*R* =	0.0360	0.0422	0.0383
R indices for all data	*R* =	0.0169	0.0177	0.0176
	wR =	0.0366	0.0427	0.0388
Extinction scheme			Lorentzian isotropic[1]	
Extinction coefficient		700(30)	650(30)	890(40)
Largest diff. peak and hole, *e* Å^{-3}		1.28 / –1.50	1.33 / –1.41	1.48 / –2.55

Table S4. Crystal data and structure refinement for $Yb_{0.68(1)}Ca_{0.32(1)}Pd_2Al_3$, $Yb_{0.34(1)}Ca_{0.66(1)}Pd_2Al_3$ and $CaPd_2Al_3$ (*P6/mmm*, $Z = 3$), measured at room temperature.

Compound		$Yb_{0.68(1)}Ca_{0.32(1)}Pd_2Al_3$	$Yb_{0.34(1)}Ca_{0.66(1)}Pd_2Al_3$	$CaPd_2Al_3$
Temperature, K			RT	
Formula weight, g mol^{-1}		424.8	379.0	333.9
Unit cell dimensions, pm			Table 1	
Calculated density, g cm^{-3}		6.69	5.92	5.17
Crystal size, µm^3		40 × 85 × 120	20 × 80 × 100	30 × 35 × 40
Absorption correction			numerical	
Absorption coefficient, mm^{-1}		24.3	17.0	10.0
$F(000)$, *e*		556	504	453
θ range for data collection, deg		2.5-33.3	2.5-33.3	2.5-33.3
Range in *hkl*		–14, +13; ±14; ±6	±14; ±14; ±6	±14; ±14; –6, +5
Total no. of reflections		4800	3732	5818
Independent reflections / R_{int}		284 / 0.0258	287 / 0.0489	288 / 0.022
Reflections with $I > 3\sigma(I)$ / R_σ		248 / 0.0064	241 / 0.0074	258 / 0.0038
Data / parameters		284 / 19	287 / 19	288 / 17
Goodness–of–fit		0.84	1.44	0.83
Final *R* indices [$I > 3\sigma(I)$]	R =	0.0084	0.0165	0.0069
	wR =	0.0206	0.0367	0.0186
R indices for all data	R =	0.0124	0.0208	0.0098
	wR =	0.0223	0.0367	0.0200
Extinction scheme			Lorentzian isotropic[1]	
Extinction coefficient		464(19)	390(30)	750(30)
Largest diff. peak and hole, *e* Å^{-3}		0.39 / –0.39	1.05 / –0.86	0.45 / –0.41

Table S5. Atomic positions and equivalent isotropic displacement parameters (pm^2) of $YbPd_2Al_3$ (*P6/mmm, Z = 3*), measured at 90, 140 and 300 K, and those of $Yb_{0.68(1)}Ca_{0.32(1)}Pd_2Al_3$, $Yb_{0.34(1)}Ca_{0.66(1)}Pd_2Al_3$ and $CaPd_2Al_3$ measured at room temperature, refined from single-crystal X-ray diffraction experiments.

Atom	Wyckoff site	*x*	*y*	*z*	U_{eq}
$YbPd_2Al_3$, 90(2) K					
Yb1	2*d*	1/3	2/3	1/2	112(1)
Yb2	1*a*	0	0	0	123(1)
Pd	6*l*	0.18485(2)	2*x*	0	109(1)
Al1	6*k*	0.30365(15)	0	1/2	121(4)
Al2	3*f*	1/2	0	0	124(5)
$YbPd_2Al_3$, 140(2) K					
Yb1	2*d*	1/3	2/3	1/2	122(1)
Yb2	1*a*	0	0	0	137(1)
Pd	6*l*	0.18577(2)	2*x*	0	117(2)
Al1	6*k*	0.30443(18)	0	1/2	129(4)
Al2	3*f*	1/2	0	0	131(6)
$YbPd_2Al_3$, 300(2) K					
Yb1	2*d*	1/3	2/3	1/2	157(1)
Yb2	1*a*	0	0	0	185(1)
Pd	6*l*	0.185995(19)	2*x*	0	146(1)
Al1	6*k*	0.30440(15)	0	1/2	161(3)
Al2	3*f*	1/2	0	0	160(5)
$Yb_{0.68(1)}Ca_{0.32(1)}Pd_2Al_3$, RT					
Yb/Ca1[a]	2*d*	1/3	2/3	1/2	85(1)
Yb/Ca2[a]	1*a*	0	0	0	111(2)
Pd	6*l*	0.185280(13)	2*x*	0	73(1)
Al1	6*k*	0.30395(10)	0	1/2	86(2)
Al2	3*f*	1/2	0	0	89(4)
$Yb_{0.34(1)}Ca_{0.66(1)}Pd_2Al_3$, RT					
Yb/Ca1[b]	2*d*	1/3	2/3	1/2	92(2)
Yb/Ca2[b]	1*a*	0	0	0	112(4)
d	6*l*	0.18431(2)	2*x*	0	79(1)
Al1	6*k*	0.30310(16)	0	1/2	94(4)
Al2	3*f*	1/2	0	0	93(6)
$CaPd_2Al_3$, RT					
Yb1	2*d*	1/3	2/3	1/2	84(1)
Yb2	1*a*	0	0	0	104(2)
Pd	6*l*	0.183557(7)	2*x*	0	68(1)
Al1	6*k*	0.30197(6)	0	1/2	81(1)
Al2	3*f*	1/2	0	0	78(2)

