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The Thermodynamics of the Divalent Metal Fluorides. III. Heat Capacity of the Fast Ion Conductor $SrSnF_4$ from 6 to 344 K*

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The heat capacity of the fast ion conductor $SrSnF_4$ was measured by adiabatic calorimetry from $6 < T/K < 344$. A phase transition was not detected, but an anomalous rise in the molar heat capacity was found above 280 K that showed no sign of lessening at 344 K. This rise is coincident with the temperature range where a rapid drop in the ^{19}F spin-lattice relaxation time T_1 occurs. Standard molar thermodynamic functions are given at selected temperatures from 5 to 345 K.

Introduction

The metal tetrafluorostannates with lead, barium, or strontium are fast ion conductors characterized by good electrical performances as shown in Table I. These solid electrolytes are of technological significance because of their applications in electronic devices and batteries. Not only do they exhibit significant anionic conduction down to 300 K (*5*, *6*), but fast ion fluorine electrolytes are often electronic insulators, which is an important property for use in electrochemical cells (*7*). Considerable experimental work has been directed recently at fluorides with the fluorite-type structure, which includes the family MSnF$_4$, where M = Pb, Ba, or Sr.

Several allotropic forms of $PbSnF_4$ are known to exist at temperatures above 273 K (*5*, *8–11*). The normal α-phase at room temperature, which depends upon the method of preparation, has a monoclinic structure (P_{112}/n of P_2/c No. 13 C^4_2h) stable to about 353 K. The β-phase is tetragonal

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TABLE I

CONDUCTIVITIES AT −20, 20, 150, AND 200°C AND ACTIVATION ENERGIES FOR $PbSnF_4$, $BaSnF_4$, $SrSnF_4$, AND β-PbF_2

	$\sigma_{-20°C}$ (Ω^{-1} cm^{-1})	ΔE (eV)	$\sigma_{20°C}$ (Ω^{-1} cm^{-1})	ΔE (eV)	$\sigma_{150°C}$ (Ω^{-1} cm^{-1})	ΔE (eV)	$\sigma_{200°C}$ (Ω^{-1} cm^{-1})	ΔE (eV)	Ref.
α-$PbSnF_4$	—	—	1×10^{-3}	0.42	—	—	—	—	(*1*)
	—	—	0.1×10^{-3}	0.52	—	—	—	—	(*2*)
	—	—	2.6×10^{-3}	0.45	—	—	—	—	(*3*)
β-$PbSnF_4$	—	—	—	—	0.08	0.14	—	—	(*1*)
	—	—	—	—	0.08	0.17	—	—	(*2*)
	—	—	—	—	0.08	0.16	0.11	0.16	(*3*)
β-$BaSnF_4$	0.2×10^{-3}	0.50	—	—	9.4×10^{-3}	0.18	13×10^{-3}	0.18	(*3*)
	8×10^{-6}	0.34	—	—	3.9×10^{-3}	0.31	6×10^{-3}	0.31	(*4*)
$SrSnF_4$	—	—	—	—	0.2×10^{-3}	—	6×10^{-3}	—	(*3*)
β-PbF_2	—	—	2×10^{-6}	0.45	7×10^{-4}	0.45	—	—	(*5*)

(*P_4/nmm* or No. 129 D_4^7h) and stable from 353 to 623 K (*9–11*). When $PbSnF_4$ is prepared using the dry method, the α-phase appears only after annealing (*10*). The variation in the electrical conductivity in the α-phase shown in Table I may be caused by insufficient annealing. The heat capacity of $PbSnF_4$ by adiabatic calorimetry was measured by us from $10 < T/K < 352$ (*12*) and a subtle anomaly found between 130 and 160 K, which correlates with changes in the ^{19}F spin-lattice relaxation time (*3*).

The $BaSnF_4$ salt is isomorphous between room temperature and 693 K with the tetragonal structure of β-$PbSnF_4$ (*4, 9, 13*). X-ray diffraction studies of the thermal expansion coefficients from $77 < T/K < 685$ show no phase transition, but decomposition occurs above 673 K (*4, 13*). Our study of the heat capacity of $BaSnF_4$ by adiabatic calorimetry from $7 < T/K < 345$ showed no phase transition (*14*). However, an anomalous rise in the heat capacity occurred in the region $210 < T/K < 310$. This rise coincides with the temperature range where a break in the slope of the electrical conductivity results in a threefold decrease in the activation energy above the break at 272 K (*3*).

