On the Phase Transition of Ammonium Hexafluoroferrate(III)

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The heat capacities of $(NH_4)_3[FeF_6]$ crystal have been measured from 15 to 350 K with an adiabatic calorimeter. A heat capacity anomaly was observed at 267.02 ± 0.05 K. The enthalpy and entropy changes of the transition are 6490 ± 500 J mol^{-1} and 24.8 ± 1.9 J K^{-1} mol^{-1}, respectively. This value of entropy was discussed in terms of a model involving orientational disorder of the ammonium as well as hexafluoroferrate(III) ions. Based on the assumption of the average fcc symmetry of the crystal and internal rigidity of the ions, the proposed model predicts the transition entropy equal to $R \ln 16=23.05$ J K^{-1} mol^{-1} which is in close agreement with the experimental value. Temperature dependent splitting of the Raman band due to the internal vibration of the anion was found to be consistent with the model. The excess heat capacity follows the prediction of the Landau theory of phase transitions of the second kind. Properties of the present and the similar crystals including ammonium and alkali salts of hexafluoro-complex ions were discussed in terms of the ionic orientational disorder.

An early X-ray diffraction work by Pauling[1] showed that ammonium hexafluoroferrate(III) has a face-centered cubic lattice at room temperature. This was confirmed later by Steward and Rooksby[2] who studied the crystal by X-ray powder method at room temperature and at 93 K. They found a tetragonal lattice at the lower temperature, a phase transition being suspected at some intermediate temperature. The phase transition was found at 263 K by Mørup and Thrane[3] in a Mössbauer line-width study of the compound. The mechanism of the phase transition has not been understood well, since the only available data are those concerned with the Bravais lattice change and Mössbauer spectrum narrowing. The latter was interpreted as indicating that the symmetry of the iron site becomes lower in the low temperature phase.[4]

There are a number of factors in the $(NH_4)_3[FeF_6]$ crystal that can lead to the phase transition. The ammonium ion is, of course, well-known for its tendency toward disordering in a number of crystals, the most notable example being ammonium chloride in which the ammonium ion takes at random one of the two allowed orientations. The ammonium ions in the present crystal are not all equivalent, but are grouped into two sets.[5] Those which belong to one set occupy the octahedral sites (the 4b positions)[6] in the fcc lattice, while those belonging to the other set are in the tetrahedral sites (the 8c positions). Consequently, the role played by the ammonium ions in this phase transition may be more complicated than in the ammonium halides. The hexafluoroferrate(III) ion, $[FeF_6]^{3-}$, has the octahedral ionic symmetry and occupies the octahedral 4a position. One might hence expect that the hexafluoroferrate(III) ions are in a uniquely determined orientation in the crystal and, as such, would play a rather passive role in the phase transition. However, consideration based on the lattice dimension and empirical radii of Fe^{3+}, F^- and NH_4^+ ions[7] shows that coincidence of the ionic and crystalline tetrad axes might not be taken for granted: the ions are too bulky to lie simultaneously on the tetrad axis. Instead, the high crystal symmetry might be a result of the orientational disorder of the $[FeF_6]^{3-}$ ions. Therefore, the orientational degree of freedom of the anion has also to be taken into account in a satisfactory description of the mechanism of the phase transition. This type of ionic disorder is an interesting possibility which the heat capacity measurement can prove or refute.

Another motivation for studying the present substance is that it belongs to a large family of crystals which contain fluorine octahedra as their major constituent and for which a vast amount of structural information has been accumulated.[5] Specifically, three closely related ammonium salts are of particular interest: $NH_4[PF_6]$,[8] $(NH_4)_2[SiF_6]$,[9] and $(NH_4)_3[AlF_6]$.[2] The structural relation among these fcc crystals are briefly as follows. The NH_4^+ ion in $NH_4[PF_6]$ crystal occupies the site corresponding to the octahedral position (4b) of the $(NH_4)_3[FeF_6]$ structure, with the 8c tetrahedral positions unoccupied. This is the rock-salt structure with the sodium and chloride ions replaced by the ammonium and the hexafluorophosphate(V) ions, respectively. In the cubic $(NH_4)_2[SiF_6]$ crystal, the occupations is just reversed, *i.e.*, the tetrahedral 8c sites are occupied by the ammonium ions while the octahedral 4b sites are vacant. In $(NH_4)_3[AlF_6]$ both the 4b and 8c positions are occupied. This last crystal is isomorphous with ammonium hexafluoroferrate(III) crystal. The heat capacities of the fluorophosphate,[10] fluorosilicate,[11] and fluoroaluminate[12] have been measured. It will be shown below that comparison of the properties of these compounds leads to an insight into the molecular mechanism of the phase transitions in these ammonium salts.

