SUPPORTING MATERIAL

FOR

Host Structure Engineering in Thermoelectric Clathrates

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Powder diffraction

All refined parameters are given in the table below. The peak shape was refined using a Thomson-Cox-Hasting Pseudo Voigt function with axial asymmetry. The background was refined through a sixth degree polynomial function. The unit cell of the standard LaB₆ was used for refining the wavelength of the measurement. The Flux grown sample contain a 10(1)% Ge impurity which was co-refined with the other two phases.

	Czo	Norm	Flux
Zero_pat1	0.0296(3)	0.0479(4)	0.0444(3)
Lambda_pat1	1.54052(1)	1.54009(2)	1.54030(1)
Bck_0_pat1	13.7(2)	13.1(2)	16.5(2)
Bck_1_pat1	2(1)	-4(1)	-6(1)
Bck_2_pat1	11(3)	10(2)	-2(1)
Bck_3_pat1	-28(3)	2(3)	6(2)
Bck_4_pat1	1(7)	-27(7)	-4(2)
Bck_5_pat1	13(6)	17(4)	1(1)
Scale_ph1_pat1	0.0001040(11)	0.0000504(5)	0.0000360(4)
Cell_A_ph1_pat1	10.83863(3)	10.84865(5)	10.85335(3)
X_Ge2_ph1	0.1842(2)	0.1844(2)	0.1843(2)
Y_Ge3_ph1	0.3072(2)	0.3065(3)	0.3089(4)
Z_Ge3_ph1	0.1158(2)	0.1155(3)	0.1175(3)
Biso_Ba1_ph1	1.03(7)	0.93(6)	0.91(5)
Biso_Ba2_ph1	2.2(1)	2.6(1)	3.4(1)
Occ_Ge1_ph1	0.014(2)	0.359(5)	0.056(2)
Occ_Ge2_ph1	0.213(4)	0.244(4)	0.280(5)
Occ_Ge3_ph1	0.499(6)	0.041(2)	0.322(5)
U_ph1_pat1	0.008(2)	0.011(2)	0.002(1)
V_ph1_pat1	-0.006(2)	-0.011(2)	-0.006(1)
W_ph1_pat1	0.0041(3)	0.0064(4)	0.0063(3)
Xpar_ph1_pat1	0.011(4)	0.038(1)	0.061(2)
Ypar_ph1_pat1	0.013(1)		
Asym1_ph1_pat1	0.05(2)	0.01(1)	-0.02(4)
Asym2_ph1_pat1	0.02(1)	0.05(6)	0.01(2)
Scale_ph2_pat1	0.03095(2)	0.00203(1)	0.00758(1)
Biso_La1_ph2	3.2(1)	-0.2(1)	2.0(1)
Biso_B1_ph2	2.8(3)	-0.9(6)	1.9(3)
U_ph2_pat1	0.003(2)	0.007(4)	0.005(1)
V_ph2_pat1	-0.002(2)	-0.007(4)	-0.007(1)

W_ph2_pat1	0.0040(3)		0.0055(7)		0.0059(3)	
Xpar_ph2_pat1	0.039(4)		0.046(4)		0.051(5)	
Ypar_ph2_pat1	0.004(1)				0.001(2)	
Scale_ph3_pat1					0.000194(5)	
Cell_A_ph3_pat1					5.66277(5)	
Biso_Ge1_ph3					0.6(1)	
U_ph3_pat1					0.02(1)	
V_ph3_pat1					-0.01(1)	
W_ph3_pat1					0.004(2)	
Xpar_ph3_pat1					0.01(3)	
Ypar_ph3_pat1					0.05(1)	
Rp/Rwp	14.5	17.8	22.4	26.8	20.5	26
Re/Chi2	13.4	1.7	17.5	2.3	20.2	1.7
Rf/RI_phase_1	5.4	8.1	8.9	12.3	7.5	8.2
Rf/RI_phase_2	3.1	7.8	4.2	7.4	3.1	4.8
Rf/RI_phase_3					7.6	14.1

Figure 1: The powder diffraction pattern of $\text{Ba}_8\text{Al}_{16}\text{Ge}_{30}\text{czo}$ on a logarithmic scale. The red circles are the measured data points, the black line corresponds to the model, the green lines are Bragg positions, and the blue line is the difference between the observed data and the calculated model.

Figure 2: The powder diffraction pattern of $\text{Ba}_8\text{Al}_{16}\text{Ge}_{30_norm}$ on a logarithmic scale. The red circles are the measured data points, the black line corresponds to the model, the green lines are Bragg positions, and the blue line is the difference between the observed data and the calculated model.

Figure 3: The powder diffraction pattern of $\text{Ba}_8\text{Al}_{16}\text{Ge}_{30_flux}$ on a logarithmic scale. The red circles are the measured data points, the black line corresponds to the model, the green lines are Bragg positions, and the blue line is the difference between the observed data and the calculated model.

Multi-temperature single crystal experiment:

The data have been modelled with 5 different models; Ba6d with Ba2 in the center of the large cage at the 6d position, Ba24j with Ba2 at the 24j site with isotropic ADPs or with anisotropic ADPs (Ba24j_a). Similarly the 24k site has been used for the Ba2 position with and without anisotropic displacement parameters. The refinements have been carried out for the three samples at the four measured temperatures.

