

Thermodynamics of divalent-metal fluorides

VI. Heat capacity and thermodynamic properties of the fast-ion conductor CaSn_2F_6 at temperatures from 6 K to 310 K

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The molar heat capacity $C_{p,m}$ of calcium hexafluorostannate CaSn_2F_6 was measured at temperatures T from 6 K to 310 K by adiabatic calorimetry. Reproducible heat capacities were obtained only after cooling the sample twice to $T < 150$ K. The curve of heat capacity against temperature is continuous and rises smoothly to $T \approx 140$ K, where a small anomaly appears. Above $T \approx 150$ K, the curve resumes its smooth path. The anomaly, whose source is unknown, is centred at $T \approx 143$ K. The greatest difference of the curve from that defined by the curve of the lattice vibrations is $0.01 \cdot C_{p,m}$, which lies outside the error in the measurements. The excess molar enthalpy associated with the anomaly amounts to $\Delta_{135\text{K}}^{150\text{K}} H_m^\circ = (1.3 \pm 0.3) \cdot R \cdot \text{K}$ ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), while the excess entropy is zero within the experimental error of the measurements. Smoothed values of the standard thermodynamic quantities for pure CaSn_2F_6 are tabulated up to $T = 310$ K and $S_m^\circ(298.15 \text{ K}) = (33.16 \pm 0.03) \cdot R$.

1. Introduction

Fast-ion conductors are solid electrolytes with ionic conductivities κ comparable, at the operating temperature, with proton conductivities in a strong acid,⁽¹⁾ i.e. $\kappa \geq 0.1 \Omega^{-1} \cdot \text{cm}^{-1}$. More loosely, these conductors are also categorized as solids with ionic conductivities comparable with those of molten salts. The ideal solid

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electrolyte shows both a high degree of ionic conductivity at $T = 300$ K and a low electronic conductivity typical of an insulator; the latter property is important when the solid electrolyte is used in electrochemical cells.^(2,3) The ability of the ions to migrate within ionic conductors is dependent either on the existence of non-equivalent lattice sites for the mobile species⁽⁴⁻⁸⁾ or on a structural phase transition.⁽⁹⁾ These materials are important technologically for use in electrochemical cells^(2,3) and other electrochemical devices.⁽¹⁰⁻¹²⁾

Considerable experimental work has been directed at fast-ion conductors containing F^- . Such materials are insulators and are predicted to be among the best anionic conductors because the anion is low in mass, small in size, and univalent. The studies on the metallic M^{2+} tetrafluorostannates include measurements on electrical conductivity,⁽¹³⁻¹⁷⁾ n.m.r.,⁽¹⁶⁾ and heat capacity.⁽¹⁸⁻²²⁾ Electrical conductivity yields information about activation energy and bulk mobility, but fails to differentiate between different ions moving on non-equivalent sites. The n.m.r. results often allow identification of both the rigid and the mobile ions. However, the effects of several interactions are sometimes superimposed, precluding an unambiguous interpretation of ionic movement within the crystal at the microscopic level. On the other hand, heat capacity is a macroscopic property that reflects all the changes occurring within the lattice and, when interpreted together with the results from other experiments, is a powerful tool for understanding these solids and for identifying other experiments that should be done.

As part of a continuing study of the ionic conductivities of the fluorostannates,⁽²³⁾ pure $CaSn_2F_6$ has been synthesized by a precipitation reaction between α - SnF_2 (monoclinic) in solution and $Ca(NO_3)_2(aq)$.⁽²⁴⁾ The absence of thermodynamic quantities in general, and heat capacities in particular, for this solid electrolyte prompted us to measure its heat capacity by adiabatic calorimetry at temperatures T from 6 K to 310 K.

2. Experimental

The sample of $CaSn_2F_6$ was provided by Dr G. Denes of Concordia University, Montreal, Canada. The Guinier-de-Wolff diffraction pattern of the $CaSn_2F_6$ sample as received by us matched the pattern for the compound described in reference 24. This compound is not yet included in the listing of the Joint Committee for Powder Diffraction Standards. Its structure has not been assigned⁽²⁴⁾ since the available software was inadequate to index the powder diffraction pattern, but the symmetry is thought to be lower than tetragonal.

