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Lattice Parameters, Magnetic Properties, and Melting Behavior of the Ternary NiAs-Phase in the Ni—Sb—Te System*

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Lattice parameter, magnetic, and DTA-measurements were performed in the range of the ternary NiAs-phase in the nickel—antimony—tellurium system which exhibits a continuous range of homogeneity. Lattice parameter and susceptibility values are reported for three sections with constant ratios of $x_{Sb}/x_{Te} = 4.00$, 1.00, and 0.25. The ternary liquidus projection is given between about 35 and 60 at % Ni.

(Keywords: Nickel—antimony—tellurium; Phase diagram: Ni—Sb—Te; *Lattice parameters:* Ni—Sb—Te; *Magnetic properties:* Ni—Sb—Te; *NiAs-Phase:* Ni—Sb—Te*)*

Gitterparameter, magnetische Eigenschaften und Schmelzverhalten der ternären NiAs-*Phase im System* Ni—Sb—Te

Im Bereich der ternären NiAs-Phase im System Nickel—Antimon—Tellur, welche einen durchgehenden Homogenitätsbereich aufweist, wurden Gitterparameter bestimmt und magnetische Messungen und Differenz-Thermo-Analysen durchgeführt. Werte für die Gitterparameter und für die Suszeptibilität werden auf drei Schnitten mit konstanten Verhältnissen x_{Sb}/x_{Te} angegeben, nämlich für $x_{Sb}/x_{Te} = 4.00$, 1.00 und 0.25. Weiters wird die Projektion der ternären Liquidusoberfläche zwischen etwa 35 und 60 At% Ni gezeigt.

Introduction

Both the nickel—antimony [1] and the nickel—tellurium [2] binary systems are characterized by the appearance of a phase with NiAs- (B8-) structure. Whereas in the latter system nonstoichiometry is due to nickel vacancies, resulting in a homogeneity range on the tellurium-rich side of

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* Dedicated to Prof. *K. L. Komarek* on the occasion of his 60th birthday.

the equiatomic composition, the nickel—antimony system is one of the few cases where the NiAs-phase has a considerable range of homogeneity on either side of stoichiometry. This is achieved by subtraction of nickel atoms from their regular lattice sites on the antimony-rich side and by addition of interstitial nickel atoms (in the trigonal-bipyramidal holes) on the nickel-rich side [3–5]. A recent thermodynamic investigation of γ-NiSb suggested, however, that the change from one defect mechanism to the other does not occur exactly at the equiatomic composition, but rather at about 50.6 at% Sb [6]. This interpretation is supported by the composition dependence of the lattice parameters, the pycnometric density, and the magnetic susceptibility [7].

For the ternary nickel—antimony—tellurium system it is expected that the homogeneity range of the NiAs-phase is shifted gradually to the nickel-rich side with increasing x_{Sb}/x_{Te}-ratio. Thus it was the purpose of the present study to investigate the extension of this ternary phase by X-ray and DTA-measurements (differential thermal analysis), to determine the composition dependence of the lattice parameters, and to establish the liquidus surface in the corresponding composition range. In addition, the variation of the magnetic susceptibility was determined by magnetic measurements.

Experimental

Starting materials were nickel sheet (Puratronic, 99.999%, Johnson Matthey, U.K.), antimony and tellurium lumps (both 99.99+%, ASARCO, New York, U.S.A.). Nickel was cut into small pieces and cleaned by p.a. acetone, antimony and tellurium were powdered and used without further cleaning. Calculated amounts of the pure elements (approx. 1 g total) were weighed on a semi-microbalance to within ±0.05 mg. They were filled into quartz capsules which were then evacuated to 10^{-1} Pa, flushed several times with Ti-gettered argon, and finally sealed under vacuum.

The samples were heated for about one week at a temperature between 1 250 and 1 375 K depending on the x_{Sb}/x_{Te}-ratio. The obtained alloys were finely ground in an agate mortar, once again sealed in quartz capsules, and homogenized for about two weeks at a temperature where a maximum extension of the NiAs-phase was expected. Thus annealing temperatures were 1 200 K for $x_{Sb}/x_{Te} = 4.00$ and 963 K for both $x_{Sb}/x_{Te} = 1.00$ and 0.25. The heat treatment was terminated by quenching in ice water.

