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SOME ASPECTS OF THE THERMAL BEHAVIOUR OF In_2Se_3

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On the basis of measurements of the specific heat capacity from 7 to 525 K and of DTA investigations from 300 K up to the melting point, it was possible to clarify the problem of the occurrence of the two room-temperature modifications of In_2Se_3.

The compound In_2Se_3 has often been discussed in the literature, but the data concerning its structure and thermal behaviour differ from author to author [1–19]. Some detailed and comprehensive works are those of Semiletov [5], Likforman et al. [12, 15], van Landuyt et al. [13] and Popović et al. [16]. During studies of the phase relations in the ternary system copper-indium-selenium, it was necessary to clarify the polymorphism of In_2Se_3, because this compound is one component of the mainly interesting quasibinary cut through the system along the line of normal valency.

Experimental

The samples were prepared by direct synthesis from a stoichiometric mixture of the elements (purity 5N) in evacuated sealed silica ampoules. In the knowledge of the reaction mechanism, the heating procedure had to be interrupted at about 500 K for one day [20]. The homogenization of the melt at 1273 K was followed either by immediate cooling or by annealing for 40 days at 393 K, 773 K or 873 K, and quenching down to room temperature. The resulting material was polycrystalline. X-ray powder diffraction and electron microprobe analysis were used for sample characterization. The thermal behaviour was studied by means of a SETARAM microthermoanalyzer and a SETARAM DSC–111 apparatus.

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Measurements of the specific heat capacity between 7 and 290 K were performed with an adiabatic vacuum calorimeter (for details see [21]). Benzoic acid was used to calibrate the measuring system. In the temperature range from 5 to 320 K, the literature data could be confirmed within error limits of 0.5% (7–20 K), 0.3% (20–80 K) and 0.1% (80–300 K). Between 330 and 525 K, the specific heat capacity was measured with a Perkin–Elmer DSC-2 apparatus, employing the scanning method (scan interval: 20 K, scan speed: 0.17 deg/s). As recommended by Perkin–Elmer Corp., the values were calculated in direct comparison with a sapphire standard. The error is about 4%.

Results and discussion

According to Popović et al. [10, 16], In_2Se_3 occurs in two modifications at room temperature (α_H: hexagonal, and α_R: rhombohedral). By X-ray powder diffration, these two modifications could be found both separately and in co-existence in one ingot, but no dependence on the preparation parameters was observed. DTA investigations showed that the temperature of the $\alpha \rightarrow \beta$ transition varies by 10 deg. The transition of α_R-In_2Se_3 takes place at 471 K, but that of α_H-In_2Se_3 only at 481 K (Fig. 1). The specific heat capacities of the two α-modifications are nearly

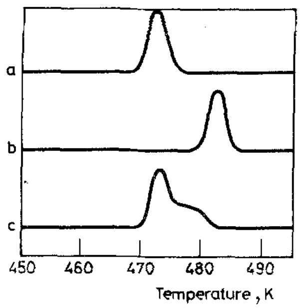

Fig. 1 Schematic representation of the heating curves for the $\alpha \rightarrow \beta$ transition of In_2Se_3 recorded by the DSC-111 apparatus (heating rate: 0.05 K/s)
a) the transition $\alpha_R \rightarrow \beta$ $T_t = 471$ K
b) the transition $\alpha_H \rightarrow \beta$ $T_t = 481$ K
c) the transition of a mixture of α_R and α_H

equal between 330 and 525 K, with respect to the given error of 4%. However, the values for α_R-In_2Se_3 are systematically somewhat higher and approximate to the values for α_H-In_2Se_3 towards the transformation point (Table 1, Fig. 2). Therefore, α_R must be a metastable In_2Se_3 modification, and α_H is the stable modification at room temperature.

Table 1 Experimental data of the specific heat capacity of α-In_2Se_3
a) α_H-In_2Se_3 (temperature range: 7–285 K)