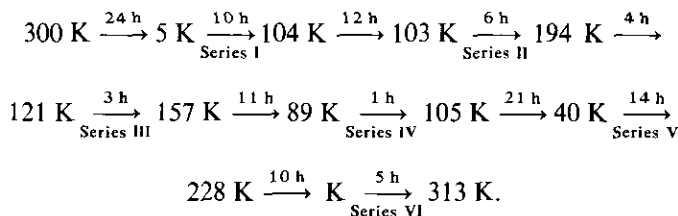
The molar heat capacity $C_{p,m}$ was measured by us from $T = 6$ K to $T = 310$ K by adiabatic calorimetry in the Mark XIII adiabatic cryostat, which is an upgraded version of the Mark II cryostat described previously.⁽²⁵⁾ A guard shield was incorporated to surround the adiabatic shield. A Leeds and Northrup capsule-type platinum resistance thermometer (Laboratory designation A-5) was used for the temperature measurements. The thermometer was calibrated at the U.S. National Bureau of Standards (N.B.S., now NIST) against the IPTS-1948 (as revised in 1960)⁽²⁶⁾ for temperatures above 90 K, against the N.B.S. (NIST) provisional scale

from 10 K to 90 K, and by the technique of McCrackin and Chang⁽²⁷⁾ below 10 K. These calibrations are estimated to reproduce thermodynamic temperatures to within 0.03 K between 10 K and 90 K and within 0.04 K above 90 K.⁽²⁸⁾ The effects of changing the temperature scale to ITS-90 vary over the range $90 \leq T/\text{K} \leq 350$ from $0.020 \geq (T_{90} - T_{48})/\text{K} \geq -0.27$, and for the range $14 \leq T/\text{K} \leq 350$ from $-0.008 \leq (T_{90} - T_{55})/\text{K} \leq 0.018$.^(29,30) Here, T_{90} , T_{55} , and T_{48} refer to the temperatures defined, respectively, by the ITS-90, the National Bureau of Standards (N.B.S.) Temperature Scale of 1955, and the IPTS-48. The changes in heat capacity, enthalpy, and entropy resulting from the conversion from IPTS-68 to ITS-90 have been shown⁽²⁹⁾ for a number of materials to lie within the experimental error of the measurements over the range from $T = 16$ K to $T = 2800$ K. Measurements of mass, current, potential difference, and time were based upon calibrations done at N.B.S. (NIST). The measurement procedures that lead to the determination of the heat capacity are described in detail in references 31 and 32.

A gold-plated copper calorimeter (laboratory designation W-99) with four internal vertical vanes and a central entrant well for (heater + thermometer) was filled with CaSn_2F_6 . After loading, the calorimeter was evacuated and pumping was continued for several hours to ensure that moisture was no longer present in the sample. After addition of helium gas to the vessel ($p = 4.7$ kPa at $T = 300$ K) to facilitate thermal equilibration, the calorimeter was sealed by means of an annealed gold gasket pressed tightly on to the stainless-steel knife edge of the calorimeter top with a screw closure about 5 mm in diameter.

Buoyancy corrections were calculated on the basis of the experimentally determined⁽²⁴⁾ density of $4.28 \text{ g} \cdot \text{cm}^{-3}$. The mass of the CaSn_2F_6 was 17.0841 g (≈ 0.0436387 mol, based on a molar mass of $391.4884 \text{ g} \cdot \text{mol}^{-1}$ calculated from the 1985 IUPAC recommended values).⁽³³⁾

The thermal history of the CaSn_2F_6 is represented by the following linear array. The arrows denote either cooling or heating, and correspond to the acquisition of the heat-capacity results.



