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A Contribution to the Ternary Phase Diagram Co–Sb–Te*

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Abstract. The melting behaviour, some phase boundaries and the lattice parameters in the region of the NiAs-type phase in the ternary system cobalt–antimony–tellurium have been determined by differential thermal analysis and X-ray diffraction. A projection of the liquidus surface and the phase relationships in different sections with constant antimony/tellurium ratios are presented. The peculiar variation of the lattice parameters with the composition of the nonstoichiometric NiAs-type phase is discussed in terms of the defect structure.

Keywords. Phase diagram: Co–Sb–Te; NiAs-type phase; Lattice parameter: Co–Sb–Te

Ein Beitrag zum ternären Phasendiagramm Co–Sb–Te

Zusammenfassung. Im Bereich der NiAs-Phase des ternären Systems Kobalt–Antimon–Tellur wurden mit Hilfe von thermischen Analysen und Röntgenbeugung das Schmelzverhalten, einige Phasengrenzen und Gitterparameter bestimmt. Neben einer Projektion der Liquidusoberfläche werden die Phasenbeziehungen in verschiedenen Schnitten mit konstanten Konzentrationsverhältnissen Antimon/Tellur vorgestellt. Die ungewöhnliche Variation der Gitterparameter mit der Zusammensetzung der nicht-stöchiometrischen NiAs-Phase wird anhand des Defektmechanismus erörtert.

Introduction

The appearance of phases with the hexagonal NiAs-(B 8)-structure and that of a marcasite-(C 18)-related structure is a common feature of the binary systems Co–Sb and Co–Te. Although the ternary phase diagram Co–Sb–Te seems to be well established [1] it was worth to supplement the existing results by additional measurements with emphasis on the range of the ternary NiAs-type phase.

It is a widely accepted view that the deviations from the ideal NiAs-type structure with the stoichiometry 1 : 1 are due to either vacant transition metal sites (subtractive type) or the insertion of additional transition metal atoms on interstitial sites (additive type). According to its cobalt deficiency $Co_{1-x}Te$ represents the subtractive type of structure extending from about 55 to 64 at%Te [2–4] while the range of $Co_{1\pm x}Sb$, located around 50 at%Sb, includes both the subtractive and the additive version of the defect structure [5, 6].

* Dedicated to Prof. K. L. Komarek on the occasion of his 65th birthday

The careful analysis of the lattice parameters in $Ni_{1\pm x}Sb$, $Co_{1\pm x}Sb$ and $Ni_{1\pm x}(Sb, Te)$ revealed a close relation between the individual type of defect mechanism and the sensitivity of the lattice parameters to changes in composition [6–8]. In this sense, the present paper is a continuation of our preceding studies on this very particular subject complemented by some additional aspects of the phase diagram.

Experimental

The alloys were prepared by direct reaction of the elements using Co wire (purity >99.997%, Johnson-Matthey, U.K.) and antimony and tellurium lumps (purity >99.99%, Asarco, New York). The appropriate mixtures (≈1 g) were evacuated, repeatedly flushed with purified argon, and finally sealed under vacuum (≈0.01 Pa) in quartz ampoules. After a first reaction period of about three days at 1350 K the ingots were rapidly cooled to room temperature, crushed in ground, subjected again to repeated evacuating-flushing cycles, and once more sealed in quartz ampoules. In order to achieve homogeneity the alloys were thermally treated at 1150 K for about two weeks. The well homogenized powders were quenched in ice water and their phase purity and structure were determined by X-ray diffraction. The diffraction patterns were taken in 57.30 mm Debye-Scherrer cameras using $Co-K_\alpha$-radiation and Fe-filters.

Thermal effects were traced on a commercial thermal analyzer (DTA 404S/3), Netzsch, Selb, F.R.G.) using samples of about 0.5 g sealed under vacuum in special quartz containers. An empty alumina crucible was used as reference. Except for some special cases, the heating and cooling rate was 2 K min^{-1}. The temperature was determined with a Pt/Pt − Rh (10% Rh) thermocouple calibrated at the melting points of high purity zinc, antimony and gold.