Ba₈Al₁₆Ge₃₀_Czo, Czochralski pulled, bottom piece @ 100K

	Ba6d	Ba24j	Ba24k	Ba_24j_a	Ba24k_a
T	100	100	100	100	100
A	10.8213(1)	10.8213(1)	10.8213(1)	10.8213(1)	10.8213(1)
Ba1					
Uiso 1e4	44(1)	42(1)	43(1)	44(1)	44(1)
Ba2 sof					
X	0.25	0.25	0.24934(30)	0.25	0.25454(195)
Y	0.5	0.49223(7)	0.5	0.49882(61)	0.5
Z	0	0.99223(7)	0.01104(10)	0.99882(61)	0.00519(181)
Dist		0.119(1)	0.120(1)	0.018(9)	0.056(20)
Uiso	79(1)	81(1)	80(1)	133(2)	124(8)
U11 / Ba2 j	79(1)			81(2)	56(23)
U22 / X	159(1)			159(3)	138(18)
U33 / Y				159(3)	177(14)
U12 / Z				-27(10)	
U13 / Uiso					60(14)
U23 /dist				23(18)	
6c					
U11	31(5)	32(6)	31(6)	31(5)	31(5)
U22	35(4)	33(4)	33(4)	35(4)	35(4)
sof Al	96.8(6)	96.7(6)	97.4(6)	96.8(6)	96.8(6)
16i					
x=y=z	0.18439(2)	0.1844(3)	0.18439(3)	0.18439(2)	0.18439(2)
U11	41(1)	41(1)	41(1)	41(1)	41(1)
U12	-5(1)	-5(1)	-5(1)	-5(1)	-5(1)
sof Al	43.6(4)	43.2(4)	43.2(4)	43.6(4)	43.6(4)
24k					
Y	0.30767(2)	0.30767(3)	0.30767(3)	0.30767(2)	0.30767(2)
Z	0.11656(3)	0.11656(3)	0.11656(3)	0.11656(3)	0.11657(3)
U11	48(1)	48(1)	48(1)	48(1)	48(1)
U22	43(1)	42(1)	42(1)	43(1)	43(1)
U33	47(1)	47(1)	47(1)	47(1)	47(1)
U23	-5(1)	-5(1)	-5(1)	-5(1)	-5(1)
sof Al	5.1(4)	4.5(4)	4.5(4)	5.3(4)	5.2(4)
Al tot	14.0(1)	13.8(1)	13.8(1)	14.1(1)	14.0(1)
Si tot	32.0(1)	32.2(1)	32.2(1)	31.9(1)	32.0(1)
Host	43(1)	42(1)	42(1)	43(1)	43(1)
Parameter constrain	22, 3	22, 3	23, 3	25, 3	26, 3
N, N(Fo>4 σ(Fo))	1060, 857	1060, 857	1060, 857	1060, 857	1060, 857
R _F , R _F (Fo>4σ(Fo))	3.08, 2.21	3.14, 2.26	3.1, 2.23	3.07, 2.20	3.07, 2.20
GoF, R _{wl} (N)	0.601, 8.3	0.61, 8.4	0.608, 8.4	0.6, 8.2	0.6, 8.2

Ba₈Al₁₆Ge₃₀_Czo, Czochralski pulled, bottom piece @ 200K

	Ba6d	Ba24j	Ba24k	Ba_24j_a	Ba24k_a
T	200	200	200	200	200
A	10.8286(1)	10.8286(1)	10.8286(1)	10.8286(1)	10.8286(1)
Ba1					
Uiso 1e4	72(1)	71(1)	71(1)	72(1)	72(1)
Ba2 sof					
X	0.25	0.25	0.24927(27)	0.25	0.24447(186)
Y	0.5	0.49053(7)	0.5	0.49286(79)	0.5
Z	0	0.99053(7)	0.01344(10)	0.99286(79)	0.01026(129)
dist		0.145(1)	0.146(1)	0.109(12)	0.111(14)
Uiso	126(2)	129(2)	128(2)	166(10)	164(11)
U11 / Ba2 j	126(2)			126(2)	89(27)
U22 / X	250(1)			186(15)	231(19)
U33 / Y				186(15)	173(21)
U12 / Z				-7(2)	
U13 / Uiso					0(10)
U23 /dist				2(9)	
6c					
U11	46(6)	46(6)	45(6)	46(6)	45(6)
U22	53(4)	51(4)	52(4)	52(4)	52(4)
sof Al	97.9(6)	97.8(6)	97.2(6)	97.9(6)	97.9(6)
16i					
X=y=z	0.18442(3)	0.18443(3)	0.18442(3)	0.18442(3)	0.18442(3)
U11	68(1)	67(1)	68(1)	68(1)	68(1)
U12	-8(1)	-8(1)	-8(1)	-8(1)	-8(1)
sof Al	43.1(4)	42.6(4)	42.6(4)	43.0(4)	42.9(4)
24k					
Y	0.30765(3)	0.30764(3)	0.30765(3)	0.30765(3)	0.30765(3)
Z	0.11666(3)	0.11665(3)	0.11665(3)	0.11666(3)	0.11666(3)
U11	77(1)	77(1)	77(1)	77(1)	77(1)
U22	67(1)	67(1)	67(1)	67(1)	67(1)
U33	76(1)	75(1)	75(1)	75(1)	75(1)
U23	-8(1)	-8(1)	-8(1)	-8(1)	-8(1)
sof Al	5.0(4)	4.3(4)	4.3(4)	4.9(4)	4.8(4)
Al tot	14.0(1)	13.7(1)	13.7(1)	13.9(1)	13.9(1)
Si tot	32.0(1)	32.3(1)	32.3(1)	32.1(1)	32.1(1)
Host	68(1)	68(1)	68(1)	68(1)	68(1)
Parameter constrain	22, 3	22, 3	23, 3	25, 3	26, 3
N, N(Fo>4 σ(Fo))	1060, 823	1060, 823	1060, 823	1060, 823	1060, 823
R _F , R _F (Fo>4σ(Fo))	3.52, 2.39	3.59, 2.43	3.58, 2.43	3.5, 2.36	3.5, 2.36
GoF, R _{wl} (N)	0.578, 8.4	0.587, 8.5	0.589, 8.5	0.575, 8.3	0.575, 8.3

