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CALORIMETRIC STUDY OF CESIUM HEXAFLUOROARSENATE $CsAsF_6$ AT ELEVATED TEMPERATURES

G. A. Sharpataya[1], *K. S. Gavrichev*[1*], *A. V. Khoroshilov*[1], *V. N. Plakhotnik*[2] *and V. M. Gurevich*[3]

[1]Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky prospect 31, Moscow 119991, Russia
[2]Dnepropetrovsk State Technical University of Transport, ul. Akademika Lazaryana 2, Dnepropetrovsk 49010, Ukraine
[3]Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, ul. Kosygina 19, Moscow 119991, Russia

The heat capacity of cesium hexafluoroarsenate, $CsAsF_6$, was measured from 300 to 850 K by differential scanning calorimetry. The results indicate that the structural transformation from the rhombohedral to cubic phase, occurring in the range 235–360 K, relates to gradual transition completed isothermally. The enthalpy of the transition is 6.015 ± 0.186 kJ mol^{-1}, and its entropy is 17.21 ± 0.58 J K^{-1} mol$^{-1}\approx R\ln8$, which suggests that this structural transition belongs to the order–disorder type. The thermodynamic properties of $CsAsF_6$ were evaluated in the range 10–760 K.

Keywords: *DSC, heat capacity, phase transition*

Introduction

This article continues the publication of results of long-term study of thermodynamic properties of inorganic substances with octahedral PF_6^- and AsF_6^- anions [1–6], which are using in electrochemical devices. Cesium hexafluoroarsenate, as well as another alkali hexafluoroarsenates, undergoes the reversible polymorphous phase transition [7]. In accordance with X-ray data, at room temperature low-temperature α-phase has the rhombohedral structure (distorted CsCl-type) [7, 8], and high-temperature β-phase has cubic structure (NaCl-type) [7]. At low-temperature heat capacity measurements in the range 10–325 K it was found that the heat capacity anomaly, related to phase transition, is observed starting already from 240 K [6].

The purpose of this work was the investigation of thermodynamic properties of cesium hexafluoroarsenate in a wide temperature range.

Experimental

Sample

$CsAsF_6$ was synthesized by the exchange reaction of lithium hexafluoroarsenate with cesium carbonate. The final product was dried carefully under dynamic vacuum at elevated temperature. According to the chemical analysis, content of $CsAsF_6$ in the product was 99.9 mass%. The molecular mass of $CsAsF_6$ was taken to be 321.8174 g mol^{-1}. Earlier the part of this sample was used in the low-temperature measurements [6].

Method

The thermal behavior of cesium hexafluoroarsenate between 300 and 850 K was studied by differential scanning calorimetry (DSC) using a Setaram DSC 111 instrument (detection limit, 15 μW; temperature reproducibility, ±0.1 K; temperature-scale uncertainty, ±0.5 K; heat capacity precision, ±0.5%). High purity metal standards (Ga, In, Sn, Pb, Zn and Al) supplied by Russian Research Institute of Standard Substances Metrology were used to calibrate the DSC instrument in respect of temperature. The enthalpy calibration was carried out by measurements of the Joule effect. Corundum sample was measured to check the heat capacity data. Since $CsAsF_6$ is nonhygroscopic substance, we used unsealed thin-walled 0.26 cm^3 platinum-rhodium crucibles. Blank experiments with the same empty crucibles were recorded to correct the baseline and to calculate the heat capacity measured in the continuous heating mode.

Results and discussion

Preliminary DSC study

The investigation of three $CsAsF_6$ samples was carried out accordingly with the programs, called as ‘run’ (in Table 1 the number of run is related to the serial number of heating of the same sample).

The initial four sequential runs of the $CsAsF_6$–1 sample were conducted as follows:

Isothermal stage (10 min) – heating from 290 to 423 (673) K (rate 5 K min^{-1}) – isothermal stage (3 min)

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[*] Author for correspondence: gavrich@igic.ras.ru

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Table 1 Parameters of endothermic effects in the heating curves of $CsAsF_6$

Sample mass, run No.	Heating rate, v/K min^{-1}	Integrating range/K	T_e/K	T_p/K	$\Delta_{tr}H$(endo)/kJ mol^{-1}
$CsAsF_6$–1 (0.0467 g)					
run 1	5	305–378	348.4	358.5	5.32±0.05
run 2	5	315–376	348.1	357.0	5.37±0.05
run 3	5	324–364	343.3	348.5	0.64±0.01
run 4	5	314–378	347.1	353.9	5.35±0.06
$CsAsF_6$–2 (0.3731 g)					
run 1	3	305–378	347.6	354.4	5.34±0.05
$CsAsF_6$–3 (0.3222 g)					
run 6	0.5	315–364	344.0	347.0	5.39±0.07
run 7	2	315–373	346.4	351.1	5.36±0.02

– cooling (rate 5 K min^{-1}). After cooling the crucible with substance was weighed and kept at room temperature to the next study (usually, 20–24 h).