Results and Discussion

Four different series of alloys were prepared with constant x_{Sb}/x_{Te} ratios of 0.33, 1, 3, and 7. The compositions of the alloys and the results of the thermal analyses

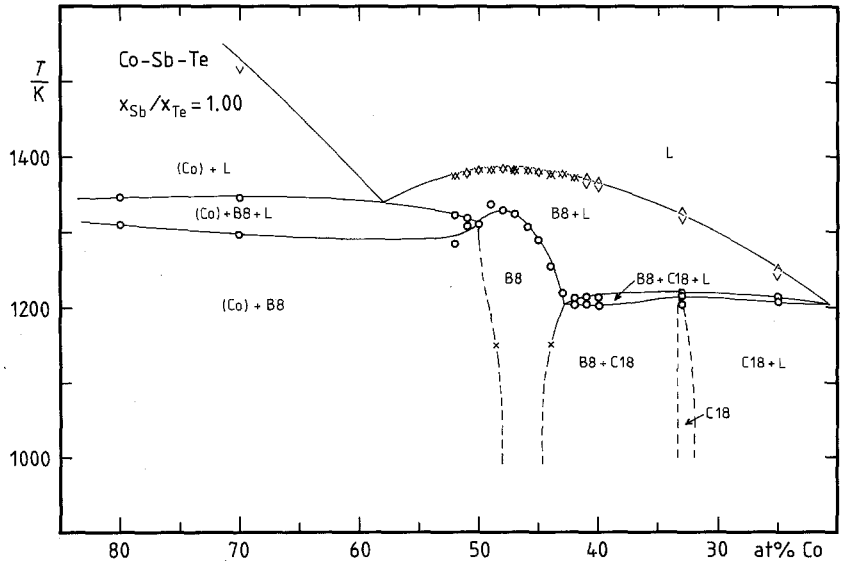

Fig. 1. Phase boundaries in the isopleth with $x_{Sb}/x_{Te}=1$. Λ, V liquidus on heating and cooling; ○ solidus and other thermal effects; × phase width deduced from lattice parameters

are listed in Table 1 together with the lattice parameters of the hexagonal-(NiAs)-phase (*a*, *c*) and those of some samples with the orthorhombic marcasite-phase (*a*, *b*, *c*).

The interpretation of the thermal effects and the resulting phase relationships in the isopleth with $x_{Sb}/x_{Te} = 1$ are presented in Fig. 1 covering the full composition range of Co investigated in this paper (25 – 80 at% Co). Those in the isopleths with $x_{Sb}/x_{Te} = 0.33$ and 3 are shown only for the vicinity of the B 8-phase (Fig. 2) in combination with the equivalent binary phase fields taken from the literature [3, 6].

Due to the likeness of the binary phase diagrams – a congruently melting B 8-type phase and a peritectically formed C 18-type phase [3, 6] – the appearance of the different phase fields remains the same throughout the ternary system, and the changes from one isopleth to the other are only gradual. According to the different stability ranges of the binary B 8-phases we observed a systematic change in the phase boundaries and in the position of the liquidus maximum. In the sequence of $x_{Sb}/x_{Te} = 0$, 0.33, 1, 3 and ∞ the liquidus maximum occurs successively at 1 288, 1 328, 1 388, 1 440, and 1 493 K being located at 43.8 46.0, 48.5, 50.0, and