Finally a peculiar property of the present crystal is noticed in Table 1 which summarizes the room temperature crystal systems and the molar volumes of $A_3[FeF_6]$ type crystals (A; alkali or ammonium ions). The

TABLE 1. ROOM-TEMPERATURE CRYSTAL PROPERTIES OF SOME CRYOLITE-TYPE COMPOUNDS $A(I)_3[FeF_6]$

A(I)	Crystal system	Molar volume/cm^3 mol^{-1}
Li	(complex)	—
Na	monoclinic	76.0
K	tetragonal	96.2
Rb	tetragonal	106.6
Cs	tetragonal	122.3
NH_4	cubic	111.3

structure of the lithium compound is complicated and is not successfully analysed, but the symmetry of the crystal is certainly the lowest.[13] The sodium compound is monoclinic, while the potassium, rubidium and cesium compounds are tetragonal. A gradual trend toward the higher symmetry with increasing cationic size is evident. The ammonium compound, whose molar volume lies between those of the rubidium and cesium compounds (this fact is itself somewhat anomalous because the apparent ionic volume of the ammonium ion is usually between those of potassium and rubidium) has the highest cubic symmetry in the series of the crystals. It should be noted that the enhancement of the crystal symmetry is caused by substitution of the less symmetric ammonium ion for spherical alkali ions. This unusual property of the ammonium salt will be explained below as an entropy effect. This paper reports on the heat capacity measurement of $(NH_4)_3[FeF_6]$ crystal and the interpretation of the experimental results in terms of the above general consideration.

Experimental

Sample Preparation. Extra-pure grade reagent of $Fe(NO_3)_3\cdot 9H_2O$ crystal (Wako Pure Chemical Industries, Ltd.) was dissolved in distilled water. This solution was added dropwise to a concentrated aqueous solution of extra-pure grade reagent of NH_4F (Wako Pure Chemical Industries, Ltd.). $(NH_4)_3[FeF_6]$ crystal precipitated rapidly as finely divided powder. The crystal was separated from the mother liquor and dried at 70 °C. Contamination of the sample with the fluorosilicate was avoided by using polyethylene ware throughout the sample preparation. Elemental analysis gave F, 50.9±0.4%; Fe, 24.94±0.04%; H, 5.39±0.2% (Fe by EDTA gravimetric method, F by thorium nitrate titration, and H by gravimetric method). The calculated values for $(NH_4)_3[FeF_6]$ are F, 50.90%; Fe, 24.94%; H, 5.40%. It was important to use an excess amount of ammonium fluoride solution slightly acidified with hydrofluoric acid. Otherwise, the hydrated crystal appeared to precipitate as noted by Cox and Sharpe.[14] Several other attempts were made until the above preparation was found to be successful. These other attempts gave less than ideal elemental analysis. As an additional guide for the preparation, the differetial thermal analysis (DTA) was employed. The crystal used for the heat capacity measurement gave a sharp endothermic peak on heating through 266±1K. Table 2 summarized the chemical analyses and the DTA results for five different preparations. It should be emphasized that, contrary to Cox and Sharpe's statement,[14] the stoichiometric $(NH_4)_3[FeF_6]$ crystal was prepared by the wet method.

Calorimetry. The heat capacities of $(NH_4)_3[FeF_6]$ crystal were measured from 15 to 350 K with an adiabatic calorimeter. The apparatus is described elsewhere.[15–18] The calorimetric sample crystal, 32.4949 g (0.14510 mol) in weight, was put in the calorimeter cell together with helium heat-exchange gas. The procedure of the measurement was standard one, *i.e.*, intermittent heating method with the temperature increment of 1 K at 20 K and 2 K above 80 K. Smaller steps were employed near the phase transition. The total enthalpy change of the transition was determined by introducing electric energy to the specimen from approximately 4 K below the transition temperature to 4 K above under the adiabatic condition.

TABLE 2. ELEMENTAL ANALYSIS AND DTA OF $(NH_4)_3[FeF_6]$ CRYSTALS PREPARED BY DIFFERENT METHODS

	Chemical composition		DTA peak
	Fe	F	
(1)	24.87%	50.0%	sharp[a]
(2)	24.95	50.2	sharp
(3)	24.61	50.5	broad
(4)	25.06	50.7	broad
(5)	24.94	50.9	sharp
Calcd	24.94	50.9	

a) A small peak was found at 257 K besides the main peak at 267 K. The crystals were prepared as follows. (1) From aqueous solutions of $Fe(NO_3)_3\cdot 9H_2O$ and $NH_4F\cdot HF$. (2) From aqueous solutions of $FeCl_3\cdot 6H_2O$ and NH_4F. (3) Direct reaction of $Fe(NO_3)_3\cdot 9H_2O$ crystal with NH_4F solution. (4) The same as described in the text but without addition of hydrofluoric acid. (5) As described in the text.

