Heat capacity of deuterated cubic ammonium hexafluorosilicate (ND$_4$)$_2$SiF$_6$ from 6 K to 343 K

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The heat capacity of deuterated cubic ammonium hexafluorosilicate (ND$_4$)$_2$SiF$_6$ was measured from 6 K to 343 K by adiabatic calorimetry. The curve of heat capacity against temperature is smooth and without anomalies. Values of the standard thermodynamic quantities are tabulated below 350 K. Analysis of our heat-capacity results yielded a librational wavenumber of the ND$_4^+$ ion of about 122 cm^{-1} and a maximum in the rotational heat capacity lying between 220 K and 230 K.

1. Introduction

The hexahalometallates of the general type A$_2$MX$_6$, where A is an alkali metal, M a polyvalent or heavy transition metal, and X a halogen, normally crystallize in the antifluorite structure with space group Fm3m (No. 225 O$_h^5$) at room temperature. Some, but not all, of the members of this family undergo structural phase transitions changing into a phase of lower symmetry with decreasing temperature.[1, 2] In some cases, the transitions involve the small-angle rotations of the MX$_6^{2-}$ octahedra, but in others the transitions appear to lead to lattice distortion without coupling to the octahedral rotations.[1-3]

When the ammonium ion, either NH$_4^+$ or ND$_4^+$, is substituted in place of the alkali metal, additional librational degrees of freedom are introduced. In compounds of the type (NH$_4$)$_2$MX$_6$, the structural phase transition is either suppressed or the

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transition temperature is diminished by the tetrahedral symmetry of the ammonium ion.[3] In addition, salts within this family exhibit a low barrier to rotation of either the NH_4^+ ion or ND_4^+ ion. As a consequence, they attract substantial interest in the study of molecular rotation. The salt $(NH_4)_2SnCl_6$ is without any phase transition between room temperature and 20 K,[4] and the low barrier to rotation of the ammonium ion varies from 600 K,[5, 7] to 740 K.[8] Our recent studies on the heat capacity of the deuterated salt, $(ND_4)_2SnCl_6$, showed a λ-shaped anomaly around 244 K whose origins are so far unknown.[9]

The ammonium hexafluorosilicate salt, $(NH_4)_2SiF_6$, exhibits two crystalline modifications which are a stable cubic phase[10] and a metastable trigonal phase,[11] the latter being stable only below 278 K. The trigonal phase[12] (P3̄m1 or No. 164 D_{3d}^3) undergoes a phase transition with hysteresis between 36.7 K and 38.6 K. It appears as a λ-shaped anomaly in the heat capacity.[13] However, the cubic phase (Fm3m or No. 225 O_h^5) shows no transition in its crystal structure below room temperature and its heat capacity is without an anomaly from 25 K to 300 K.[13] The barrier to rotation of the NH_4^+ corresponds to 1107 K based on n.m.r.[5] or 1616 K derived from the heat capacity.[8]

Cubic ammonium fluorosilicate $(NH_4)_2SiF_6$ has the CaF_2 structure with the calcium ions replaced by SiF_6^{2-} groups and the fluorine atoms by NH_4^+ groups.[12, 14] The cell constant is $a = 0.8395$ nm,[15] with four molecules per unit cell.

In experiments designed to get a more sensitive indicator of the nature of the hydrogen motion in $(NH_4)_2SiF_6$, Blinc and Lahajnar[16] measured the deuteron magnetic resonance spectrum of $(ND_4)_2SiF_6$. The scarcity of experimental results in general and of heat capacities in particular to assist in understanding molecular motion in the deuterated salt led us to undertake a study of the adiabatic calorimetry as part of our ongoing work involving ammonium salts.