3. Results

The experimental molar heat capacities for CaSn_2F_6 are presented in table 1 where the temperature T represents the midpoint of the temperature intervals. The measurements were made in seven series spanning the interval $T = 5$ K to $T = 313$ K. The standard errors in our heat-capacity values vary from $\approx 0.01 \cdot C_{p,m}$ at $T = 10$ K to $\leq 0.005 \cdot C_{p,m}$ at $T \geq 25$ K. The heat capacity of the sample amounted to about

TABLE I. Experimental molar heat capacity of CaSn_2F_6
($M = 391.48841 \text{ g} \cdot \text{mol}^{-1}$; $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Series I		51.53	7.740	171.35	20.46	55.28	7.446	175.21	20.78
6.22	0.0263	54.81	8.371	176.38	20.85	59.70	8.142	181.86	21.11
8.35	0.100	58.37	9.058	181.43	21.15	64.39	8.896	188.48	21.54
9.00	0.141	62.14	9.794	186.47	21.44	69.05	9.663	194.33	21.90
9.74	0.205	65.97	10.48	191.56	21.72	73.81	10.41	199.45	22.17
10.68	0.306	69.75	11.17	Series III		78.64	11.13	204.63	22.45
11.80	0.407	73.84	11.85	123.60	16.55	83.52	11.83	209.80	22.68
13.08	0.545	78.18	12.55	128.79	17.08	88.40	12.51	214.98	22.88
14.39	0.701	82.56	13.17	133.84	17.56	93.32	13.15	220.15	23.06
15.76	0.901	87.19	13.77	136.95	17.85	98.27	13.76	225.31	23.22
17.18	1.113	92.05	14.36	138.38	17.99	103.27	14.32	Series VI	
18.65	1.342	96.96	14.93	140.38	18.26	108.29	14.88	230.74	23.60
20.11	1.590	101.88	15.50	142.84	18.51	113.31	15.44	236.14	23.85
21.59	1.866	Series II		145.49	18.68	118.32	15.99	241.82	24.12
23.22	2.142	105.56	16.07	148.20	18.85	123.35	16.54	247.51	24.32
24.98	2.469	110.50	16.64	150.71	19.05	128.41	17.04	253.23	24.52
26.74	2.827	115.52	17.18	153.12	19.24	133.48	17.54	258.96	24.71
28.53	3.160	120.48	17.69	155.59	19.43	137.04	17.88	264.67	24.90
30.35	3.533	125.47	18.16	Series IV		139.09	18.13	270.36	25.07
32.18	3.889	130.48	18.59	91.99	13.00	141.15	18.47	276.07	25.26
33.86	4.256	135.50	19.02	97.07	13.74	143.22	18.63	281.77	25.44
35.45	4.573	140.53	19.60	102.07	14.27	145.29	18.72	287.44	25.64
37.54	5.021	145.71	19.63	Series V		147.35	18.84	293.12	25.82
40.18	5.549	150.91	19.06	43.12	5.458	150.71	19.05	298.85	25.98
42.90	6.088	156.08	19.46	45.42	5.810	155.82	19.46	304.55	26.12
45.67	6.616	161.19	19.85	47.81	6.169	161.94	19.90	310.25	26.24
48.48	7.151	166.30	20.18	51.11	6.739	168.57	20.32		

0.52 to 0.76 of the measured total heat capacity away from the regions of the anomalies.

The sample was supplied as a fine white powder and was judged not to require further grinding. Because CaSn_2F_6 is sensitive to moisture,⁽²⁴⁾ the sample was handled within a dry box. Particle size and thermal history are factors that influence hysteresis effects in some salts. Morphee and Staveley discovered that the apparent heat capacities of NH_4PF_6 and RbPF_6 ,⁽³⁴⁾ as well as those of $(\text{NH}_4)_2\text{SnCl}_6$, K_2SnCl_6 , and Rb_2SnCl_6 ,⁽³⁵⁾ were diminished by repeated cooling to temperatures of liquid nitrogen or liquid air. Reproducible results were obtained only after repeated cooling. In the case of NH_4PF_6 , the curve through their first values of heat capacity diverged gradually upwards from the points taken as the final values, and amounted to a $0.03 \cdot C_{p,m}$ increase at $T = 300 \text{ K}$. In the n.m.r. study of KPF_6 and RbPF_6 by Miller and Gutowsky,⁽³⁶⁾ the temperature dependence of the fluorine resonance depended upon the particle size, and reproducible results were obtained only after the sample was in the form of a fine powder.