X-ray measurements were made with a Kristalloflex 4 (Siemens, Karlsruhe, F.R.G.) in *Debye-Scherrer* cameras with a diameter of 57.3 mm using filtered CoK_α-radiation. The lattice constants were obtained by linear regression and extrapolation to zero using the function $(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)/2$.

DTA-measurements were performed with a commercial thermal analyzer (DTA 404 S/3, Netzsch, Selb, F.R.G.) using samples of about 0.5 g sealed under vacuum in special quartz containers and an empty alumina crucible as reference. The Pt/Pt 10%Rh-thermocouples were calibrated at the melting points of high purity zinc, antimony, and gold. The heating rate was 2 K min^{-1}.

Magnetic susceptibilities were measured at room temperature on a *Faraday*-type balance calibrated with *Mohr's* salt as reference material. Ferromagnetic contributions due to traces of ferromagnetic components were subtracted by extrapolating the magnetic susceptibilities to infinite field strength.

Results and Discussion

The compositions of the investigated samples are listed in Table 1 together with the corresponding lattice constants. Values of the parameter a are generally thought to be accurate within ± 0.002 Å, those of the parameter c within ± 0.005 Å. Their variation with changing nickel content is shown in Fig. 1 for three different ratios x_{Sb}/x_{Te}; also shown are the values of c/a and of the unit cell volume. For comparison the corresponding data for the binary systems are added; they are taken from the recent investigations by *Leubolt* et al. [7] (Ni—Sb) and *Terzieff* et al. [8] (Ni—Te).

One can see that the lattice parameters increase with increasing tellurium content; this effect, however, is much more pronounced for c than it is for a. The opposite is true for the variation with the nickel content; in this case a increases much stronger on going to higher nickel concentrations. The flat maximum in c close to the nickel-rich phase boundary which has been reported for the Ni—Te binary system [8] starts to develop already for $x_{Sb}/x_{Te} = 0.25$ (cf. Fig. 1 b). A change of slope can be observed at about 50 at% Ni for $x_{Sb}/x_{Te} = 4.00$ which is certainly due to the different defect mechanisms on both sides of this composition. The experimental data do not allow to pinpoint it more exactly as in the case of the Ni—Sb binary where it was found to be shifted slightly to the antimony-rich side [7]. For the other investigated sections the stoichiometric composition is already outside the homogeneity range at the corresponding quenching temperature.

It is interesting to observe that the variation of the unit cell volume with the nickel content is nearly the same throughout the whole ternary system, i.e. between about 68 and 72 Å^3 (cf. Fig. 1 d). Whether this is fortuitous or indeed a factor which determines the extension of the ternary phase would have to be proved by investigating other ternary systems of transition metals with antimony and tellurium.

A comparison of the present lattice parameter values with the results of *Makovetskii* and *Shakhlevich* [9] who investigated the "NiSb—NiTe system" shows good agreement for the parameter c; their parameter a, however, is somewhat lower on the Ni—Sb side, and this deviation increases with increasing tellurium content. The reason for this discrepancy is obviously the shifting of the nickel-rich phase boundary which crosses 50 at% Ni somewhere in the vicinity of $x_{Sb}/x_{Te} = 1.00$ depending,

