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Lattice parameter and electronic properties of the solid solution $CoSb_2-CoTe_2$

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Abstract

The lattice parameter, the magnetic susceptibility, and the thermoelectric power of the marcasite-type solid solution in the system cobalt-antimony-tellurium are reported. Systematic changes are observed if tellurium is successively replaced by antimony. The peculiar variations of the unit cell dimensions with composition are found to be correlated with some characteristic changes in the electronic properties. The magnetic behaviour varies in a systematic manner from paramagnetic on the tellurium-rich side to diamagnetic on the antimony-rich side. The thermoelectric power adopts negative values of about $-20 \ \mu V \ K^{-1}$ on the tellurium-rich side, increases in magnitude on the antimony-rich side of the solid solution, and abruptly changes its sign in the vicinity of $CoSb_2$. The trends in the properties are discussed in terms of a schematic band model and the structural changes occurring in the system.

Keywords: Lattice parameter; Magnetic susceptibility; Thermoelectric power; Marcasite-type phases

1. Introduction

The formation of phases with marcasite-related structures is a common feature of the binary systems Co–Sb and Co–Te. While $CoTe_2$ crystallizes in the orthorhombic marcasite structures [1,2], $CoSb_2$ takes the monoclinic arsenopyrite structure, a slightly distorted variant of the marcasite structure [3]. The complete mutual solubility between $CoSb_2$ and $CoTe_2$ and the gradual transition from one structure to the other have been approved by different authors [4,5]. However, some discrepancies in the lattice parameter on the Sb-rich side of the solid solution suggested a reinvestigation. In a way, this paper is also a continuation of a previous study of the phase relationships in the system Co–Sb–Te [6].

2. Experimental

The alloys were prepared by direct reaction of the elements using Co wire (purity > 99.997%, Johnson-Matthey, UK), and lumps of antimony and tellurium (purity > 99.99%, Asarco, New York). The appropriate mixtures (approximately 1 g) were repeatedly

evacuated, flushed with purified argon, and finally sealed under vacuum (about 0.01 Pa) in quartz ampoules. After a first reaction period of about 3 days at 1350 K the ingots were rapidly cooled to room temperature, crushed and ground, subjected again to repeated evacuating-flushing cycles, and once more sealed in quartz ampoules. In general, the alloys were homogeneized at 650 K or 900 K for more than 4 weeks. The numbers given to the samples are related to the systematic numbering used in our previous article [6]. In graphical presentations the compositions refer to a constant content of Co (mole fraction x_{Co} or at.% Co), and to a variable fraction of Sb according to the notation $y_{Sb} = x_{Sb}/(x_{Sb} + x_{Te})$.

The well homogenized powders were quenched in ice-water and their phase purities and structures were determined by X-ray diffraction applying either the Guinier-Huber (Cu K α) or Debye-Scherrer technique (114.59 mm, Cr K α or Co K α).

The magnetic measurements were performed on a Faraday-type balance applying magnetic fields from 3 to 15 kOe, and using Mohr's salt as reference material $(32.31 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1} \text{ at } 293 \text{ K})$. Superimposed ferromagnetic contributions were subtracted by extrapolation to infinite field strength. The thermoelectric

measurements refer to a vertical arrangement of two massive copper blocks which provided the thermal and the electrical contact to the samples. The temperature gradient across the sample was varied between -10 and $10 \,^{\circ}$ C. The thermoelectric power was derived from the initial slope of the thermoelectric voltage vs. temperature difference. Further details are given elsewhere [7].

3. Results and discussion

On account of the differences in composition and phase width of the marcasite-like phases $CoTe_2$ and $CoSb_2$, four series of alloys at constant Co-concentrations of 32, 33, 34 and 34.6 at.% have been synthesized. $CoTe_2$ crystallizes in the orthorhombic C18-structure ranging in composition from 32.4 to 33.3 at.% Co at 608 K [1], or from 30.4 to 33.3 at.% Co at 803 K according to Ref. [2]. At high temperatures $CoSb_2$ crystallizes in the same structure, but at room temperature the true symmetry is monoclinic [3] with a slight departure from stoichiometry according to $CoSb_{1.85}$ [8,9].

Both Yamaguchi et al. [4] and Abrikosov and Petrova [5] claimed the complete mutual solubility of the phases occurring obviously via a gradual change of the structure. However, comparing their lattice parameter we found some divergences on the antimony-rich side. At the outset of our experiments it was not clear whether this points to a more complex phase relationship or not.