For our CaSn_2F_6 sample, hysteresis was experienced for the first set of measurements in Series I and II from $T \approx 30 \text{ K}$ to $T \approx 150 \text{ K}$. When the sample was cooled for the second and subsequent times at $T < 150 \text{ K}$, the $C_{p,m}$ results were lower and reproducible. No differences are apparent in the regions of overlap. The values

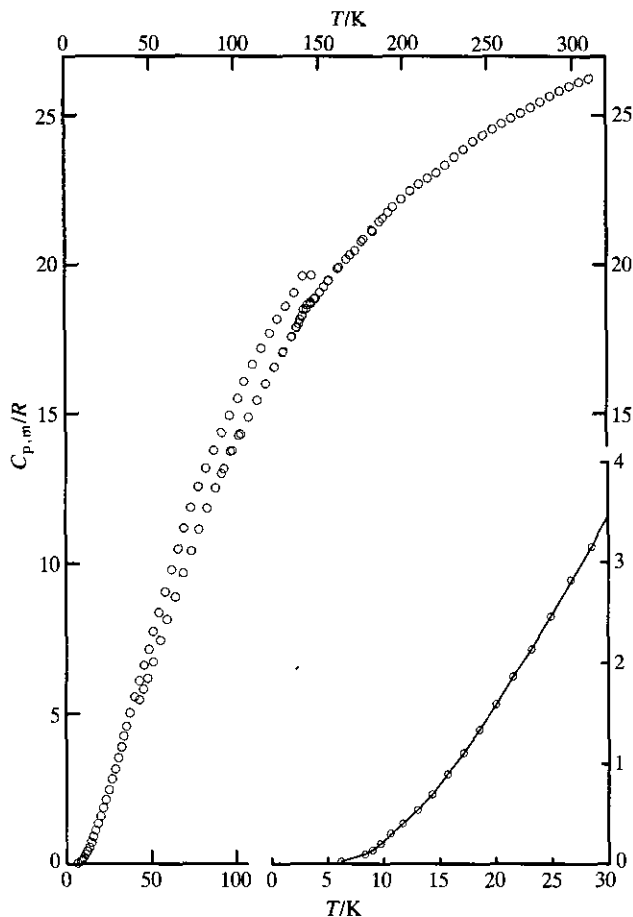


FIGURE 1. Experimental molar heat capacities $C_{p,m}$ at constant pressure plotted against temperature T for CaSn_2F_6 . The values lying above the smooth curve at $T < 150$ K are due to hysteresis (see text). The region $T \leq 30$ K is enlarged in the lower right-hand corner.

of our $C_{p,m}$ from Series I and II between $T = 30$ K and $T = 150$ K diverged gradually from the points defined by the $C_{p,m}$ from Series III through VI ($0.05 \cdot C_{p,m}$ to $0.07 \cdot C_{p,m}$). They were greater by $0.8 \cdot R$ at $T = 50$ K ($0.12 \cdot C_{p,m}$) and $1.4 \cdot R$ at $T = 100$ K through $T = 140$ K ($0.1 \cdot C_{p,m}$ to $0.08 \cdot C_{p,m}$). Since the sample removed from the calorimeter had the same appearance, a fine powder, as it did when placed in the calorimeter, it seems that sample subdivision was not a factor in the hysteresis observed. The fact that differences of $0.05 \cdot C_{p,m}$ to $0.08 \cdot C_{p,m}$ were observed before the repeated cooling, and that after the cooling the differences were $0.001 \cdot C_{p,m}$ to $0.0015 \cdot C_{p,m}$, do point to thermal history as an explanation.

A plot of experimental values of $C_{p,m}/R$ against T from 6 K to 310 K is shown in figure 1, where the hysteresis noted above is evident. The curve of final values is continuous and rises smoothly to $T \approx 140$ K, at which temperature an anomaly appears. Above $T \approx 150$ K, the curve resumes its smooth path. The anomaly centred