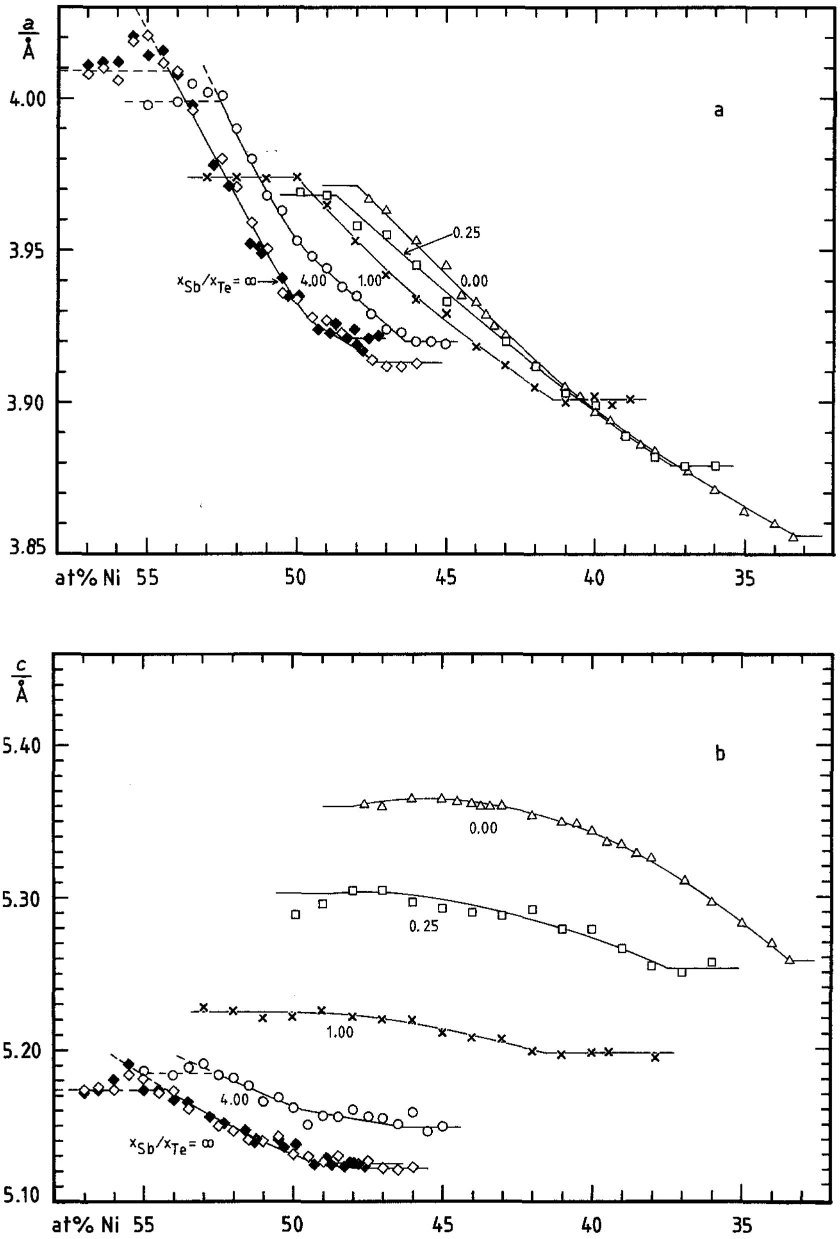
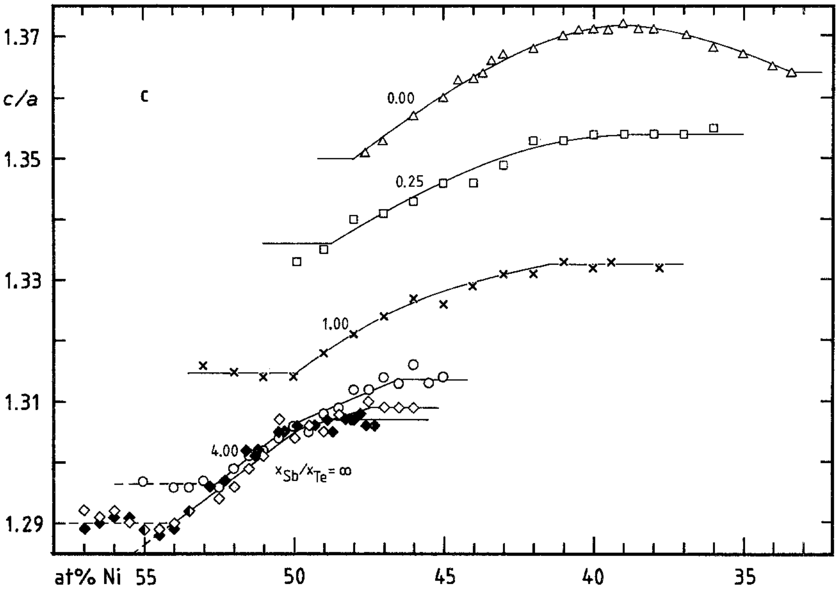


Fig. 1. Variation of the lattice parameters *a* and *c*, of the ratio *c*/*a*, and of the unit cell volume with nickel content; ◇, ◆ : $x_{Sb}/x_{Te} = \infty$ (open symbol: quenched from 1 173 K, full symbol: 1 300 K) [7]; ○: $x_{Sb}/x_{Te} = 4.00$ (1 200 K); × : $x_{Sb}/x_{Te} = 1.00$ (963 K); □: $x_{Sb}/x_{Te} = 0.25$ (963 K); △: $x_{Sb}/x_{Te} = 0.00$ (873 K) [8]


c
c/a
1.37
1.35
1.33
1.31
1.29
0.00
0.25
1.00
4.00
$x_{Sb}/x_{Te}=\infty$
at% Ni
55
50
45
40
35