Ba₈Al₁₆Ge₃₀_Czo, Czochralski pulled, bottom piece @ 300K

	Ba6d	Ba24j	Ba24k	Ba_24j_a	Ba24k_a
T	300	300	300	300	300
A	10.8402(1)	10.8402(1)	10.8402(1)	10.8402(1)	10.8402(1)
Ba1					
Uiso 1e4	103(1)	100(1)	100(1)	102(1)	101(1)
Ba2 sof					
X	0.25	0.25	0.24904(25)	0.25	0.24611(167)
Y	0.5	0.48915(7)	0.5	0.49161(62)	0.5
Z	0	0.98915(7)	0.01547(10)	0.99161(62)	0.01283(91)
dist		0.166(1)	0.168(1)	0.129(10)	0.139(10)
Uiso	175(2)	181(2)	178(2)	226(10)	215(9)
U11 / Ba2 j	175(2)			176(2)	156(17)
U22 / X	343(2)			250(14)	257(18)
U33 / Y				250(14)	231(14)
U12 / Z				-10(3)	
U13 / Uiso					12(11)
U23 /dist				-19(12)	
6c					
U11	81(6)	81(7)	82(7)	82(6)	82(6)
U22	82(5)	77(5)	79(5)	80(5)	80(5)
sof Al	97.6(6)	97.6(6)	97.4(6)	97.5(6)	97.5(6)
16i					
X=y=z	0.18451(3)	0.18451(3)	0.1845(3)	0.18451(3)	0.1845(3)
U11	94(1)	94(1)	94(1)	94(1)	94(1)
U12	-9(1)	-10(1)	-10(1)	-10(1)	-10(1)
sof Al	43.8(4)	43.1(4)	43.1(4)	43.5(4)	43.4(4)
24k					
Y	0.30764(3)	0.30763(3)	0.30764(3)	0.30764(3)	0.30764(3)
Z	0.11669(3)	0.11668(3)	0.11669(3)	0.11669(3)	0.11669(3)
U11	108(1)	108(1)	108(1)	108(1)	108(1)
U22	94(1)	94(1)	94(1)	94(1)	94(1)
U33	104(1)	103(1)	104(1)	104(1)	104(1)
U23	-12(1)	-12(1)	-12(1)	-12(1)	-12(1)
sof Al	5.4(4)	4.4(4)	4.4(4)	5.0(4)	4.9(4)
Al tot	14.2(1)	13.8(1)	13.8(1)	14.0(1)	14.0(1)
Si tot	31.8(1)	32.2(1)	32.2(1)	32.0(1)	32.0(1)
Host	97(1)	96(1)	96(1)	96(1)	96(1)
Parameter constrain	22, 3	22, 3	23, 3	25, 3	26, 3
N, N(Fo>4 σ(Fo))	1061, 761	1061, 761	1061, 761	1061, 761	1061, 761
R _F , R _F (Fo>4σ(Fo))	3.74, 2.34	3.9, 2.45	3.79, 2.38	3.7, 2.30	3.7, 2.30
GoF, R _{wl} (N)	0.549, 8.4	0.567, 8.7	0.559, 8.6	0.542, 8.3	0.542, 8.3

Ba₈Al₁₆Ge₃₀_Czo, Czochralski pulled, bottom piece @ 400K

	Ba6d	Ba24j	Ba24k	Ba_24j_a	Ba24k_a
T	400	400	400	400	400
A	10.8469(1)	10.8469(1)	10.8469(1)	10.8469(1)	10.8469(1)
Ba1					
Uiso 1e4	136(1)	133(1)	133(1)	134(1)	134(1)
Ba2 sof					
X	0.25	0.25	0.24906(24)	0.25	0.25141(181)
Y	0.5	0.48778(7)	0.5	0.49059(59)	0.5
Z	0	0.98778(7)	0.01739(10)	0.99059(59)	0.01470(59)
dist		0.187(1)	0.189(1)	0.144(9)	0.159(6)
Uiso	223(2)	231(2)	229(2)	289(10)	273(8)
U11 / Ba2 j	223(2)			224(2)	221(8)
U22 / X	441(2)			321(16)	307(15)
U33 / Y				321(16)	290(14)
U12 / Z				-12(3)	
U13 / Uiso					12(11)
U23 /dist				-42(17)	
6c					
U11	117(7)	(7)	116(7)	117(7)	117(7)
		114			
U22	120(5)	(5)	114(5)	116(5)	116(5)
		110			
sof Al	97.0(6)	97.4(6)	97.2(6)	97.1(6)	97.1(6)
16i					
X=y=z	0.18445(3)	0.18446(3)	0.18444(3)	0.18445(3)	0.18445(3)
U11	126(1)	126(1)	126(1)	126(1)	126(1)
U12	-16(1)	-16(1)	-16(1)	-16(1)	-16(1)
sof Al	43.7(4)	43.0(4)	42.9(4)	43.3(4)	43.3(4)
24k					
Y	0.3076(3)	0.3076(3)	0.3076(3)	0.3076(3)	0.3076(3)
Z	0.1167(3)	0.11669(3)	0.11669(3)	0.1167(3)	0.1167(3)
U11	147(1)	146(1)	146(1)	147(1)	146(1)
U22	120(1)	120(1)	120(1)	120(1)	120(1)
U33	135(1)	135(1)	135(1)	135(1)	135(1)
U23	-15(1)	-15(1)	-15(1)	-15(1)	-15(1)
sof Al	5.1(4)	4.2(4)	4.2(4)	4.6(4)	4.6(4)
Al tot	14.0(1)	13.7(1)	13.7(1)	13.9(1)	13.9(1)
Si tot	32.0(1)	32.3(1)	32.3(1)	32.1(1)	32.1(1)
Host	129(1)	128(2)	128(1)	129(1)	129(1)
Parameter constrain	22, 3	22, 3	23, 3	25, 3	26, 3
N, N(Fo>4 σ(Fo))	1066, 707	1066, 707	1066, 707	1066, 707	1066, 707
R _F , R _F (Fo>4σ(Fo))	4.34, 2.39	4.51, 2.50	4.43, 2.45	4.27, 2.33	4.27, 2.33
GoF, R _{wl} (N)	0.53, 8.6	0.555, 9.0	0.54, 8.7	0.518, 8.4	0.519, 8.4

