

**Tuning structural instability in the  
 $\text{Cu}_{12-x}\text{Ni}_x\text{Sb}_4\text{S}_{13}$  ( $x = 0, 0.05, 0.2, 0.5$ ) tetrahedrites**

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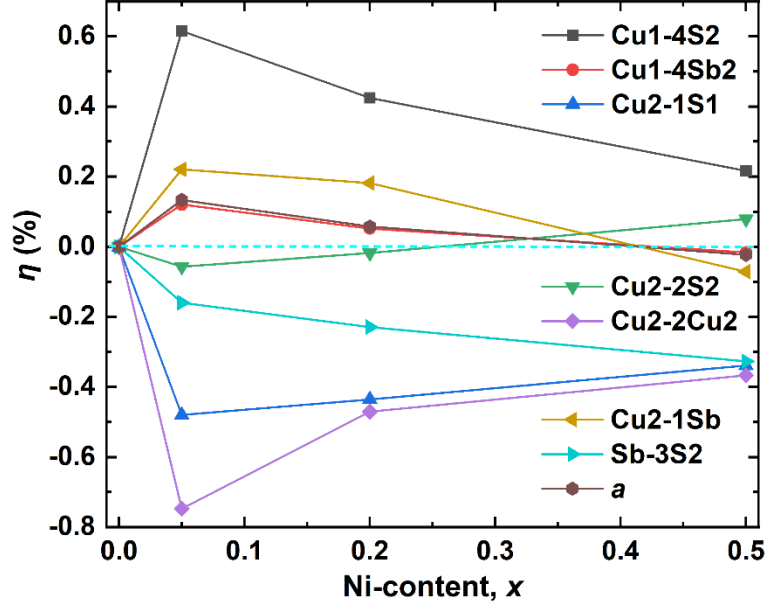
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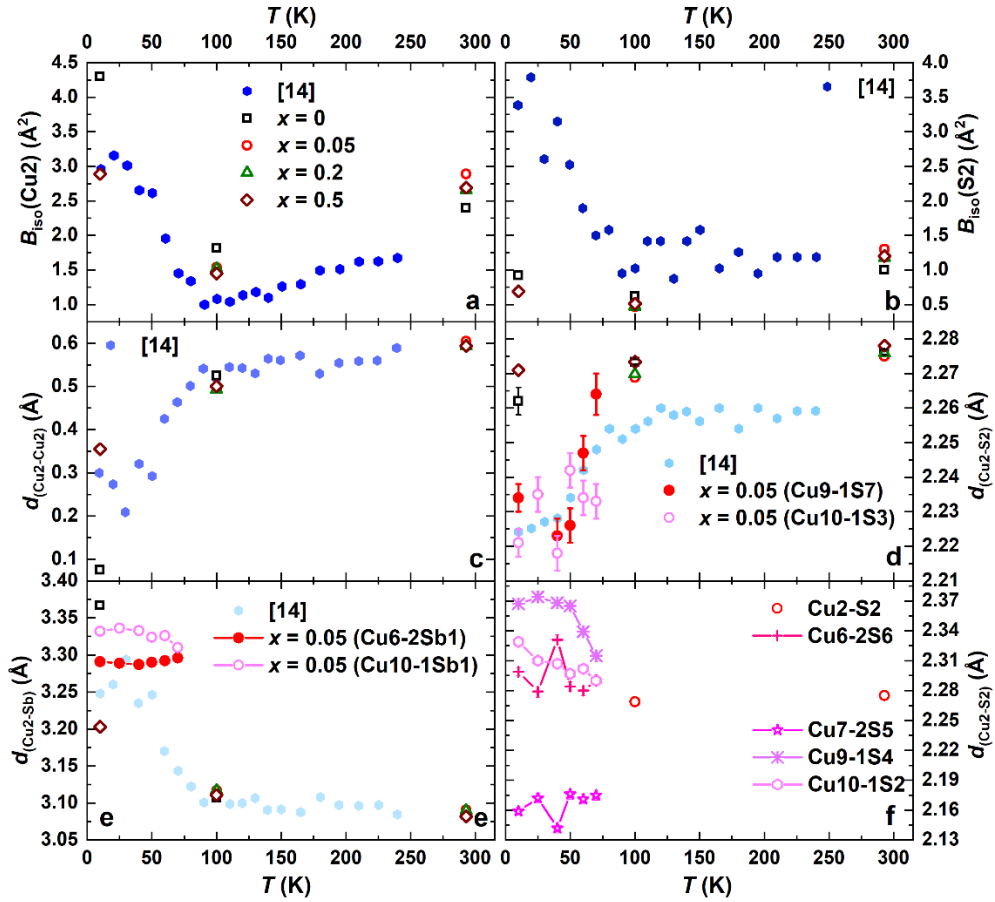
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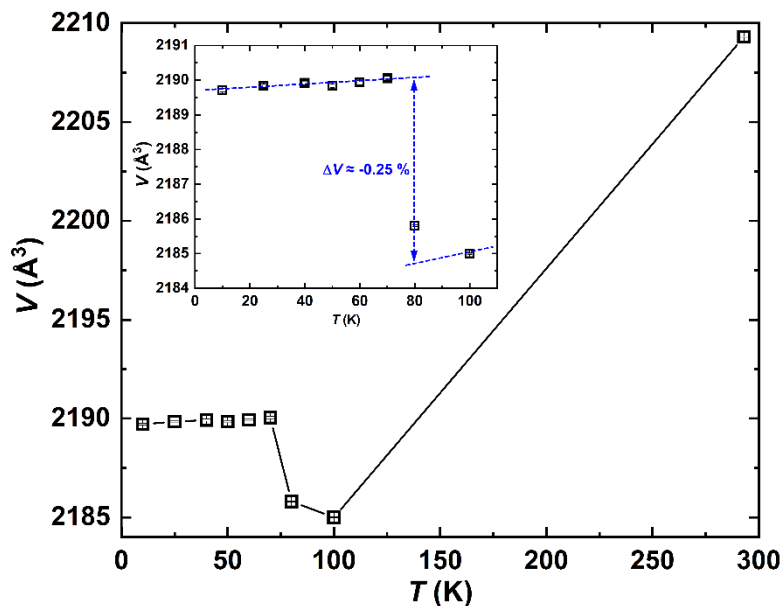
**Supplemental Materials**



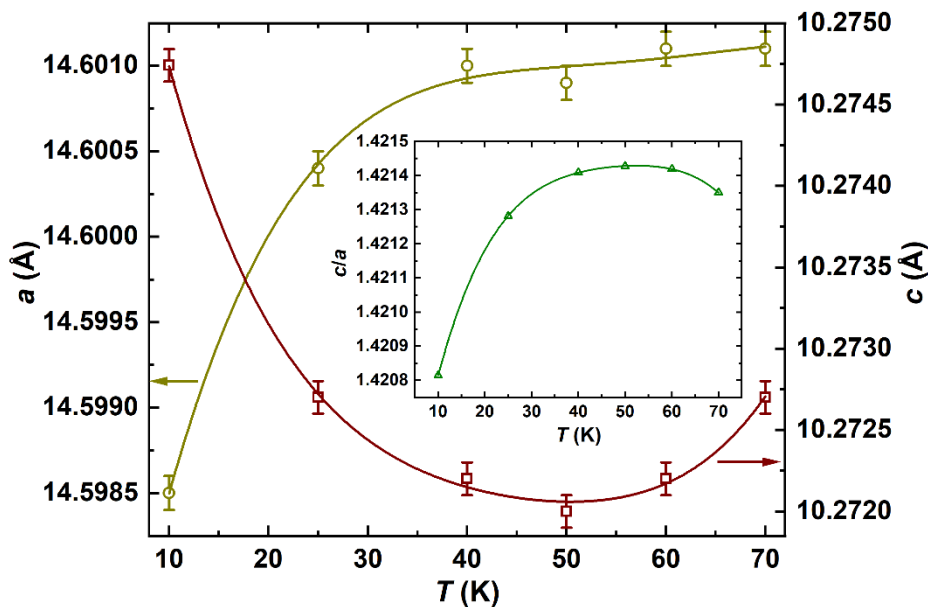
**Fig. S1.** Relative expansion (positive)/contraction (negative) in  $\text{Cu}_{12-x}\text{Ni}_x\text{Sb}_4\text{S}_{13}$  for the bonding interatomic distances in comparison with unit cell parameter  $a$  at room temperature as function of Ni-content  $x$ . Solid lines are guides for eyes only.