As a matter of fact, all of our diffraction patterns expecting those close to $CoSb_2$ – could be indexed as orthorhombic. On the cobalt-rich boundary of CoTe₂ we found a = 5.328 Å, b = 6.321 Å and c = 3.906 Å, in good accordance with the numerous literature data discussed in Ref. [2]. For the monoclinic cell of CoSb₂ we obtained a = 6.504 Å, b = 6.387 Å, c = 6.538 Å and $\beta = 117.64^{\circ}$, which is nearly identical to that reported by Siegrist and Hulliger [10] (a = 6.5051 Å, b =6.3833 Å, c = 6.5410 Å, $\beta = 117.65^{\circ}$), and also very close to that given by Kjekshus [9] (a = 6.5077 Å,b = 6.3879 Å, c = 6.5430 Å, and $\beta = 117.66^{\circ}$). Throughout the paper we will use the orthorhombic setting; the conversion from the monoclinic to the orthorhombic setting is accomplished with $\boldsymbol{a}_{mon} = \boldsymbol{a}_{orth} + \boldsymbol{c}_{orth}$, $\boldsymbol{b}_{\text{mon}} = \boldsymbol{b}_{\text{orth}}$, and $\boldsymbol{c}_{\text{mon}} = -\boldsymbol{a}_{\text{orth}} + \boldsymbol{c}_{\text{orth}}$. Following the systematic changes of the lattice

Following the systematic changes of the lattice parameter into the ternary phase field we observe an excellent agreement with the data reported by Yamaguchi et al. [4] (Fig. 1). The divergence of the values taken from Fig. 2 of Abrikosov and Petrova [5] on the antimony-rich side is possibly due to a different thermal treatment of the samples, which in view of the



Fig. 1. Lattice parameter (a, b, c), volume V, and axial ratios (c/a, c/b) of the marcasite-type solid solution $CoTe_2-CoSb_2$ as function of the Sb-fraction y_{Sb} $(x_{Co} = 0.33; \bigcirc$, this paper; \times , data from Ref. [4]; \diamond , points taken from Ref. [5]).



Fig. 2. Magnetic susceptibility of the marcasite-type solid solution $CoTe_2-CoSb_2$ as function of temperature ($x_{Co} = 0.33$).

structural changes in the system might be of special importance. It has to be remarked that Fig. 1 (and also Fig. 2 and Fig. 3) refers to a nominal composition of 33 at.% Co, ignoring the fact that in the vicinity of $CoSb_2$ this section lies slightly outside of the range of homogeneity; however, the influence on the shape of the curves is negligible.

The compositions and the lattice parameter of the alloys are listed in Table 1 together with phase purities and some other experimental details. It turned out to be extremely difficult to attain thermodynamic equilibrium on the antimony-rich side; even annealing times of more than 6 months were not sufficient to transform the alloys completely into the equilibrium phase. Thus, based on our own analyses, we assume the phase relationships reported by Abrikosov and Petrova [5] to be basically correct.

It is remarkable that the successive substitution of Te by Sb yields such complex variations of the lattice parameter. The initial decrease of a and b, and also that of c, is certainly due to the smaller size of the Sb-atoms, which is definitely evidenced by the linear decrease of the cell volume V. Despite the progressive substitution, the axial ratios c/a and c/b remain constant up to an Sb-fraction of $y_{Sb} \approx 0.5$ with values typical of 'anomalous' or 'class B' d⁷ marcasites which



Fig. 3. Magnetic susceptibility, thermoelectric power, and angle of monoclinic distortion in the marcasite-type solid solution $CoTe_2$ - $CoSb_2$ as function of the Sb-fraction y_{Sb} at 293 K (×, $x_{Co} = 0.32$; \bigcirc , $x_{Co} = 0.33$; +, $x_{Co} = 0.346$).

show increased ratios of $c/a \approx 0.74$ and $c/b \approx 0.62$ [11-13]. The further replacement leads to a pronounced increase of *a* and *b* accompanied by a likewise drastic decrease of *c* which signals a significant change in the electronic band structure of the system. There are reasons to assume that the d⁷ configuration of Co in CoTe₂ transforms smoothly into a d⁶ around CoSbTe, and finally into a d⁵ configuration which favours the monoclinically distorted arsenopyrite structure in CoSb₂ [12,13].

In both structures the Co atoms are coordinated by six anion neighbours placed at the corners of more or less distorted octahedra. Owing to the octahedral crystal field, the degenerate d orbitals of the transition atom split into three t_{2g} and two e_g levels. Together with the anion s and p orbitals, the eg orbitals form bonding σ and antibonding σ^* bands; those with $t_{2\sigma}$ symmetry form narrow bands located in the gap between σ and σ^* and are assumed not to be involved in chemical bonding. The distortion of the octahedral arrangement removes the t_{2g} degeneracy by destabilizing the a₁₁ level relative to the twofold degenerate b levels. According to the band schemes proposed by Hulliger and Mooser [11], Brostigen and Kjekshus [12] and Goodenough [13], the marcasite and the arsenopyrite structure differ by the degree of splitting of the non-bonding a₁₁ and b bands. In regular marcasites the splitting is strong enough to raise a_{11} up into the range of σ^* ; in anomalous marcasites a_{11} is still above b but sufficiently below σ^* ; in arsenopyrites the monoclinic distortion of the cell is accompanied by a splitting of a_{11} into one sub-band $a_{1\alpha}$ overlapping with σ^* and another sub-band a_{16} overlapping with the b band. In the same sequence, the non-bonding bands are expected to host a maximum number of 4, 6, and 5 d electrons respectively.

