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# A study of cationic disorder in nitrosyl tetrafluoroborate, by comparison of the heat capacity of this salt with that of potassium tetrafluoroborate from 9 to 304 K

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The heat capacity  $C_p$  of the salt nitrosyl tetrafluoroborate, NOBF<sub>4</sub>, has been measured from 10 to 304 K, and that of potassium tetrafluoroborate from 9 to 295 K. The heat capacity-temperature curve of the nitrosyl compound has a  $\lambda$ -type anomaly with  $C_p$  reaching a maximum at  $\sim 67$  K, and with an associated entropy gain estimated at  $0.54R$ . Using  $C_p$  of the potassium salt as a reference, it appears that just above the  $\lambda$  point  $C_p$  of the nitrosyl salt once more starts to rise anomalously. The two-dimensional librational or rotational movement of the nitrosyl ion is probably that of a restricted rotator in a somewhat unsymmetrical potential field, and admittedly it is difficult to estimate reliably the contribution to  $C_p$  from this mode of motion. Nevertheless, the total heat capacity of the nitrosyl salt for at least 200 K is such that it seems certain that it embodies a component reflecting the gradual gain by the nitrosyl ion of orientational disorder. We estimate that the total configurational entropy acquired on reaching 300 K is approximately  $2.3R$ , or about  $R \ln 10$ , and since  $C_p$  at this temperature is still anomalously high, this entropy term must rise even higher with a further increases in temperature.

## INTRODUCTION

The simplest ions capable of orientational disorder in a crystal are, of course, diatomic. In the great majority of salts with one or more phases in which diatomic ions are orientationally disordered, these ions are the anions, examples being CN<sup>-</sup>, SH<sup>-</sup>, SeH<sup>-</sup>, NH<sub>2</sub><sup>2-</sup>, and C<sub>2</sub><sup>2-</sup>. A series of salts which might be expected to be capable of similar disorder of the cations is that containing the nitrosyl ion NO<sup>+</sup>. It has long been known that some nitrosyl salts [e.g., the perchlorate, fluoroborate, and hexachlorostannate (IV)] are isomorphous with the corresponding ammonium salts and indeed with the alkali metal salts.<sup>1</sup> Thus, at room temperature, NOBF<sub>4</sub>, NH<sub>4</sub>BF<sub>4</sub>, and the salts MBF<sub>4</sub> with M=K, Rb, Cs, Tl, or Ag are all orthorhombic, space group *Pnma*.<sup>2</sup> This implies that the NO<sup>+</sup> and NH<sub>4</sub><sup>+</sup> ions in the first two salts are sufficiently orientationally disordered to simulate the spherical symmetry of monatomic cations.

Accordingly, just as salts with disordered ammonium ions frequently undergo a transition to an ordered condition on cooling, so also one might expect with high probability to find a low-temperature transition in a salt such as NOBF<sub>4</sub>. If at room temperature the cations in this salt are orientationally disordered in that each undergoes torsional oscillations about two or more axes, then the crystal could change on cooling so that the torsional oscillations of each ion are limited to just one axis. However, it would still be possible for any one cation to have two orientations in that particular direction (NO<sup>+</sup> and ON<sup>+</sup>). For the isoelectronic species carbon monoxide, the dipole moment is so small that there is no

strong directional preference, and crystalline carbon monoxide exhibits frozen-in disorder arising from two orientations per molecule. The same might happen for NO<sup>+</sup>, but if the species is sufficiently polar and the activation energy for reorientation not too high, a nitrosyl salt might undergo a further transition on cooling leading to a uniquely ordered condition of the cations.