Raman Spectrum. Temperature dependence of Raman spectra were recorded with a laser-excited Raman apparatus. The high symmetry of $[FeF_6]^{3-}$ ion is particularly suitable for the vibrational-spectroscopic study because changes in its ionic environment affect the degenerate internal vibration, causing well-resolved splitting of the spectral band. The same situation was exploited in a study of the phase transition in $[Co(NH_3)_6]Cl_2$,[19] in which the hexaamminecobalt(II) ion has a similar high ionic symmetry. The sample crystal was sealed in a thin wall glass ampule and attached to the cold finger in a cryostat. The sample temperature was controlled by adjusting the amount of liquid nitrogen introduced into the coolant chamber and monitored with a copper-constantan thermocouple fixed to the glass ampule.

Results

The experimental values of the molar heat capacity of $(NH_4)_3[FeF_6]$ crystal are given in Table 3 and also shown in Fig. 1. Graphically smoothed heat capacities and derived thermodynamic functions are given in Table 4. The heat capacity changes smoothly with temperature except in the transition region which spans approximately from 180 to 270 K. The highest value of the heat capacity reaching 20000 J K^{-1} mol^{-1} was observed at 267.02±0.05 K. This temperature is 4 K higher than the line width transition temperature 263 K reported by

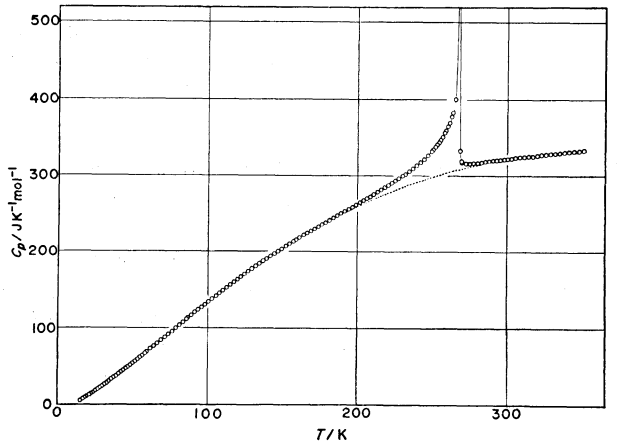

Fig. 1. Molar heat capacity of $(NH_4)_3[FeF_6]$.