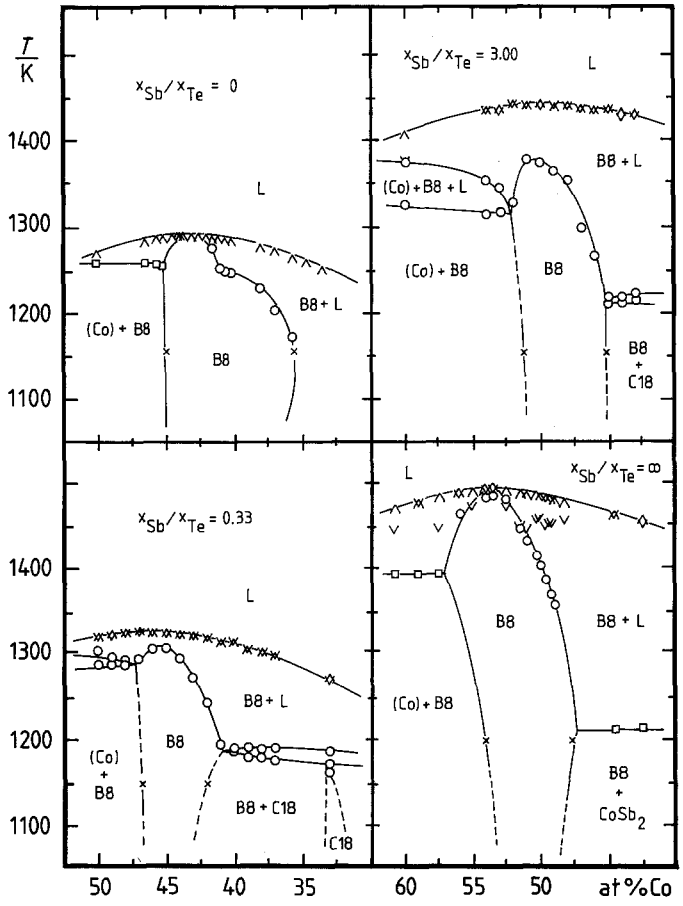

Fig. 2. The phase width of the B 8-type phase in the binary systems [3, 6] and in the isopleths with $x_{Sb}/x_{Te} = 0.33$ and 3. Λ, V liquidus on heating and cooling; ○ solidus and other thermal effects; × phase with deduced from lattice parameters

53.5 at% Co, respectively. At 1150 K – our reference temperature for the lattice parameters – the range of homogeneity shifts progressively from 36.5–44.7 to 42–47, 44–48.5, 45–51, and 47.4–54.8 at% Co.

A projection of the liquidus surface and the variation of the peritectic and the eutectic troughs across the ternary phase field are shown in Fig. 3. As already apparent from Fig. 2, the system shows a very simple melting behaviour. Both the eutectic and the peritectic trough as well as the liquidus surface itself rise in a continuous manner from the Te-rich towards Sb-rich side. As far as comparable to previous investigations in this system [1] it has to be noted that the form of the liquidus surface and the phase relationships are in principal agreement with our findings. In fact, the phase boundaries reported for the section from Co to Sb_2Te_3 have a strong resemblance to the isopleths presented in this paper (cf. Fig. 2), and even the somewhat distorted form of the B 8-phase field is almost the same as that of our isopleth with $x_{Sb}/x_{Te}=1$ (cf. Fig. 1).

The variation of the lattice parameters (a, c), the axial ratio (c/a), and the volume of unit cell (V) with the composition of the B 8-type phase is shown in Fig. 4 a–d. The additional isopleth with $x_{Sb}/x_{Te}=7$ has been prepared in order to elaborate some of the details on the antimony-rich side of the system.

The separately marked discontinuities in the lattice parameters manifest the phase boundaries which have also been included in Fig. 1 and Fig. 2. As to the width itself, we observed a narrowing of the ternary phase field around $x_{Sb}/x_{Te}=1$. The numerical values are already discussed in a previous section of this paper.