The nitrosyl salts have been relatively little studied, and virtually no thermodynamic work has yet been reported on them. It therefore seemed worthwhile to measure the heat capacity of at least one such salt down to  $\sim 10$  K. We chose the tetrafluoroborate partly because this salt is commercially available in reasonable purity, and partly because the limited amount of work so far carried out on it at least includes a room temperature diffraction study,<sup>3</sup> some spectroscopy,<sup>3</sup> and an <sup>19</sup>F NMR investigation<sup>4</sup> which gave some information on the torsional movement of the BF<sub>4</sub><sup>-</sup> ions, to which we briefly refer later. With suitable data, one could attempt an analysis of the  $C_p$  vs  $T$  curve for NOBF<sub>4</sub>. One would need the coefficients of expansion and compressibility to evaluate  $(C_p - C_v)$ , and in particular the torsional oscillational frequencies of the two ions in the lattice. Unfortunately, for none of these quantities is an experimental value available. In their absence, some guidance in interpreting the experimental  $C_p$  vs  $T$  curve can be provided by the corresponding curve for a similar salt with a monatomic cation. We have therefore also measured the heat capacity of KBF<sub>4</sub>, as being that salt of this kind which is isomorphous with NOBF<sub>4</sub> and which has the cation nearest in size and mass to the NO<sup>+</sup> ion. (At room temperature, the molar volumes of NOBF<sub>4</sub> and KBF<sub>4</sub>, as evaluated from the lattice parameters,<sup>3,5</sup> are 53.2 and 50.2 cm<sup>3</sup> mol<sup>-1</sup>, respectively.)

## EXPERIMENTAL

The heat capacities were measured in the smaller of the two calorimeters described by Waterfield and Staveley.<sup>6</sup> Temperatures are recorded on IPTS-68.

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The specimen of the nitrosyl salt was a commercial sample, which was used without further purification. This substance is readily hydrolyzed, and was loaded into the calorimeter sample vessel in a dry box. The specimen of the potassium salt was obtained by re-crystallizing a commercial sample from water. Analysis for potassium by atomic absorption spectroscopy gave 30.91% K (theory, 31.06%).

## RESULTS

The experimental  $C_p$  results for  $\text{NOBF}_4$  are given in Table I, and a representative selection of them is plotted in Fig. 1. The corresponding results for the potassium salt are presented in Table II and Fig. 1. Smoothed values of  $C_p$  at regular temperature intervals and the values of derived thermodynamic functions are given in Table III for the nitrosyl salt and in Table IV for the potassium salt. As a check on the estimation of the entropy gain associated with the  $\lambda$  transition in  $\text{NOBF}_4$ , the enthalpy intake across an interval covering the major part of this transition was measured. This gave  $\Delta H = 1363.0 \text{ J mol}^{-1}$  for the interval 55.92–75.78 K.

There are no  $C_p$  data for the nitrosyl salt with which comparison can be made and none for the potassium salt below 298 K. Dworkin and Bredig<sup>7</sup> determined the enthalpy difference  $H_T - H_{298}$  for  $\text{KBF}_4$  as a function of temperature by drop calorimetry. Their expression for this difference gives  $C_p = 114.9 \text{ J K}^{-1} \text{ mol}^{-1}$  at 300 K, as compared with our value of  $116.4 \text{ J K}^{-1} \text{ mol}^{-1}$ . The agreement is reasonable since each value is at a limit of the temperature range covered. The two sets of results for  $\text{KBF}_4$  give  $C_p$  from 10 K to the melting point (843 K).

## DISCUSSION

The heat capacity results for the potassium salt show no sign of any transition or anomaly, whereas the nitrosyl salt has a  $\lambda$ -type transition, giving a maximum in the heat capacity at  $\sim 67 \text{ K}$ . However, perhaps the most interesting outcome of the  $C_p$  measurements on  $\text{NOBF}_4$  is the disclosure of the high values which prevail over much of the temperature range covered. At 300 K,  $\Delta C_p(\text{NO-K}) = C_p(\text{NOBF}_4) - C_p(\text{KBF}_4)$  is  $40.9 \text{ J K}^{-1} \text{ mol}^{-1}$ , or  $\sim 4.9R$ . If the nitrosyl ions at this temperature were to execute effectively classical simple harmonic torsional oscillations, their contribution to  $C_p$  on this account would be  $2R$ . If this motion is not yet quite "classical," the contribution would be somewhat less. It is more realistic to consider this movement of the cations as that of a two-dimensional restricted rotator, for which the heat capacity would pass through a maximum with rising temperature. It is true that the maximum value of this heat capacity contribution can sometimes exceed  $2R$ , but the excess over  $2R$  would be relatively small—certainly much less than the difference between  $4.9R$  and  $2R$ . We may add that a study of ammonium tetrafluoroborate at present in progress in this laboratory has shown that at 300 K,  $C_p$  for this salt (after making allowance for the small contribution from the internal vibrations of the  $\text{NH}_4^+$  ion) exceeds that of the potassium salt by  $\sim 27 \text{ J K}^{-1} \text{ mol}^{-1}$ , which is slightly above the classical figure of  $3R (= 24.9$