Endothermic effects, related to the α→β transition, were observed in all heating curves, while in the cooling curves no effects, related to the reverse β→α transition, were recorded (for illustration in Fig. 1 the heating–cooling cycle (run 7) for the $CsAsF_6$–3 sample is presented). As one can see in Table 1, after the second heating the complete transformation of β- to α-phase was not reached (run 3). The complete transformation was attained in 5 days (time interval from third to fourth run). So, in contrast with the isostructural $RbAsF_6$ [5] and $KAsF_6$ [9], the reverse β→α-$CsAsF_6$ transition proceeds very slowly. This circumstance explains the fact, that in [10] at the study of electrical conductivity of hexafluoroarsenates, carried out just after the cooling of annealed at 423 K samples, the phase transition only for $CsAsF_6$ was not observed.

Endothermic effect values were determined by the graphical integration of peaks in DSC curves (the error of integration was 1%). For the temperature ranges, listed in Table 1, the transition enthalpy $\Delta_{tr}H$(endo) is 5.36±0.07 kJ mol^{-1} (average from six runs at heating rates of 0.5–5 K min^{-1}). This value is certainly less than the full enthalpy of transition, starting at 240 K, as far as, in the initial stages of extended transitions, small increments in anomalous enthalpy are included in the baseline of DSC curve. To compare obtained data with literature ones, temperatures of thermal effects were determined as extrapolated peak onset (T_e) and as maximum peak temperature (T_p). It is a common knowledge that T_e and T_p values depend on heating rate (Table 1 and Fig. 2). From plotted in [7] DTA curve, recorded at the heating rate of 9 K min^{-1}, T_e and T_p values for $CsAsF_6$ were around 348 and 378 K, relatively. Based on NMR data [11], the phase transition from rhombohedral to cubic structure occurs at 318 K.

Heat capacity study

The heat capacity of cesium hexafluoroarsenate was measured in continuous ($C_{p,cont}$) and step ($C_{p,step}$) heating modes.

The $C_{p,cont}$ heat capacity of the $CsAsF_6$–2 sample (0.3731 g) was measured in the range 300–850 K using the continuous heating at the rate of 3 K min^{-1}. The data points (at the temperature spacing of 1 K in the anomaly region and of 5 K above this region) are presented in Table 2. For the convenience of thermodynamic computations, the $C_p(T)$ values in this and the next tables are given with one extra significant digit.