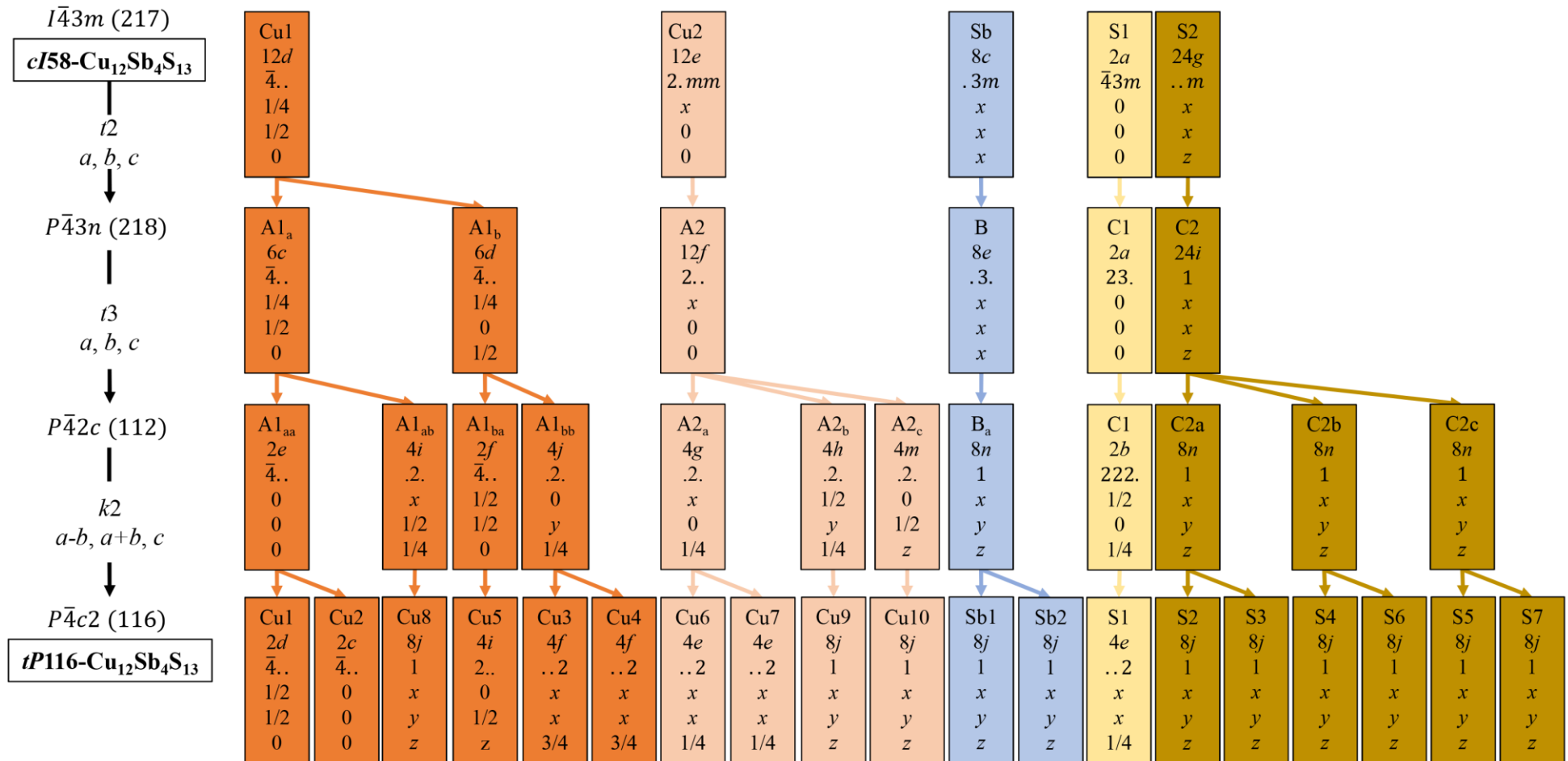
**Fig. S2.** Temperature dependences of  $B_{\text{iso}}$  of Cu2- (a) and S2-atoms (b), as well as interatomic distances Cu2-Cu2 (c), Cu2-S2 (d), Cu2-Sb (e) reported in [14] for cubic  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  in comparison with our data. In (d), (e) and (f) we present some analogous distances observed in the tetragonal structure of  $\text{Cu}_{11.95}\text{Ni}_{0.05}\text{Sb}_4\text{S}_{13}$ .