2. Experimental

The sample of $(ND_4)_2 SiF_6$ was prepared from $(NH_4)_2SiF_6$. Some 25 g of $(NH_4)_2SiF_6$, 99.999 mass per cent pure, certified by Certificate of Analysis from the Aldrich Chemical Company, was dissolved completely in 92 cm³ of D_2O, which was of 99.9 moles per cent minimum isotopic purity. The salt dissolved completely at 332 K. A partially deuterated product was obtained by recrystallization at 293 K. This procedure, executed in a dry atmosphere, was repeated four times, and 25.7 g of $(ND_4)_2SiF_6$ was obtained. To remove most of the D_2O trapped in the lattice upon recrystallization, the crystals were placed under an infrared lamp within the dry box and warmed gently for 16 d with the temperature increased gradually to 370 K. A thermogravimetric analysis (t.g.a.) using a Mettler TA 3000 was done on 10 mg samples removed at intervals.

The Guinier–de Wolff diffraction pattern of our sample was in perfect agreement with the standard pattern for this compound, No. 7-13 as determined by the Joint Committee for Powder Diffraction Standards. The structure is face-centred cubic at room temperature with $a = (0.83818 \pm 0.00004)$ nm.

To ascertain if any D_2O was trapped within our "dried" sample of $(ND_4)_2SiF_6$, the
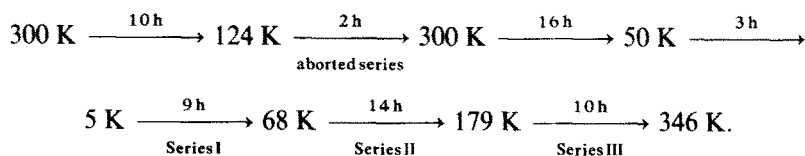
final t.g.a. was made using 10 mg of the sample which was loaded into the calorimeter. On heating the 10 mg to 413 K, a mass loss of 0.2 per cent was apparent and might be associated with adsorbed or trapped water. When the temperature was raised to 453 K, decomposition began slowly and became rapid above 533 K. A platinum resistance thermometer was used in the t.g.a. instrument to measure temperature. It was calibrated using the ice point and the fixed points of the Curie transition in alumel at 422.5 K, nickel at 631.2 K, and "trafoperm" (97 mass per cent of Fe, 3 mass per cent of Si) at 1018.8 K. The estimated precision was ± 2 K and $\pm 1 \times 10^{-6}$ g.

The molar heat capacity $C_{p,m}$ was measured from 5.4 K to 346 K by adiabatic calorimetry in the Mark XIII adiabatic cryostat, which is an upgraded version of the Mark II cryostat described previously.[17] The acquisition of heat capacities was assisted [18,19] by a computer programmed for a series of determinations. During the drift periods, both the calorimeter temperature and its first and second time derivatives were recorded to establish the equilibrium temperatures of the calorimeter between the energy inputs. During energy inputs the heater current and potential and the duration of the heating interval were obtained. Also recorded were the apparent heat capacity of the system including the calorimeter, heater, thermometer, and sample.

A gold-plated copper calorimeter (laboratory designation W-139) with four internal vertical vanes and a central entrant well for (heater + thermometer) was loaded with $(ND_4)_2SiF_6$ within a dry box. After loading, the calorimeter was evacuated and pumping was continued for several hours to ensure that moisture was no longer released from the sample. After addition of about 3.2 kPa (at 300 K) of helium gas to the vessel so as to facilitate thermal equilibration, it was then sealed by means of an annealed gold gasket tightly pressed on to the stainless-steel knife edge of the calorimeter top using a screw closure about 5 mm in diameter.

Buoyancy corrections were calculated on the basis of a crystallographic density of $2.100 \text{ g} \cdot \text{cm}^{-3}$ derived from the X-ray diffraction of our sample. The mass of the $(ND_4)_2SiF_6$ was 20.36033 g, i.e. 0.1093529 mol based on its molar mass of $186.1892 \text{ g} \cdot \text{mol}^{-1}$ from IUPAC 1983 relative atomic masses.