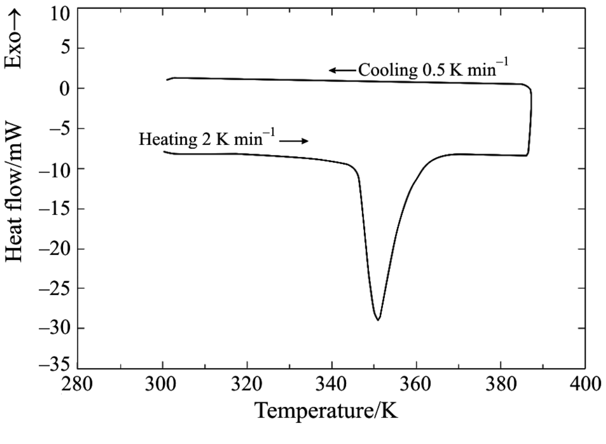

Fig. 1 'Heating–cooling' cycle for $CsAsF_6$–3 sample

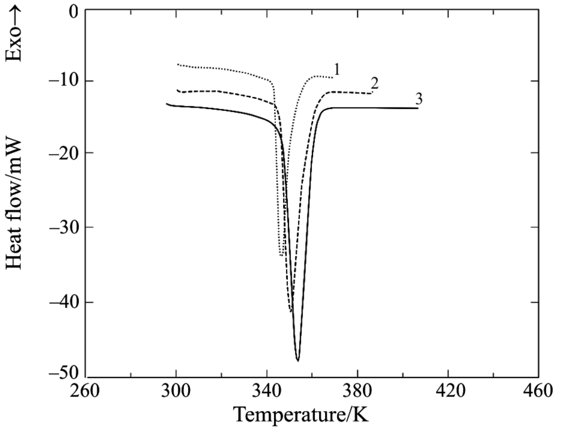

Fig. 2 Portions of heating curves in the region of α→β phase transition at heating rates of 1 – 0.5, 2 – 2 and 3 – 3 K min^{-1}

In the overlapping temperature range, 300–325 K, our DSC data are in good agreement with the low-temperature adiabatic calorimetry data [6]. As one can see in Fig. 3, the curve of heat capacity exhibits a pronounced λ-type anomaly, related to $\alpha \rightarrow \beta$ transition in $CsAsF_6$. The transformation takes place in the range from 235 to 412 K (a change in the sign of the second order derivative of heat capacity was

Table 2 Heat capacity of $CsAsF_6$ measured in continuous heating mode

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
299	181.2	340	217.5	381	183.5	450	186.6	655	203.7
300	182.0	341	219.5	382	183.5	455	186.7	660	204.5
301	182.8	342	221.8	383	183.5	460	185.6	665	204.7
302	183.3	343	225.1	384	183.6	465	186.1	670	205.0
303	184.1	344	229.6	385	183.3	470	186.0	675	205.0
304	184.6	345	237.3	386	183.3	475	186.3	680	205.0
305	185.0	346	250.1	387	183.3	480	186.6	685	205.3
306	185.7	347	268.2	388	183.3	485	187.6	690	205.9
307	186.5	348	297.3	389	183.3	490	188.1	695	205.9
308	187.2	349	356.8	390	183.3	495	188.7	700	206.2
309	187.9	350	439.8	391	183.3	500	189.2	705	206.5
310	188.9	351	543.9	392	183.3	505	189.9	710	207.4
311	189.6	352	638.4	393	183.0	510	190.4	715	207.7
312	190.2	353	721.2	394	183.0	515	190.8	720	208.1
313	190.9	354	762.9	395	183.0	520	191.6	725	208.1
314	191.9	355	754.3	396	183.0	525	192.4	730	208.7
315	192.5	356	688.7	397	183.0	530	193.1	735	208.4
316	193.4	357	585.0	398	183.0	535	193.6	740	209.1
317	194.0	358	487.9	399	182.7	540	194.0	745	209.7
318	194.7	359	397.1	400	182.7	545	194.1	750	209.7
319	195.3	360	326.5	401	182.7	550	194.3	755	210.0
320	196.2	361	276.8	402	182.7	555	194.4	760	212.0
321	196.7	362	242.0	403	182.7	560	194.6	765	210.7
322	197.6	363	219.2	404	182.7	565	194.7	770	212.6
323	198.5	364	204.7	405	182.7	570	194.8	775	212.7
324	199.1	365	196.2	406	182.7	575	194.9	780	212.7
325	199.9	366	191.1	407	182.7	580	195.7	785	214.0
326	200.8	367	188.0	408	182.6	585	195.8	790	214.6
327	201.6	368	186.1	409	182.6	590	196.8	795	215.9
328	202.8	369	185.2	410	182.6	595	197.5	800	217.2
329	203.6	370	184.6	411	182.6	600	198.2	805	217.8
330	204.6	371	184.3	412	182.6	605	198.7	810	218.8
331	205.4	372	184.3	413	182.9	610	199.7	815	219.8
332	206.5	373	184.0	414	182.9	615	200.1	820	220.7
333	207.6	374	183.7	415	183.2	620	201.2	825	222.0
334	208.7	375	183.7	420	183.5	625	201.3	830	223.6
335	210.1	376	183.8	425	183.8	630	202.7	835	224.9
336	211.6	377	183.5	430	184.2	635	203.1	840	228.0
337	212.7	378	183.8	435	184.8	640	203.6		
338	214.1	379	183.8	440	185.5	645	203.1		
339	215.8	380	183.8	445	185.9	650	203.4		