TABLE I. Experimental values of the molar heat capacity  $C_p$  of nitrosyl tetrafluoroborate.

$T$ (K)	$C_p$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )
10.74	1.27
13.18	2.52
15.24	3.79
17.00	5.13
18.96	6.86
21.04	8.80
23.37	11.41
25.71	14.03
28.03	16.72
30.75	19.90
31.70	20.86
35.02	25.71
37.76	29.70
38.99	31.50
42.50	36.35
46.53	41.73
51.02	47.85
55.90	54.90
57.40	57.09
59.88	61.40
61.09	64.23
62.21	65.99
64.56	72.38
66.32	82.85
66.88	83.63
69.09	80.86
71.50	65.65
72.34	66.79
74.07	66.65
79.28	69.78
79.36	69.34
83.24	71.33
89.49	74.57
95.49	77.63
101.28	80.38
107.58	83.37
114.38	86.62
120.95	89.71
127.34	92.70
133.55	95.55
139.60	98.36
144.88	100.85
151.57	103.9
158.10	107.1
166.96	111.4
173.24	114.3
179.29	117.05
185.62	120.05
192.25	122.8
199.20	125.9
206.42	129.0
213.88	132.2
221.65	135.55
226.22	137.2
233.78	140.3
241.92	143.45
248.49	145.8
255.70	147.55
262.82	149.5
269.86	151.3
276.81	153.0
283.69	154.4
290.53	155.85
297.46	156.7
304.17	158.1