The thermal history of the $(ND_4)_2SiF_6$ is shown by the linear array. The solid arrows indicate cooling or heating, which correspond to acquisition of heat capacity results.

$$300 \text{ K} \xrightarrow{10\text{h}} 124 \text{ K} \xrightarrow[\text{aborted series}]{2\text{h}} 300 \text{ K} \xrightarrow{16\text{h}} 50 \text{ K} \xrightarrow{3\text{h}}$$

$$5 \text{ K} \xrightarrow[\text{Series I}]{9\text{h}} 68 \text{ K} \xrightarrow[\text{Series II}]{14\text{h}} 179 \text{ K} \xrightarrow[\text{Series III}]{10\text{h}} 346 \text{ K}.$$

3. Results and discussion

The experimental molar heat capacities for $(ND_4)_2SiF_6$ are presented in table 1. The probable errors in our heat-capacity results decrease from about 1 per cent at 10 K

TABLE 1. Experimental molar heat capacity of $(ND_4)_2SnCl_6$ (molar mass: 186.189 g·mol^{-1}; $R = 8.31451$ J·K^{-1}·mol^{-1})

$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$
Series I		65.42	9.954	194.26	24.39
6.25	0.04317	Series II		200.40	24.90
7.40	0.08954	70.59	10.73	206.52	25.38
8.23	0.1375	76.01	11.52	212.66	25.86
9.28	0.2177	80.87	12.21	218.80	26.32
10.35	0.3155	85.78	12.88	224.96	26.77
11.46	0.4349	90.73	13.53	231.13	27.21
12.57	0.5680	95.70	14.15	237.31	27.62
13.81	0.7329	100.68	14.74	243.47	28.01
15.27	0.9518	105.69	15.34	249.62	28.41
16.74	1.186	110.71	15.94	255.79	28.78
18.40	1.465	115.72	16.52	261.96	29.16
20.26	1.791	120.77	17.10	268.16	29.56
22.13	2.130	126.07	17.69	274.32	29.94
24.37	2.549	131.61	18.30	280.24	30.30
26.94	3.040	137.17	18.91	286.69	30.67
29.55	3.541	142.74	19.50	292.86	30.97
32.21	4.061	148.33	20.08	299.08	31.23
35.12	4.628	153.92	20.65	305.33	31.45
38.28	5.232	159.50	21.21	311.50	31.66
41.47	5.833	165.09	21.75	317.69	31.87
44.71	6.431	170.70	22.28	323.87	32.10
48.43	7.100	176.32	22.80	330.05	32.31
52.61	7.842	Series III		336.25	32.52
56.84	8.568	182.10	23.33	342.45	32.72
61.11	9.273	188.11	23.86		

to less than 0.15 per cent at temperatures above 30 K. The heat capacity of our sample represented about 70 to 87 per cent of the measured total heat capacity.

A plot of $C_{p,m}/R$ against T from 6 K to 343 K is presented in figure 1. The curve is smooth and without anomalies. No rise in the heat capacity is evident around 270 K to 275 K where fusion of any D_2O trapped in the lattice is expected to occur. However, 0.2 mass per cent of trapped D_2O would have been expected to give about a 9 per cent increment in the heat capacity over the 5 K interval of a single run. This was not detected. It is, therefore, presumed that the volatile contaminant was adsorbed water removed in the evacuation of the sample at room temperature prior to measurement.

Integration of the smoothed values for heat capacity yielded the thermodynamic functions. Values of $C_{p,m}/R$ and the derived functions are shown at selected temperatures in table 2. The heat capacities of $(ND_4)_2SiF_6$ below 7 K were obtained by fitting our experimental results below 20 K to the limiting form of the Debye equation, using a plot of $C_{p,m}/T^3$ against T^2 and extrapolating to $T \to 0$.