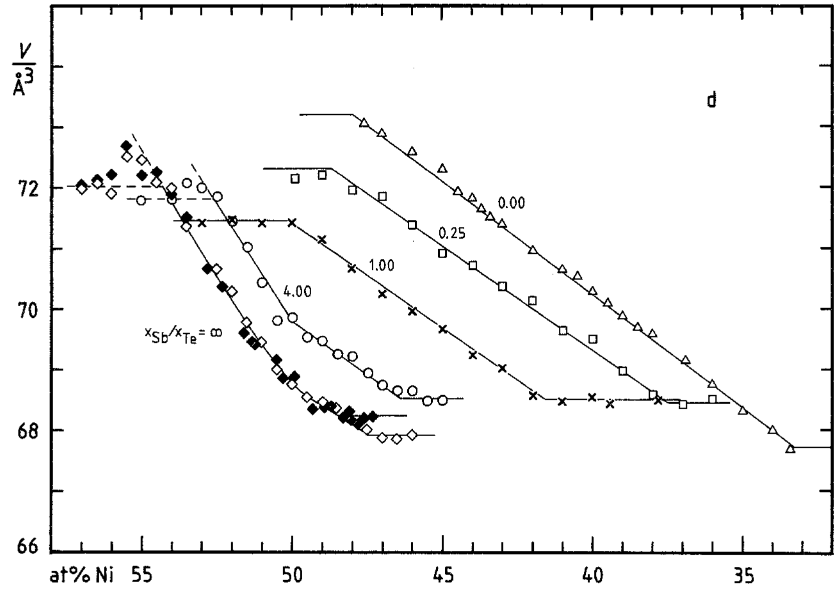

d
V/Å³
72
70
68
66
0.00
0.25
1.00
4.00
$x_{Sb}/x_{Te}=\infty$
at% Ni
55
50
45
40
35

Table 1. *Composition of the samples, lattice parameters, and thermal effects*

Sample No.	$\frac{x_{Sb}}{x_{Te}}$	at% Ni	a(Å)	c(Å)	Solidus (K)	Liquidus	
						Heating (K)	Cooling (K)
12	4.00	45.0	3.919	5.149			
12A	4.00	45.5	3.920	5.146	1 087	1 373	1 372
13	4.00	46.0	3.920	5.159			
13A	4.00	46.5	3.923	5.151			
14	4.00	47.0	3.924	5.155	1 228	1 379	1 372
14A	4.00	47.5	3.929	5.156			
15	4.00	48.0	3.935	5.161	1 276	1 383	1 378
15A	4.00	48.5	3.938	5.156			
16	4.00	49.0	3.944	5.157	1 301	1 378	1 375
16A	4.00	49.5	3.948	5.151			
17	4.00	50.0	3.953	5.162	1 327	1 387	1 373
17A	4.00	50.5	3.963	5.169			
18	4.00	51.0	3.968	5.166			
18A	4.00	51.5	3.980	5.177	1 323	1 381	1 377
19	4.00	52.0	3.990	5.182			
19A	4.00	52.5	4.001	5.184	1 318	1 381	1 375
20	4.00	53.0	4.002	5.191			
20A	4.00	53.5	4.005	5.189			
21	4.00	54.0	3.999	5.184	1 274	1 376	1 373
22	4.00	55.0	3.998	5.187	1 260	1 373	1 370
41	1.00	37.8	3.901	5.196			
40	1.00	39.4	3.899	5.198			
39	1.00	40.0	3.902	5.198			
26	1.00	41.0	3.900	5.197	955	1 294	1 285
27	1.00	42.0	3.905	5.199	1 013	1 294	1 286
28	1.00	43.0	3.912	5.207	1 068	1 299	1 289
29	1.00	44.0	3.918	5.208	1 159	1 307	1 291
30	1.00	45.0	3.929	5.211	1 204	1 309	1 299
31	1.00	46.0	3.934	5.220	1 221	1 311	1 302
32	1.00	47.0	3.942	5.220	1 236	1 310	
33	1.00	48.0	3.953	5.222	1 244	1 311	1 304
34	1.00	49.0	3.965	5.226	1 235	1 313	1 306
35	1.00	50.0	3.974	5.222	1 217	1 305	1 305
36	1.00	51.0	3.974	5.221	1 191	1 311	1 302
37	1.00	52.0	3.974	5.226	[a]	1 304	1 300
38	1.00	53.0	3.974	5.220	[a]	1 301	1 296
56	0.25	36.0	3.879	5.257			
55	0.25	37.0	3.879	5.251	910	1 170	1 165
54	0.25	38.0	3.882	5.255	1 011	1 181	1 170
53	0.25	39.0	3.889	5.266	1 053	1 185	
52	0.25	40.0	3.899	5.279	1 088	1 194	1 189
51	0.25	41.0	3.903	5.279	1 108	1 199	1 187
50	0.25	42.0	3.912	5.292	1 133	1 205	1 195