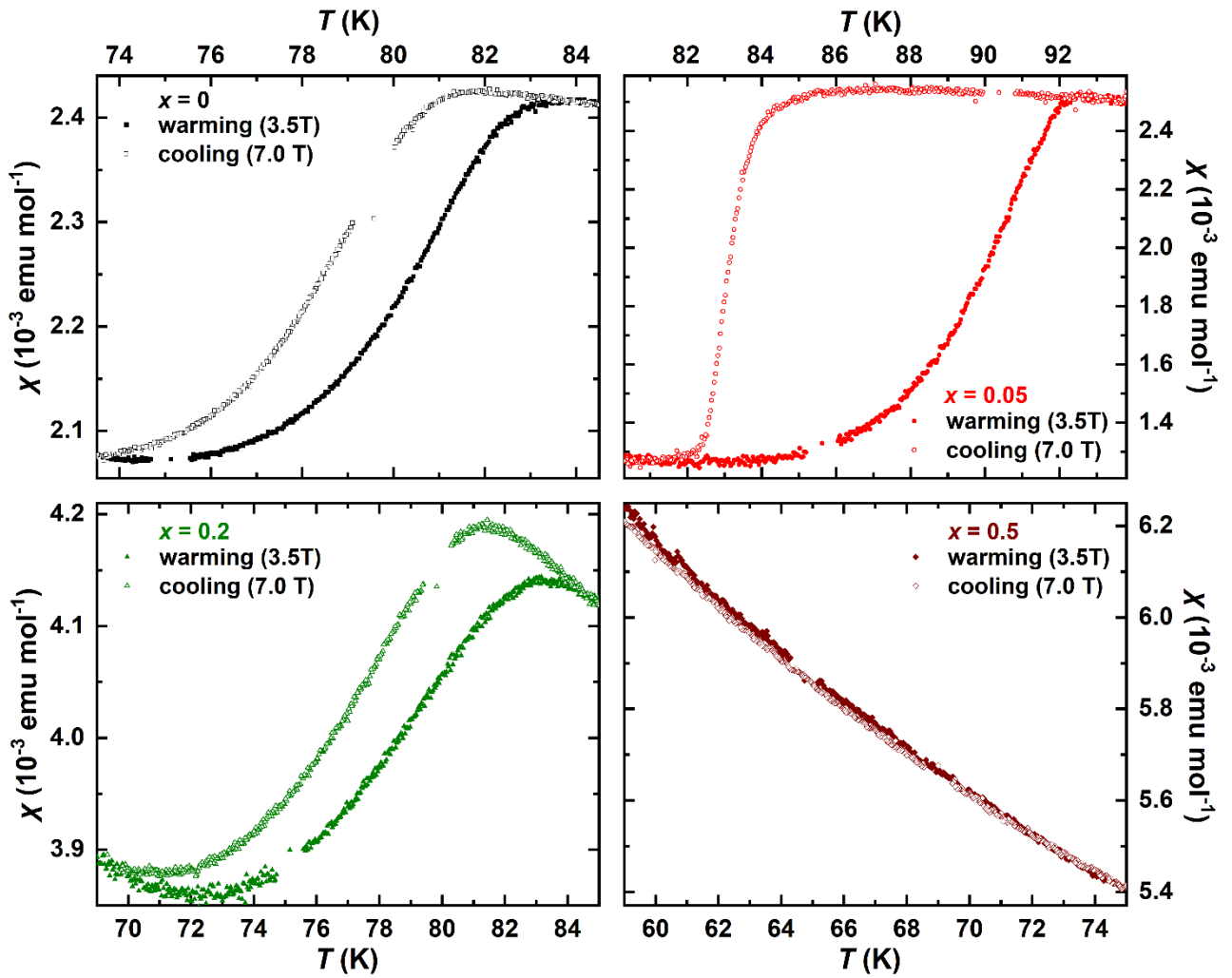
**Fig. S3.** Temperature dependence of the unit cell volume (UCV) of  $\text{Cu}_{11.95}\text{Ni}_{0.05}\text{Sb}_4\text{S}_{13}$ . UCV refined for the cubic modification of this compound (i.e., at 100 K and 293 K) were multiplied by a factor of 2 to make them comparable with those of the tetragonal structures. Solid line is guides for eyes only. Inset: temperature dependence of UCV in low temperature regime and near the structural phase transition. Estimation of the  $\Delta V \approx -0.25\%$  jump is tentative, due to the lack of the of the measured points above 100 K.



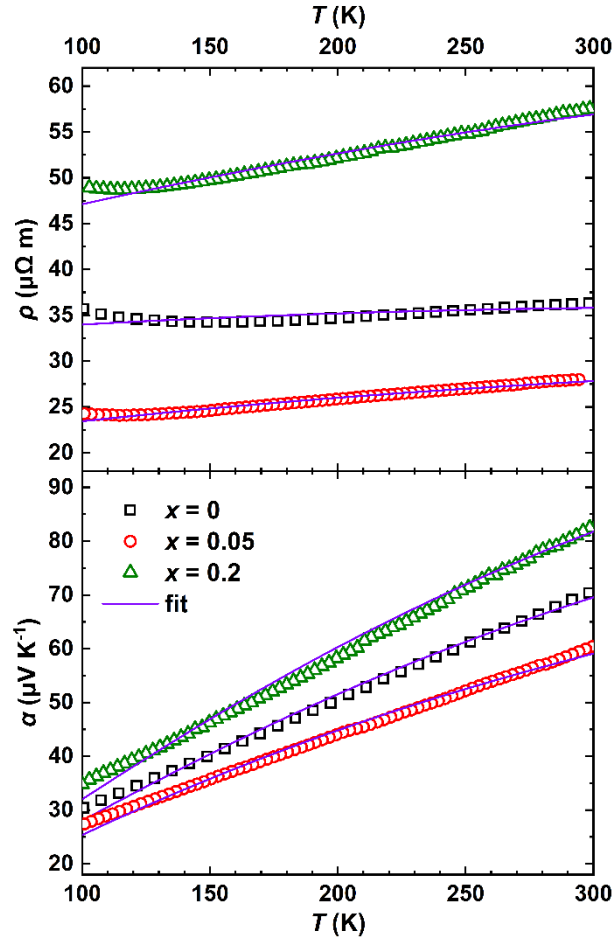
**Fig. S4.** Temperature dependence of the unit cell parameters (UCP) of  $\text{Cu}_{11.95}\text{Ni}_{0.05}\text{Sb}_4\text{S}_{13}$ . Inset: temperature dependence of the  $c/a$ -ratio of tetragonal  $\text{Cu}_{11.95}\text{Ni}_{0.05}\text{Sb}_4\text{S}_{13}$ . Solid lines are guides for eyes only.



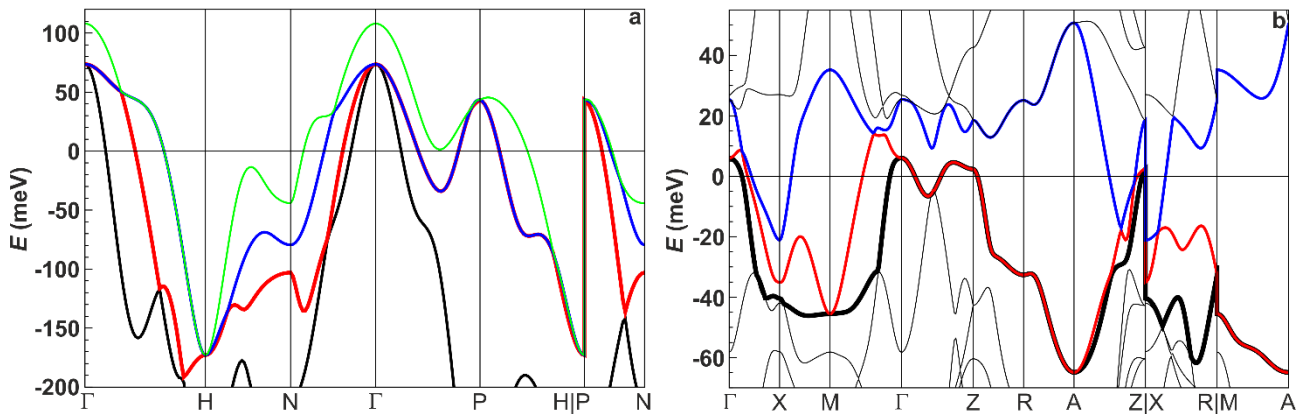
**Fig. S5.** Group-subgroup scheme of symmetry reduction operations needed to transform high temperature cubic ( $I\bar{4}3m$ )  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  tetrahedrite into its low temperature tetragonal ( $P\bar{4}c2$ ) modification. First two *translationsgleiche* ( $t$ ) transformations of indexes 2 and 3, respectively do not assume any changes in unit cell parameters whereas *klassengleiche* ( $k$ ) symmetry reduction of index 2 indicates  $a_{\text{tetr}} \approx a_{\text{cub}}\sqrt{2}$ ;  $c_{\text{tetr}} \approx a_{\text{cub}}$ .



**Fig. S6.** Hystereses in the temperature dependencies of magnetic susceptibilities of  $\text{Cu}_{12-x}\text{Ni}_x\text{Sb}_4\text{S}_{13}$  compounds at the structural phase transitions.