Between about 77 and 693 K, the solid electrolyte $SrSnF_4$ is also isomorphous with the tetragonal structure of β-$PbSnF_4$. At 293 K, the lattice parameters of $SrSnF_4$ were found to be $a = 0.41754$ and $c = 1.1448$ nm with $Z = 2$ and a space group $P_{4/nmm}$ (*9*). Their X-ray diffraction work on the thermal expansion coefficients from $77 < T/K < 693$ showed no phase transition. However, decomposition began above 673 K (*9*).

Chadwick *et al.* (*3*) have examined the conduction mechanism in $PbSnF_4$, $BaSnF_4$, and $SrSnF_4$ using nuclear magnetic resonance (NMR) techniques. They found the behavior of the relaxation to be broadly similar in all three compounds. To assist in understanding the conduction mechanism in $SrSnF_4$, its heat capacity, heretofore unreported, was measured by us from $6 < T/K < 344$ by adiabatic calorimetry.

Experimental

The $SrSnF_4$ sample was prepared by a solid-state reaction of a 1 : 1 stoichiometric mixture of SrF_2 and SnF_2, which was ground to a fine powder and thoroughly mixed in an agate mortar and pestle. Pellets were then pressed from the powder contained in a stainless-steel die and loaded into a specially designed copper tube evacuated to 0.13×10^{-3} MPa. The pellets in the copper tube were next annealed inside an evacuated silica tube for 12 hr at 523 K. After sintering, the copper tube showed no visible signs of reaction with the pellets. Annealing was carried out in two stages. First the pellets were annealed for 1 hr at 473 K and then for 1 hr at 773 K, a treatment similar to that used for the $BaSnF_4$ salt (*3*, *12*). Then the pellets of $SrSnF_4$ were cooled to room temperature where they remained until they were loaded into the calorimeter. Once loaded, they were cooled to 5 K for the measurements of heat capacity. The X-ray powder pattern at room temperature confirmed the structure of the $SrSnF_4$ as tetragonal in agreement with Pannetier *et al.* (*9*, *15*).

The calorimetric results were determined using the Mark XIII cryostat, which is an upgraded version of the Mark II cryostat already described (*16*). A guard shield was incorporated around the adiabatic shield. A capsule-type platinum resistance thermometer (laboratory designation A-5) was used for temperature measurements. The thermometer was calibrated at the U.S. National Bureau of Standards (NBS) against the IPTS-1948 (as revised in 1960) (*17*) for temperatures above 90 K, against the NBS provisional scale from 10 to 90 K, and by the technique of McCracken and Chang (*18*) below 10 K. These calibrations are judged to reproduce thermodynamic temperatures to within 0.03 K between 10 and 90 K and within 0.04 above 90 K (*19*). Measurements of mass, current, voltage, and time are based upon calibrations done at NBS. The heat capacities from about 10 to 352 K were acquired with the assistance of a computer (*20*, *21*), which was programmed for a series of determinations. During the drift periods both the calorimeter temperature and the first and second derivatives of temperature with respect to time were recorded to establish the equilibrium temperature of the calorimeter before and after the energy input. While the calorimeter heater was on, the heater current and voltage as well as the duration of the heating interval were determined. The apparent heat capacity of the system, which included the calorimeter, heater, thermometer, and sample, was also recorded.

The gold-plated, copper calorimeter (laboratory designation W-UK) without internal vanes was loaded with the $SrSnF_4$ specimen, which was in the form of a single cylindrical-shaped pellet. The calorimeter vessel contained an entrant well that was located off center for the heater and thermometer, thereby allowing the accommodation of massive samples. After loading, the removable lid with a diameter equal to that of the calorimeter vessel was soldered in place using a low melting point (bismuth/tin/indium) solder. The calorimeter was then evacuated through the stainless-steel seal-off tip provided in the lid. Helium gas was admitted to the vessel to a pressure of 3.7 kPa at 295 K to facilitate thermal equilibration. The vessel was then sealed by melting a drop of low melting point solder on the seal-off tip in the low-pressure helium atmosphere.

The empty calorimeter vessel has a mass of 18.70 g and an internal volume of 17.0×10^{-6} m^3. Buoyancy corrections were calculated on the basis of the crystallographic density of 4696.9 kg m^{-3} from the X-ray diffraction studies on the salt (*9*). The mass of $SrSnF_4$ amounted to 10.754398 g or 0.03809515 mole based on its molar mass of 282.3036 g mole^{-1} calculated from the 1983 IUPAC recommended atomic masses of the elements.