Sample No.	$\frac{x_{Sb}}{x_{Te}}$	at% Ni	a(Å)	c(Å)	Solidus (K)	Liquidus	
						Heating (K)	Cooling (K)
49	0.25	43.1	3.920	5.288	1 162	1 207	1 192
48	0.25	44.0	3.929	5.290	1 183	1 213	1 209
47	0.25	45.0	3.933	5.293	1 195	1 214	1 201
46	0.25	46.0	3.945	5.297	1 191	1 213	1 201
44	0.25	47.0	3.955	5.305	1 178	1 211	1 212
45	0.25	48.0	3.958	5.305	1 183	1 213	1 206
43	0.25	49.0	3.968	5.296	[a]	1 210	1 203
42	0.25	49.9	3.969	5.289			

[a] Other effects; outside single phase region.

of course, on the temperature. It has been known for quite some time that stoichiometric "NiTe" lies outside the homogeneity range of the NiAs-phase in a two-phase region [2, 10, 11], a fact ignored by *Makovetskii* and *Shakhlevich* [9]. At their quenching temperature of 1 120 K the phase boundary is at about 46 at% Ni [2]; and in fact, their value for "NiTe", $a = 3.953$ Å, corresponds exactly to this composition on the curve for the Ni—Te binary system in Fig. 1 a. This discrepancy is less pronounced for the parameter c since its composition dependence is very flat in the vicinity of the nickel-rich phase boundary (cf. Fig. 1 b).

Table 1 contains also the solidus and liquidus temperatures for most of the ternary samples obtained from DTA-measurements. Isopleths were constructed for the three sections with constant x_{Sb}/x_{Te}-ratio, and the disappearance of the solidus together with the observation of other effects allowed to fix the phase boundary down to relatively low temperatures in some instances. From these isopleths the homogeneity ranges shown in Fig. 1 were deduced which are evidently in good agreement with the phase boundaries obtained from the variation of the lattice parameters. An exception is the nickel-rich boundary at $x_{Sb}/x_{Te} = 4.00$ where a maximum appears in both parameters. This is probably caused—similarly as in the Ni—Sb binary system [7]—by the shape of the phase boundary with temperature. Apparently the true equilibrium could not be retained in this region by our quenching method.

The liquidus temperatures from Table 1 were combined with the relevant data on the two limiting binary systems [2, 7] to construct the liquidus surface between about 35 and 60 at% Ni. The result is shown in Fig. 2. As can be seen, the surface drops continuously with increasing

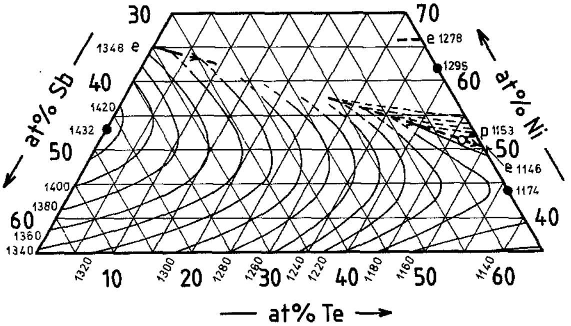


Fig. 2. Ternary liquidus projection in the range of the NiAs-phase in the nickel—antimony—tellurium system; e = binary eutectic point, p = binary peritectic point, ● = congruent melting point, ○ = ternary four-phase equilibrium

tellurium content. The melting point maximum is shifted gradually from 1 432 K and 53 at% Ni in the Ni—Sb binary to 1 174 K and 44 at% Ni in the Ni—Te binary. It is assumed that the two troughs originating from the points e and p in the Ni—Te system which mark the positions of a eutectic and a peritectic point, resp., combine with a third one to form a class II four-phase equilibrium whose position is shown schematically in Fig. 2. No attempt is made to estimate the location of the other four-phase equilibria.