Table 3. Heat capacity of $(NH_4)_3[FeF_6]$

T_{av}	C_p	T_{av}	C_p	T_{av}	C_p	T_{av}	C_p	T_{av}	C_p
K	J K^{-1} mol^{-1}	K	J K^{-1} mol^{-1}	K	J K^{-1} mol^{-1}	K	J K^{-1} mol^{-1}	K	J K^{-1} mol^{-1}
		78.39	100.2	163.96	223.2	239.62	315.2	332.34	331.1
1 st series		80.87	104.3	166.43	225.6	242.20	319.5	335.38	331.9
		83.26	108.0	168.88	228.8	244.74	323.6	338.48	332.6
15.06	6.23	85.58	112.0	171.33	231.7	247.26	328.8	341.62	333.7
15.81	7.05			173.75	234.5	249.75	333.8	344.85	334.0
16.89	8.34	3 rd series		176.13	237.5	252.22	339.5	348.16	334.6
18.13	9.75			178.50	239.9	254.65	345.5	351.47	335.3
19.20	11.08	81.43	106.4	181.02	243.0	257.05	352.7		
20.15	12.25	84.22	109.7	183.68	246.0	259.41	361.1	9 th series	
21.14	13.48	86.49	113.4	186.29	249.0	261.73	371.2		
22.25	14.88	88.85	117.2	188.88	251.9	264.01	384.9	233.06	305.3
23.58	16.46	91.14	121.4	191.45	254.8	266.10	545.6	235.72	309.1
25.01	18.52	93.38	124.4	193.99	257.9	266.94	15270	238.36	313.0
26.65	20.70	95.62	128.0	196.51	260.6	267.01	26580	240.98	317.3
28.10	22.62	97.87	131.5	199.01	263.6	267.07	20030	243.57	321.6
29.61	24.66	100.23	135.2	201.49	266.4	267.96	623.2	246.12	326.6
31.18	26.83	102.68	139.0	203.94	269.3	270.15	319.7	248.65	331.6
32.61	28.85	105.08	142.7	206.38	271.9	272.79	318.1	250.57	335.9
34.04	30.86	107.42	146.2			275.39	318.1	251.93	338.9
35.63	33.11	109.83	149.9	5 th series		277.96	318.7	253.29	342.4
37.27	35.50	112.31	153.5			280.58	318.8	254.64	345.9
38.92	37.75	114.75	157.2	201.15	266.0	283.27	319.6	255.89	349.0
40.60	40.28	117.15	160.8	203.63	269.1	285.78	320.6	257.21	353.2
42.16	42.60	119.50	164.1	206.10	271.7	288.29	321.0	258.51	358.3
43.62	44.85	121.80	167.4	208.54	274.0	290.80	321.9	259.40	360.9
45.11	47.16	124.23	170.8	210.96	277.2	293.32	322.6	260.69	366.6
46.65	49.20	126.78	174.5	213.42	280.3	295.83	322.7	261.96	372.8
48.23	51.95	129.27	178.0	215.91	283.3	298.32	323.6	263.21	379.8
49.87	54.36	131.78	181.8	218.38	286.2	300.80	324.2	264.45	388.6
51.42	56.92	134.25	184.7	220.80	289.3	303.28	324.8	265.66	402.9
53.03	59.25	136.64	188.1	223.23	292.4	305.75	325.2	266.58	892.9
54.70	62.21	139.12	191.2					266.93	11690
56.40	64.55	141.70	194.8	6 th series		8 th series		266.98	20520
58.16	67.57	144.25	198.1					267.01	24700
		146.76	201.4	222.96	291.8	301.04	324.4	267.04	23880
2 nd series		149.24	204.6	225.42	295.4	303.60	324.8	267.07	21650
		149.71	205.2	227.86	298.2	306.16	325.5	267.11	11550
56.51	64.82	152.03	208.1	230.29	301.8	308.89	326.2	267.52	733.6
59.33	69.39	154.43	211.2	232.71	304.9	311.72	326.8	268.58	334.9
61.54	73.63	157.01	214.6			314.49	327.5	269.95	321.3
64.02	76.95	159.56	217.4	7 th series		317.36	327.5	271.34	319.0
66.33	80.69					320.30	329.0	272.73	318.3
68.83	84.70	4 th series		232.14	303.9	323.23	329.5	274.41	318.1
71.21	88.62			234.67	307.8	326.23	330.0	276.37	318.4
73.57	92.51	158.96	216.8	237.11	311.0	329.31	330.7	278.32	318.7
75.96	96.18	161.12	220.0						

Mørup and Thrane in the Mössbauer study. The difference between these two temperatures is well beyond the claimed accuracies of the temperature measurements. The origin of the discrepancy is not clear at present. The time required for thermal equilibration in the calorimeter increased near the phase transition to about an hour compared with ten minutes normally required. Such a behavior is often observed in first order transitions.

In order to evaluate the enthalpy and the entropy of transition, the "normal" heat capacity has to be estimated. However, the spectroscopic data on which the estimation of the vibrational heat capacity should be based are insufficient at present, because not only the long wavelength optical vibrations but also the normal modes of the every branch from the entire Brillouin zone contribute to the heat capacity. Thermal motion of the ammonium ions adds further difficulty since their torsional lattice vibration is certainly highly anharmonic. One of the practicable resorts is to interpolate the low and high temperature heat capacities smoothly into the transition region and to make the

Table 4. Thermodynamic functions of $(NH_4)_3[FeF_6]$

$\frac{T}{K}$	$\frac{C_p^\circ}{J\,K^{-1}\,mol^{-1}}$	$\frac{S^\circ}{J\,K^{-1}\,mol^{-1}}$	$\frac{[H^\circ-H_0^\circ]/T}{J\,K^{-1}\,mol^{-1}}$	$\frac{-[G^\circ-H_0^\circ]/T}{J\,K^{-1}\,mol^{-1}}$
10	(1.93)	(0.66)	(0.49)	(0.17)
20	12.10	4.60	3.38	1.22
30	25.16	11.91	8.41	3.50
40	39.48	21.09	14.36	6.73
50	54.57	31.49	20.88	10.61
60	70.37	42.82	27.80	15.02
70	86.54	54.89	35.04	19.85
80	102.8	67.51	42.50	25.01
90	119.0	80.56	50.10	30.46
100	134.9	93.96	57.79	36.17
110	150.2	107.5	65.50	42.04
120	164.8	121.2	73.17	48.07
130	178.9	135.0	80.76	54.23
140	192.4	148.7	88.26	60.49
150	205.6	162.5	95.65	66.83
160	218.3	176.2	102.9	73.23
170	230.2	189.7	110.1	79.69
180	241.8	203.2	117.1	86.18
190	253.2	216.6	123.9	92.69
200	264.6	229.9	130.7	99.22
210	276.2	243.1	137.3	105.8
220	288.2	256.2	143.9	112.3
230	301.2	269.3	150.5	118.8
240	315.7	282.4	157.0	125.4
250	334.4	295.7	163.7	132.0
260	363.7	309.3	170.8	138.5
270	321.4	340.7	195.2	145.5
280	319.0	352.3	199.6	152.6
290	321.7	363.5	203.8	159.7
300	324.1	374.4	207.8	166.7
310	326.3	385.1	211.6	173.5
320	328.6	395.5	215.2	180.3
330	330.8	405.6	218.7	187.0
340	332.9	415.6	222.0	193.6
350	335.0	425.2	225.2	200.1