Results

The experimental molar heat capacities, $C_{p,m}$, of our $SrSnF_4$ sample are given in Table II, where the results are presented in

TABLE II

EXPERIMENTAL MOLAR HEAT CAPACITY OF $SrSnF_4$

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
5.94	0.03366	100.30	9.646
6.88	0.05719	105.30	10.06
7.60	0.07425	110.31	10.46
8.41	0.09542	115.34	10.85
9.23	0.1214	120.64	11.25
10.16	0.1581	126.19	11.64
11.22	0.2068	131.76	12.01
12.27	0.2644	137.34	12.35
13.34	0.3315	142.94	12.66
14.55	0.4171	148.54	12.96
15.87	0.5203	154.15	13.26
17.20	0.6328	159.77	13.54
18.56	0.7549	165.66	13.81
20.05	0.8982	171.81	14.08
21.68	1.063	177.96	14.34
23.31	1.237	184.12	14.58
24.97	1.418	190.29	14.82
26.77	1.620	196.46	15.04
28.71	1.842	202.64	15.24
30.66	2.075	208.82	15.44
32.79	2.334	215.00	15.64
35.12	2.615	221.19	15.81
37.46	2.897	227.37	15.99
40.00	3.199	233.57	16.16
42.74	3.529	239.94	16.35
45.49	3.866	246.08	16.54
48.50	4.231	252.96	16.75
51.75	4.618	259.99	16.92
55.03	5.004	267.01	17.05
58.57	5.424	274.04	17.17
62.35	5.875	281.05	17.32
66.16	6.309	288.07	17.48
70.01	6.728	295.04	17.65
73.90	7.135	302.01	17.77
77.81	7.546	309.02	17.85
81.73	7.984	316.00	17.96
85.92	8.419	322.99	18.13
86.21	8.450	329.96	18.40
90.36	8.828	336.86	18.81
95.33	9.231	343.80	19.25

Note. Molar mass = 282.3036 g mole^{-1}; R = 8.3145 J K^{-1} mole^{-1}.

the order of increasing temperature. The measurements were made in one series beginning at 5.4 K and finishing at 347 K. The probable errors in heat capacity decrease from about 1% at 10 K to less then 0.15% at temperatures above 30 K. The heat capacity of the $SrSnF_4$ sample amounted to 54 to 30% of the total heat capacity of the sample plus calorimeter vessel. The heat capacity plot for $SrSnF_4$ is shown in Fig. 1 from 6 to 344 K as $C_{p,m}/R$ where R is the gas constant.

TABLE III

STANDARD MOLAR THERMODYNAMIC FUNCTIONS FOR $SrSnF_4$

T/K	$C_{p,m}/R$	$\Delta_0^T S_m^\circ(T)/R$	$\Delta_0^T H_m^\circ(T)/R$ K	ϕ_m°/R
5	(0.020)	(0.007)	(0.026)	(0.0017)
10	0.154	0.052	0.391	0.0130
15	0.451	0.164	1.82	0.0424
20	0.900	0.352	5.15	0.0947
25	1.419	0.607	10.95	0.1687
30	2.000	0.915	19.50	0.2654
35	2.604	1.268	31.01	0.3820
40	3.197	1.654	45.51	0.5160
45	3.807	2.065	63.02	0.6646
50	4.413	2.497	83.57	0.8258
55	5.009	2.946	107.1	0.9978
60	5.593	3.406	133.6	1.179
65	6.180	3.877	163.1	1.368
70	6.726	4.355	195.3	1.565
75	7.245	4.837	230.3	1.767
80	7.791	5.322	267.8	1.974
85	8.325	5.810	308.1	2.185
90	8.794	6.299	350.9	2.400
95	9.205	6.786	395.9	2.618
100	9.615	7.268	443.0	2.838
105	10.03	7.747	492.1	3.061
110	10.44	8.224	543.3	3.285
120	11.21	9.165	651.5	3.736
130	11.90	10.09	767.1	4.189
140	12.50	10.99	889.1	4.643
150	13.04	11.87	1016.8	5.096
160	13.55	12.73	1149.7	5.547
170	14.00	13.57	1287.5	5.994
180	14.42	14.38	1429.6	6.437
190	14.81	15.17	1575.7	6.876
200	15.15	15.94	1725.6	7.310
210	15.48	16.69	1878.8	7.739
220	15.79	17.41	2035.2	8.163
230	16.07	18.12	2194.5	8.580
240	16.35	18.81	2356.5	8.992
250	16.66	19.49	2521.6	9.399
260	16.92	20.14	2689.6	9.799
270	17.11	20.79	2859.7	10.19
280	17.29	21.41	3031.7	10.58
290	17.54	22.02	3205.8	10.97
300	17.74	22.62	3382.3	11.35
310	17.86	23.20	3560.3	11.72
320	18.04	23.77	3739.7	12.09
330	18.41	24.33	3921.8	12.45
340	18.97	24.89	4108.7	12.81
345	19.33	25.17	4204.5	12.99
298.15	17.71 ± 0.03	22.51 ± 0.04	3349.5 ± 5.4	11.28 ± 0.02