If the present liquidus data are compared with the "NiSb—NiTe phase diagram" by *Makovetskii* and *Shakhlevich* [9], the same general trend can be observed; only the temperatures in Ref. [9] are consistently lower by 10 to 15 K except for the melting point of "NiTe" given as 1 170 K. This value agrees well with the congruent melting point determined by *Klepp* and *Komarek* [2] (1 174 K) which is, however, situated at 44 at% Ni. Furthermore, the transformation within the NiAs-phase shown in Ref. [9] on the tellurium-rich side between 1 140 and 1 150 K must be rejected. Neither the present investigation of the ternary system nor any previous study of the Ni—Te binary phase diagram [2, 10, 11] gave any evidence of such a transformation. The observed thermal effects are probably caused by the binary eutectic at 1 146 K between δ-NiTe and the high temperature phase γ_2 which melts peritectically at 1 153 K [2] and the corresponding phase equilibria in the ternary system.

The magnetic behavior of the system can be considered as superposition of a weak paramagnetic contribution which is proportional to the density of states (*Pauli*-paramagnetism) on the underlying diamagnetism of the core atoms. The variation of the room temperature susceptibility with the nickel content is shown in Fig. 3. The slight change of slope observed for Ni—Te has been explained in terms of structural changes [8].

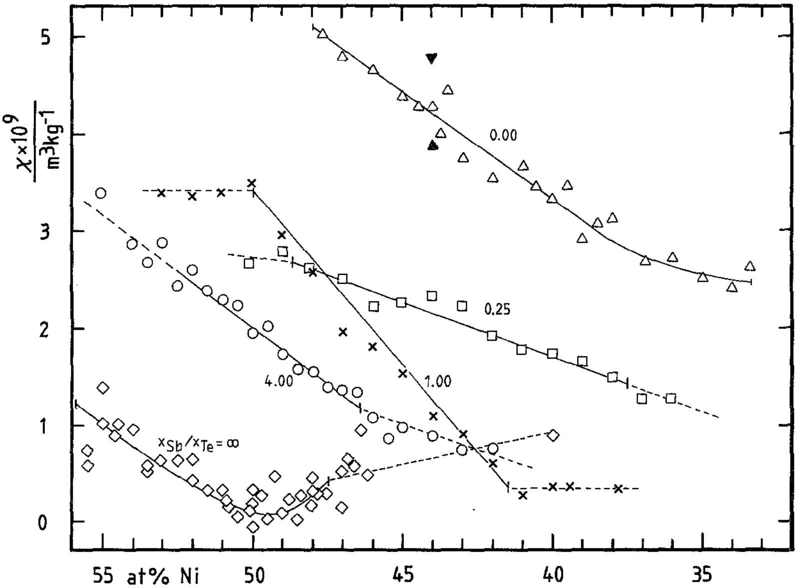


Fig. 3. Magnetic susceptibility in the range of the NiAs-phase in the nickel—antimony—tellurium system as function of the nickel content (the symbols are those of Fig. 1 with the exception of ▲ and ▼ which are single crystal data [8])

The extremely small and even negative values around 50 at% Sb in Ni—Sb have been assigned to a low density of states most likely due to the filling of the nickel d-band which seems not to be the case for Ni—Te [7, 8]. As a consequence, the susceptibilities are expected to increase with increasing tellurium content. For the ternary sections and particularly for $x_{Sb}/x_{Te} = 4.00$ we observed a linear variation with the nickel content, although the lattice parameters yielded a discontinuity around 50 at% Ni pointing to the change in the defect mechanism as discussed above. The decrease of the susceptibilities with decreasing nickel content, most pronounced for $x_{Sb}/x_{Te} = 1.00$, is stronger than expected simply from the variation of the underlying diamagnetism indicating that the density of states varies considerably with the composition.

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