Analysis of the observed heat capacities of ammonium compounds is normally done by subtracting the heat capacities arising from the lattice and internal vibrational motion to yield the heat capacity due to the hindered motion of the
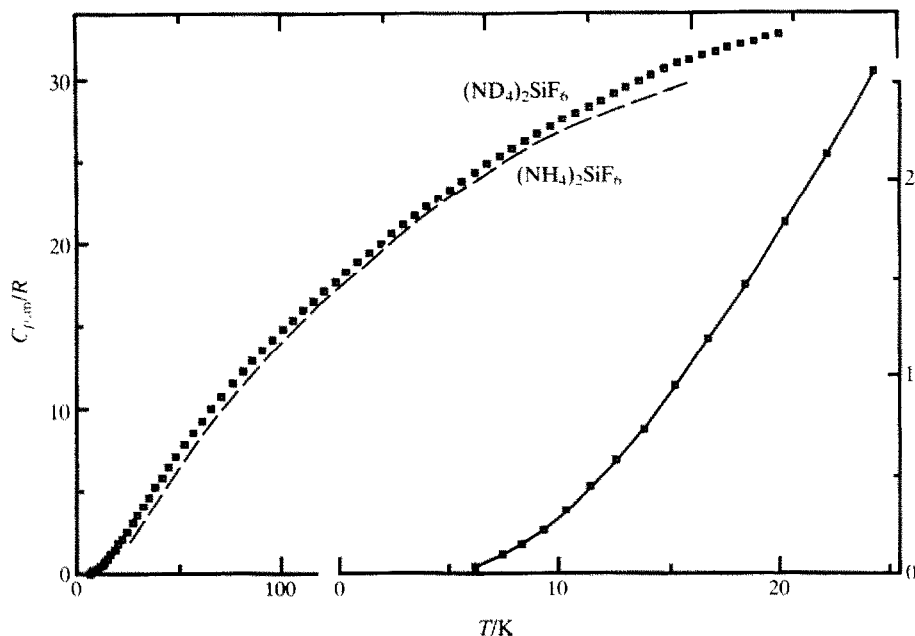
FIGURE 1. Experimental molar heat capacities at constant pressure $C_{p,m}/R$ plotted against temperature for cubic $(ND_4)_2SiF_6$ ($\square$, this work) and cubic $(NH_4)_2SiF_6$ (— — —, Stephenson et al.).[13]

ammonium ion. Various methods are available to do this, but their use depends upon the availability of spectroscopic information, thermal expansion, and compressibility over a range of temperature for the ammonium salt concerned. The lattice heat capacity of the ammonium solid has been estimated from the potassium or rubidium analogues,[4] but the method is applicable only when the thermal expansion of the ammonium crystal is isotropic.[20] The lattice heat capacity has also been calculated using corresponding states to adjust the lattice heat capacity of the potassium compound in order to represent that of the ammonium ion,[21] while in other methods, either a sum of the Debye/Einstein functions is used[13,22] or lattice frequencies from infra-red and Raman spectra are employed.[20,23]

The heat-capacity results of undeuterated $(NH_4)_2SiF_6$ and $(NH_4)_2SnCl_6$ have been analyzed previously by a procedure described by Stephenson et al.[8,13,24] in which the heat capacity of these solids was represented by a sum of both Debye and Einstein functions. This procedure has also been used to determine librational frequencies of a number of tetrahedral ions in solids:[22] viz. AlH_4^-, BH_4^-, GaH_4^-, NH_4^+. The limited experimental information available for $(ND_4)_2SiF_6$ describing its spectroscopic properties, thermal expansion, and compressibility have forced us to adopt the same procedure to analyze the heat capacity of our deuterated salt.