Note. Molar mass = 332.014 g mole^{-1}; P° = 101.325 kPa; R = 8.3145; $\phi_m^\circ(T, 0)^{\mathrm{def}} = -\Delta_0^T H_m^\circ(T)/T + \Delta_0^T S_m^\circ(T)$; $\Delta_0^T X(T) = [X(T) - x(0)]$.

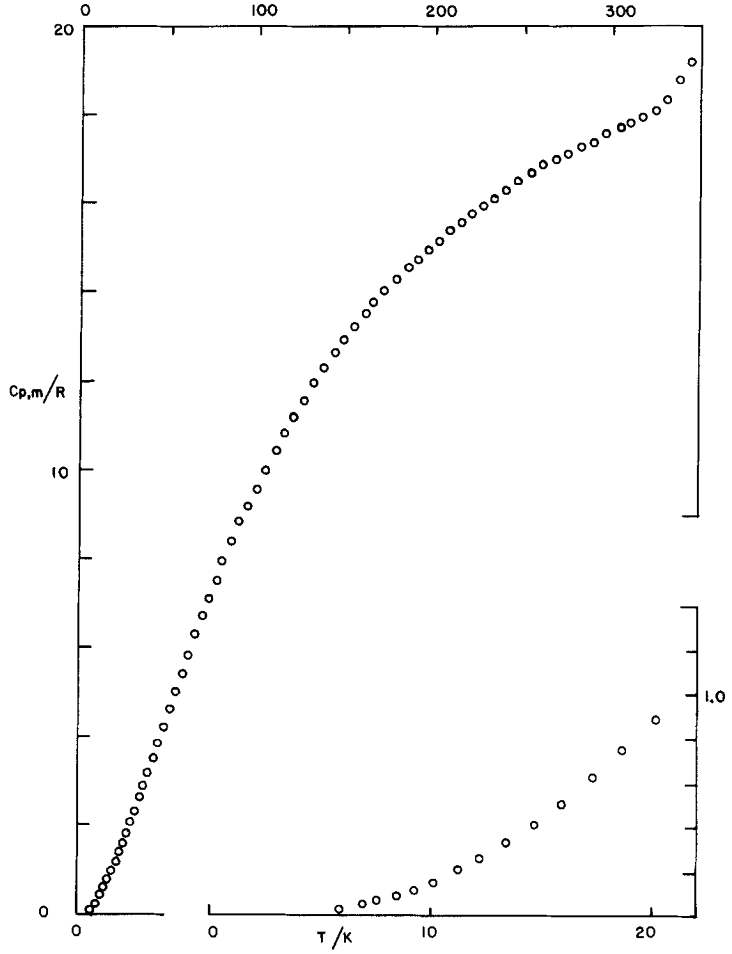

FIG. 1. The molar heat capacity as $C_{p,m}/R$ for $SrSnF_4$.

The standard molar thermodynamic functions derived from the smoothed heat capacity curve are tabulated at selected temperatures in Table III. Below 7 K, our heat capacities were obtained by fitting our experimental values below 20 K to the limiting form of the Debye equation, using a plot of $C_{p,m}/T$ against T^2 and extrapolating to 0 K. Because the temperatures achieved in this study were not sufficiently low to reach the linear region below the maximum in a plot of $C_{p,m}/T^3$ against T^2, this relationship could not be used for the extrapolation.

