Supporting Information

Centric and Non-centric $Ca_3Au_{\sim 7.5}Ge_{\sim 3.5}$: Electron-Poor Derivatives of La_3Al_{11}. Syntheses, Structures, and Bonding Analyses

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Table S1 Atomic Coordinates of nonstandard setting (*Pmnn*) for Crystals **3,** $Ca_3Au_{7.50(1)}Ge_{3.50(1)}$, and **4**, $Ca_3Au_{8.01(1)}Ge_{2.99(1)}$, in sequence.

Atom*	Wyck.	Occ. (≠1)	x	y	z
Au1	2a		½	½	0
			½	½	0
Au2	4g		½	0.9969(1)	0.3016(1)
			½	0.9967(1)	0.2988(1)
Au3	4g		½	0.1584(1)	0.1122(1)
			½	0.1595(1)	0.1108(1)
Ge4	4g		½	0.8168(1)	0.1478(1)
			½	0.8170(2)	0.1517(2)
Au5	4g		½	0.6380(1)	0.7605(1)
			½	0.6364(1)	0.7623(1)
M6	4g	0.251/0.749(5)	½	0.6274(1)	0.2229(1)
		0.506/0.496(7)	½	0.6299(1)	0.2218(1)
Ca1	2d		0	0	0
			0	0	0
Ca2	4g		½	0.8108(3)	0.4995(3)
			½	0.8105(4)	0.5018(4)

* M = Au/Ge

Table S2 Anisotropic Displacement Parameters for Crystals **1**, $Ca_3Au_{7.16(6)}Ge_{3.84(6)}$, **2**, and $Ca_3Au_{7.43(5)}Ge_{3.57(5)}$, listed in sequence.

Atom*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M1	0.019(2)	0.025(1)	0.029(1)	0.00000	0.00000	0.00000
	0.0151(7)	0.0140(8)	0.0146(7)	0.00000	0.00000	0.00000
Au2	0.010(2)	0.016(1)	0.039(2)	0.00000	0.00000	0.00000
	0.0113(9)	0.0070(8)	0.027(1)	0.00000	0.00000	0.00000
Au3	0.025(2)	0.019(2)	0.032(1)	0.00000	0.00000	0.00000
	0.021(1)	0.011(1)	0.0221(9)	0.00000	0.00000	0.00000
M4	0.019(1)	0.020(1)	0.030(1)	0.00000	0.00000	-0.0011(7)
	0.0234(8)	0.0141(7)	0.0186(7)	0.00000	0.00000	-0.0063(5)
M5	0.011(3)	0.015(3)	0.028(3)	0.00000	0.00000	0.005(2)
	0.010(2)	0.035(2)	0.046(2)	0.00000	0.00000	0.027(2)
M6	0.010(1)	0.018(1)	0.030(1)	0.00000	0.00000	0.0003(8)
	0.0113(7)	0.0108(7)	0.0155(8)	0.00000	0.00000	-0.0010(5)
M7	0.008(4)	0.021(4)	0.026(3)	0.00000	0.00000	0.001(2)
	0.011(1)	0.021(2)	0.029(2)	0.00000	0.00000	0.006(1)
Ca1	0.026(9)	0.020(6)	0.031(7)	0.00000	0.00000	0.00000
	0.027(4)	0.009(3)	0.016(3)	0.00000	0.00000	0.00000
Ca2	0.013(5)	0.026(5)	0.027(4)	0.00000	0.00000	0.004(5)
	0.015(2)	0.008(2)	0.017(3)	0.00000	0.00000	-0.006(4)

* M = Au/Ge

Table S3 Anisotropic Displacement Parameters for Crystals **3**, $Ca_3Au_{7.50(1)}Ge_{3.50\ (1)}$, and **4**, $Ca_3Au_{8.01(1)}Ge_{2.99(1)}$. *