Table 5. Normal heat capacity of $(NH_4)_3[FeF_6]$

$\frac{T}{K}$	$\frac{C_p}{J\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{J\,K^{-1}\,mol^{-1}}$
160	217.8	260	306.5
170	229.5	270	311.2
180	240.8	280	315.5
190	251.3	290	319.3
200	261.3	300	322.6
210	270.8	310	325.5
220	279.5	320	328.2
230	287.5	330	330.6
240	294.6	340	340.8
250	301.0	350	350.9

"normal" heat capacity thus estimated available to the reader, as is done here (Table 5). The dotted curve in Fig. 1 represents the assumed normal heat capacity. The enthalpy and entropy of the phase transition based on this normal heat capacity are 6490±500 J mol^{-1} and 24.8±1.9 J K^{-1} mol^{-1}, respectively.

The Raman spectra are shown in Fig. 2. The frequency of the $\nu_1(A_{1g})$ mode of the $[FeF_6]^{3-}$ ion is 535 cm^{-1} at 280 K, which is compared favorably with 538 cm^{-1} reported by Wieghardt and Eysel.[20] The $\nu_5(F_{2g})$ vibration was observed at 256 cm^{-1} compared with Wieghardt and Eysel's value at 253 cm^{-1}.[20] The weak band at 374 cm^{-1} was assigned to the $\nu_2(E_g)$ mode. Raman bands of the ammonium ion were not informative because of their low intensity. They are not discussed in the following. Effect of the phase transition on the Raman spectra is most explicitly shown in the temperature dependence of the A_{1g} and F_{2g} modes. On cooling to 103 K, the A_{1g} band narrows appreciably but does not show any splitting. On the other hand, the triply degenerate F_{2g} mode, which is relatively broad at 280 K, broadens further on cooling through the transition temperature with a gradually emerging structure resulting in a well-resolved triplet at 103 K. In view of the relatively large separation between the component frequencies, this splitting is a site group splitting of the threefold degenerate vibration rather than a Davydov splitting. Another explanation that assumes presence of three distinct sets of octahedral sites for the $[FeF_6]^{3-}$ ions may be a least probable possibility and will not be considered further. We conclude, therefore, that the site symmetry of $[FeF_6]^{3-}$ ion is lower than axial. This low site symmetry is rather surprising, because structural and spectroscopic investigations of the related compounds containing octahedral hexafluoride complex have shown that the site symmetry is trigonal or higher if the counter-cation is potassium or a larger ion.[5,21]

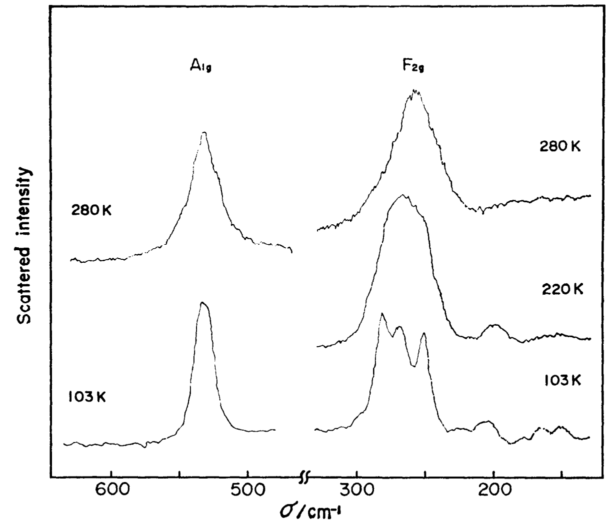

Fig. 2. Temperature dependence of the Raman scattering from the $\nu_1(A_{1g})$ and $\nu_5(F_{2g})$ modes of $[FeF_6]^{3-}$ ion.

The Mössbauer spectra of the present compound have also been interpreted on the assumption of the tetragonal axial symmetry.[3,4] The present Raman data seem to require revision of the interpretation of the Mössbauer results.