T, K	C_p, J/K·mol	T, K	C_p, J/K·mol	T, K	C_p, J/K·mol
6.85	0.767	104.18	93.22	189.81	115.0
7.60	1.066	106.76	94.43	192.46	115.4
8.69	1.612	108.08	94.82	192.84	115.1
9.78	2.254	111.74	96.53	195.85	115.4
10.85	3.067	112.38	96.19	196.25	115.6
11.91	3.982	114.15	97.57	198.84	115.7
12.94	5.004	116.31	98.73	200.00	116.4
14.10	6.485	119.91	99.58	201.80	116.2
15.19	7.697	123.63	100.7	203.99	116.8
16.29	8.940	127.06	101.8	208.52	116.9
17.44	10.25	130.60	103.0	209.50	116.7
18.55	11.62	134.68	104.4	212.82	117.0
19.74	13.11	138.91	105.4	213.84	117.6
20.89	14.66	143.05	106.4	216.51	117.2
21.92	15.98	144.05	106.6	219.64	118.0
25.36	20.18	146.93	107.2	220.17	118.0
26.84	22.36	147.10	107.2	223.79	118.3
31.88	28.81	147.15	107.3	225.37	118.6
33.82	31.23	149.78	107.5	227.39	119.2
39.28	37.91	150.21	107.8	231.02	119.5
41.43	40.61	150.81	107.3	231.53	119.4
47.18	47.75	152.60	108.4	236.18	119.3
49.65	50.70	152.79	108.6	236.60	119.8
55.13	55.89	154.29	108.3	240.79	119.7
57.21	58.20	155.16	108.9	245.36	120.0
60.16	61.66	155.34	109.1	245.89	120.2
63.33	64.88	157.70	109.6	249.89	120.5
65.89	67.24	157.72	109.0	252.06	120.5
68.75	69.74	157.87	109.7	254.08	120.3
71.81	72.47	160.22	110.1	254.38	120.6
74.75	75.06	161.10	109.9	258.15	120.8
77.52	77.25	163.68	110.6	259.67	121.3
82.30	80.68	164.43	110.7	260.30	120.4
84.59	82.28	167.71	111.5	264.17	120.9
86.91	83.88	168.14	111.6	266.44	120.8
87.22	84.13	170.98	111.9	267.50	120.3
90.02	86.16	172.26	112.5	270.12	121.1
90.36	86.23	174.20	112.5	271.72	120.4
93.09	87.95	176.32	113.3	272.50	121.0
93.36	88.03	177.38	113.1	276.00	121.2
96.00	89.13	180.54	113.6	276.06	120.7
96.26	89.39	180.56	113.8	278.50	121.0
98.81	90.80	183.66	113.9	280.36	120.8
99.69	91.05	184.75	114.6	281.83	121.4
101.54	92.09	186.75	114.2	284.44	121.4
103.85	92.72	188.63	114.5	285.17	121.1

Table 1 Experimental data of the specific heat capacity of α-In_2Se_3
b) α_H-In_2Se_3 and α_R-In_2Se_3
(temperature range: 330–465 K)

T, K	C_p, J/K·mol	
	α_H-In_2Se_3	α_R-In_2Se_3
333	121.1	128.0
338	122.1	127.8
343	124.7	128.2
353	120.8	126.5
358	122.2	128.2
363	122.8	127.6
373	121.8	125.4
378	121.4	124.7
383	121.9	124.8
393	123.7	125.2
398	123.8	124.9
403	124.4	124.5
413	123.5	125.9
418	124.7	127.3
423	124.0	127.5
433	122.2	122.9
438	123.1	122.1
443	121.8	122.8
453	124.1	125.1
458	125.7	125.2
463	123.6	123.2

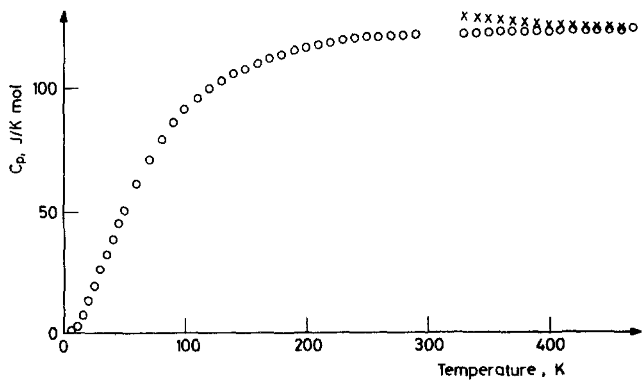

Fig. 2 Representation of the smoothed values of the specific heat capacities
○ α_H-In_2Se_3; × α_R-In_2Se_3

In the low-temperature range, only the specific heat capacity of α_H-In_2Se_3 was determined (Table 1). The resulting values are in good correspondence with those of Koščenko et al. [17] for α-In_2Se_3. We have not found the additional phase transition observed at 148 K by van Landuyt et al. [13].

The low and the high-temperature measurements on α_H-In_2Se_3 give a nearly continuous curve over the whole temperature range up to the phase transition $\alpha \to \beta$.

It should be mentioned that the transition $\beta \to \alpha$ always takes place at about 330 K (see also [13, 16]). Although the β-modification exhibits considerable supercooling, we could not detect this phase at room temperature by X-ray investigations. Therefore, it seems possible that the data given by Koščenko et al. [17] for β-In_2Se_3 (C_p (300 K) = 127.7 J/deg·mol) really refer to α_R-In_2Se_3.

In the temperature range from 773 K up to the melting point, several phase transitions were observed, similarly to the results of Popović et al. [16]. A γ-like superstructure could be obtained in quenching experiments from about 780 K. The lattice parameters are

$$a = 0.712 \text{ nm} \sim a_\gamma,$$

and

$$c = 9.65 \text{ nm} \sim 5 \times c_\gamma.$$

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Zusammenfassung — Anhand von DTA-Untersuchungen im Bereich zwischen 300 K und dem Schmelzpunkt und durch Messung der spezifischen Wärmekapazität im Bereich von 7 K bis 525 K konnte eine Klärung hinsichtlich des Auftretens von zwei In_2Se_3-Raumtemperatur-Modifikationen gegeben werden.

Резюме — ДТА измерения селенида индия, проведенные от 300 К до температуры его плавления, а также измерения удельной теплоемкости в интервале температур 7–525 К, представили возможность объяснить существование двух его модификаций при комнатной температуре.