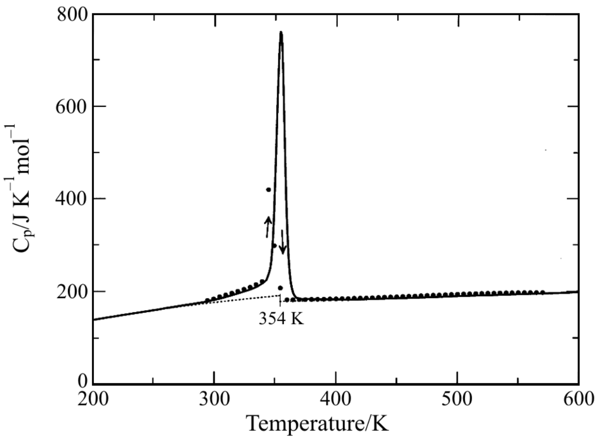

Fig. 3 Heat capacity of $CsAsF_6$ in the range from 200 to 600 K: solid line – joint smoothed data of adiabatic calorimetry [6] and DSC data measured in continuous heating mode, circles – DSC data (series **I** and **IV**) measured in step heating mode, dashed lines – normal parts of heat capacity

taken as the anomaly onset) with maximum of heat capacity at 354 K. From DTA and DTG study [7] and our DSC data on $CsAsF_6$ heat capacity it follows that above 760 K decomposition of the compound begins.

In evaluating the thermodynamic functions of cesium hexafluoroarsenate the range 0–760 K was divided into three portions:

- 0–235 K (α-$CsAsF_6$);
- 235–412 K ($\alpha\to\beta$ transition);
- 412–760 K (β-$CsAsF_6$).

The joint smoothing of low-temperature heat capacity data, measured by adiabatic calorimetry [6], and our $C_{p,cont}$ data was conducted using the algorithm, described in [12, 13]. In the 0–235 K range smoothed heat capacity data for α-$CsAsF_6$ were obtained by *DE* equation:

$$C_p(T)=9.219D_1(117\text{ K})+7.788D_2(1273\text{ K})+\\+7.110D_3(1308\text{ K})+2.086E(442\text{ K}) \qquad (1)$$

where $D_{1,2,3}$ are the Debye functions and E is the Einstein function.

The heat capacity data for β-$CsAsF_6$ in the range 412–760 K were also smoothed by *DE* equation:

$$C_p(T)=6.502D_1(65\text{ K})+7.090D_2(127\text{ K})+\\+7.550D_3(127\text{ K})+3.160E(2446\text{ K}) \qquad (2)$$

The experimental values of $C_p(T)$ in the transition region were smoothed by method of least square using the [14] program.

As was noted earlier, at the heating rate of 3 K min^{-1} the $\alpha\to\beta$ transition in $CsAsF_6$ takes place in the range 235–412 K. The enthalpy and entropy of transition were evaluated by graphical integrating the $C_{p,an}(T)$ and $C_{p,an}(T)/T$ plots. The anomalous heat capacity was found as $C_{p,an}(T)=C_p(T)–C_{p,n}(T)$. The normal (or regular) component of heat capacity, $C_{p,n}(T)$, was determined by extrapolating low-temperature (α-phase) and high-temperature (β-phase) portions of $C_p(T)$ curve, laying beyond the transition region, to temperature T_{max}=354 K (Fig. 3). The values of normal and anomalous heat capacity, and the corresponding thermodynamic functions for the range 235–412 K are presented in Table 3. The transition enthalpy and entropy are $\Delta_{tr}H(\alpha\to\beta$, cont$)=6.015\pm0.186$ kJ mol^{-1} and $\Delta_{tr}S(\alpha\to\beta$, cont$)=17.21\pm0.58$ J K^{-1} mol^{-1}. The indicated errors are the uncertainties arise from scattering of the experimental data about the smoothed heat capacity values.