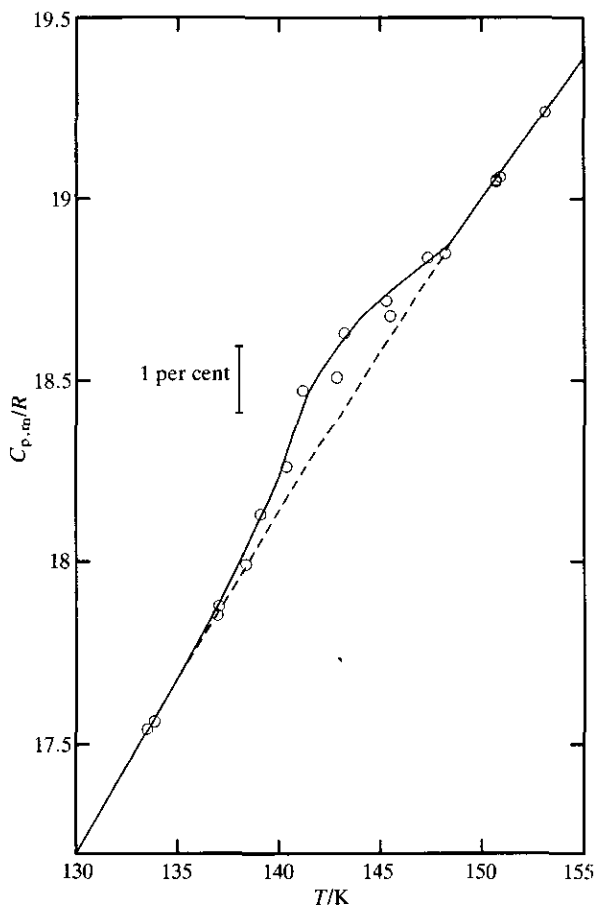


FIGURE 2. Experimental heat capacities $C_{p,m}$ at constant pressure plotted against temperature T through the region of the anomaly from $T \approx 138$ K to $T \approx 148$ K for CaSn_2F_6 . ---, The lattice heat capacity.

at $T \approx 143$ K is shown in detail in figure 2. The greatest difference of the curve from that defined by the broken line of the lattice is $0.01 \cdot C_{p,m}$, which lies outside the error in the measurements. The excess molar enthalpy associated with the anomaly amounts to $\Delta_{135\text{K}}^{150\text{K}} H_m^\circ = (1.3 \pm 0.3) \cdot R \cdot \text{K}$. The excess entropy is zero within the experimental error of the measurements.

The experimental values of energy and the equilibrium temperatures before and after heating were used to calculate the experimental heat capacities. The smoothed heat capacities were obtained by a spline-fit to the experimental results. Integration of the smoothed heat capacities yielded the thermodynamic functions. Values of $C_{p,m}/R$ and the derived functions are presented at selected temperatures in table 2. The corresponding lattice heat capacities beneath the anomaly, drawn by smooth interpolation of the curve, are shown in parentheses and plotted in figure 2 as a

TABLE 2. Standard molar thermodynamic functions for CaSn₂F₆

$$\{M = 391.48841 \text{ g} \cdot \text{mol}^{-1}; p^\circ = 101.325 \text{ kPa}; R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}; \Phi_m^\circ = \Delta_0^T S_m^\circ - \Delta_0^T H_m^\circ / T\}$$