**Fig. S7.** Temperature dependencies of electrical resistivity [ $\rho(T)$ ] and Seebeck coefficient [ $\alpha(T)$ ] of  $\text{Cu}_{12-x}\text{Ni}_x\text{Sb}_4\text{S}_{13}$  together with the fits to a two-parabolic bands model for  $T > 100$  K performed by using *SeeBand* software



**Fig. S8.** Bands crossing the Fermi level ( $E_F = 0$  meV) in the electronic structure of cubic ( $I\bar{4}3m$ ) (a) and of tetragonal ( $P\bar{4}c2$ ) (b)  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ . The bands 249, 250, 251, 252 (a) are given in black, red, blue and green colors, respectively. The bands 1003, 1004, 1005 (b) are presented in black, red and blue, respectively.

**Table S1.** Crystallographic data for cubic (space group  $I\bar{4}3m$ )  $\text{Cu}_{12-x}\text{Ni}_x\text{Sb}_4\text{S}_{13}$  tetrahedrites refined from HR PXRD at different temperatures.

Ni-content	$x = 0$			$x = 0.05$		$x = 0.2$		$x = 0.5$		
EDX composition	$\text{Cu}_{12.0(1)}\text{Sb}_{4.1(1)}\text{S}_{12.9(1)}$			$\text{Cu}_{12.0(1)}\text{Ni}_{0.03(10)}\text{Sb}_{4.1(1)}\text{S}_{12.7(1)}$		$\text{Cu}_{11.9(1)}\text{Ni}_{0.2(1)}\text{Sb}_{4.1(1)}\text{S}_{12.8(1)}$		$\text{Cu}_{11.5(1)}\text{Ni}_{0.5(1)}\text{Sb}_{4.1(1)}\text{S}_{12.7(1)}$		
$T$ , K	10 K	100 K	293 K	100 K	293 K	100 K	293 K	10 K	100 K	293 K
$a$ , Å	10.30679(3)	10.30422(3)	10.32356(3)	10.29929(3)	10.33731(5)	10.29886(2)	10.32947(2)	10.29754(4)	10.29974(2)	10.32116(3)
$V$ , Å <sup>3</sup>	1094.89(9)	1094.07(1)	1100.24(1)	1092.500(8)	1104.65(2)	1092.365(6)	1102.134(6)	1091.95(2)	1092.646(7)	1099.475(8)
$\rho$ , g cm <sup>-3</sup>	5.05(1)	5.0584(1)	5.0301(1)	5.0657(1)	5.0100(1)	5.0663(1)	5.0214(0)	5.0683(1)	5.0650(1)	5.0336(1)
$2\theta_{\max}$ (°), $\sin\theta/\lambda_{\max}$	40, 0.964	40, 0.964	40, 0.964	40, 0.964	40, 0.964	40, 0.964	40, 0.964	40, 0.964	40, 0.964	40, 0.964
$N_{\text{reflections}}$	443	443	443	443	443	443	443	443	443	443
$h_{\min}, k_{\min}, l_{\min}$	0, 0, 1	0, 0, 1	0, 0, 1	0, 0, 1	0, 0, 1	0, 0, 1	0, 0, 1	0, 0, 1	0, 0, 1	0, 0, 1
$h_{\max}, k_{\max}, l_{\max}$	11, 14, 20	11, 14, 20	11, 14, 20	11, 14, 20	11, 14, 20	11, 14, 20	11, 14, 20	11, 14, 20	11, 14, 20	11, 14, 20
$N_{\text{free parameters}}$	11	11	11	11	11	11	11	11	11	11
Residual peaks ( $e^- \text{Å}^{-3}$ )	-0.63/1.37	-0.44/0.56	-0.41/0.71	-0.45/0.67	-0.53/0.76	-0.43/0.67	-0.56/0.78	-0.42/0.68	-0.38/0.60	-0.32/0.40
$R_I$	0.048	0.0462	0.0431	0.0446	0.0328	0.0361	0.0351	0.0444	0.0428	0.0498
$R_P$	0.036	0.0322	0.0367	0.0409	0.0698	0.0323	0.0348	0.0660	0.0301	0.0402

**Table S2.** Crystallographic data for tetragonal (space group  $P\bar{4}2c$ )  $\text{Cu}_{12-x}\text{Ni}_x\text{Sb}_4\text{S}_{13}$  tetrahedrites refined from HR PXRD at different temperatures.

$T$ , K	$x = 0.05$							$x = 0.2$
	10 K	25 K	40 K	50 K	60 K	70 K	80 K	10 K
$a$ , Å	14.5985(1)	14.6004(1)	14.6010(1)	14.6009(1)	14.6011(1)	14.6011(1)	14.5757(3)	14.5897(2)
$c$ , Å	10.27474(9)	10.2727(1)	10.2722(1)	10.2720(1)	10.2722(1)	10.2727(1)	10.2886(3)	10.2819(2)
$V$ , Å <sup>3</sup>	2189.71(5)	2189.84(6)	2189.92(6)	2189.84(6)	2189.93(6)	2190.05(6)	2185.8(2)	2188.60
$\rho$ , g cm <sup>-3</sup>	5.0548(1)	5.0538(2)	5.0536(2)	5.0545(2)	5.0543(2)	5.0540(2)	5.06(3)	5.0574(2)
$2\theta_{\max}$ (°), $\sin\theta/\lambda_{\max}$	40.00, 0.964	29.99, 0.730	29.99, 0.730	29.99, 0.730	29.99, 0.730	29.99, 0.730	29.99, 0.730	40.00, 0.964
$N_{\text{reflections}}$	4430	1967	1968	1968	1967	1968	1960	4428
$h_{\min}, k_{\min}, l_{\min}$	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0
$h_{\max}, k_{\max}, l_{\max}$	20, 28, 20	20, 28, 20	15, 22, 15	15, 22, 15	15, 22, 15	15, 22, 15	15, 22, 15	20, 28, 20
$N_{\text{free parameters}}$	59	59	59	59	59	59	59	59
Residual peaks ( $e^- \text{Å}^{-3}$ )	-0.76/0.99	-0.56/0.79	-0.41/0.57	-0.40/0.51	-0.47/0.61	-0.57/0.75	-0.59/0.81	-0.81/1.32
$R_I$	0.0524	0.0435	0.0399	0.0423	0.0522	0.0538	0.083	0.0421
$R_P$	0.0649	0.0715	0.0715	0.0670	0.0679	0.0643	0.062	0.1025

**Table S3.** Atomic coordinates, thermal displacement ( $B_{\text{iso}}$ ) and occupational ( $G$ ) parameters as well as interatomic distances ( $d$ ) for cubic (space group  $I\bar{4}3m$ )  $\text{Cu}_{12-x}\text{Ni}_x\text{Sb}_4\text{S}_{13}$  tetrahedrites refined from HR PXRD at different temperatures.\*