Refined occupancies: [a] Yb1:Ca1 = 79(1):21(1), Yb2:Ca2 = 46(1):54(1); [b] Yb1:Ca1 = 44(1):56(1), Yb2:Ca2 = 15(1):85(1)

Table S6. Interatomic distances (in pm) of $YbPd_2Al_3$ (*P6/mmm, Z = 3*), measured at 90, 140 and 300 K, and those of $Yb_{0.68(1)}Ca_{0.32(1)}Pd_2Al_3$, $Yb_{0.34(1)}Ca_{0.66(1)}Pd_2Al_3$ and $CaPd_2Al_3$ measured at room temperature, refined from single-crystal X-ray diffraction. Standard deviations are smaller or equal to ±0.3 pm, all distances of the first coordination sphere are given.

$YbPd_2Al_3$, 90(2) K				$YbPd_2Al_3$, 140(2) K				$YbPd_2Al_3$, 300(2) K			
Yb1	6	Pd	318.6	Yb1	6	Pd	316.7	Yb1	6	Pd	316.9
	6	Al1	324.0		6	Al1	323.6		6	Al1	324.1
	6	Al2	341.1		6	Al2	340.3		6	Al2	340.8
Yb2	6	Pd	297.1	Yb2	6	Pd	298.6	Yb2	6	Pd	299.5
	12	Al1	352.1		12	Al1	351.9		12	Al1	352.4
Pd	2	Al2	254.5	Pd	2	Al2	253.9	Pd	2	Al2	254.2
	4	Al1	259.3		4	Al1	258.6		4	Al1	259.1
	1	Yb2	297.1		1	Yb2	298.6		2	Pd	299.5
	2	Pd	297.1		2	Pd	298.6		1	Yb2	299.5
	2	Yb1	318.6		2	Yb1	316.7		2	Yb1	316.9
Al1	4	Pd	259.3	Al1	4	Pd	258.6	Al1	4	Pd	259.1
	2	Al2	278.9		2	Al2	277.4		2	Al2	277.8
	2	Al1	281.8		2	Al1	282.5		2	Al1	283.0
	2	Yb1	324.0		2	Yb1	323.6		2	Yb1	324.1
	2	Yb2	352.1		2	Yb2	351.9		2	Yb2	352.4
	1	Al1	364.4		1	Al1	363.0		1	Al1	363.6
Al2	4	Pd	254.5	Al2	4	Pd	253.9	Al2	4	Pd	254.2
	4	Al1	278.9		4	Al1	277.4		4	Al1	277.8
	4	Yb1	341.1		4	Yb1	340.3		4	Yb1	340.8
$Yb_{0.68(1)}Ca_{0.32(1)}Pd_2Al_3$				$Yb_{0.34(1)}Ca_{0.66(1)}Pd_2Al_3$				$CaPd_2Al_3$			
Yb/Ca1	6	Pd	318.4	Yb/Ca1	6	Pd	320.5	Ca1	6	Pd	322.4
	6	Al1	324.9		6	Al1	326.2		6	Al1	327.8
	6	Al2	341.5		6	Al2	342.5		6	Al2	343.5
Yb/Ca2	6	Pd	298.8	Yb/Ca2	6	Pd	298.0	Ca2	6	Pd	297.7
	12	Al1	352.8		12	Al1	353.2		12	Al1	353.4
Pd	2	Al2	255.1	Pd	2	Al2	256.4	Pd	2	Al2	257.7
	4	Al1	259.4		4	Al1	259.8		4	Al1	260.2
	2	Pd	298.8		2	Pd	298.0		2	Pd	297.7
	1	Yb/Ca2	298.8		1	Yb/Ca2	298.0		1	Ca2	297.7
	2	Yb/Ca1	318.4		2	Yb/Ca1	320.5		2	Ca1	322.4
Al1	4	Pd	259.4	Al1	4	Pd	259.8	Al1	4	Pd	260.2
	2	Al2	278.8		2	Al2	280.1		2	Al2	281.6
	2	Al1	283.0		2	Al1	283.0		2	Al1	282.7
	2	Yb/Ca1	324.9		2	Yb/Ca1	326.2		2	Ca1	327.8
	2	Yb/Ca2	352.8		2	Yb/Ca2	353.2		2	Ca2	353.4
	1	Al1	365.0		1	Al1	367.6		1	Al1	370.8
Al2	4	Pd	255.1	Al2	4	Pd	256.4	Al2	4	Pd	257.7
	4	Al1	278.8		4	Al1	280.1		4	Al1	281.6
	4	Yb/Ca1	341.5		4	Yb/Ca1	342.5		4	Ca1	343.5

References

(1) Becker, P. J.; Coppens, P. *Acta Crystallogr. A* **1974**, *30*, 129.