Based on diatomic anions of the type Te_2^{2-} , $SbTe^{3-}$ and Sb_2^{4-} , the formal valency of Co is assumed to vary from 2 in $CoTe_2$ (d⁷), to 3 in CoSbTe (d⁶), and to 4 in $CoSb_2$ (d⁵). As already indicated by the axial ratios, our experimental findings are well explained in terms of a gradual transition from the anomalous marcasite to the arsenopyrite structure which implies a configu-ration of $b^4 a_{11}^2 \sigma^{*1}$ in CoTe₂, $b^4 a_{11}^2$ in CoSbTe, and $b^4 a_{1\alpha}^1$ in CoSb₂. The depletion of the σ^* band as Te is substituted by Sb apparently has no influence on the axial ratios c/a and c/b; the decrease in a, b, c and V up to about CoSbTe result from the smaller atomic volume of Sb as discussed above. The depletion of the a_{11} band, however, obviously reduces the expanding forces along the c-axis which are assumed to be responsible for the increased axial ratios [11-13]. As a consequence, c decreases at the expense of a and bkeeping the volume constant, while c/a and c/bincrease towards the values typical of the arsenopyrite structure. The physical origin of the expanding forces

Table 1 Composition and lattice parameter of the marcasite-type solid solution CoSb₂-CoTe₂

No.	Composition		Lattice parameter					Temperature (K)	Technique ^b	Radiation	Phases ^c
	x _{Co}	y _{sb} ^a	а	b	с (Å)	V	β				
67	0.320	0	5.328	6.318	3.904	131.42	90	650	D	Со	m
73		0.250	5.555	4.444	5.555	123.34	90	650	D	Cr	m + t
72		0.500	5.253	6.245	3.826	125.51	90	650	D	Cr	m + t
171		0.750	5.379	6.302	3.637	123.29	90	650	D	Cr	m + t
70		0.875	5.500	6.352	3.491	121.96	90	650	D	Cr	m + c + h
211		0.926	5.536	6.366	3.428	120.81	90.15	650	G	Cu	m + c
64		1	5.579	6.386	3.376	120.27	90.60	650	G	Cu	$\mathbf{m} + \mathbf{c}$
68	0.330	0	5.327	6.317	3.907	131.47	90	650	D	Cr	m
77		0.250	5.273	6.266	3.884	128.33	90	900	D	Cr	m
116		0.400	5.254	6.248	3.876	127.24	90	650	G	Cu	m + t + c
76		0.500	5.250	6.244	3.826	125.42	90	900	D	Cr	m
115		0.600	5.255	6.245	3.788	124.31	90	650	G	Cu	m + c
75		0.750	5.376	6.301	3.633	123.06	90	900	D	Cr	m + c
215		0.896	5.522	6.366	3.476	122.21	90.14	650	G	Cu	m + c
214		0.933	5.546	6.375	3.431	121.31	90.44	650	G	Cu	m + c
213		0.966	5.567	6.381	3.410	121.13	90.61	650	G	Cu	m + c
65		1	5.579	6.387	3.377	117.65	90.58	900	D	Cr	m + c
69	0.340	0	5.328	6.321	3.906	131.55	90	900	D	Со	m + h
81		0.250	5.275	6.263	3.890	128.52	90	900	D	Cr	m + h
80		0.500	5.250	6.244	3.836	125.75	90	900	D	Cr	m +
79		0.750	5.372	6.301	3.641	123.24	90	900	D	Со	m +
78		0.875	5.493	6.350	3.496	121.94	90	900	D	Cr	m +
66		1	5.578	6.387	3.376	120.27	90.56	650	D	Cr	m + c
102	0.346	0.750	5.379	6.395	3.635	125.04	90	650	D	Cr	m + h
101		0.875	5.490	6.352	3.495	121.88	90	650	D	Cr	m +
100		1	5.579	6.387	3.377	120.33	90.60	650	D	Cr	m
			5.579	6.388	3.376	120.31	90.63	650	D	Со	m

^a $y_{Sb} = x_{Sb} / (x_{Sb} + x_{Te}).$ ^b D, Debye; G, Guinier.

^c m, marcasite; h, hexagonal NiAs-type; t, trigonal Sb₂Te₃; c, cubic CoSb₃.

has been assigned either to the repulsion between doubly occupied orbitals of neighbouring cations along the c-axis [12] or to antibonding electrons the a_{11} band [13].