Discussion

In the present section we will be concerned with interpretation of the experimental transition entropy, ΔS_{tr}=24.8±1.9 J K^{-1} mol^{-1}, by assuming that it is related to the ionic configurations by the expression

$$\Delta S_{\mathrm{tr}} = R \ln (W_{\mathrm{h}}/W_{\mathrm{l}}).$$

Here, R is the gas constant, W_{h} and W_{l} the numbers of accessible ionic configurations in the high and low temperature phases, respectively. We assume that W_{l} is equal to unity, *i.e.*, the ionic configuration is uniquely determined in the low temperature phase. The ionic disorder in the high temperature phase is assumed to be orientational rather than positional in the sense that the positions of the nitrogen and iron atoms are fixed. We assume further that the $[\mathrm{FeF_6}]^{3-}$ and $\mathrm{NH_4^+}$ ions themselves are rigid so that they retain the $\mathrm{O_h}$ and $\mathrm{T_d}$ symmetries, respectively, in the crystal. Our problem is then to enumerate the allowed ionic orientations compatible with the average face-centered cubic symmetry. The ammonium ion in the 8c position is surrounded by twelve fluorine atoms. At first sight, this seems to offer large number of orientations to the ammonium ion. However, a closer examination of the ionic environment shows that this is not the case. The twelve fluorine atoms are grouped into four sets, each belonging to one of the four iron atoms that form a tetrahedron around the ammonium ion. The other four corners, which, together with the four iron atoms, form the cube around the ammonium ion, are occupied by the other set (4b) of the ammonium ions. Therefore, the environment of the 8c ammonium ion is predominantly tetrahedral. The ammonium ion will settle snugly into this tetrahedral environment without disorder. We assign zero configurational entropy to the 8c ammonium ions.

The ammonium ion in the 4b position is surrounded octahedrally by six fluorine atoms. We associate two distinct orientations with this ammonium ion, assuming that the stable orientation of the ion is such that each of the N–H bonds is directed to the unoccupied corner of the cube surrounding the ammonium ion. Evidently, there are two equivalent orientations of this type for each of the 4b ammonium ions. These orientations would be the most favorable, because it avoids too close a contact between the hydrogen and fluorine atoms. Thus far, we have treated the fluorine atoms as situated on the 24e position on the tetrad axis of the crystal. We consider next the possibility of the orientational disorder of the $[\mathrm{FeF_6}]^{3-}$ ion. There are in general twelve types of positions (one general and eleven special) in the fcc lattice. Of these positions, only 192a and 24e are acceptable as the fluorine site. The other special positions are incompatible with the rigid $[\mathrm{FeF_6}]^{3-}$ ion. These statements are derived algebraically as follows. We express the position of the fluorine atom by $(u\ v\ w)$, where the first, second and third positions in the parentheses designate, respectively, the x, y, and z coordinates of the atom. The coordinate axes are so chosen as to coincide with the cubic axes, the Fe atom being on the origin. Without loss of generality we may put

$$u \geqq v \geqq |w|.$$

Here, u, v, and w are related to the Fe–F bond length r by the following expression:

$$u^2 + v^2 + w^2 = r^2.$$

The rigidity assumption requires that the coordinates of the six fluorine atoms belonging to the iron atom should be

$$\begin{array}{ll} (u \quad v \quad w), & (\bar{u} \quad \bar{v} \quad \bar{w}), \\ (w \quad u \quad v), & (\bar{w} \quad \bar{u} \quad \bar{v}), \\ (v \quad w \quad u), & (\bar{v} \quad \bar{w} \quad \bar{u}). \end{array} \tag{1}$$

The three fluorine atoms on the left column in (1) are related to the three on the right through the inversion about the origin. The orthogonality condition of the first three Fe–F bonds are expressed by

$$vw + wu + uv = 0. \tag{2}$$

One solution of this equation is

$$\begin{aligned} u &= r \\ v &= 0 \\ w &= 0. \end{aligned} \tag{3}$$

The six fluorine coordinates corresponding to this solution are

$$\begin{array}{ll} (r \quad 0 \quad 0), & (\bar{r} \quad 0 \quad 0), \\ (0 \quad r \quad 0), & (0 \quad \bar{r} \quad 0), \\ (0 \quad 0 \quad r), & (0 \quad 0 \quad \bar{r}). \end{array}$$