The heat capacity of $(ND_4)_2SiF_6$ can be represented by

$$C_{V,m} = 3D(\theta_1/T) + 3E(\theta_2/T) + 6E(\theta_3/T) + C_{int,m} + 2C_{rot,m}, \tag{1}$$

$$C_{p,m} = C_{V,m} + (aC_{V,m})^2 T, \tag{2}$$

TABLE 2. Standard molar thermodynamic quantities for $(ND_4)_2SiF_6$; $M = 186.189 \text{ g} \cdot \text{mol}^{-1}$. $p^\circ = 101.325 \text{ kPa}$, $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $\Phi_m^\circ \overset{\text{def}}{=} \Delta_0^T S_m^\circ - \Delta_0^T H_m^\circ / T$

$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{\Delta_0^T S_m^\circ}{R}$	$\dfrac{\Delta_0^T H_m^\circ}{R \cdot K}$	$\dfrac{\Phi_m^\circ}{R}$	$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{\Delta_0^T S_m^\circ}{R}$	$\dfrac{\Delta_0^T H_m^\circ}{R \cdot K}$	$\dfrac{\Phi_m^\circ}{R}$
0	0	0	0	0	175	22.70	22.35	2124.7	10.21
5	(0.0184)	(0.0051)	(0.0204)	(0.0010)	180	23.17	23.00	2239.4	10.56
10	0.295	0.0773	0.621	0.015	185	23.62	23.64	2356.3	10.90
15	0.906	0.303	3.51	0.069	190	24.03	24.27	2475.5	11.24
20	1.755	0.676	10.10	0.171	195	24.44	24.90	2596.6	11.59
25	2.683	1.166	21.18	0.318	200	24.86	25.53	2718.9	11.93
30	3.640	1.738	36.98	0.507	205	25.27	26.15	2845.2	12.27
35	4.628	2.373	57.67	0.725	210	25.64	26.76	2972.5	12.60
40	5.588	3.056	83.31	0.973	215	26.03	27.37	3101.7	12.94
45	6.469	3.764	113.4	1.243	220	26.42	27.97	3232.8	13.28
50	7.385	4.493	148.1	1.532	225	26.80	28.57	3365.8	13.61
55	8.270	5.238	187.2	1.834	230	27.15	29.16	3500.7	13.94
60	9.100	5.993	230.6	2.149	235	27.48	29.75	3637.3	14.27
65	9.905	6.753	278.1	2.474	240	27.81	30.33	3775.5	14.60
70	10.66	7.515	328.5	2.807	245	28.12	30.91	3915.3	14.93
75	11.36	8.274	384.6	3.146	250	28.43	31.48	4056.7	15.25
80	12.08	9.030	443.2	3.490	255	28.72	32.04	4199.6	15.57
85	12.81	9.784	505.4	3.839	260	29.05	32.60	4344.0	15.90
90	13.45	10.54	571.0	4.190	265	29.37	33.16	4489.0	16.22
95	14.06	11.27	639.8	4.543	270	29.67	33.71	4637.7	16.54
100	14.66	12.01	711.6	4.899	275	29.98	34.26	4786.7	16.85
105	15.27	12.74	786.4	5.255	280	30.29	34.80	4937.3	17.17
110	15.85	13.47	864.2	5.612	285	30.56	35.34	5088.5	17.48
115	16.44	14.19	944.9	5.969	290	30.84	35.87	5243.0	17.80
120	17.01	14.90	1028.5	6.326	295	31.08	36.40	5397.7	18.11
125	17.55	15.60	1114.9	6.683	300	31.28	36.93	5553.8	18.42
130	18.13	16.30	1204.1	7.040	305	31.44	37.45	5710.4	18.72
135	18.67	17.00	1296.1	7.396	310	31.60	37.96	5868.0	19.03
140	19.21	17.69	1390.8	7.751	315	31.77	38.47	6026.4	19.33
145	19.74	18.37	1488.1	8.105	320	31.96	38.97	6185.8	19.64
150	20.24	19.05	1588.0	8.459	325	32.14	39.46	6346.0	19.94
155	20.72	19.72	1690.4	8.811	330	32.32	39.96	6507.1	20.24
160	21.22	20.38	1795.3	9.162	335	32.50	40.44	6669.2	20.54
165	21.72	21.04	1902.6	9.512	340	32.65	40.93	6832.1	20.83
170	22.21	21.70	2012.4	9.861	345	32.80	41.40	6995.7	21.13
					298.15	29.87	36.73	5495.8	18.30
						±0.03	±0.05	±5.5	±0.03

where D represents the Debye function, E the Einstein function, θ_n represents the characteristic temperatures, C_{int} the heat capacity due to the internal vibrations, C_{rot} the heat capacity due to the hindered rotation of ND_4^+, and a is an empirical parameter which is a measure of $(C_{p,m} - C_{V,m})$.