The results of the magnetic measurements are represented in Fig. 2 and Fig. 3. It is evident that the magnetic properties change rapidly with y_{sb} , i.e. the substitution of Te by Sb. Judged from the band structure discussed above, it is obvious why the magnetic character changes in such a remarkable manner. Owing to the occupation of the σ^* band, CoTe₂ is paramagnetic with obviously metallic character [14,15]. The rapid loss of the paramagnetism, and probably also that of the metallic behaviour, is associated with the depletion of the σ^* band which is completed at CoSbTe. The small paramagnetic contribution beyond CoSbTe is probably due to unfilled a_{11} bands but, as the splitting into $a_{1\alpha}$ and $a_{1\beta}$ proceeds, a diamagnetic and semiconducting behaviour [10] prevails near $CoSb_2$ due to completely filled b and $a_{1\alpha}$ bands. Concerning the binary phases CoTe₂ and CoSb₂, the

experimental results of our magnetic measurements are in accordance with the values quoted in the literature [9,10,15-17].

Regarding the classification of the paramagnetism in $CoTe_2$, a clear assignment cannot be given. The marked temperature dependence of the magnetic susceptibility seems to hint at magnetic moments associated with the Co atoms. The $1/\chi$ vs. T plot is not strictly linear, but we may tentatively deduce an effective magnetic moment of $1.7 \,\mu_{\rm B}$ per Co atom. Experimentally, this is in good accordance with the earlier observations [16,17] but not justified by the band structure which rather would imply a temperature dependent Pauli paramagnetism, as has been suggested by Saut [15]. Based on our own data we are unable to distinguish between the two cases, a situation quite similar to that observed in NiAs-type CoTe [18].

It has already been noted that it was practically impossible to prepare samples in the range close to CoSb₂ absolutely free of neighbouring phases (see

Table 1). Minor amounts of these had practically no influence on the lattice parameter and the magnetic susceptibility; the thermoelectric power, however, was found to be extremely sensitive to the presence of foreign phases. As a result, the experimental accuracy was low, as evident from Fig. 4, and also from Fig, 3, which shows the variation of the thermoelectric power with the composition at room temperature. Despite the scattering of the data of at least $\pm 5 \,\mu V \, K^{-1}$ ' a systematic trend seems to be indicated. Irrespective of the changing occupancy of the non-bonding bands the thermoelectric power remains constant at a negative value of about $-20 \,\mu V \, K^{-1}$ throughout the range of the orthorhombic marcasite phase. The obvious increase in magnitude on the antimony-rich side correlates with the transition to the monoclinic arsenopyrite structure which occurs around $y_{sb} = 0.87$ as inferred from our crystallographic data. The abrupt change of sign at $CoSb_2$, however, is most likely due to the absence of tellurium which seems to be responsible for n-type behaviour of the solid solution. The discrepancies of the literature data on the binary compounds are symptomatic of the difficulties associated with the measurement of the thermoelectric power on powdered specimens. Our best estimate of $-20 \,\mu\text{V}\,\text{K}^{-1}$ for CoTe₂ is about an order of magnitude more negative than the values reported by Bither et al. [14] or Saut [15], and identical in magnitude but



Fig. 4. Thermoelectric power of the marcasite-type solid solution $CoTe_2$ -CoSb₂ as function of temperature (compositions of alloys are given in Table 1).

definitely opposite in sign to that claimed by Dudkin and Dyuldina [19]. On the contrary, we find excellent agreement with the results of Siegrist and Hulliger [10]. Similar to the trend observed in this study, they reported that the thermoelectric power of $CoSb_2$ (about 40 μ V K⁻¹, single crystal) changes its sign abruptly if a small amount of Sb is substituted by Te (-80 μ V K⁻¹, polycrystalline $CoSb_{1.9}Te_{0.1}$). Although they emphasized that their crystals might have been impure or off stoichiometry – similar to our own findings – we assume our results to be representative of the pure marcasite phase; to our knowledge, further literature data on $CoSb_2$ are not available.

In conclusion we may state that the trends observed in the lattice parameter, the magnetic susceptibility, and possibly also in the thermoelectric power are explicable in terms of some very elementary concepts. The conclusion drawn in this paper correlate well with the findings reported for the marcasite-type solid solutions of the systems Fe-Sb-Te [20] and Fe-As-Se [21]. We admit, however, that some of the details, e.g. the paramagnetism of CoTe₂ or the sign of the thermoelectric power in view of the metal deficiency in $CoTe_2$ [1,2] or the metal excess in $CoSb_2$ [8,9], are still not completely understood. Based on our experience with the system, we would suggest complementary conductivity and Hall effect measurements on welldefined samples and, if possible, a reinvestigation of the electronic properties of the system based on single crystalline samples.

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