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Au1	0.0103(4)	0.0218(5)	0.0128(5)	0.0031(3)	0.00000	0.00000
	0.0131(6)	0.0213(8)	0.0199(7)	0.0047(6)	0.00000	0.00000
Au2	0.0166(4)	0.0116(3)	0.0112(3)	0.0018(2)	0.00000	0.00000
	0.0177(5)	0.0078(5)	0.0156(5)	0.0013(4)	0.00000	0.00000
Au3	0.0110(3)	0.0139(3)	0.0195(3)	0.0018(2)	0.00000	0.00000
	0.0106(4)	0.0111(5)	0.0251(5)	0.0020(4)	0.00000	0.00000
Ge4	0.0096(7)	0.0161(8)	0.0076(7)	-0.0032(6)	0.00000	0.00000
	0.010(1)	0.011(1)	0.014(1)	-0.001(1)	0.00000	0.00000
Au5	0.0127(3)	0.0146(3)	0.0079(3)	-0.0013(2)	0.00000	0.00000
	0.0128(4)	0.0135(5)	0.0127(5)	-0.0014(4)	0.00000	0.00000
M6	0.0120(6)	0.0192(7)	0.0085(7)	-0.0001(4)	0.00000	0.00000
	0.0135(8)	0.0170(9)	0.0137(8)	-0.0008(5)	0.00000	0.00000
Ca1	0.014(2)	0.012(2)	0.018(2)	0.001(2)	0.00000	0.00000
	0.016(4)	0.004(3)	0.027(4)	0.003(3)	0.00000	0.00000
Ca2	0.011(2)	0.014(2)	0.011(2)	0.003(1)	0.00000	0.00000
	0.011(2)	0.009(2)	0.016(2)	0.002(2)	0.00000	0.00000

* M = Au/Ge

Table S4 Important Interatomic Distances in crystals **1**, $Ca_3Au_{7.16(6)}Ge_{3.84(6)}$, **2**, $Ca_3Au_{7.43(5)}Ge_{3.57(5)}$, **3**, $Ca_3Au_{7.50(1)}Ge_{3.50\ (1)}$, and **4**, $Ca_3Au_{8.01(1)}Ge_{2.99(1)}$.

1		**2**		**3**		**4**	
Bond*	Dist. (Å)	Bond*	Dist. (Å)	Bond*	Dist. (Å)	Bond*	Dist. (Å)
Ca1—Au4	3.243(7)	Ca1—M4	3.233(4)	Ca1—Au3	3.219(1)	Ca1—Au3	3.238(1)
Ca1—Ge5	3.474(8)	Ca1—M5	3.443(5)	Ca1—Ge4	3.559(1)	Ca1—Ge4	3.585(2)
Ca1—Au6	3.01(2)	Ca1—M6	3.07(1)	Ca1—Au5	3.080(1)	Ca1—Au5	3.066(1)
Ca1—M7	3.19(2)	Ca1—M7	3.14(1)	Ca1—M6	3.133(1)	Ca1—M6	3.141(1)
Ca1—Au2	3.60 (2)	Ca1—Au2	3.64(1)	Ca1—Au2	3.634(1)	Ca1—Au2	3.591(1)
Ca1—Au3	3.75(2)	Ca1—Au3	3.68(1)				
Ca2—Au1	3.326(8)	Ca2—M1	3.328(4)	Ca2—Au1	3.326(3)	Ca2—Au1	3.351(4)
Ca2—Au4	3.152(8)	Ca2—M4	3.162(4)	Ca2—Au3	3.167(3)	Ca2—Au3	3.172(4)
Ca2—Ge5	3.109(8)	Ca2—M5	3.126(5)	Ca2—Ge4	3.115(3)	Ca2—Ge4	3.129(4)
Ca2—Au6	3.254(9)	Ca2—M6	3.236(6)	Ca2—Au5	3.250(2)	Ca2—Au5	3.247(3)
Ca2—Ge7	3.193(9)	Ca2—M7	3.208(6)	Ca2—M6	3.179(2)	Ca2—M6	3.142(3)
Ca2—Au2	3.13(1)	Ca2—Au2	3.111(6)	Ca2—Au2	3.158(3)	Ca2—Au2	3.123(5)
Ca2—Au3	3.10(1)	Ca2—Au3	3.115(6)	Ca2—Au2	3.089(3)	Ca2—Au2	3.173(5)
Ca2—Au4	3.71(1)	Ca2—M4	3.715(8)	Ca2—Au3	3.734(3)	Ca2—Au3	3.681(4)
Ca2—Ge5	3.41(1)	Ca2—M5	3.430(5)	Ca2—Ge4	3.363(3)	Ca2—Ge4	3.308(4)
Ca2—Au6	3.41(1)	Ca2—M6	3.430(7)	Ca2—Au5	3.369(3)	Ca2—Au5	3.371(5)
Ca2—M7	3.49(1)	Ca2—M7	3.464(7)	Ca2—M6	3.576(4)	Ca2—M6	3.566(5)
Au1—Au2	2.909(3)	M1—Au2	2.910(2)	Au1—Au2	2.913(1)	Au1—Au2	2.923(1)
Au1—Au3	2.853(3)	M1—Au3	2.880(2)				
Au1—Au6	2.883(3)	M1—M6	2.870(2)	Au1—Au5	2.920 (1)	Au1—Au5	2.882(1)
Au1—M7	2.764(5)	M1—M7	2.798(3)	Au1—M6	2.709(1)	Au1—M6	2.710(1)
Au2—Au6	2.833(1)	Au2—M6	2.845(1)	Au2—Au5	2.860(1)	Au2—Au5	2.856(1)
Au3—M7	2.815(3)	Au3—M7	2.837(2)	Au2—M6	2.807(1)	Au2—M6	2.843(1)
Au2—Ge5	2.791(5)	Au2—M5	2.787(3)	Au2—Au3	2.788 (1)	Au2—Au3	2.793(1)
Au3—Au4	2.777(3)	Au3—M4	2.764(2)	Au2—Ge4	2.785(2)	Au2—Ge4	2.754(3)
Au4—Ge5	2.523(5)	M4—M5	2.439(3)	Au3—Ge4	2.506(2)	Au3—Ge4	2.499(2)
Au4—M7	2.688(3)	M4—M7	2.681(1)	Au3—M6	2.746(1)	Au3—M6	2.754(1)
Ge5—Au6	2.543(3)	M5—M6	2.573(2)	Ge4—Au5	2.530(1)	Ge4—Au5	2.530(1)
Au4—Au6	2.957(3)	M4—M6	2.951(2)	Au3—Au5	2.938(1)	Au3—Au5	2.956(1)
Ge5—M7	2.592(7)	M5—M7	2.654(4)	Ge4— M6	2.588(2)	Ge4— M6	2.565(3)