Atom	Site	$T$	$x = 0$			$x = 0.05$		$x = 0.2$		$x = 0.5$		
			10 K	100 K	293 K	100 K	293 K	100 K	293 K	10 K	100 K	293 K
Cu1	12d, (1/4 1/2 0)	$B_{\text{iso}}, \text{\AA}$	0.965(8)	0.805(8)	1.65(1)	0.632(7)	1.91(1)	0.590(8)	1.731(8)	0.81(1)	0.645(8)	1.792(10)
		-4S2	2.3035(5)	2.3044(5)	2.3076(5)	2.3034(5)	2.3218(6)	2.3028(5)	2.3174(4)	2.2991(7)	2.3019(5)	2.3126(5)
		-4Sb	3.6562(2)	3.6588(2)	3.6650(2)	3.6574(2)	3.6694(2)	3.6574(2)	3.6669(2)	3.6552(2)	3.6579(2)	3.6644(2)
Cu2	24g ( $x x z$ )	$x$	0.0026(5)	0.01801(5)	0.02037(5)	0.01702(5)	0.02068(6)	0.01691(5)	0.02033(4)	0.0122(1)	0.01720(5)	0.02034(5)
		$z$	0.78388(5)	0.78192(5)	0.78163(5)	0.78171(5)	0.78306(5)	0.78186(5)	0.78273(4)	0.78298(7)	0.78176(5)	0.78233(5)
		$B_{\text{iso}}, \text{\AA}$	4.30(2)	1.82(2)	2.40(2)	1.54(1)	2.89(2)	1.52(2)	2.66(2)	2.89(3)	1.45(2)	2.69(2)
		$G$	0.50(1)	0.50(1)	0.50(1)	0.50(1)	0.50(1)	0.50(1)	0.50(1)	0.50(1)	0.50(1)	0.50(1)
		-1Cu2	0.075(7)	0.5247(8)	0.5946(8)	0.4955(8)	0.6045(8)	0.4923(8)	0.5937(6)	0.355(2)	0.5009(8)	0.5937(7)
		-1S1	2.2279(5)	2.2625(5)	2.2739(6)	2.2619(5)	2.2630(6)	2.2600(5)	2.2640(5)	2.2420(7)	2.2617(6)	2.2662(5)
		-2S2	2.262(4)	2.2734(7)	2.2763(8)	2.2688(7)	2.2750(8)	2.2698(7)	2.2759(6)	2.271(1)	2.2734(8)	2.2781(7)
		-2Cu2	3.113(5)	2.9156(7)	2.8909(8)	2.9318(7)	2.8693(8)	2.9310(8)	2.8773(6)	2.983(2)	2.9285(8)	2.8803(7)
		-1Sb	3.367(5)	3.1069(6)	3.0841(6)	3.1169(6)	3.0909(6)	3.1168(6)	3.0897(5)	3.203(1)	3.1110(6)	3.0819(6)
Sb	8c ( $x x x$ )	$x$	0.26674(2)	0.26899(1)	0.26860(2)	0.26918(1)	0.26817(2)	0.26929(2)	0.26842(1)	0.26810(2)	0.26941(2)	0.26874(1)
		$B_{\text{iso}}, \text{\AA}$	0.954(4)	0.774(3)	1.279(4)	0.554(3)	1.472(4)	0.536(3)	1.308(3)	0.740(4)	0.587(3)	1.343(4)
		-3S2	2.4342(5)	2.4352(5)	2.4438(5)	2.4365(5)	2.4399(6)	2.4380(5)	2.4382(4)	2.4352(7)	2.4368(5)	2.4358(5)
S1	2a (0 0 0)	$B_{\text{iso}}, \text{\AA}$	4.36(7)	1.61(4)	1.66(5)	1.27(4)	1.73(5)	1.34(4)	1.92(4)	3.09(8)	1.17(4)	2.01(5)
		-12Cu2	2.2279(5)	2.2625(5)	2.2739(6)	2.2619(5)	2.2630(6)	2.2600(5)	2.2640(5)	2.2420(7)	2.2617(6)	2.2662(5)
S2	24g ( $x x z$ )	$x$	0.11458(4)	0.11586(4)	0.11537(5)	0.11581(4)	0.11508(5)	0.11579(4)	0.11536(4)	0.11536(6)	0.11603(4)	0.11574(4)
		$z$	0.36406(6)	0.36363(5)	0.36388(6)	0.36363(5)	0.36217(6)	0.36370(5)	0.36254(5)	0.36434(8)	0.36386(6)	0.36295(5)
		$B_{\text{iso}}, \text{\AA}$	0.920 (10)	0.621(8)	1.00(1)	0.466(8)	1.30(1)	0.469(8)	1.178(8)	0.69(1)	0.511(8)	1.203(9)
		-2Cu2	2.262(4)	2.2734(7)	2.2763(8)	2.2688(7)	2.2750(8)	2.2698(7)	2.2759(6)	2.271(1)	2.2734(8)	2.2781(7)
		-2Cu1	2.3035(5)	2.3044(5)	2.3076(5)	2.3034(5)	2.3218(6)	2.3028(5)	2.3174(4)	2.2991(7)	2.3019(5)	2.3126(5)
		-1S2	3.3399(7)	3.3767(6)	3.3684(7)	3.3736(6)	3.3649(7)	3.3729(6)	3.3704(5)	3.3602(9)	3.3802(7)	3.3785(6)

\* - Ni-content  $x$  cannot be refined from this data due to the small difference (i.e.  $1e^-$ ) in the electronic density between Ni and Cu. Hence, Ni can occupy any of the Cu-atom sites.

**Table S4.** Atomic coordinates and thermal displacement ( $B_{\text{iso}}$ ) for tetragonal (space group  $P\bar{4}2c$ )  $\text{Cu}_{12-x}\text{Ni}_x\text{Sb}_4\text{S}_{13}$  tetrahedrites refined from HR PXRD at different temperatures. \*