T K	$C_{p,m}$ R	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{R \cdot K}$	$\frac{\Phi_m^\circ}{R}$	T K	$C_{p,m}$ R	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{R \cdot K}$	$\frac{\Phi_m^\circ}{R}$
0	0	0	0	0	160	19.76	18.84	1680.4	8.342
5	(0.0101)	(0.0027)	(0.0109)	(0.0005)		(19.76)	(18.84)	(1679.1)	(8.341)
10	0.232	0.0514	0.423	0.0091	170	20.42	20.06	1881.4	8.996
15	0.780	0.242	0.870	0.0509		(20.42)	(20.05)	(1880.1)	(8.994)
20	1.570	0.568	1.745	0.131	180	21.07	21.25	2088.9	9.644
25	2.440	1.009	3.177	0.258		(21.07)	(21.24)	(2087.6)	(9.642)
30	3.280	1.526	4.623	0.424	190	21.63	22.40	2302.5	10.29
35	4.100	2.092	6.070	0.620		(21.63)	(22.39)	(2301.2)	(10.28)
40	4.930	2.693	7.517	0.841	200	22.20	23.53	2521.6	10.92
45	5.730	3.320	8.964	1.081		(22.20)	(23.52)	(2520.3)	(10.92)
50	6.550	3.966	10.411	1.337	210	22.68	24.62	2746.1	11.55
55	7.370	4.628	11.858	1.605		(22.68)	(24.61)	(2744.8)	(11.54)
60	8.190	5.304	13.305	1.885	220	23.09	25.69	2975.0	12.16
65	9.000	5.992	14.752	2.174		(23.09)	(25.68)	(2973.7)	(12.16)
70	9.810	6.688	16.199	2.472	230	23.55	26.72	3208.1	12.7
75	10.59	7.392	17.646	2.776		(23.55)	(26.71)	(3206.8)	(12.77)
80	11.33	8.099	19.093	3.087	240	24.02	27.74	3446.0	13.38
85	12.03	8.806	20.540	3.402		(24.02)	(27.73)	(3444.7)	(13.37)
90	12.72	9.514	21.987	3.722	250	24.41	28.72	3688.2	13.97
95	13.36	10.22	23.434	4.046		(24.41)	(28.72)	(3686.9)	(13.97)
100	13.96	10.92	24.881	4.372	260	24.75	29.69	3934.0	14.56
105	14.50	11.61	26.328	4.700		(24.75)	(29.68)	(3932.7)	(14.55)
110	15.06	12.30	27.775	5.030	270	25.06	30.63	4183.0	15.14
115	15.62	12.98	29.222	5.361		(25.06)	(30.62)	(4181.7)	(15.13)
120	16.16	13.66	30.669	5.693	280	25.39	31.55	4435.3	15.71
125	16.70	14.33	32.116	6.025		(25.39)	(31.54)	(4434.0)	(15.70)
130	17.20	14.99	33.563	6.357	290	25.72	32.44	4690.8	16.27
135	17.68	15.65	35.010	6.689		(25.72)	(32.43)	(4689.5)	(16.26)
140	18.23	16.30	36.457	7.021	300	26.01	33.32	4949.5	16.82
	(18.14)	(16.30)	(36.457)	(7.021)		(26.01)	(33.31)	(4948.2)	(16.82)
145	18.72	16.96	37.904	7.352	310	26.25	34.18	5210.8	17.37
	(18.58)	(16.95)	(37.904)	(7.352)		(26.25)	(34.17)	(5209.5)	(17.36)
150	19.00	17.59	39.351	7.683	298.15	25.96	33.16	4901.4	16.72
	(19.00)	(17.58)	(39.351)	(7.683)		± 0.02	± 0.03	± 4.4	± 0.02

^a Quantities in parentheses represent the values estimated for the lattice curve.

broken line. The heat capacities of CaSn₂F₆ at $T \leq 6$ K were obtained by fitting our experimental values at $T \leq 20$ K to the limiting form of the Debye equation, with a plot of $C_{p,m}/T^3$ against T^2 and extrapolation to $T \rightarrow 0$.

4. Discussion

The quantity measured calorimetrically is $C_{\text{sat},m}$, the heat capacity of the solid or liquid in equilibrium with its saturated vapour. For solid CaSn₂F₆, $C_{\text{sat},m}$ is virtually identical with $C_{p,m}$ as the right-hand side of the equation:

$$C_{\text{sat},m} - C_{p,m} = (\partial p / \partial T)_{\text{sat}} \{ (\partial H_m / \partial p)_T - V_m \}. \quad (1)$$