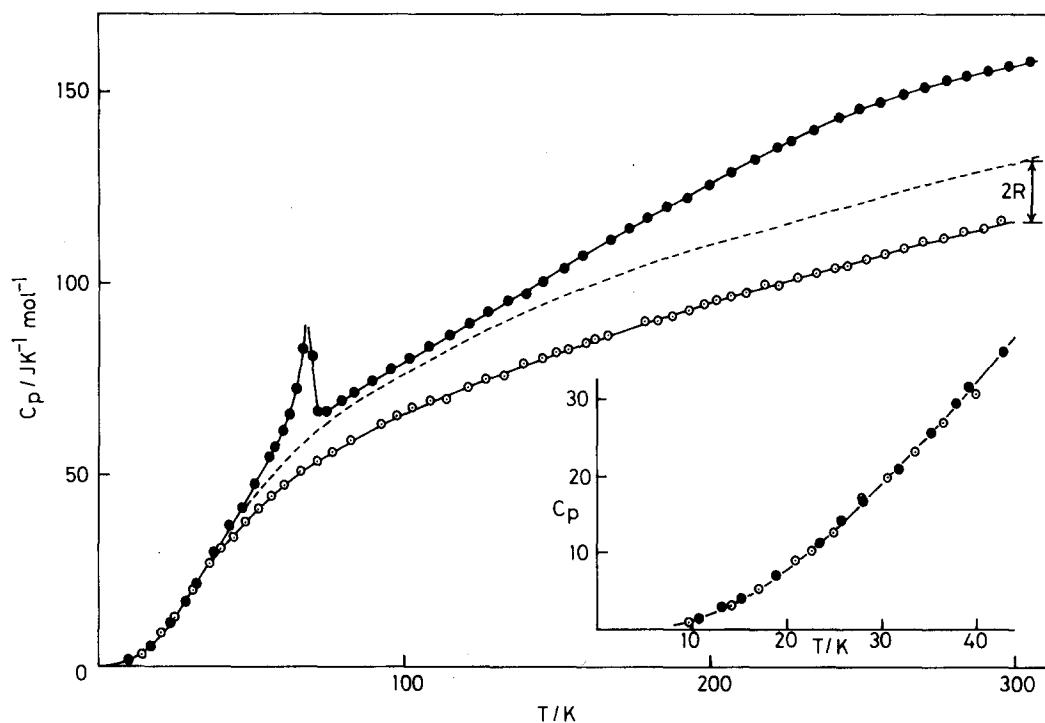


FIG. 1. Molar heat capacity ( $C_p$ ) vs temperature ( $T$ ) plotted from a representative selection of the experimental points for  $\text{NOBF}_4$  (full circles) and  $\text{KBF}_4$  (open circles). The dotted curve is the estimated base line heat capacity for  $\text{NOBF}_4$  (see the text).

$\text{J K}^{-1} \text{mol}^{-1}$ ) for three-dimensional oscillations, so that  $C_p$  for the ammonium salt at 300 K is actually considerably less than that of the nitrosyl salt with its fewer degrees of freedom. It therefore seems certain that there is an "abnormal" contribution to  $C_p$  of the nitrosyl salt which amounts to roughly  $3R$  at room temperature and which persists over a considerable temperature range. Thus, even at 180 K, which is about midway

between room temperature and the  $\lambda$  point,  $\Delta C_p(\text{NO-K})$  is already  $\sim 3.2R$ .

In attempting an analysis of the experimental  $C_p$ ,  $T$  curve for  $\text{NOBF}_4$ , we are admittedly handicapped by ignorance of the torsional oscillation frequencies of the cation and anion. Nevertheless, some progress can be made towards establishing a plausible "base line"  $C_p$

TABLE II. Experimental values of the molar heat capacity  $C_p$  of potassium tetrafluoroborate.

$T$ (K)	$C_p$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$T$ (K)	$C_p$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$T$ (K)	$C_p$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )
9.34	0.91	81.18	58.92	167.02	86.84
14.16	2.97	87.55	62.52	177.86	89.89
17.01	5.24	91.64	63.31	182.65	90.76
19.01	7.15	97.31	65.51	187.46	91.69
19.87	8.19	101.95	67.17	192.44	93.05
20.85	8.99	108.06	68.96	197.58	94.45
22.76	10.17	113.21	69.85	202.17	95.16
24.97	12.47	120.20	72.89	206.52	96.73
27.86	16.98	121.08	72.51	211.67	97.71
30.60	19.93	126.11	74.99	217.48	99.48
33.44	23.16	128.00	74.56	222.31	99.36
36.43	26.92	132.17	76.09	228.40	101.25
39.72	30.76	138.44	79.28	234.56	102.7
43.50	33.83	138.92	78.54	240.68	103.95
47.44	37.45	144.31	80.34	244.36	104.7
51.87	40.97	144.90	80.93	250.78	106.2
56.40	44.32	149.61	81.87	257.15	107.55
60.90	47.55	149.81	82.59	263.45	109.2
65.91	50.76	152.95	82.69	269.74	110.5
71.11	53.61	157.70	84.58	276.28	111.8
76.19	56.31	161.93	85.62	282.51	113.65
79.63	58.19	166.07	86.47	288.86	114.25
				295.18	116.1

curve, i. e., the curve which would be expected in the absence of any abnormal contribution from order-disorder changes or phase transitions. We first observe that for  $\text{KBF}_4$  at 300 K the contributions from the internal vibrations of the  $\text{BF}_4^-$  ion (for which we have used the frequencies assigned by Goubeau and Bues<sup>8</sup>) is  $36.2 \text{ J K}^{-1} \text{ mol}^{-1}$ . This, added to  $9R$ , the limiting classical value for the lattice vibrations and torsional oscillations of the anions, is  $111.0 \text{ J K}^{-1} \text{ mol}^{-1}$ . The experimental value is  $116.4 \text{ J K}^{-1} \text{ mol}^{-1}$ . Probably the  $9R$  is a slight overestimate, but the implication is that at 300 K the  $(C_p - C_v)$  contribution is of the order of 5% of  $C_p$ , so that it is reasonable to assume, from the similarity of the structures of  $\text{NOBF}_4$  and  $\text{KBF}_4$ , that there is no significant difference between the heat capacities of the two salts due to differences in the  $(C_p - C_v)$  contribution. Moreover, the single internal vibration frequency of the  $\text{NO}^+$  ion is so high ( $2340 \text{ cm}^{-1}$ )<sup>3</sup> that the contribution from this to  $C_p$  is quite negligible even at 300 K.