Ba₈Al₁₆Ge₃₀_norm, conventionally synthesised @ 100K

	Ba6d	Ba24j	Ba24k	Ba_24j_a	Ba24k_a
T	100	100	100	100	100
A	10.8489(3)	10.8489(3)	10.8489(3)	10.8489(3)	10.8489(3)
Ba1					
Uiso 1e4	53(1)	48(1)	48(1)	51(1)	51(1)
Ba2 sof					
X	0.25	0.25	0.24946(19)	0.25	0.24924(289)
Y	0.5	0.48672(6)	0.5	0.48985(38)	0.5
Z	0	0.98672(6)	0.01916(9)	0.98985(38)	0.01597(39)
dist		0.204(1)	0.208(1)	0.156(6)	0.173(4)
Uiso	76(2)	103(2)	96(2)	188(8)	168(6)
U11 / Ba2 j	76(2)			78(2)	77(6)
U22 / X	391(3)			243(12)	224(12)
U33 / Y				243(12)	203(10)
U12 / Z				-9(2)	
U13 / Uiso					-5(30)
U23 /dist				-52(13)	
6c					
U11	53(5)	49(6)	51(5)	53(4)	53(4)
U22	55(3)	42(4)	48(4)	52(3)	52(3)
sof Al	65.9(8)	65.9(1.1)	65.8(1.1)	65.6(8)	65.6(8)
16i					
X=y=z	0.18448(3)	0.18452(4)	0.18449(3)	0.18448(3)	0.18448(3)
U11	54(1)	55(2)	55(2)	54(1)	54(1)
U12	-8(1)	-9(1)	-9(1)	-8(1)	-8(1)
sof Al	30.2(7)	27.8(9)	27.6(8)	29.3(6)	29.3(7)
24k					
Y	0.3085(4)	0.3085(5)	0.30851(5)	0.30851(4)	0.30851(4)
Z	0.11625(4)	0.11622(5)	0.11624(5)	0.11626(4)	0.11626(4)
U11	50(2)	52(2)	52(2)	51(2)	51(2)
U22	48(2)	51(2)	50(2)	48(2)	48(2)
U33	55(2)	57(2)	57(2)	55(2)	55(2)
U23	-8(1)	-8(1)	-7(1)	-8(1)	-8(1)
sof Al	29.5(6)	26.5(7)	26.6(7)	28.5(5)	28.5(5)
Al tot	15.9(2)	14.8(2)	14.7(2)	15.5(2)	15.5(2)
Si tot	30.1(2)	31.2(2)	31.3(2)	30.5(2)	30.5(2)
Host	52(1)	52(2)	53(2)	52(1)	52(1)
Parameter constrain	22, 3	22, 3	23, 3	25, 3	26, 3
N, N(Fo>4 σ(Fo))	1298, 906	1298, 906	1298, 906	1298, 906	1298, 906
R _F , R _F (Fo>4σ(Fo))	6.39, 3.38	7.26, 4.18	7.13, 4.10	6.2, 3.22	6.2, 3.22
GoF, R _{wl} (N)	0.829, 13.0	0.994, 15.5	0.936, 14.6	0.802, 12.5	0.802, 12.5

Ba₈Al₁₆Ge₃₀_norm, conventionally synthesised @ 200K

	Ba6d	Ba24j	Ba24k	Ba_24j_a	Ba24k_a
T	200	200	200	200	200
A	10.851(2)	10.851(2)	10.851(2)	10.851(2)	10.851(2)
Ba1					
Uiso 1e4	82(1)	77(2)	77(2)	81(1)	81(1)
Ba2 sof					
X	0.25	0.25	0.24908(23)	0.25	0.24829(393)
Y	0.5	0.48593(8)	0.5	0.4891(45)	0.5
Z	0	0.98593(8)	0.02015(11)	0.9891(45)	0.01613(71)
dist		0.216(1)	0.219(1)	0.167(7)	0.175(8)
Uiso	124(2)	154(3)	149(3)	248(10)	239(11)
U11 / Ba2 j	124(2)			126(2)	123(17)
U22 / X	475(3)			309(15)	318(19)
U33 / Y				309(15)	276(14)
U12 / Z				-17(3)	
U13 / Uiso					-8(37)
U23 /dist				-37(13)	
6c					
U11	81(5)	75(6)	78(6)	79(5)	79(5)
U22	76(4)	64(5)	70(5)	74(4)	74(4)
sof Al	66.1(9)	66.0(1.1)	63.9(1.1)	65.9(9)	65.9(9)
16i					
X=y=z	0.18453(3)	0.18456(4)	0.18453(4)	0.18453(3)	0.18453(3)
U11	80(2)	80(2)	81(2)	80(1)	80(1)
U12	-9(1)	-10(1)	-10(1)	-9(1)	-9(1)
sof Al	29.3(7)	27.1(8)	27.0(8)	28.6(7)	28.6(7)
24k					
Y	0.30852(4)	0.30854(5)	0.30852(5)	0.30852(4)	0.30852(4)
Z	0.11632(5)	0.11631(6)	0.11631(5)	0.11633(4)	0.11633(4)
U11	80(2)	80(2)	81(2)	80(2)	80(2)
U22	71(2)	74(2)	73(2)	71(2)	71(2)
U33	80(2)	83(2)	82(2)	80(2)	80(2)
U23	-13(1)	-12(2)	-12(2)	-13(1)	-13(1)
sof Al	29.4(6)	26.6(7)	26.7(7)	28.6(6)	28.6(6)
Al tot	15.7(2)	14.7(2)	14.6(2)	15.4(2)	15.4(2)
Si tot	30.3(2)	31.3(2)	31.4(2)	30.6(2)	30.6(2)
Host	78(2)	78(2)	79(2)	78(1)	78(1)
Parameter constrain	22, 3	22, 3	23, 3	25, 3	26, 3
N, N(Fo>4 σ(Fo))	1302, 851	1302, 851	1302, 851	1302, 851	1302, 851
R _F , R _F (Fo>4σ(Fo))	7.02, 3.41	7.67, 4.12	7.69, 4.06	6.88, 3.33	6.88, 3.33
GoF, R _{wl} (N)	0.858, 14.1	0.982, 16.1	0.959, 15.7	0.831, 13.7	0.832, 13.7