Atom Site			$x = 0.05$							$x = 0.2$
1	2	3	4	5	6	7	8	9	10	11
		$T$	10 K	25 K	40 K	50 K	60 K	70 K	80 K	10 K
Cu1	2d, (1/2 1/2 0)	$B_{\text{iso}}, \text{\AA}^2$	0.44(8)	0.847(6)	0.782(6)	0.76(3)	0.70(3)	0.66(3)	0.64(3)	0.60(15)
Cu2	2c, (0 0 0)	$B_{\text{iso}}, \text{\AA}^2$	0.46(7)	0.880(6)	0.844(6)	0.83(3)	0.81(3)	0.80(3)	0.75(3)	0.6(2)
Cu3	4f, (x, x, 3/4)	$x$	0.1376(6)	0.1376(2)	0.1376(2)	0.1380(7)	0.1383(7)	0.1385(7)	0.1376(10)	0.1348(6)
		$B_{\text{iso}}, \text{\AA}^2$	0.39(5)	0.756(6)	0.676(6)	0.64(3)	0.58(3)	0.53(3)	0.47(3)	0.57(10)
Cu4	4f, (x, x, 3/4)	$x$	0.3808(6)	0.3796(2)	0.3796(2)	0.3796(7)	0.3799(7)	0.3798(8)	0.3754(12)	0.3780(7)
		$B_{\text{iso}}, \text{\AA}^2$	0.25(5)	0.712(6)	0.625(6)	0.59(3)	0.52(3)	0.48(3)	0.44(3)	0.46(10)
Cu5	4i, (0, 1/2, z)	$z$	0.0274(12)	0.0245(4)	0.0258(4)	0.026(2)	0.026(2)	0.026(2)	0.016(3)	0.0188(15)
		$B_{\text{iso}}, \text{\AA}^2$	0.63(6)	0.783(6)	0.703(6)	0.67(3)	0.62(3)	0.57(3)	0.55(3)	0.77(13)
Cu6	4e, (x, x, 1/4)	$x$	0.3525(6)	0.3522(2)	0.3513(2)	0.3524(7)	0.3522(7)	0.3520(7)	0.3561(11)	0.3547(6)
		$B_{\text{iso}}, \text{\AA}^2$	1.82(6)	0.919(6)	0.990(6)	1.02(3)	1.09(3)	1.14(3)	1.20(3)	0.95(9)
Cu7	4e, (x, x, 1/4)	$x$	0.1263(6)	0.1265(2)	0.1257(2)	0.1262(7)	0.1264(7)	0.1265(7)	0.1308(9)	0.1284(6)
		$B_{\text{iso}}, \text{\AA}^2$	0.97(5)	0.866(6)	0.830(6)	0.82(3)	0.81(3)	0.81(3)	0.91(3)	0.75(8)
Cu8	8j, (x, y, z)	$x$	0.6257(7)	0.6248(2)	0.6247(2)	0.6247(8)	0.6252(8)	0.6249(8)	0.6262(11)	0.6246(7)
		$y$	0.1223(6)	0.1215(2)	0.1214(2)	0.1214(7)	0.1213(7)	0.1210(7)	0.1246(12)	0.1241(7)
		$z$	0.2403(9)	0.2401(3)	0.2400(3)	0.2396(11)	0.2393(11)	0.2387(11)	0.245(2)	0.2432(10)
		$B_{\text{iso}}, \text{\AA}^2$	0.61(4)	0.617(6)	0.512(6)	0.47(3)	0.39(3)	0.31(3)	0.24(3)	0.59(7)
Cu9	8j, (x, y, z)	$x$	0.3613(5)	0.3621(2)	0.3615(2)	0.3615(7)	0.3611(7)	0.3603(7)	0.3550(10)	0.3592(6)
		$y$	0.1512(6)	0.1508(2)	0.1502(2)	0.1501(7)	0.1494(7)	0.1496(7)	0.1425(10)	0.1521(6)
		$z$	0.2178(7)	0.2162(2)	0.2164(2)	0.2168(8)	0.2168(9)	0.2170(9)	0.2273(14)	0.2223(8)
		$B_{\text{iso}}, \text{\AA}^2$	1.02(4)	0.988(6)	0.976(6)	0.97(3)	0.99(3)	0.99(3)	1.13(3)	0.88(7)
Cu10	8j, (x, y, z)	$x$	0.2721(5)	0.2718(1)	0.2720(1)	0.2717(6)	0.2718(6)	0.2713(6)	0.2637(10)	0.2694(5)
		$y$	0.2510(6)	0.2496(2)	0.2501(2)	0.2506(7)	0.2509(7)	0.2513(7)	0.2630(11)	0.2522(6)
		$z$	0.0417(6)	0.0420(2)	0.0413(2)	0.0414(8)	0.0413(8)	0.0415(8)	0.039(2)	0.0428(7)
		$B_{\text{iso}}, \text{\AA}^2$	0.93(4)	0.974(6)	0.954(6)	0.95(3)	0.95(3)	0.93(3)	1.07(3)	0.73(6)
Sb1	8j, (x, y, z)	$x$	0.2536(4)	0.2538(1)	0.2532(1)	0.2531(5)	0.2526(5)	0.2521(4)	0.2485(6)	0.2514(4)
		$y$	0.4776(2)	0.47732(6)	0.47735(6)	0.4770(3)	0.4771(3)	0.4768(3)	0.4793(6)	0.4787(3)
		$z$	0.0235(4)	0.0242(1)	0.0244(1)	0.0244(5)	0.0244(5)	0.0242(5)	0.0221(9)	0.0219(4)
		$B_{\text{iso}}, \text{\AA}^2$	0.70(2)	0.573(5)	0.509(5)	0.49(2)	0.45(2)	0.40(2)	0.46(3)	0.47(3)
Sb2	8j, (x, y, z)	$x$	0.2556(4)	0.2562(1)	0.2563(1)	0.2563(4)	0.2568(4)	0.2570(4)	0.2531(6)	0.2548(4)
		$y$	0.0073(2)	0.00709(6)	0.00723(6)	0.0071(3)	0.0071(3)	0.0071(3)	0.0136(5)	0.0093(2)
		$z$	0.0083(4)	0.0079(1)	0.0081(1)	0.0083(4)	0.0084(4)	0.0088(4)	0.0173(8)	0.0114(4)

Continuation of **Table S4**

1	2	3	4	5	6	7	8	9	10	11
			10 K	25 K	40 K	50 K	60 K	70 K	80 K	10 K
Sb2		$B_{\text{iso}}, \text{\AA}^2$	0.76(2)	0.513(5)	0.422(5)	0.39(2)	0.37(2)	0.34(2)	0.47(3)	0.47(3)
S1	4e, (x, x, 1/4)	x	0.2329(8)	0.2326(2)	0.2333(2)	0.2331(9)	0.2337(9)	0.2345(9)	0.2423(14)	0.2341(7)
		$B_{\text{iso}}, \text{\AA}^2$	1.08(9)	0.972(6)	0.955(6)	0.95(3)	0.92(3)	0.90(3)	0.87(3)	0.87(15)
S2	8j, (x, y, z)	x	0.2508(14)	0.2502(4)	0.2509(4)	0.250(2)	0.250(2)	0.250(2)	0.251(3)	0.251(2)
		y	0.1479(11)	0.1472(3)	0.1483(3)	0.1470(14)	0.1470(14)	0.1474(14)	0.146(2)	0.1444(13)
		z	0.5973(13)	0.5987(4)	0.5985(4)	0.599(2)	0.599(2)	0.600(2)	0.601(3)	0.6017(14)
		$B_{\text{iso}}, \text{\AA}^2$	0.45(7)	0.845(6)	0.780(6)	0.75(3)	0.69(3)	0.65(3)	0.54(3)	0.56(13)
S3	8j, (x, y, z)	x	0.251(2)	0.2505(5)	0.2510(5)	0.252(2)	0.251(2)	0.252(2)	0.252(3)	0.251(2)
		y	0.6282(11)	0.6284(3)	0.6284(4)	0.6282(14)	0.6285(14)	0.6280(15)	0.629(3)	0.6296(13)
		z	0.1229(14)	0.1218(4)	0.1217(4)	0.122(2)	0.122(2)	0.122(2)	0.116(3)	0.119(2)
		$B_{\text{iso}}, \text{\AA}$	0.44(6)	0.790(6)	0.708(6)	0.67(3)	0.59(3)	0.53(3)	0.44(3)	0.47(12)
S4	8j, (x, y, z)	x	0.0162(13)	0.0162(4)	0.0171(4)	0.016(2)	0.016(2)	0.017(2)	0.010(3)	0.0177(14)
		y	0.3720(14)	0.3719(4)	0.3719(4)	0.372(2)	0.372(2)	0.372(2)	0.373(3)	0.3718(15)
		z	0.153(2)	0.1526(6)	0.1529(6)	0.153(3)	0.153(2)	0.153(2)	0.140(4)	0.153(2)
		$B_{\text{iso}}, \text{\AA}$	0.55(9)	0.851(6)	0.785(6)	0.76(3)	0.70(3)	0.65(3)	0.55(3)	0.53(14)
S5	8j, (x, y, z)	x	0.0009(11)	0.0013(3)	0.0021(3)	0.0011(13)	0.0009(13)	0.0008(14)	0.007(2)	0.0051(12)
		y	0.123(2)	0.1226(5)	0.1241(5)	0.123(2)	0.123(2)	0.124(2)	0.122(3)	0.120(2)
		z	0.138(2)	0.1370(6)	0.1376(6)	0.138(3)	0.138(3)	0.139(3)	0.140(4)	0.132(3)
		$B_{\text{iso}}, \text{\AA}$	0.82(9)	0.876(6)	0.824(6)	0.80(3)	0.75(3)	0.71(3)	0.63(3)	0.67(14)
S6	8j, (x, y, z)	x	0.4850(11)	0.4849(3)	0.4866(3)	0.4851(14)	0.4844(14)	0.4847(14)	0.489(2)	0.4863(13)
		y	0.3720(15)	0.3725(5)	0.3741(5)	0.373(2)	0.373(2)	0.372(2)	0.373(3)	0.374(2)
		z	0.133(2)	0.1337(6)	0.1339(6)	0.134(3)	0.134(3)	0.134(3)	0.130(5)	0.131(3)
		$B_{\text{iso}}, \text{\AA}$	0.39(7)	0.833(6)	0.774(6)	0.75(3)	0.70(3)	0.66(3)	0.60(3)	0.59(14)
S7	8j, (x, y, z)	x	0.4940(11)	0.4941(3)	0.4945(3)	0.4943(14)	0.4949(14)	0.4954(14)	0.494(2)	0.4900(14)
		y	0.1245(15)	0.1251(5)	0.1255(5)	0.125(2)	0.125(2)	0.126(2)	0.125(3)	0.124(2)
		z	0.119(2)	0.1177(5)	0.1173(5)	0.118(2)	0.119(2)	0.120(2)	0.130(4)	0.126(2)
		$B_{\text{iso}}, \text{\AA}$	0.52(8)	0.825(6)	0.746(6)	0.71(3)	0.64(3)	0.58(3)	0.50(3)	0.7(2)