Accordingly, we may seek to establish an acceptable base line curve by adding to  $C_p$  for  $\text{KBF}_4$  a contribution from the two-dimensional oscillations of the  $\text{NO}^+$  ion. As will be seen from Tables I and II and from the inset in Fig. 1, the values of  $C_p$  for the two salts at low temperatures (e. g., from 12 to 30 K) are almost identical the difference at a given temperature nowhere exceeding ~2%. In this temperature range—or at least certainly at the lower end of it—the contribution from the torsional oscillations of the  $\text{NO}^+$  ion to  $C_p$ , on any frequency for this motion which by analogy with known values for ions in other salts would appear reasonable, would be negligible. The near equality of  $C_p$ , therefore, for the two

TABLE III. Molar thermodynamic properties of nitrosyl tetrafluoroborate,  $\text{NOBF}_4$ .

$T$ (K)	$C_p$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$(H_T^* - H_0^*)$ ( $\text{J mol}^{-1}$ )	$s_T^*$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$[-(G_T^* - H_0^*)/T]$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )
10	(0.99)	(2.4)	0.31	0.07
20	7.60	40.8	2.70	0.66
30	18.95	172.6	7.85	2.10
40	32.8	430.5	15.15	4.39
50	46.3	826.8	23.93	7.39
60	61.5	1363	33.65	10.94
70	67.5	2104	45.02	14.96
80	69.6	2977	54.0	19.3
90	74.8	3199	62.5	23.6
100	79.8	4272	70.65	27.9
110	84.5	5093	78.45	32.15
120	89.3	5962	86.05	36.35
130	93.9	6878	93.35	40.45
140	98.6	7841	100.5	44.5
150	103.2	8850	107.45	48.45
160	107.9	9905	114.25	52.35
170	112.8	11010	120.95	56.2
180	117.4	12160	127.55	60.0
190	121.9	13360	134.0	63.7
200	126.2	14600	140.35	67.4
210	130.6	15880	146.65	71.0
220	134.9	17210	152.8	74.6
230	138.9	18580	158.9	78.1
240	142.5	19980	164.9	81.6
250	146.0	21430	170.75	85.05
260	148.7	22900	176.55	88.45
270	151.3	24400	182.2	91.85
280	153.6	25920	187.75	95.15
290	155.7	27470	193.2	98.45
298.15	157.0	28750	197.5	101.1
300	157.3	29040	198.5	101.7

TABLE IV. Molar thermodynamic properties of potassium tetrafluoroborate,  $\text{KBF}_4$ .

$T$ (K)	$C_p$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$(H_T^* - H_0^*)$ ( $\text{J mol}^{-1}$ )	$s_T^*$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$[-(G_T^* - H_0^*)/T]$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )
10	1.14	2.9	0.38	0.08
20	7.62	42.1	2.82	0.71
30	19.05	171.2	7.89	2.18
40	30.8	422.8	15.04	4.47
50	39.55	775.7	22.88	7.36
60	46.95	1208	30.74	10.61
70	53.2	1709	38.46	14.04
80	58.4	2267	45.91	17.56
90	62.8	2875	53.05	21.1
100	66.5	3521	59.85	24.65
110	69.8	4203	66.35	28.15
120	72.9	4916	72.55	31.6
130	76.0	5661	78.5	34.95
140	79.2	6437	84.25	38.3
150	82.2	7244	89.85	41.55
160	82.0	8079	95.2	44.75
170	87.6	8942	100.45	47.85
180	90.2	9831	105.55	50.9
190	92.5	10750	110.5	53.9
200	94.8	11680	115.3	56.85
210	97.0	12640	119.95	59.75
220	99.2	13620	124.5	62.6
230	101.4	14620	129.0	65.4
240	103.6	15650	133.35	68.15
250	105.9	16700	137.6	70.85
260	108.2	17770	141.8	73.5
270	110.4	18860	145.95	76.1
280	112.4	19970	150.0	78.65
290	114.5	21110	153.95	81.2
298.15	116.1	22070	157.15	83.2
300	116.4	22260	157.9	83.65