Ba₈Al₁₆Ge₃₀_norm, conventionally synthesised @ 300K

	Ba6d	Ba24j	Ba24k	Ba_24j_a	Ba24k_a
T	300	300	300	300	300
A	10.8513(2)	10.8513(2)	10.8513(2)	10.8513(2)	10.8513(2)
Ba1					
Uiso 1e4	118(2)	115(2)	113(2)	116(2)	116(2)
Ba2 sof					
X	0.25	0.25	0.24891(26)	0.25	0.24959(504)
Y	0.5	0.48503(8)	0.5	0.48776(40)	0.5
Z	0	0.98503(8)	0.02137(12)	0.98776(40)	0.01737(60)
dist		0.230(1)	0.232(1)	0.188(6)	0.189(7)
Uiso	179(3)	211(3)	204(3)	296(10)	296(12)
U11 / Ba2 j	179(3)			182(3)	184(14)
U22 / X	565(4)			353(15)	386(23)
U33 / Y				353(15)	318(15)
U12 / Z				-19(3)	
U13 / Uiso					-26(49)
U23 /dist				-35(12)	
6c					
U11	115(6)	108(7)	113(7)	114(6)	114(6)
U22	106(5)	90(5)	98(5)	101(4)	102(4)
sof Al	66.6(10)	68.0(1.0)	65.8(1.1)	66.3(9)	66.3(9)
16i					
X=y=z	0.18459(3)	0.18462(4)	0.18459(4)	0.18459(3)	0.18459(3)
U11	110(2)	108(2)	111(2)	110(2)	110(2)
U12	-14(1)	-14(1)	-14(1)	-14(1)	-14(1)
sof Al	30.4(7)	30.5(6)	28.1(8)	29.5(7)	29.5(7)
24k					
Y	0.30846(5)	0.30844(5)	0.30846(5)	0.30846(4)	0.30846(4)
Z	0.11635(5)	0.11637(6)	0.11634(6)	0.11637(5)	0.11637(5)
U11	112(2)	111(2)	114(2)	113(2)	113(2)
U22	103(2)	103(2)	105(2)	103(2)	103(2)
U33	112(2)	113(2)	115(2)	113(2)	113(2)
U23	-12(1)	-13(2)	-12(2)	-13(1)	-13(1)
sof Al	30.0(6)	29.3(4)	27.5(7)	29.0(6)	29.0(6)
Al tot	16.1(2)	16.0(1)	15.0(2)	15.7(2)	15.7(2)
Si tot	29.9(2)	30.0(1)	31.0(2)	30.3(2)	30.3(2)
Host	109(2)	107(2)	110(2)	109(2)	109(2)
Parameter constrain	22, 3	22, 5	23, 3	25, 3	26, 3
N, N(Fo>4 σ(Fo))	1307, 799	1307, 799	1307, 799	1307, 799	1307, 799
R _F , R _F (Fo>4σ(Fo))	8.4, 3.86	8.87, 4.36	8.97, 4.38	8.22, 3.72	8.22, 3.72
GoF, R _{wl} (N)	0.877, 15.1	0.981, 16.9	0.956, 16.5	0.853, 14.7	0.853, 14.7

Ba₈Al₁₆Ge₃₀_norm, conventionally synthesised @ 400K

	Ba6d	Ba24j	Ba24k	Ba_24j_a	Ba24k_a
T	400	400	400	400	400
A	10.8693(6)	10.8693(6)	10.8693(6)	10.8693(6)	10.8693(6)
Ba1					
Uiso 1e4	154(2)	148(2)	149(2)	151(2)	151(2)
Ba2 sof					
X	0.25	0.25	0.24897(32)	0.25	0.25185(155)
Y	0.5	0.48431(10)	0.5	0.48662(40)	0.5
Z	0	0.98431(10)	0.02247(14)	0.98662(40)	0.01972(52)
dist		0.241(2)	0.244(2)	0.206(6)	0.214(6)
Uiso	233(4)	261(4)	257(4)	336(11)	323(10)
U11 / Ba2 j	233(4)			238(4)	232(10)
U22 / X	650(5)			385(17)	399(21)
U33 / Y				385(17)	337(16)
U12 / Z				-16(4)	
U13 / Uiso					-26(49)
U23 /dist				-58(15)	
6c					
U11	169(8)	163(9)	164(8)	164(8)	164(8)
U22	140(6)	129(6)	131(6)	135(5)	135(5)
sof Al	64.1(1.1)	64.2(1.1)	63.9(1.1)	64.0(1.0)	64.0(1.0)
16i					
X=y=z	0.1845(4)	0.18452(5)	0.18447(4)	0.18448(4)	0.18448(4)
U11	146(2)	146(2)	147(2)	146(2)	146(2)
U12	-16(1)	-16(1)	-16(1)	-16(1)	-16(1)
sof Al	28.6(8)	26.6(9)	26.5(8)	27.4(8)	27.4(8)
24k					
Y	0.30845(6)	0.30843(6)	0.30844(6)	0.30845(6)	0.30845(6)
Z	0.11642(6)	0.11645(6)	0.11639(6)	0.11643(6)	0.11643(6)
U11	155(3)	155(3)	156(3)	156(3)	156(3)
U22	134(3)	136(3)	135(3)	134(3)	134(3)
U33	148(3)	149(3)	149(3)	148(3)	148(3)
U23	-14(2)	-14(2)	-14(2)	-14(2)	-14(2)
sof Al	28.3(7)	26.1(7)	26.2(7)	27.1(7)	27.0(7)
Al tot	15.2(2)	14.4(2)	14.4(2)	14.7(2)	14.7(2)
Si tot	30.8(2)	31.6(2)	31.6(2)	31.3(2)	31.3(2)
Host	146(2)	145(2)	146(2)	146(2)	146(2)
Parameter constrain	22, 3	22, 3	23, 3	25, 3	26, 3
N, N(Fo>4 σ(Fo))	1312, 700	1312, 700	1312, 700	1312, 700	1312, 700
R _F , R _F (Fo>4σ(Fo))	10.12, 4.01	10.67, 4.27	10.49, 4.17	9.99, 3.78	10.01, 3.78
GoF, R _{wl} (N)	0.922, 17.2	0.97, 18.0	0.945, 17.6	0.895, 16.6	0.895, 16.6