These are the 24e positions mentioned above and corresponds to the ordered orientation of the fluorine octahedron. It should be noted that application of the $\mathrm{O_h}$ site symmetry operations to this arrangement does not produce any different orientations. Another solution, which is of more interest, is given by

$$u > v > 0, \quad w < 0.$$

This solution corresponds to the disordered orientation of the $[\mathrm{FeF_6}]^{3-}$ ion. There are eight distinct orientations of this type. The other seven are derived from the general expression (1) by successive application of the operations of the site symmetry $\mathrm{O_h}$ as follows:

$$(u \quad v \quad \bar{w}) \quad (w \quad u \quad \bar{v}) \quad (\bar{v} \quad \bar{w} \quad u), \tag{4}$$

$$(u \quad \bar{w} \quad v) \quad (\bar{v} \quad u \quad \bar{w}) \quad (w \quad \bar{v} \quad u), \tag{5}$$

$$(u \quad w \quad v) \quad (v \quad u \quad w) \quad (w \quad v \quad u), \tag{6}$$

$$(u \quad \bar{v} \quad \bar{w}) \quad (\bar{w} \quad u \quad v) \quad (\bar{v} \quad w \quad u), \tag{7}$$

$$(u \quad \bar{v} \quad w) \quad (\bar{w} \quad u \quad \bar{v}) \quad (v \quad \bar{w} \quad u), \tag{8}$$

$$(u \quad w \quad \bar{v}) \quad (v \quad u \quad \bar{w}) \quad (\bar{w} \quad \bar{v} \quad u), \tag{9}$$

$$(u \quad \bar{w} \quad \bar{v}) \quad (\bar{v} \quad u \quad w) \quad (\bar{w} \quad v \quad u). \tag{10}$$

Here, we have given only the coordinates of three fluorine atoms corresponding to the three on the left column of the expression (1). Other three are easily derived from them by the inversion operation. Figure 3 illustrates the above argument. The eight orientations given by the expressions (1), (4), (5), ···, (10) correspond to the fluorine positions numbered as 1, 2, 3, ···, 8 in the Fig. 3. We conclude that the orientational entropy of the fluorine octahedra is either zero or R ln 8. Intermediate values of R ln N (N=2, 3, 4, or 6) often encountered in various models or orientational disorder are incompatible with the rigidity of the ion or the equivalence of the fluorine atoms in the ion in the present crystal.

Morfee *et al.*[22] considered a similar situation in connection with a phase transition in $\mathrm{K_2[SnCl_6]}$, but seem to have failed to take into account the restrictive nature of the fcc symmetry. The transition entropy ($\simeq R$ ln 2) of $\mathrm{K_2[SnCl_6]}$ is too small to support this

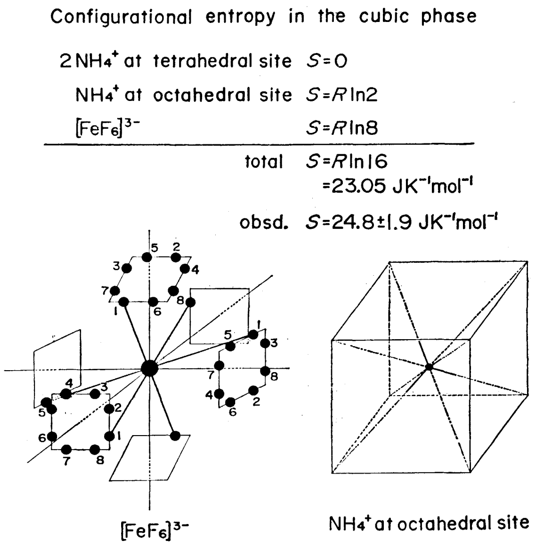

Fig. 3. Orientational disorder of $[FeF_6]^{3-}$ and NH_4^+ ions in the cubic phase of $(NH_4)_3[FeF_6]$.

mechanism in this crystal. The total entropy ΔS of the ionic orientation is given by the sum of the contributions from the ammonium and hexafluoroferrate(III) ions:

$$\begin{aligned}\Delta S &= R\ln 2 + R\ln 8 \\ &= 23.05\ \mathrm{J\ K^{-1}\ mol^{-1}}\end{aligned}$$

The experimental value of the transition entropy $24.8 \pm 1.9\ \mathrm{J\ K^{-1}\ mol^{-1}}$ is in close agreement with this value, giving a support to the disorder mechanism considered above. In recent papers Heyns and Pistorius[23,24] considered a closely related structural disorders in $K[PF_6]$ and $K[AsF_6]$. From an entropy argument they concluded that the location of the fluorine atom may be smeared into a torus-like distribution instead of the eight distinct positions considered here. Precise determination of the electron distribution in these disordered crystals will be rewarding in this respect.

Next we compare the behavior of the present crystal with those of $NH_4[PF_6]$ and $(NH_4)_2[SiF_6]$ crystals. $NH_4[PF_6]$ has the NaCl structure at room temperature and undergoes phase transitions at 131.3 and 191.8 K. The total entropy change of the transitions is 19.7 $\mathrm{J\ K^{-1}\ mol^{-1}}$.[10] The cubic modification of $(NH_4)_2[SiF_6]$, on the other hand, has no phase transitions down to 25 K,[11] although a disordering of ammonium ion with quite different nature has been suspected.[9] These observations, in conjunction with the structural information outlined in the introduction, lead to a conjecture that presence of ammonium ion at the 4b site causes lattice instability which is restored at the higher temperatures by increased orientational entropy pertaining both to the ammonium and hexafluoro-complex ions. If the ammonium ions are absent from the 4b positions, the cubic symmetry is maintained without invoking the ionic disorder. Consequently the crystal is expected to remain cubic down to the lowest temperature as does ammonium hexafluorosilicate.