To correct our experimental values of $C_{p,m}$ to $C_{V,m}$, equation (2) was used in which the value of a was derived from the value of $(C_{p,m} - C_{V,m}) = 2.8 \cdot R$ at 273 K, which was determined from the values of thermal expansion and compressibility for the undeuterated salt.[25] This value of $2.8 \cdot R$ is much higher than values for similar

compounds.[25, 26] The resulting value of a is $0.0028 \; \text{mol}^{1/2} \cdot \text{J}^{-1/2}$. To calculate the $C_{\text{int,m}}$, the following internal vibrational wavenumbers[27-30] $\tilde{\nu}$ were used: $\tilde{\nu}_1 = 646 \; \text{cm}^{-1}$, $\tilde{\nu}_2 = 466 \; \text{cm}^{-1}$, $\tilde{\nu}_3 = 721 \; \text{cm}^{-1}$, $\tilde{\nu}_4 = 476 \; \text{cm}^{-1}$, $\tilde{\nu}_5 = 403 \; \text{cm}^{-1}$. The $\tilde{\nu}_6$, which is inactive in the infrared, was determined from the relation:[31] $\tilde{\nu}_6 = \tilde{\nu}_5/2^{1/2} = 285 \; \text{cm}^{-1}$. The internal vibrations of ND_4^+ were taken as[32] $\tilde{\nu}_1 = 3233 \; \text{cm}^{-1}$, $\tilde{\nu}_2 = 1701 \; \text{cm}^{-1}$, $\tilde{\nu}_3 = 3314 \; \text{cm}^{-1}$, $\tilde{\nu}_4 = 1427 \; \text{cm}^{-1}$.

At low temperatures, the molar heat capacity $C_{\text{rot,m}}$ due to the hindered rotation of the ND_4^+ ion is set equal to an Einstein function with three degrees of freedom. However, in $(ND_4)_2SiF_6$, the heat capacity from the hindered rotation of the ND_4^+ ion is lower than that determined from the Einstein function. In an harmonic oscillator, the third librational level has twice the energy of the second librational level, but in both the hexafluorides and hexachlorides, due to the nature of the rotational potential function, the third level has more than twice the energy of the second level. In ammonium solids with strong hydrogen bonding, all the terms in the potential function are negative, which leads to the third librational level having an energy less than twice that of the second librational level. In the hexafluorides and hexachlorides, the $J = 6$ term in the potential function is positive, which influences the rotational properties of the ammonium ion.[22] For our $(ND_4)_2SiF_6$ salt, the heat capacity from the ND_4^+ ion was calculated from the energy levels derived from the potential function based on atom–atom potentials[22] using the crystal structure at room temperature. Using these results to determine the deviation from the harmonic-oscillator heat-capacity values for ND_4^+, the parameters in equation (1) were computed. The librational wavenumber of the ND_4^+ ion in $(ND_4)SiF_6$ was determined by analyzing the observed heat-capacity values using equation (1) and found to lie between $120 \; \text{cm}^{-1}$ and $130 \; \text{cm}^{-1}$. Using a value of $122 \; \text{cm}^{-1}$, the values of the parameters in equation (1) are $\theta_1 = 88 \; \text{K}$, $\theta_2 = 115 \; \text{K}$, and $\theta_3 = 310 \; \text{K}$. The temperature dependence of $C_{\text{rot,m}}$ determined from the observed heat capacity is illustrated in figure 2 together with the heat capacity computed from the energy levels derived from the rotational potential function.[22] The maximum in $C_{\text{rot,m}}$ may vary between $220 \; \text{K}$ and $280 \; \text{K}$ depending on the values of $(C_{p,m} - C_{V,m})$ as a function of temperature. By taking $a = 0.0028 \; \text{mol}^{1/2} \cdot \text{J}^{-1/2}$ as described above, the maximum in $C_{\text{rot,m}}$ occurs between $220 \; \text{K}$ and $230 \; \text{K}$.