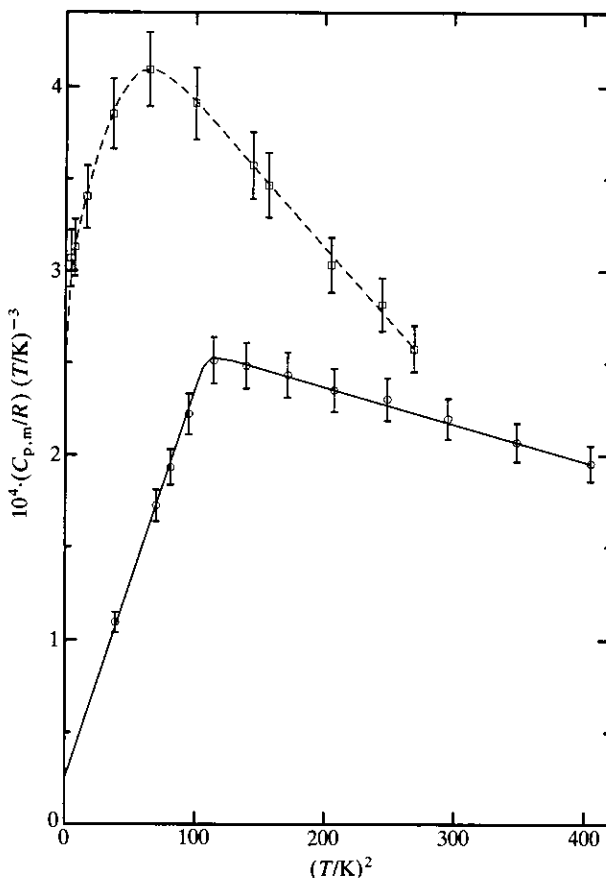


FIGURE 3. Experimental values of $C_{p,m}/RT^3$ plotted against T^2 for CaSn_2F_6 . —, This work; ---, argon (references 38 and 39). The vertical bars indicate about $0.1 \cdot C_{p,m}$ and are not precision indices.

is negligible. The pressure effect of the helium exchange gas ($p = 0.2$ kPa of helium at $T = 20$ K) on the heat capacity of solid CaSn_2F_6 , *i.e.* $(\partial C_{p,m}/\partial p)_T$, is also negligible. However, analysis of heat-capacity results requires $C_{V,m}$, which is related to $C_{p,m}$:

$$C_{p,m} - C_{V,m} = V_m T \alpha^2 / \kappa_T, \quad (2)$$

where $\alpha = V_m^{-1}(\partial V_m/\partial T)_p$ is the isobaric expansivity, V_m is the molar volume, and $\kappa_T = -V_m^{-1}(\partial V_m/\partial p)_T$ is the isothermal compressibility. Values of α and κ_T are unavailable for CaSn_2F_6 but, fortunately, at $T < 20$ K, $(C_{p,m} - C_{V,m}) \approx 0$.

The heat capacity of an insulator at very low temperatures can be described by a power series of the form:

$$C_{V,m} = aT^3 + bT^5 + cT^7 + \dots, \quad (3)$$

in which the parameters a , b , and c are directly related to the corresponding power series for the frequency spectrum at low frequencies.⁽³⁷⁾ As $T \rightarrow 0$, the lattice heat

capacity of the crystal should become equal to that of an elastic continuum and, as such, can be described by the "Debye T^3 " law:

$$C_{v,m} = aT^3, \quad (4)$$

$$\Theta_0^c = (12\pi^4 Lk/5a)^{1/3}, \quad (5)$$

where Θ_0^c is the Debye temperature derived from heat capacity and L and k are the Avogadro constant and the Boltzmann constant.

A plot of $C_{p,m}/RT^3$ against T^2 shown in figure 3 is also useful for identifying any non-vibrational contributions to the heat capacity at low temperatures. In the region $36 < (T^2/\text{K}^2) < 400$, the graph of our experimental heat capacities for CaSn_2F_6 resembles that for argon^(38,39) and suggests that only lattice vibrations make significant contributions to the heat capacity in this temperature range. By extrapolating the points below $T^2 = 37 \text{ K}^2$ to intersect the $C_{p,m}/RT^3$ axis at $T^2 = 0$, we found $10^4 \cdot a/R = (0.33 \pm 0.08) \text{ K}^{-3}$ or $10^4 \cdot a = (2.74 \pm 0.42) \text{ J} \cdot \text{K}^{-4} \cdot \text{mol}^{-1}$. This yields, from equation (5), $\Theta_0^c = (192.1 \pm 10.8) \text{ K}$, which is more than double the value for argon at $T = 93.3 \text{ K}$.⁽³⁸⁾ Therefore, the corresponding lattice frequency of vibration at $T \rightarrow 0$ must also be more than double that of argon. Values of Θ_0^c for the M^{2+} tetrafluorostannates are not available for comparison.^(18,22) No other information is available for CaSn_2F_6 at temperatures below 310 K. Zhu⁽²⁴⁾ has measured its electrical and ionic conductivity from $T \approx 310 \text{ K}$ to $T \approx 450 \text{ K}$ and, over this range, there is no indication of a structural phase transition.

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