salts at the lowest temperatures suggests that their Debye temperatures are almost identical, and we shall assume this to be the case.

The range of somewhat higher temperatures available to us in which the heat capacity would appear to be unaffected by the onset of the  $\lambda$  transition is admittedly rather limited, but it seems (Fig. 1) that at 40 K the transition might be said not to have begun, whereas this could not be maintained at 50 K. At 40 K,  $\Delta C_p(\text{NO-K})$  is  $2.0 \text{ J K}^{-1} \text{ mol}^{-1}$ , and if this is regarded as the contribution (calculated from an Einstein function) for the two-dimensional librations of the  $\text{NO}^+$  ion, the frequency for this motion is  $155 \text{ cm}^{-1}$ . Using this value, we have calculated the base line heat capacity curve shown by the dotted line in Fig. 1, where  $C_p$  (base line) is the experimental  $C_p$  of the potassium salt plus the contribution from the two-dimensional librations of the  $\text{NO}^+$  ion. If the view is taken that even at 40 K there is a not negligible component arising from the beginning of the gradual transition, then we have underestimated the librational frequency and our suggested base line is an upper limit for the "normal" heat capacity. Accordingly, the estimates we shall present of the abnormal entropy gained by the nitrosyl salt should be regarded as lower limit values.

It will be seen from Fig. 1 that nowhere above the  $\lambda$  transition does the base line curve quite reach the experimental  $C_p$  curve for the nitrosyl salt. The difference is smallest at ~80 to 100 K, being ~ $2.1 \text{ J K}^{-1} \text{ mol}^{-1}$  in this region. To force a fit between the base line curve  $C_p$  and the experimental value for  $\text{NOBF}_4$  at, say, 90 K, the libration frequency of the  $\text{NO}^+$  ion must be re-

duced from  $\sim 155$  to  $\sim 125$   $\text{cm}^{-1}$ , but with the latter value one would then expect  $C_p(\text{NOBF}_4)$  to exceed  $C_p(\text{KBF}_4)$  at 30 K by  $\sim 1.55$   $\text{J K}^{-1} \text{mol}^{-1}$ , which is not the case. The upper part of the base line curve would be relatively little altered by modest variations in the values adopted for the  $\text{NO}^+$  torsional oscillation frequency. Therefore, all in all, we consider the dotted curve of Fig. 1 to be a plausible reference, the use of which to assess the abnormal component of  $C_p(\text{NOBF}_4)$  should not grossly overestimate this component.

From the experimental  $C_p(\text{NOBF}_4)$  values and our base line curve, the extra entropy gained from the start of the  $\lambda$  transition to 80 K is  $4.5$   $\text{J K}^{-1} \text{mol}^{-1}$ , while from 80 to 300 K a further  $14.6$   $\text{J K}^{-1} \text{mol}^{-1}$  is acquired, making a total of  $19.1$   $\text{J K}^{-1} \text{mol}^{-1}$ , or  $R \ln 10$ . As the heat capacity of this salt must continue to be abnormally high above room temperature, on heating above 300 K this extra entropy must be still further increased. Above the  $\lambda$  transition, the rate at which it is gained with respect to rise in temperature is a maximum at  $\sim 250$  K.