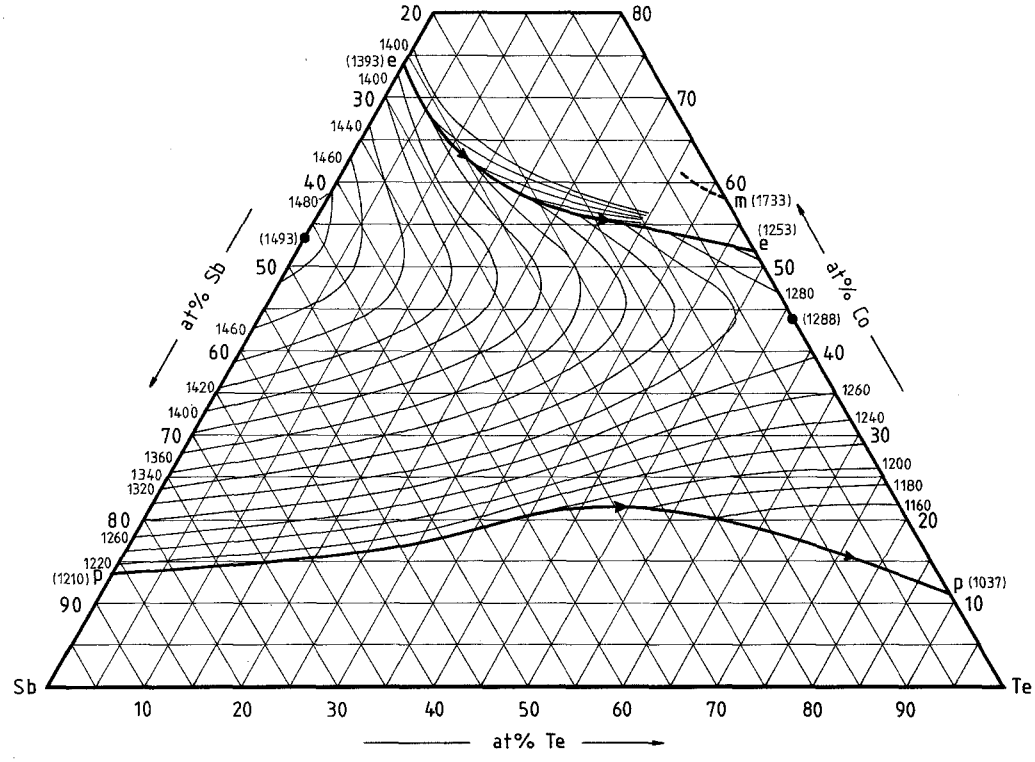

Fig. 3. Projection of the liquidus surface in the Co–Sb–Te system. e binary eutectic point, p binary peritectic point, m binary monotectic, ● congruent melting point