Ba₈Al₁₆Ge₃₀_flux, flux grown @ 100K

	Ba6d	Ba24j	Ba24k	Ba_24j_a	Ba24k_a
T	100	100	100	100	100
A	10.8300(1)	10.8300(1)	10.8300(1)	10.8300(1)	10.8300(1)
Ba1					
Uiso 1e4	54(2)	46(2)	45(2)	48(1)	48(1)
Ba2 sof					
X	0.25	0.25	0.24951(16)	0.25	0.24782(51)
Y	0.5	0.48384(7)	0.5	0.48604(13)	0.5
Z	0	0.98384(7)	0.02319(8)	0.98604(13)	0.02142(14)
dist		0.248(1)	0.251(1)	0.214(2)	0.232(2)
Uiso	60(2)	104(3)	96(2)	186(4)	157(4)
U11 / Ba2 j	60(2)			67(2)	60(4)
U22 / X	560(4)			245(6)	232(7)
U33 / Y				245(6)	178(5)
U12 / Z				-6(2)	
U13 / Uiso					22(8)
U23 /dist				-83(6)	
6c					
U11	65(5)	62(7)	64(5)	59(3)	59(3)
U22	43(4)	31(5)	39(4)	40(3)	40(3)
sof Al	55.8(8)	55.0(11)	54.8(9)	55.0(6)	54.9(6)
16i					
X=y=z	0.18447(3)	0.18452(4)	0.18449(3)	0.18448(2)	0.18448(2)
U11	55(2)	57(2)	58(2)	56(1)	56(1)
U12	-9(1)	-9(1)	-9(1)	-9(1)	-9(1)
sof Al	23.5(6)	19.9(7)	19.5(6)	21.2(4)	21.1(4)
24k					
Y	0.30903(5)	0.30899(6)	0.30903(5)	0.30902(3)	0.30902(3)
Z	0.11604(5)	0.11599(7)	0.11602(5)	0.11602(3)	0.11602(3)
U11	53(2)	56(3)	58(2)	55(2)	55(2)
U22	44(2)	51(3)	51(2)	47(2)	47(2)
U33	57(2)	60(3)	61(3)	59(2)	59(2)
U23	-12(1)	-11(2)	-11(2)	-11(1)	-11(1)
sof Al	39.7(6)	35.7(8)	35.4(7)	37.1(4)	37.0(4)
Al tot	16.6(2)	15.0(2)	14.8(2)	15.6(1)	15.5(1)
Si tot	29.4(2)	31.0(2)	31.2(2)	30.4(1)	30.5(1)
Host	52(2)	54(2)	56(2)	54(1)	54(1)
Parameter constrain	22, 3	22, 3	23, 3	25, 3	26, 3
N, N(Fo>4 σ (Fo))	986, 779	986, 779	986, 779	986, 779	986, 779
R _F , R _F (Fo>4 σ (Fo))	5.24, 3.65	6.29, 4.65	5.52, 3.89	3.9, 2.39	3.89, 2.38
GoF, R _{wl} (N)	0.961, 13.5	1.208, 16.8	1.037, 14.5	0.704, 9.9	0.701, 9.8

Ba₈Al₁₆Ge₃₀_flux, flux grown @ 200K

	Ba6d	Ba24j	Ba24k	Ba_24j_a	Ba24k_a
T	200	200	200	200	200
A	10.8397(1)	10.8397(1)	10.8397(1)	10.8397(1)	10.8397(1)
Ba1					
Uiso 1e4	84(1)	76(2)	75(1)	79(1)	78(1)
Ba2 sof					
X	0.25	0.25	0.24926(19)	0.25	0.25233(45)
Y	0.5	0.48331(7)	0.5	0.48578(15)	0.5
Z	0	0.98331(7)	0.02389(9)	0.98578(15)	0.02162(17)
dist		0.256(1)	0.259(1)	0.218(2)	0.234(2)
Uiso	108(2)	152(3)	144(3)	244(5)	217(4)
U11 / Ba2 j	108(2)			112(2)	103(4)
U22 / X	626(4)			310(7)	302(8)
U33 / Y				310(7)	245(6)
U12 / Z				-12(2)	
U13 / Uiso					-51(6)
U23 /dist				-83(7)	
6c					
U11	76(3)	59(4)	62(4)	66(2)	66(2)
U22	76(3)	59(4)	62(4)	66(2)	66(2)
sof Al	55.9(8)	55.2(10)	55.6(8)	55.5(6)	55.4(6)
16i					
X=y=z	0.18451(3)	0.18454(4)	0.18451(3)	0.18451(2)	0.18451(2)
U11	80(1)	81(2)	82(1)	81(1)	81(1)
U12	-11(1)	-11(1)	-12(1)	-11(1)	-11(1)
sof Al	24.5(5)	20.9(7)	20.5(6)	22.4(4)	22.2(4)
24k					
Y	0.30899(4)	0.309(6)	0.30901(5)	0.30899(3)	0.30899(3)
Z	0.11615(4)	0.1162(6)	0.11617(5)	0.11616(3)	0.11617(3)
U11	77(2)	78(3)	80(2)	78(1)	78(1)
U22	69(2)	72(3)	72(2)	70(1)	70(1)
U33	82(2)	84(3)	84(2)	83(1)	83(1)
U23	-14(1)	-12(2)	-13(2)	-14(1)	-14(1)
sof Al	39.7(5)	36.2(7)	36.0(6)	37.6(4)	37.5(4)
Al tot	16.8(2)	15.3(2)	15.2(2)	15.9(1)	15.9(1)
Si tot	29.2(2)	30.7(2)	30.8(2)	30.1(1)	30.1(1)
Host	78(1)	77(2)	78(2)	77(1)	77(1)
Parameter constrain	22, 3	22, 3	23, 3	25, 3	26, 3
N, N(Fo>4 σ (Fo))	991, 756	991, 756	991, 756	991, 756	991, 756
R _F , R _F (Fo>4 σ (Fo))	5.1, 3.23	6.22, 4.32	5.66, 3.84	4.16, 2.42	4.19, 2.41
GoF, R _{wl} (N)	0.987, 7.1	1.339, 9.5	1.157, 8.2	0.754, 5.4	0.752, 5.3