To study the phase transition in details, the $C_{p,step}$ heat capacity of the $CsAsF_6$–3 sample (0.3692 g) was measured between 298 and 573 K in the step (discrete) heating mode, that is, under quasi-equilibrium experimental conditions. The $C_{p,step}(T)$ data obtained in five series of measurements, each consisting of 7–30 cycles (data points), are given in Table 4. In series **I** and **IV** each cycle included heating at the rate of 1.5 K min^{-1} for 200 s and isothermal stage for 400 s. T_{hus}, the temperature was raised by 5 K per cycle. In series **I** the highest anomalous heat capacity was observed at T_{max}=344.5±5.0 K, but after 400 s isothermal stage no thermal equilibrium could be reached in that cycle, as well as in four next cycles of series **I** (Table 4). For this reason two additional series **II** and **III**, at the heating rate of 0.6 K min^{-1} (temperature step of 2 K), were conducted. In series **II**, isothermal stage during 900 s was also insufficient for thermal equilibrium. The highest anomalous heat capacity value in this series was already observed at T_{max}=343.0±2.0 K. Near to equilibrium conditions were only reached in series **III** (isothermal stage during 1800 s). The temperature T_{max}=340.0 K from this series was taken as the transition temperature, $T_{tr}(\alpha\to\beta–CsAsF_6)$. Data in series **V** refer to the descending branch of the heat capacity curve in the region of the transition.

In the stepwise mode of heat capacity measurements the main part of $\alpha\to\beta$ transition occurs in the range 300–360 K (series **I**), i.e. it finishes sufficiently earlier than at continuous heating at the rate of 3 K min^{-1}. It must be reminded that at continuous heating of the $CsAsF_6$–3 sample at the rate of 0.5 K min^{-1}, the range of transformation narrowed to 315–363 K (Table 1, Fig. 2). The transition enthalpy and entropy, calculated from the $C_{p,step}(T)$ data (series **I**) for the range 235–360 K, are $\Delta_{tr}H(\alpha\to\beta$, step$)=2.778\pm0.103$ kJ mol^{-1} and $\Delta_{tr}S(\alpha\to\beta$, step$)=8.240\pm0.305$ J K^{-1} mol^{-1}, respectively. The value $\Delta_{tr}H(\alpha\to\beta$, step) is by a factor of 2 less than the value $\Delta_{tr}H(\alpha\to\beta$, cont). It shows that $\alpha\to\beta$ transition in $CsAsF_6$ has a latent heat and so, in part is a first-order transition. Consequently, the correct values of enthalpy and entropy of transition could be obtained only from C_p,cont(T) data.

Table 3 Thermodynamic functions of $CsAsF_6$ in the transition region (235–412 K)

Temperature/ K	$C_{p,n}(T)$/ J K^{-1} mol^{-1}	$S_n(T)$/ J K^{-1} mol^{-1}	$H_n(T)$–$H_n(0)$/ J mol^{-1}	$C_{p,an}(T)$/ J K^{-1} mol^{-1}	$\Delta_{an}S(T)$/ J K^{-1} mol^{-1}	$\Delta_{an}H(T)$/ J mol^{-1}
Ascending branch						
235	153.8	198.7	21800	0.00	0.00	0.0
240	155.8	202.0	22570	0.01	0.00	0.0
250	159.6	208.4	24150	0.26	0.01	1.1
260	163.3	214.7	25770	0.78	0.03	6.0
270	166.8	221.0	27420	1.62	0.08	17.9
280	170.3	227.1	29100	2.35	0.15	38.5
290	173.5	233.1	30820	3.25	0.24	65.7
298.15	176.1	238.0	32250	4.93	0.37	98.4
300	176.6	239.1	32570	5.46	0.39	108.0
310	179.6	244.9	34350	9.10	0.62	179.7
320	182.4	250.6	36160	13.70	0.98	293.3
330	185.1	256.3	38000	19.29	1.49	456.6
340	187.7	261.9	39870	30.06	2.19	695.3
350	190.2	267.3	41760	251.8	4.36	1449
354*	191.1	269.5	42520	570.7	9.30	3186
Descending branch						
354*	178.7	269.5	42520	583.2	9.30	3186
360	179.0	272.5	43590	150.1	15.98	5567
370	179.6	277.4	45390	4.41	16.96	5923
380	180.3	282.2	47180	3.38	17.07	5962
390	180.9	286.9	48990	2.32	17.14	5990
400	181.6	291.5	50800	1.23	17.19	6008
410	182.4	296.0	52620	0.12	17.21	6015
412	182.5	296.9	52990	0.00	17.21	6015

*temperature of the maximum value of heat capacity

Table 5 summarizes the heat capacity $C_p^0(T)$, entropy $S^0(T)$, reduced Gibbs energy $\Phi^0(T)=-(G^0(T)-H^0(0)/T$ and enthalpy increment $H^0(T)-H^0(0)$. The thermodynamic properties of $CsAsF_6$ in the range 10–760 K, as well as values of enthalpy and entropy of transition, were calculated based on $C_{p,cont}(T)$ values. The transition range (235–360 K) and the transition temperature (340 K) were found from $C_{p,step}(T)$ data. The values of thermodynamic properties at 298.15 K are given in Table 3.