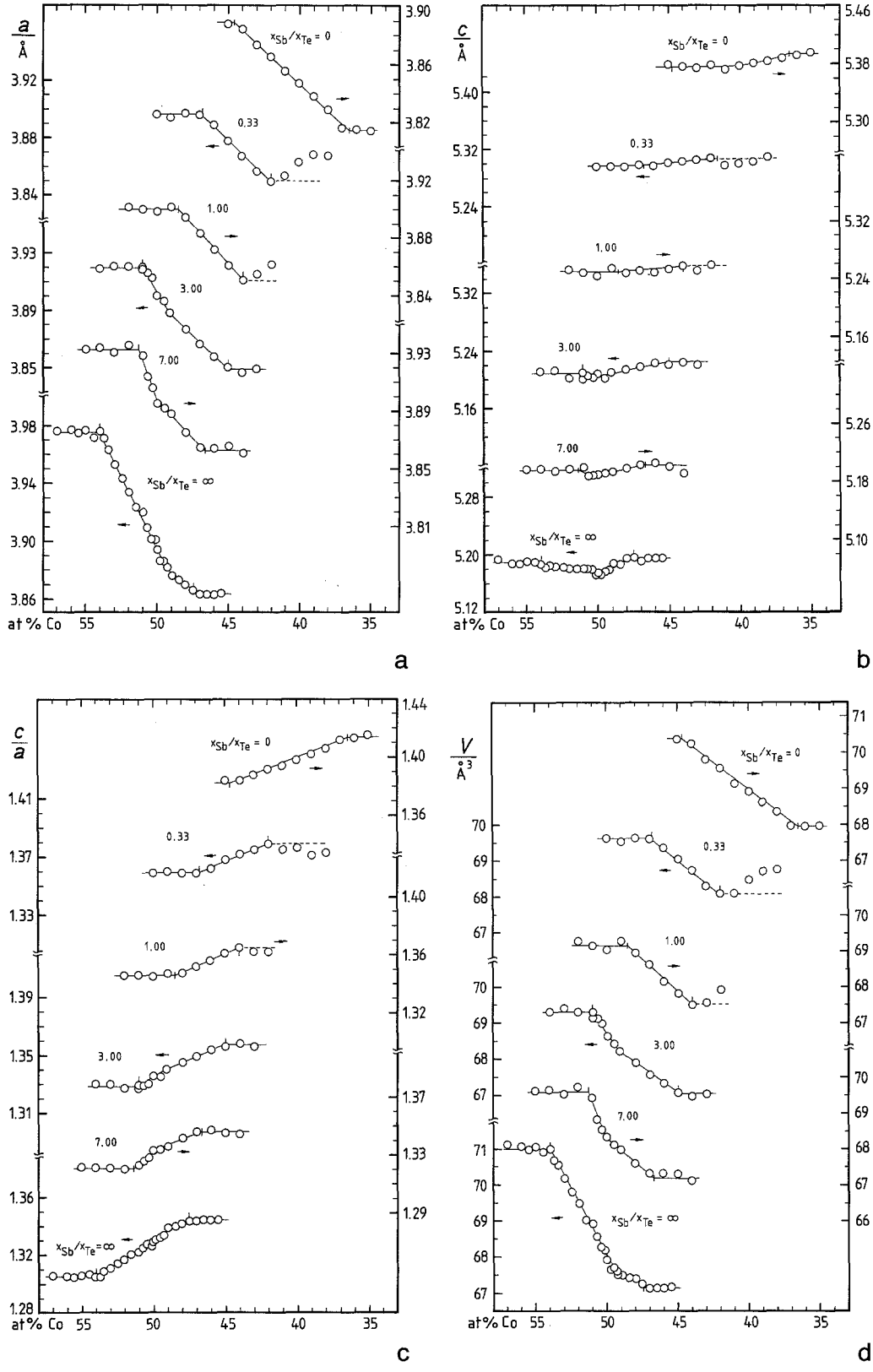

Fig. 4 a–d. Variation of the lattice parameters a and c, the axial ratio c/a, and the unit cell volume V in the binary systems [4, 6] and in four isopleths with $x_{Sb}/x_{Te}=0.33$, 1, 3, and 7 (1 150 K)

Table 1. Composition, lattice parameters, liquidus and solidus temperatures, and other thermal effects in ternary Co – Sb – Te alloys

Composition			Liquidus		Solidus	Others	Lattice Parameter		
No.	$\frac{x_{Sb}}{x_{Sb}}$	at%Co	(↑)	(↓)	(↑) (K)	(↑)	*a*	*b* (Å)	*c*
51	7.00	44.0	1 453	1 438		1 196–1 205	3.861		5.192
52		45.0					3.866		5.201
53		46.0	1 461	1 451		1 197–1 208	3.864		5.207
54		47.0					3.865		5.204
55		48.0	1 461	1 445	1 328		3.875		5.199
56		49.0					3.888		5.195
94		49.5					3.892		5.193
57		50.0	1 468	1 454	1 403		3.899		5.191
95		50.3					3.906		5.189
96		50.7					3.914		5.188
58		51.0					3.928		5.196
59		52.0	1 467	1 455	1 420		3.936		5.198
60		53.0					3.931		5.195
61		54.0	1 464	1 447	1 397		3.934		5.198
62		55.0					3.933		5.198
82	3.00	25.0	1 303	1 285		1 197–1 204; a			
75		33.0	1 371	1 359		1 198–1 211; a	5.376	6.301	3.633
40		43.0	1 431	1 418		1 209–1 218	3.850		5.221
2		44.0	1 431	1 415		1 207–1 213	3.847		5.226
3		45.0	1 437	1 428		1 206–1 215	3.851		5.222
4		46.0	1 435	1 428	1 261		3.858		5.224
5		47.0	1 437	1 430	1 294		3.867		5.218
6		48.0	1 439	1 432	1 350		3.887		5.215
7		49.1	1 438	1 433	1 360		3.888		5.211
97		49.5					3.897		5.203
8		50.0	1 442	1 431	1 370		3.900		5.210
98		50.3					3.913		5.204
99		50.7					3.916		5.206
9		51.0	1 440	1 432	1 374		3.919		5.210
10		52.0	1 441	1 434	1 323		3.921		5.203
11		53.0	1 435	1 424		1 313–1 340	3.921		5.213
12		54.0	1 434	1 428		1 310–1 349	3.919		5.212
83		60.0	1 406	1 368		1 322–1 371			
84		70.0	1 472	1 446		1 340–1 379; a			
85		80.0		>1 530		1 349–1 378			
87	1.33	63.0	n.o.	1 400		1 317–1 360			
86	1.00	25.0	1 257	1 235		1 208–1 214; a			
76		33.0	1 333	1 311		1 216–1 220; a	5.250	6.244	3.826
13		40.0	1 372	1 354		1 203–1 214			
14		41.0	1 378	1 359		1 205–1 215			
15		42.0	1 376	1 368		1 204–1 213	3.862		5.259
16		43.0	1 382	1 372	1 219		3.855		5.251
17		44.0	1 379	1 373	1 255		3.851		5.258
18		45.0	1 385	1 375	1 290		3.861		5.254