An analysis of the heat-capacity results of $(NH_4)_2SiF_6$ was attempted next by a comparison with our deuterated salt. However, this was complicated by the fact that the $C_{p,m}$ measurements of the undeuterated salt are available only down to $25 \; \text{K}$.[13] While the heat capacity of $(NH_4)_2SiF_6$ could also be represented by equation (1), only a lower limit of $168 \; \text{cm}^{-1}$ for the librational wavenumber could be determined from an analysis of the available heat capacities. The determination of the values of the parameters in equation (1) depends upon the value of the librational wavenumber of the NH_4^+ ion, which was chosen as $174 \; \text{cm}^{-1}$ because it is the value computed from the rotational potential function in reference 22. This value is close to the observed value of $168 \; \text{cm}^{-1}$.[33] The parameters in equation (1) were then determined and the rotational heat capacity was calculated. The values are illustrated in figure 2.

The practice[34] of subtracting the heat capacity of the undeuterated salt from that of the deuterated salt to help determine the librational wavenumber of the
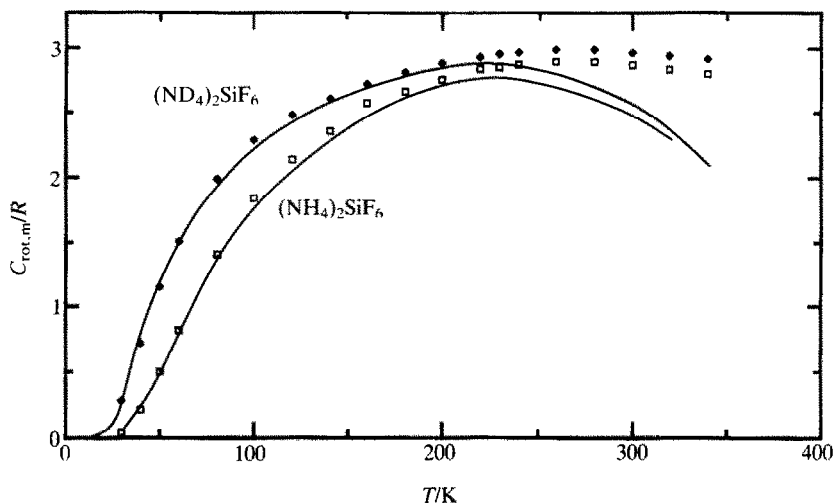
FIGURE 2. Calculated heat capacities $C_{rot,m}/R$ due to the hindered rotation of ND_4^+ and NH_4^+ derived from the observed molar heat capacities plotted against temperature for cubic $(ND_4)_2SiF_6$ and cubic $(NH_4)_2SiF_6$ (———). $\square$, $\triangle$, The heat capacities $C_{rot,m}/R$ computed from the hindered rotational levels determined from the rotational potential function given by Smith.[22]

ammonium ion could not be used, because for the $(NH_4)_2SiF_6$ and $(ND_4)_2SiF_6$ salts their lattice heat capacities determined from the observed heat capacities differ significantly from one another.

The heat capacity due to the hindered rotation of the ammonium ion computed from the rotational energy levels derived from the rotational potential function has a maximum at a higher temperature than that derived from the observed heat capacity. The discrepancy has been found in a number of other solids.[22, 34, 35] As a result of this discrepancy, the computed heat capacities match well with those derived from the observed heat capacities only on the low-temperature side of the maximum in the rotational heat capacities.

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