*M = Au/Ge

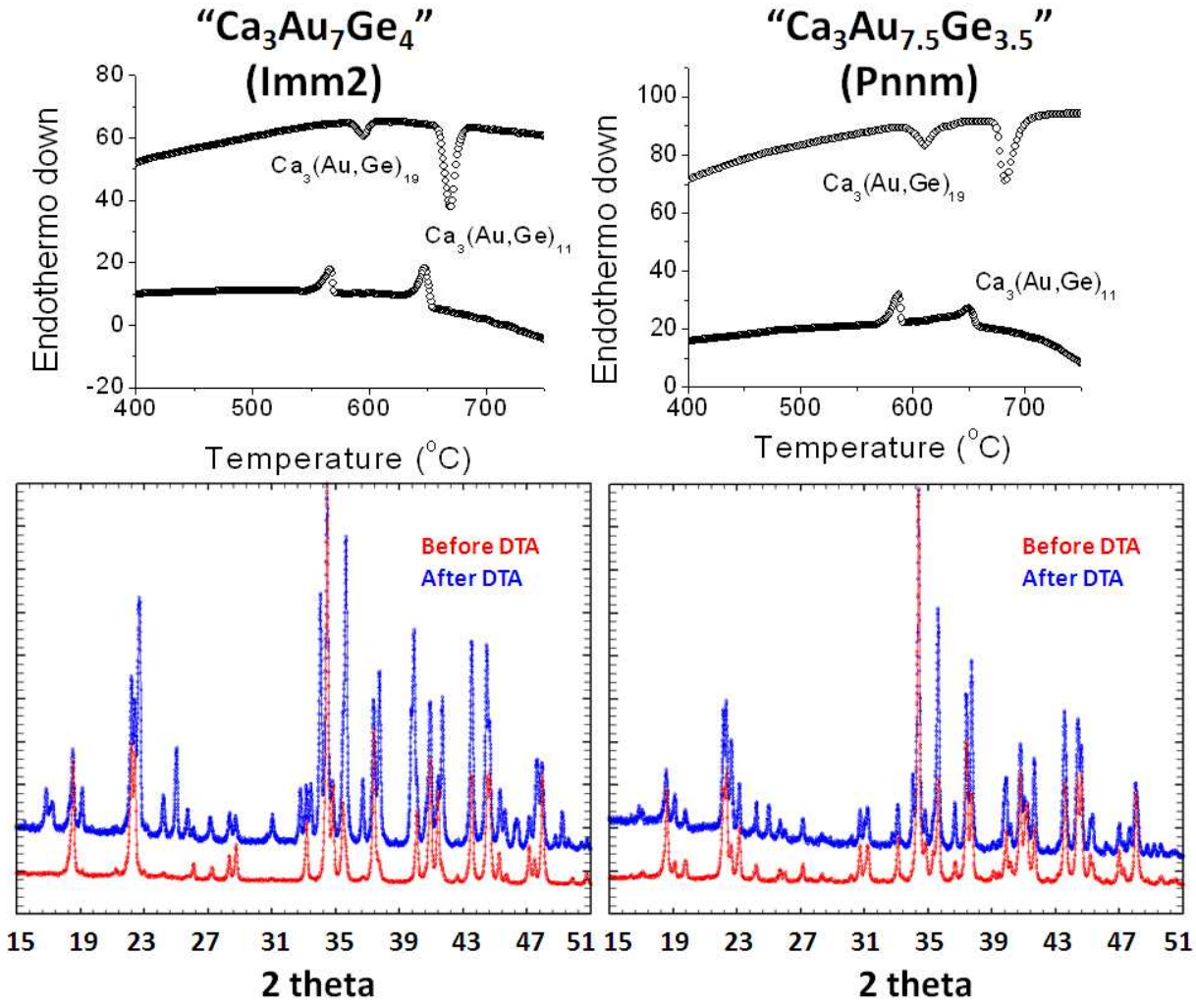

Figure S1. The DTA data for products from nominal $Ca_3Au_7Ge_4$ (left) and $Ca_3Au_{7.5}Ge_{3.5}$ (right), both arc melted samples (Table 1), together with powder patterns before and after DTA measurements. The peaks at about 570 – 600 °C in both DTA patterns occurred from the melting/freezing of the $Ca_3(Au,Ge)_{19}$ (*Im*3) phases,[20] and the second, of the studied $Ca_3(Au, Ge)_{11}$ phases. According to powder patterns, peritectic decompose reactions occurred from $Ca_3(Au, Ge)_{11}$ to $Ca_3(Au, Ge)_{19}$ (*Im*3) and Ca(Au, $Ge)_2$ (*Imm*2) after DTA measurements, see text and Figure 1.

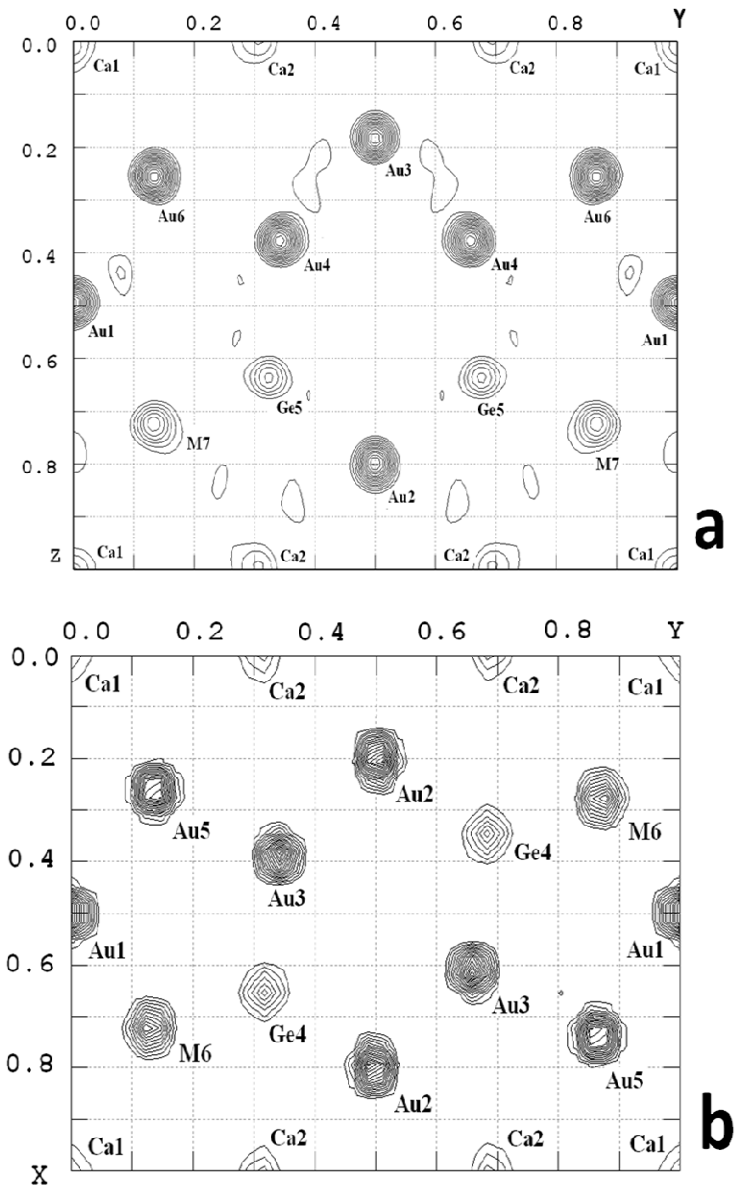

Figure S2. Observed electron density sections for (a) $x = 0$ in $Ca_3Au_{7.16}Ge_{3.84}$ (*Imm*2), and (b) $z = 0$ in $Ca_3Au_{7.50}Ge_{3.50}$ (*Pnnm*), showing the different symmetries in corresponding directions. Electron densities with different numbers of contour lines in both drawings correspond to different atoms (as marked) in respective structural plots shown in Figure 2b and 2c. Contour lines were drawn at 15 e/Å^3.