Composition			Liquidus		Solidus	Others	Lattice Parameter		
No.	$\frac{x_{Sb}}{x_{Sb}}$	at%Co	(↑)	(↓)	(↑) (K)	(↑)	*a*	*b* (Å)	*c*
19		45.9	1385	1376	1307		3.872		5.249
42		47.0	1385	1377	1324		3.884		5.253
20		47.1	1358	1382	1321		3.884		5.253
21		48.0	1390	1378	1329		3.895		5.248
22		49.0	1388	1379	1337		3.902		5.225
23		50.0	1388	1377	1311		3.899		5.244
24		510	1385	1372		1308–1319	3.900		5.249
25		52.0	1380	1371		1285–1323	3.902		5.253
88		70.0	n.o.	1511		1298–1346			
89		80.0		>1530		1310–1347			
90	0.33	25.0	1204	1184		1159–1170; a			
77		33.0	1276	1261		1171–1185; a	5.273	6.266	3.884
26		37.0	1300	1293		1174–1189	3.878		5.294
27		38.0	1305	1294		1177–1188	3.867		5.310
28		39.0	1307	1300		1177–1190	3.868		5.303
29		49.1	1315	1311		1185–1189	3.863		5.300
30		41.0	1315	1310	1194		3.853		5.297
31		42.0	1319	1314	1241		3.849		5.308
32		43.0	1324	1317	1271		3.856		5.304
33		44.0	1325	1317	1294		3.867		5.303
34		45.0	1328	1318	1306		3.878		5.301
35		46.0	1328	1318	1306		3.889		5.296
36		47.0	1330	1320	1293		3.896		5.298
37		48.0	1328	1322		1286–1293	3.897		5.295
38		49.0	1326	1317		1286–1296	3.894		5.296
39		50.0	1322	1316		1286–1303	3.896		5.296
91		60.0	n.o.	1501		1274–1310			
92		70.0		>1530		1281–1303			
93		80.0		>1530		1284 – 1304			

↑ heating; ↓ cooling; *a* additional thermal effect(s); *n.o.* not observed

In general, the *hcp* metalloid sublattice of the B 8-structure is assumed to be invariable, i.e. completely filled throughout the range of homogeneity, thus any increase in transition metal content implies a filling up of the structure, irrespective of the prevailing type of defect. As a consequence, it is not surprising to find both *a* and *V* expanding with increasing Co-content. Along the *c*-axis, this effect is possibly compensated by increased direct bonding interactions between neighbouring Co atoms, however, the trends in *c* are very weak and the interpretation is tentative.

The most striking feature of the lattice parameter vs. composition curves is the change of the slope around 50 at%Co clearly apparent for *a* and *V*, and less pronounced for *c*. It is obvious to attribute this to the transition from the subtractive (cobalt deficient) to the additive type of defect structure (cobalt atoms in interstices) which is expected to occur at about the stoichiometric composition (1 : 1). On the

cobalt-deficient side ($x_{Co} < 0.5$) the filling up occurs via the octahedral holes of the *hcp* (Sb, Te)-network, up to the stoichiometry of 1 : 1. The additional cobalt atoms on the cobalt-rich side ($x_{Co} > 0.5$) are positioned on the smaller bipyramidel sites of the structure. Accordingly, it is a consequence of the space requirements that the lattice expansion is more pronounced for the additive type of the structure.

All this is in good agreement with conclusions drawn in the preceding articles on the systems Ni – Sb, Co – Sb, and Ni – Sb – Te [6–8] where we also found two definitely different slopes reflecting the difference in defect mechanism.

Taking the cell volume – in general the most pronounced parameter – as measure of the lattice expansion we may assign the average slope of about 0.3 Å^3 per atomic percent to the subtractive type and 0.8 Å^3 per atomic percent to the additive type of structure. Furthermore, it is once more interesting to note that the range covered by the volume of the unit cell – extending from about 67 to 71 Å^3 – remains the same throughout the ternary phase field of both Co – Sb – Te and Ni – Sb – Te.

All in all, the coincidences are certainly remarkable, however, the differences in size between cobalt and nickel are only small and the significance of the argumentation for the whole class of NiAs-phases is doubtful. We may also state that some of the trends observed in the lattice parameters are explicable in terms of very elementary concepts, but we also admit that some of the details are still not completely understood.

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