Phase transition

As was shown above, the structural phase transition in $CsAsF_6$ relates to so-called gradual transition completed isothermally. Examples of such transitions can be found in [15]. The fact that the value of transition entropy, $\Delta_{tr}S$ ($\alpha\rightarrow\beta$-$CsAsF_6$), is close to $R\ln 8$ provides evidence that this $\alpha\rightarrow\beta$ phase transition belongs to order-disorder transitions and is accompanied by the 8-fold increase in the number of equilibrium (energetically indistinguishable) states in the high-temperature disordered β-phase in comparison with low-temperature structurally ordered α-phase. In the face-centered cubic cell, the octahedral AsF_6^- anion is situated in the center of an octahedral coordination polyhedron, formed by six Cs^+ cations. Speculatively, it is easy to find in the NaCl-type structure the eight equivalent orientations of the AsF_6^- group about the crystal axes. But such model of orientational disordering must be confirmed by another experimental data in addition to thermodynamic and structural ones.

For $KAsF_6$ [9] and $RbAsF_6$ [5] the entropy of analogous phase transitions was found to be equal $R\ln 24$. In accordance with NMR study [11], spectra of ^{19}F and ^{75}As of isostructural hexafluoroarsenates $KAsF_6$, $RbAsF_6$ and $CsAsF_6$ are the same and as in low-temperature, as in high-temperature phases AsF_6^- anions are tetragonally distorted. Gabuda *et al*. [11] suggest that phase transition in heavy alkali metal hexafluoroarsenates are connected with the statistical disordering of nonequivalent As–F bonds of asymmet-

Table 4 Heat capacity of $CsAsF_6$ measured in step heating mode

Temperatre/K	C_p/J K^{-1} mol^{-1}	Temperature/K	C_p/J K^{-1} mol^{-1}	Temperature/K	C_p/J K^{-1} mol^{-1}
Series **I**		337.0	209.2	484.5	193.4
(ΔT=5 K, 400 s)		339.0	207.0*	489.5	193.2
		341.0	339.1*	494.5	192.7
294.5	180.6	343.0	450.3*	499.5	192.7
299.5	183.7	345.0	323.4*	504.5	194.1
304.5	189.9	347.0	224.0*	509.5	192.6
309.5	191.8	349.0	199.0*	514.5	190.9
314.5	195.3	351.0	183.7	519.4	194.5
319.5	199.4	353.0	179.4	524.4	196.3
324.5	204.1	355.0	175.4	529.4	195.7
329.5	208.9	357.0	175.5	534.4	198.1
334.5	214.5	359.0	174.3	539.4	197.6
339.5	210.2*	361.0	176.6	544.4	197.0
344.5	419.2*			549.4	197.2
349.5	297.9*	Series **III**		554.4	197.4
354.5	207.0*	(ΔT=2 K, 1800 s)		559.3	196.9
359.5	181.0*			564.3	197.7
364.5	180.6	338.0	251.1	569.3	198.1
369.5	181.8	340.0	558.3*		
374.5	182.1	342.0	397.5*	Series **V**	
379.5	182.2	344.0	236.6	(ΔT=3 K, 600 s)	
384.5	183.2	346.0	201.9		
389.5	183.6	348.0	185.6	348.7	238.7*
394.5	183.4	350.0	176.3	351.7	205.5*
399.5	184.0			354.7	185.5
404.5	184.6	Series **IV**		357.7	179.0
409.5	185.8	(ΔT=5 K, 400 s)		360.7	178.2
414.4	186.1			363.7	178.4
419.4	185.4	429.7	189.9	366.7	179.1
424.4	186.7	434.6	186.4	369.7	178.9
429.4	186.7	439.6	186.4	372.7	178.9
434.4	186.4	444.6	187.7	375.7	179.0
439.4	188.3	449.6	189.1	378.7	179.7
		454.6	188.0	381.7	180.0
Series **II**		459.6	188.4	384.7	180.4
(ΔT=2 K, 900 s)		464.6	189.0	387.7	179.1
		469.5	190.8	390.7	180.8
333.0	208.3	474.5	191.1		
335.0	207.7	479.5	191.8		

* - obtained under nonequilibrium experimental conditions

ric AsF_6^- anions. For potassium salt Heyns and Pistorius [9] proposed a model according to which in high-temperature disordered phase the fluorine atoms, located in 24*e* positions of cubic structure, are offset from K–As lines (crystal axes) and rotate around them.