Any attempt to interpret the abnormal heat capacity of  $\text{NOBF}_4$  and the associated extra entropy in terms of ionic disorder can almost certainly be confined to the nitrosyl ion. There is nothing in the diffraction evidence to suggest that the  $\text{BF}_4^-$  ions are disordered at room temperature. Moreover, Heuttner *et al.*<sup>4</sup> concluded from their  $^{19}\text{F}$  NMR study that the activation energy for re-orientation of the  $\text{BF}_4^-$  ion in tetrafluoroborates is quite high, being  $37$   $\text{kJ mol}^{-1}$  in the potassium salt and  $41$   $\text{kJ mol}^{-1}$  in the nitrosyl salt. In fact, the salts  $\text{MBF}_4$  with  $M = \text{K, Rb, Cs, NH}_4, \text{Tl, and Ag}$  all undergo a transition at a fairly high temperature (between 430 and 560 K) to a cubic form,<sup>2</sup> and it is this transition which is probably associated with the development of orientational disorder of the anions. According to Huettnner *et al.*,<sup>4</sup>  $\text{NOBF}_4$  itself undergoes a transition at 433 K, which is almost certainly of the same kind. We may add that the high heat capacity of the nitrosyl salt cannot be attributed to incipient thermal decomposition. This is not observed until a much higher temperature is reached ( $\sim 530$  K).<sup>9</sup>

We therefore suggest that at room temperature the cations in  $\text{NOBF}_4$  are in a condition of orientational disorder, having available to them a number of distinguishable orientations. As the salt is cooled, the change to an ordered state apparently takes place rather gradually, though the final stage could well be associated with the  $\lambda$ -type transition at 67 K. It is possible, though at present this is speculation, that when on cooling the  $\lambda$  point is approached, the axis of any one cation has become limited to libration in one direction, corresponding to an ordered lattice, but that there is still some disorder remaining from the availability to a cation of the two positions  $\text{NO}^+$  and  $\text{ON}^+$  and that it is with the resolution of this on further cooling that the  $\lambda$  transition is concerned.

In the orthorhombic form of  $\text{KBF}_4$ , each potassium ion is surrounded by eight fluorine atoms at a separation  $< 3.0$   $\text{\AA}$  (though these are not all equidistant from

the cation), and two fluorine atoms at  $3.075$   $\text{\AA}$ .<sup>5</sup> If the potassium ion is replaced by  $\text{NO}^+$  to give the isomorphous  $\text{NOBF}_4$ , the potential energy of this ion on rotation in three dimensions could then have several minima, not all of the same depth. In this event, the barrier between one minimum and another could be relatively low, so that the torsional motion of the  $\text{NO}^+$  ion, while one of libration rather than true rotation, would be to some degree anharmonic. This possibility complicates any attempt to interpret the "extra" entropy of the  $\text{NOBF}_4$  salt simply on a configurational basis, i.e., in terms of the number of distinguishable orientations available to the  $\text{NO}^+$  ion. Indeed, it affects the assessment of the extra entropy, since the base line we have used was constructed on the assumption that the cations librate in two degrees of freedom with simple harmonic motion. Anharmonicity in this motion might raise or lower the base line, but by analogy with simpler systems it could scarcely seriously change the very considerable difference between our base line and the much higher, actual  $C_p$  vs  $T$  curve for  $\text{NOBF}_4$ . Accordingly, we believe that our estimate of the extra entropy is approximately right, and that the acquisition of this entropy probably represents the combined effects of the use by the  $\text{NO}^+$  ions of several different orientations, and of the greater freedom of the torsional movement of these ions.

Two further useful investigations at once suggest themselves. From the thermodynamic point of view it would be desirable to extend the heat capacity measurements above room temperature to as far as the thermal stability of the salt permits. On the structural side, it would be valuable to compare the results of a diffraction study carried out at room temperature with those obtained at suitable low temperatures such as the nitrogen boiling point (i.e., just above the  $\lambda$  transition) and the helium boiling point. In view of the interest attaching to the possibility that an  $\text{NO}^+$  ion can have two distinguishable orientations in a given direction, it would be informative to be able to distinguish between the two atoms in the ion, and therefore a neutron diffraction study would be particularly helpful, as the coherent scattering amplitudes of N and O atoms for neutrons differ considerably. Studies of the far infrared spectrum and of the  $^{14}\text{N}$  NQR spectrum might also be rewarding.

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