Discussion

The heat capacity curve in Fig. 1 is without a discontinuity and thus consistent with the absence of a phase transition from 6 to 344 K. The X-ray diffraction study by Pannetier *et al.* (*9*) also showed no phase transition from 77 to 693 K. However, our heat capacity work shows an abnormal rise in $C_{p,m}/R$ above 280 K; this rise is presented on an expanded plot in Fig. 2. An approximate estimate of the smoothed background curve is shown as the broken line. Because our measurements did not extend to tem-

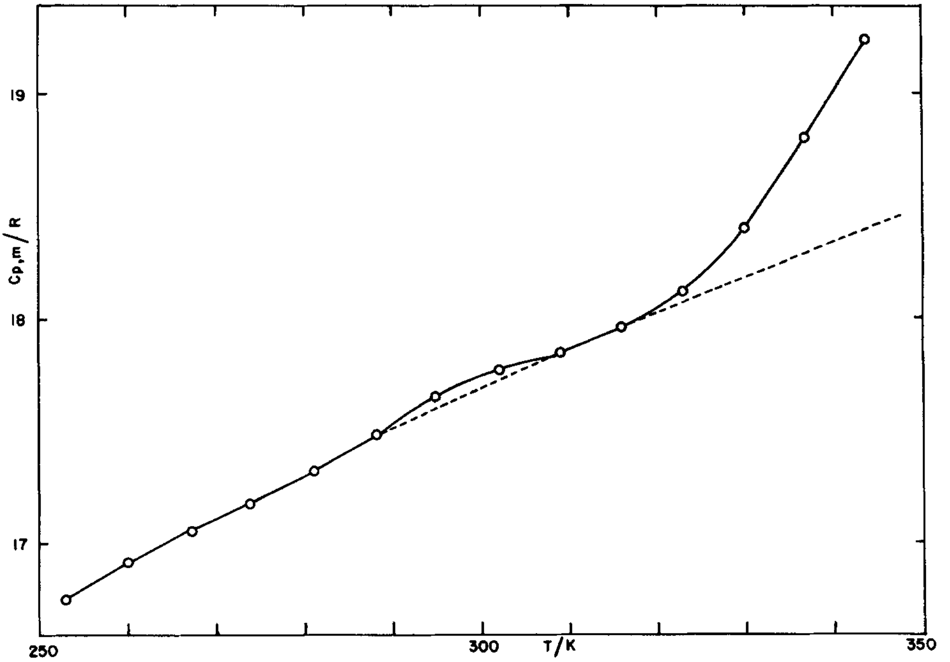

FIG. 2. The molar heat capacity as $C_{p,m}/R$ for $SrSnF_4$ in the region of the anomaly (—, experimental; ---, smoothed background curve).

peratures where the heat capacity reverted to its normal shape, it is impossible to determine the entropy change associated with the anomalous rise. The equilibrium times for our sample were normal through the temperature region covered in Fig. 2. No anomalies were detected below 280 K.

The increase in heat capacity between 280 and 340 K amounts to about 10%, which is substantially greater than the corresponding rises in the $BaSnF_4$ salt at 2% (*14*) and in $PbSnF_4$ at 6% (*12*). The rise in the $PbSnF_4$ salt is associated with the transition from the monoclinic form to the tetragonal structure around 353 K.

An examination of results of other experiments on the $SrSnF_4$ salt in the range from 280 to 340 K yielded some interesting finds. No hint of any anomaly is given by data on lattice parameters over a wide range from 77 to 673 K, and changes in lattice parameters with temperature parallel those in the $BaSnF_4$ salt (*9*). The electrical conductivity measurements are smooth, with a constant activation energy from about 310 to 420 K (*3*). A change in activation occurs above 452 K, which is well above the temperatures of our heat capacity work.

However, it is from the NMR investigation by Chadwick *et al.* (*3*) that changes are noted in the $SrSnF_4$ lattice above about 300 K. The rise in our experimental heat capacity coincides in temperature with a drop in the ^{19}F spin-lattice relaxation time T_1. Their T_1 falls slowly up to 300 K and then drops rapidly until 452 K is reached, where a break occurs in the slope of their plot of electrical conductivity with temperature. Although their $T_{1\rho}$ curve shows a similar shape, the $T_{1\rho}$ falls rapidly as temperature rises from 250 to 452 K.

This NMR work confirmed the absence of any phase transition from 167 to 650 K. For both the $BaSnF_4$ and $SrSnF_4$ salts, the free induction decay signal was made up to two components, indicating the presence of two nonequivalent sublattices of fluoride ions. One of these sublattices of F^- ions was rigid and the other mobile depending upon the range of temperature. Their model provides a qualitative explanation of both the conductivity and NMR results. It allows for the fast mobile F^- ions on interstitial sites to move by direct interstitial jumps. More detailed structural information than is currently available is required to confirm the model. Our heat capacity data by themselves do not permit discrimination between this model of single-ion excitations by Chadwick and that of the cluster-excitations suggested by Goodenough (*22*).

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