It is possible, that the number of possible equilibrium orientations of AsF_6^- anions in β-phase of $CsAsF_6$ is, also, equal to 24. In this case the number of indistinguishable equilibrium orientations of AsF_6^- anions in rhombohedral lattice can be equal to 3

Table 5 Thermodynamic properties of $CsAsF_6$ in the range 10–760 K

Temperature/K	$C_p^0(T)$/J K^{-1} mol^{-1}	$S^0(T)$/J K^{-1} mol^{-1}	$\Phi^0(T)$/J K^{-1} mol^{-1}	$H^0(T)$–$H^0(0)$/J mol^{-1}
10	3.702	1.249	0.3079	9.409
15	11.30	4.052	1.031	45.31
20	21.44	8.666	2.327	126.8
25	31.37	14.53	4.165	259.2
30	39.84	21.03	6.429	437.9
35	46.69	27.70	8.991	654.9
40	52.15	34.31	11.74	902.5
45	56.59	40.71	14.61	1175
50	60.33	46.87	17.53	1467
60	66.61	58.44	23.40	2103
70	72.25	69.14	29.18	2797
80	77.74	79.15	34.81	3547
90	83.21	88.62	40.26	4352
100	88.68	97.67	45.55	5212
110	94.10	106.4	50.69	6126
120	99.47	114.8	55.69	7093
130	104.7	123.0	60.55	8115
140	109.9	130.9	65.29	9188
150	115.0	138.7	69.93	10310
160	120.0	146.3	74.46	11490
170	124.9	153.7	78.90	12710
180	129.7	161.0	83.27	13990
190	134.4	168.1	87.53	15310
200	138.9	175.1	91.74	16670
210	143.3	182.0	95.88	18090
220	147.6	188.8	99.95	19540
230	151.8	195.4	103.9	21040
235	153.8	198.7	105.9	21800
340(α)	187.7	261.9	144.6	39870
340(β)	178.0	279.1	144.1	45880
360	179.0	289.3	151.9	49450
400	181.6	308.3	166.6	56660
450	185.5	330.3	183.7	65990
500	189.7	350.1	199.3	75370
550	194.1	368.4	213.9	84970
600	198.5	385.5	227.5	94780
650	202.7	401.5	240.2	104800
700	206.7	416.7	252.3	115000
750	210.4	431.1	263.8	125500
760	211.1	433.9	266.0	127600

(*R*ln24/3). It counts in the favor of this suggestion that at the room temperature structure of $CsAsF_6$ is still rhombohedral [7, 8], although α→β transition develops from 235–240 K. Gabuda *et al*. [11] showed that mobility of fluorine atoms, observed at room temperature, does not effect sufficiently on the structure symmetry and suggested that it can be connected with low frequency of reorientation processes. As one can see in Table 3, in the range 235–300 K the anomaly enthalpy and entropy increments are 108 J mol^{-1} and

0.39 J K^{-1} mol^{-1}, respectively, that are only near 2% from $\Delta_{tr}H$ ($\alpha\rightarrow\beta$-$CsAsF_6$) and $\Delta_{tr}S$($\alpha\rightarrow\beta$-$CsAsF_6$) values. It is possible that the structural transition in $CsAsF_6$ proceeds in two stages. In the interval 235–300 K it proceeds as the transition with atomic displacement, characterized by small anomaly entropy [16, 17], and then as the order–disorder transition. In this case at room temperature number of energetically equivalent states may be equal to 3, and then the transformation of varied rhombohedral structure to cubic one proceeds via the orientational disordering with the $\Delta_{tr}S$ value near to Rln8.

Conclusions

It was shown that the structural transition from rhombohedral to cubic phase in $CsAsF_6$ proceeds in wide temperature range. The thermodynamic parameters of this transition were determined. The reverse transition to rhombohedral phase proceeds very slowly. It was confirmed that high-temperature cubic phase of $CsAsF_6$ has a highly disordered structure.

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