Ba₈Al₁₆Ge₃₀_flux, flux grown @ 300K

	Ba6d	Ba24j	Ba24k	Ba_24j_a	Ba24k_a
T	300	300	300	300	300
A	10.8533(1)	10.8533(1)	10.8533(1)	10.8533(1)	10.8533(1)
Ba1					
Uiso 1e4	122(1)	114(2)	113(2)	117(1)	116(1)
Ba2 sof					
X	0.25	0.25	0.24914(21)	0.25	0.24688(72)
Y	0.5	0.48273(8)	0.5	0.48535(19)	0.5
Z	0	0.98273(8)	0.02463(10)	0.98535(19)	0.02218(23)
dist		0.265(1)	0.267(1)	0.225(3)	0.241(3)
Uiso	160(3)	204(3)	199(3)	302(6)	275(5)
U11 / Ba2 j	160(3)			164(2)	150(7)
U22 / X	698(4)			372(9)	371(10)
U33 / Y				372(9)	305(8)
U12 / Z				-15(2)	
U13 / Uiso					22(10)
U23 /dist				-80(8)	
6c					
U11	106(4)	94(5)	94(4)	97(3)	97(3)
U22	106(4)	94(5)	94(4)	97(3)	97(3)
sof Al	55.6(8)	54.9(10)	54.8(9)	55.2(6)	55.2(6)
16i					
x=y=z	0.18452(3)	0.18454(4)	0.18452(3)	0.18452(2)	0.18452(2)
U11	112(1)	113(2)	112(2)	112(1)	112(1)
U12	-12(1)	-12(1)	-12(1)	-12(1)	-12(1)
sof Al	24.1(5)	21.0(7)	20.8(6)	22.3(4)	22.2(4)
24k					
y	0.30897(5)	0.30899(6)	0.30899(5)	0.30897(3)	0.30897(3)
z	0.1162(5)	0.11626(6)	0.11623(5)	0.11621(3)	0.11621(3)
U11	114(2)	114(3)	116(3)	115(2)	115(2)
U22	101(2)	103(3)	103(2)	101(2)	101(2)
U33	115(2)	116(3)	116(2)	115(2)	115(2)
U23	-16(2)	-14(2)	-16(2)	-16(1)	-16(1)
sof Al	38.9(5)	36.0(6)	35.9(6)	37.2(4)	37.1(4)
Al tot	16.5(1)	15.3(2)	15.2(2)	15.8(1)	15.8(1)
Si tot	29.5(1)	30.7(2)	30.8(2)	30.2(1)	30.2(1)
Host	111(1)	110(2)	110(2)	110(1)	110(1)
Parameter constrain	22, 3	22, 3	23, 3	25, 3	26, 3
N, N(Fo>4 σ (Fo))	996, 707	996, 707	996, 707	996, 707	996, 707
R _F , R _F (Fo>4 σ (Fo))	5.53, 3.28	6.46, 4.04	6.39, 3.82	4.84, 2.56	4.84, 2.55
GoF, R _{wl} (N)	1.003, 6.1	1.306, 7.9	1.189, 7.1	0.822, 5.0	0.82, 5.0

Ba₈Al₁₆Ge₃₀_flux, flux grown @ 400K

	Ba6d	Ba24j	Ba24k	Ba_24j_a	Ba24k_a
T	400	400	400	400	400
a	10.8650(1)	10.8650(1)	10.8650(1)	10.8650(1)	10.8650(1)
Ba1					
Uiso 1e4	154(2)	146(2)	146(2)	149(1)	149(1)
Ba2 sof					
x	0.25	0.25	0.24925(24)	0.25	0.25238(71)
y	0.5	0.48207(9)	0.5	0.48499(25)	0.5
z	0	0.98207(9)	0.02555(11)	0.98499(25)	0.02284(26)
dist		0.276(1)	0.278(1)	0.231(4)	0.248(3)
Uiso	203(3)	251(4)	246(3)	362(8)	331(6)
U11 / Ba2 j	203(3)			208(3)	198(6)
U22 / X	780(5)			438(12)	428(12)
U33 / Y				438(12)	366(10)
U12 / Z				-14(3)	
U13 / Uiso					22(10)
U23 /dist				-94(11)	
6c					
U11	129(4)	117(5)	117(4)	121(3)	121(3)
U22	129(4)	117(5)	117(4)	121(3)	121(3)
sof Al	56.1(7)	55.5(9)	0.0()	55.8(6)	55.8(6)
16i					
x=y=z	0.18456(3)	0.18458(4)	0.18455(3)	0.18456(2)	0.18455(2)
U11	138(1)	138(2)	138(2)	138(1)	137(1)
U12	-16(1)	-16(1)	-16(1)	-16(1)	-16(1)
sof Al	24.1(5)	21.3(7)	21.1(6)	22.5(4)	22.4(5)
24k					
y	0.30888(5)	0.3089(6)	0.30891(6)	0.30888(4)	0.30888(4)
z	0.1163(5)	0.11637(6)	0.11633(6)	0.11631(4)	0.11631(4)
U11	141(2)	142(3)	143(3)	142(2)	142(2)
U22	124(2)	126(3)	127(3)	125(2)	125(2)
U33	140(2)	141(3)	141(3)	140(2)	140(2)
U23	-17(2)	-14(2)	-16(2)	-16(1)	-16(1)
sof Al	39.4(5)	36.8(6)	36.7(6)	37.9(4)	37.8(4)
Al tot	16.7(1)	15.6(2)	15.5(2)	16.1(1)	16.0(1)
Si tot	29.3(1)	30.4(2)	30.5(2)	29.9(1)	30.0(1)
Host	136(2)	135(2)	136(2)	135(1)	135(1)
Parameter constrain	22, 3	22, 3	23, 3	25, 3	26, 3
N, N(Fo>4 σ(Fo))	995, 688	995, 688	995, 688	995, 688	995, 688
R _F , R _F (Fo>4σ(Fo))	6.02, 3.47	7.15, 4.39	6.69, 3.90	5.44, 2.86	5.41, 2.84
GoF, R _{wl} (N)	0.978, 6.3	1.25, 7.9	1.135, 7.2	0.834, 5.3	0.833, 5.3