\* - Ni-content  $x$  cannot be refined from this data due to the small difference (i.e.  $1e^-$ ) in the electronic density between Ni and Cu. Hence, Ni can occupy any of the Cu-atom sites.

**Table S5.** Interatomic distances ( $d$ ) in tetragonal (space group  $P\bar{4}2c$ )  $\text{Cu}_{12-x}\text{Ni}_x\text{Sb}_4\text{S}_{13}$  tetrahedrites

			$x = 0.05$							$x = 0.2$
1	2	3	4	5	6	7	8	9	10	11
Atom	Site	CN	10 K	25 K	40 K	50 K	60 K	70 K	80 K	10 K
Cu1	-4S6	4	2.323(5)	2.325(6)	2.304(6)	2.325(6)	2.324(6)	2.312(6)	2.29(4)	2.29(2)
	-4Cu4		3.555(1)	3.561(2)	3.574(2)	3.564(2)	3.563(2)	3.558(2)	3.662(5)	3.598(7)
	-4Sb1		3.621(1)	3.624(2)	3.627(2)	3.629(2)	3.637(2)	3.647(2)	3.686(8)	3.647(6)
Cu2	-4S5	4	2.286(5)	2.287(6)	2.298(6)	2.294(6)	2.296(6)	2.322(6)	2.29(4)	2.22(2)
	-4Sb2		3.738(1)	3.742(4)	3.745(2)	3.740(2)	3.750(1)	3.752(1)	3.699(8)	3.722(5)
Cu3	-2S2	4	2.273(4)	2.270(5)	2.276(6)	2.274(5)	2.262(5)	2.268(5)	2.26(4)	2.28(2)
	-2S5		2.342(4)	2.345(5)	2.351(5)	2.329(5)	2.339(5)	2.308(5)	2.40(4)	2.38(2)
	-2Cu8		3.458(3)	3.462(4)	3.480(4)	3.462(3)	3.456(3)	3.465(4)	3.45(2)	3.52(2)
	-2Sb2		3.692(2)	3.694(2)	3.695(2)	3.691(2)	3.696(2)	3.694(2)	3.66(2)	3.674(8)
Cu4	-2Sb2	4	3.693(2)	3.695(2)	3.696(2)	3.696(2)	3.701(2)	3.705(2)	3.70(2)	3.694(7)
	-2S6		2.292(4)	2.316(5)	2.290(6)	2.290(6)	2.322(5)	2.306(6)	2.33(4)	2.33(2)
	-2S3		2.318(5)	2.307(6)	2.297(6)	2.309(5)	2.296(6)	2.270(6)	2.27(4)	2.29(2)
Cu5	-2Cu1	4	3.555(1)	3.561(2)	3.574(2)	3.564(2)	3.563(2)	3.558(2)	3.662(2)	3.598(7)
	-2S4		2.279(5)	2.291(6)	2.295(6)	2.292(6)	2.294(6)	2.297(6)	2.25(4)	2.34(2)
	-2S7		2.357(5)	2.352(6)	2.350(7)	2.361(6)	2.359(6)	2.393(7)	2.37(4)	2.34(3)
Cu6	-2Cu8	3	3.506(3)	3.393(4)	3.499(4)	3.494(3)	3.498(4)	3.499(4)	3.57(2)	3.55(2)
	-2S6		2.299(4)	2.279(6)	2.331(6)	2.284(5)	2.280(5)	2.290(6)	2.31(4)	2.29(2)
	-1S1		2.472(3)	2.482(4)	2.438(4)	2.481(3)	2.461(4)	2.444(4)	2.34(3)	2.49(2)
	-2Cu10		2.857(2)	2.863(3)	2.850(3)	2.867(3)	2.865(3)	2.862(3)	2.89(2)	2.88(2)
Cu7	-2Cu9	3	2.962(3)	2.963(3)	2.961(3)	2.973(3)	2.977(4)	2.979(4)	3.12(2)	2.97(2)
	-2Sb1		3.291(2)	3.289(2)	3.287(2)	3.290(2)	3.292(2)	3.296(2)	3.34(2)	3.323(8)
	-2S5		2.159(4)	2.172(5)	2.142(5)	2.176(5)	2.171(5)	2.175(5)	2.14(4)	2.17(2)
Cu8	-1S1	4	2.197(3)	2.180(4)	2.222(4)	2.181(3)	2.199(4)	2.213(4)	2.30(2)	2.18(2)
	-2Sb2		3.572(2)	3.577(2)	3.578(2)	3.572(2)	3.579(2)	3.579(2)	3.44(2)	3.527(7)
	-1S7		2.291(4)	2.294(5)	2.282(6)	2.292(5)	2.277(5)	2.249(6)	2.26(4)	2.30(2)
	-1S4		2.313(5)	2.293(6)	2.303(6)	2.289(5)	2.295(6)	2.324(6)	2.30(4)	2.33(2)
Cu9	-1S2	3	2.341(5)	2.360(6)	2.359(6)	2.355(5)	2.342(6)	2.349(6)	2.34(4)	2.35(2)
	-1S3		2.350(5)	2.360(6)	2.366(6)	2.358(6)	2.375(6)	2.406(6)	2.34(4)	2.33(2)
	-1S7		2.234(4)	2.235(5)	2.223(5)	2.226(5)	2.247(5)	2.264(6)	2.27(4)	2.19(2)
	-1S1		2.247(3)	2.245(4)	2.257(4)	2.245(3)	2.244(3)	2.230(2)	2.21(2)	2.20(2)
	-1S4		2.367(5)	2.374(6)	2.368(6)	2.365(5)	2.339(6)	2.315(6)	2.38(4)	2.35(2)
Cu10	-1Cu10	3	2.663(3)	2.650(3)	2.659(3)	2.670(3)	2.680(3)	2.696(3)	2.93(2)	2.70(2)
	-1Cu6		2.962(3)	2.963(3)	2.961(3)	2.973(3)	2.977(4)	2.979(4)	3.12(2)	2.97(2)
	-1Sb2		3.381(2)	3.377(3)	3.360(2)	3.370(2)	3.364(2)	3.363(3)	3.22(2)	3.371(9)
	-1Sb1		3.485(2)	3.489(3)	3.495(2)	3.488(2)	3.483(2)	3.475(3)	3.51(2)	3.472(9)
	-1S3		2.221(4)	2.235(5)	2.218(5)	2.242(5)	2.234(5)	2.233(5)	2.24(4)	2.23(2)
	-1S1		2.231(2)	2.227(2)	2.231(2)	2.233(2)	2.231(2)	2.230(2)	2.21(2)	2.208(7)
	-1S2		2.329(4)	2.310(4)	2.307(5)	2.297(4)	2.302(4)	2.290(5)	2.25(3)	2.35(2)
Sb1	-1Cu9	3	2.663(3)	2.650(3)	2.659(3)	2.670(3)	2.680(3)	2.696(3)	2.93(2)	2.70(2)
	-1Cu6		2.857(2)	2.863(3)	2.850(3)	2.867(3)	2.865(3)	2.862(3)	2.89(2)	3.323(8)
	-1Sb1		3.332(2)	3.336(3)	3.333(3)	3.324(2)	3.326(3)	3.310(3)	3.16(2)	3.32(2)
	-1S7		2.420(5)	2.404(6)	2.402(6)	2.414(6)	2.406(6)	2.386(6)	2.41(4)	2.45(2)
	-1S3		2.423(4)	2.419(5)	2.421(5)	2.427(4)	2.420(5)	2.433(5)	2.39(4)	2.42(2)
	-1S6		2.431(5)	2.436(6)	2.458(6)	2.442(6)	2.449(6)	2.467(6)	2.44(4)	2.43(3)