Neutron diffraction data

Czochralski pulled sample

The sample had a mass of 47.3 mg. It was mounted on an aluminum pin using a small amount of epoxy glue. Full data coverage was obtained by 12 crystal orientations. Two detectors are used to measure the diffraction data, giving a total of 24 histograms of data. Each orientation was measured for 2 hours.

Model	6d	24k
a	10.803(2)	10.803(2)
Ba1		
U _{iso} (10 ⁻⁴ Å ²)	40(2)	40(2)
Ba2		
x	0.25	0.2477(13)
y	0.5	0.5
x	0	0.0082(8)
U _{iso} (10 ⁻⁴ Å ²)	94(2)	65(8)
U ₁₁ (10 ⁻⁴ Å ²)	71(4)	
U ₂₂ (10 ⁻⁴ Å ²)	106(3)	
6c		
U _{iso} (10 ⁻⁴ Å ²)	47.8(4)	47.8(4)
sof Al (%)	96.0(5)	95.9(5)
16i	0	0
x=y=z	0.18439(3)	0.18439(3)
U _{iso} (10 ⁻⁴ Å ²)	47.8(4)	47.8(4)
sof Al (%)	43.4(6)	43.3(6)
24k		
y	0.30774(3)	0.30774(3)
z	0.11654(3)	0.11654(3)
U _{iso} (10 ⁻⁴ Å ²)	47.8(4)	47.8(4)
sof Al (%)	8.6(7)	8.4(7)
Al tot	14.8(3)	14.7(3)
Ge tot	31.2(3)	31.3(3)
U _{iso} (host) (10 ⁻⁴ Å ²)	47.8(4)	47.8(4)
N _{par} , N _{constrains}	45, 4	46, 4
N, N(l>3σ(l))	14478, 6125	14478, 6125
R _F , R _F (l>3σ(l))	27.8, 13.3	27.8, 13.3
R _{wF} , R _{wF} (l>3σ(l))	9.8, 12.8	9.8, 12.8
R _{wI} , R _{wI} (l>3σ(l))	16.2, 7.3	16.2, 7.3

Conventional synthesis

The sample had a mass of 109.4 mg. It was mounted on an aluminum pin using a small amount of epoxy glue. Full data coverage was obtained with 10 crystal orientations. Two detectors were used to measure the diffraction data, giving a total of 20 data histograms. Each orientation was measured for 2 hours.

Model	6d	24k
a	10.810(2)	10.810(2)
Ba1		
U _{iso} (10 ⁻⁴ Å ²)	25(2)	21(2)
Ba2		
x	0.25	0.2496(5)
y	0.5	0.5
x	0	0.0174(2)
U _{iso} (10 ⁻⁴ Å ²)	211(4)	61(4)
U ₁₁ (10 ⁻⁴ Å ²)	47(4)	
U ₂₂ (10 ⁻⁴ Å ²)	292(6)	
6c		
U _{iso} (10 ⁻⁴ Å ²)	39.3(3)	39.2(3)
sof Al (%)	66.5(7)	64.5(7)
16i	0	0
x=y=z	0.18440(2)	0.18440(2)
U _{iso} (10 ⁻⁴ Å ²)	0.00393(3)	0.00392(3)
sof Al (%)	31.2(8)	28.9(8)
24k		
y	0.30844(3)	0.30845(3)
z	0.11639(3)	0.11639(3)
U _{iso} (10 ⁻⁴ Å ²)	39.3(3)	39.2(3)
sof Al (%)	27.1(8)	24.8(8)
Al tot	15.5(4)	14.4(4)
Ge tot	30.5(4)	31.6(4)
U _{iso} (host) (10 ⁻⁴ Å ²)	39.3(3)	39.2(3)
N _{par} , N _{constrains}	41, 4	42, 4
N, N(l>3σ(l))	19605, 7421	19605, 7421
R _F , R _F (l>3σ(l))	32.9, 13.5	32.8, 13.5
R _{wF} , R _{wF} (l>3σ(l))	13.1, 14.8	13.1, 14.8
R _{wI} , R _{wI} (l>3σ(l))	20.8, 9.	20.8, 9.

Thermal transport

The measured thermal conductivity has been corrected for the electronic contribution using the Wiedemann-Franz law and the measured resistivity. Figure 4 shows the effect of the correction.

Figure 4: The measured thermal conductivity (black squares), the contribution from the charge carriers estimated from Wiedemann-Franz law (blue triangles) and the resulting lattice thermal conductivity (red circles).