Continuation of Table S5.

1	2	3	$x = 0.05$							$x = 0.2$
			4	5	6	7	8	9	10	11
Sb2	-1S4	3	2.400(5)	2.394(6)	2.389(6)	2.400(5)	2.405(5)	2.391(6)	2.41(4)	2.43(2)
	-1S2		2.437(4)	2.451(4)	2.455(5)	2.455(4)	2.457(4)	2.457(5)	2.48(3)	2.43(2)
	-1S5		2.458(5)	2.460(6)	2.444(7)	2.468(6)	2.467(6)	2.466(6)	2.52(4)	2.47(3)
S1	-1Cu9	6	3.381(2)	3.377(3)	3.360(2)	3.370(2)	3.364(2)	3.363(3)	3.22(2)	3.371(9)
	-1Cu7		2.197(3)	2.180(4)	2.222(4)	2.181(3)	2.199(4)	2.213(4)	2.30(2)	2.18(2)
	-2Cu10		2.231(2)	2.227(2)	2.331(2)	2.233(2)	2.231(2)	2.230(2)	2.21(2)	2.208(7)
S2	-2Cu9	4	2.247(3)	2.245(4)	2.257(4)	2.245(3)	2.244(3)	2.233(4)	2.21(2)	2.20(2)
	-1Cu6		2.472(3)	2.482(4)	2.438(4)	2.481(4)	2.461(4)	2.444(4)	2.34(3)	2.49(2)
	-1Cu3		2.273(4)	2.270(5)	2.276(6)	2.274(5)	2.262(5)	2.268(5)	2.26(4)	2.28(2)
S3	-1Cu10	4	2.329(4)	2.310(4)	2.307(5)	2.297(4)	2.302(4)	2.290(5)	2.25(3)	2.35(2)
	-1Cu8		2.341(5)	2.360(6)	2.359(6)	2.355(5)	2.342(6)	2.349(6)	2.34(4)	2.35(2)
	-1Sb2		2.437(4)	2.451(4)	2.455(5)	2.455(4)	2.457(4)	2.457(5)	2.48(3)	2.43(2)
S4	-1Cu10	4	2.221(4)	2.235(5)	2.218(5)	2.242(5)	2.234(5)	2.234(5)	2.24(4)	2.23(2)
	-1Cu4		2.318(5)	2.307(6)	2.297(6)	2.290(6)	2.296(6)	2.270(6)	2.27(4)	2.29(2)
	-1Cu8		2.350(5)	2.360(6)	2.366(6)	2.358(6)	2.375(6)	2.406(6)	2.34(4)	2.33(2)
S5	-1Sb1	4	2.423(4)	2.419(5)	2.421(5)	2.427(4)	2.420(5)	2.433(5)	2.39(4)	2.42(2)
	-1Cu5		2.279(5)	2.291(6)	2.295(6)	2.292(6)	2.294(6)	2.297(6)	2.25(4)	2.34(2)
	-1Cu8		2.313(5)	2.293(6)	2.303(6)	2.289(5)	2.295(6)	2.324(6)	2.30(4)	2.33(2)
S6	-1Cu9	4	2.367(5)	2.374(6)	2.368(6)	2.365(5)	2.339(6)	2.315(6)	2.38(4)	2.35(2)
	-1Sb2		2.400(5)	2.394(6)	2.389(6)	2.400(5)	2.405(5)	2.391(6)	2.41(4)	2.43(2)
	-1Cu7		2.159(4)	2.172(5)	2.142(5)	2.176(5)	2.171(5)	2.175(5)	2.14(4)	2.17(2)
S7	-1Cu2	4	2.286(5)	2.287(6)	2.298(6)	2.294(6)	2.296(6)	2.322(6)	2.29(4)	2.22(2)
	-1Cu3		2.342(4)	2.345(5)	2.351(5)	2.329(5)	2.339(5)	2.308(5)	2.40(4)	2.38(2)
	-1Sb2		2.458(5)	2.460(6)	2.447(7)	2.468(6)	2.449(6)	2.466(6)	2.52(4)	2.47(3)
S8	-1Cu4	4	2.292(4)	2.316(5)	2.290(6)	2.309(5)	2.322(5)	2.306(6)	2.33(4)	2.33(2)
	-1Cu6		2.299(4)	2.279(6)	2.331(6)	2.284(5)	2.280(5)	2.290(6)	2.31(4)	2.29(2)
	-1Cu1		2.323(5)	2.325(6)	2.304(6)	2.325(6)	2.324(6)	2.312(6)	2.29(4)	2.29(2)
S9	-1Sb1	4	2.420(5)	2.436(6)	2.458(6)	2.442(6)	2.449(6)	2.467(6)	2.44(4)	2.43(3)
	-1Cu9		2.234(4)	2.235(5)	2.223(5)	2.226(5)	2.247(5)	2.264(6)	2.27(4)	2.19(2)
	-1Cu8		2.291(4)	2.294(5)	2.282(6)	2.292(5)	2.277(5)	2.249(6)	2.26(4)	2.30(2)
S10	-1Cu5	4	2.357(5)	2.352(6)	2.350(7)	2.361(6)	2.359(6)	2.393(7)	2.37(4)	2.34(3)
	-1Sb1		2.420(5)	2.404(6)	2.402(6)	2.414(6)	2.406(6)	2.386(6)	2.41(4)	2.45(2)