The concept of the ionic disorder is useful also for rationalizing the structural relation of $(NH_4)_3[FeF_6]$ with other alkali hexafluoroferrates(III). As pointed out earlier, replacement of the spherical ion by the tetrahedral ammonium ion enhances the symmetry of the crystal (Table 1). This observation is understood if the orientational disorder is taken into account as follows. As is well known, the relative stability of phases of a substance is determined by the enthalpy and entropy of the phases involved. In the ammonium salt, the highly symmetric environment of the ammonium ion is stabilized relative to the less symmetric ordered arrangement by the increased entropy due to the increased ionic disorder at the higher temperatures even if the disordered arrangement may be enthalpically less favorable. In contrast, such a stabilization due to the entropy effect is not available for the alkali salts because the alkali ions do not possess orientational degree of freedom. This explains the apparent paradox that less symmetric ammonium ion enhances the crystal symmetry in the $A_3[FeF_6]$ type crystals. Other effects may also be responsible for the stabilization of the cubic phase of the ammonium salts. For instance, change in the ionic radius of the alkali ion will change the (tetragonal) axial ratio of the crystal. The axial ratio might happen to be unity with the ammonium ion. This would augment the tendency toward ionic disorder, and hence toward stabilization of the cubic phase.

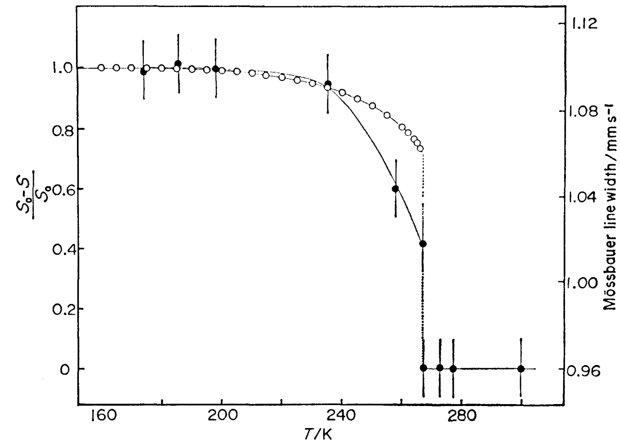

Fig. 4. Temperature dependence of the reduced anomalous entropy $(S_0 - S(T))/S_0$ (−○−○−, present data) and the Mössbauer line width (−●−●−●−, from Ref. 3).

Finally we discuss briefly the temperature dependence of the anomalous heat capacity of $(NH_4)_3[FeF_6]$ crystal. In Fig. 4, the quantity $(S_0 - S(T))/S_0$ is plotted against the temperature, together with the temperature dependence of the Fe Mössbauer line width.[3] Here, $S(T)$ is the anomalous part of the entropy at the temperature T and S_0 is the high temperature limit of the entropy. This quantity is equivalent to the square of the order parameter in the Landau theory of phase transitions of the second kind.[25] These two quantities change similarly with the temperature, implying that there is a close relation between the ionic ordering and the relaxation mechanism of the iron nuclear spin. In the Mössbauer study,[3] the nuclear quadrupole effect is *a priori* neglected in the cubic phase. Although the iron environment is certainly cubic on the average, our model proposed above for the ionic disorder implies that it deviates from the cubic symmetry if observed in a short duration of time.[26] The Mössbauer data[3] seem to set an upper limit for the time during which the proposed local non-cubic ionic arrangement persists: it is less than the electronic relaxation time 10^{-9}—10^{-11}. It may be noted that the averaging to the octahedral symmetry is effected by random jumping of the $[FeF_6]^{3-}$ ion over the eight configurations illustrated in Fig. 3. It is not necessary for the anion to reorient by 90°. The former smaller-scale reorientation would involve a smaller barrier to be overcome, and thus would be consistent with the small value of the orientational life time. In passing, Fig. 4 indicates clearly that the phase transition is of the first order. The total entropy change, 24.8 ± 1.9 J K^{-1} mol^{-1} is absorbed gradually up to 6.3 J K^{-1} mol^{-1} and the remaining part is absorbed isothermally at the transition point.

Landau's thermodynamic theory predicts that the anomalous heat capacity C_{an} follows the temperature dependence:

$$\frac{C_{an}}{T} = A(T_k - T)^{-1/2},$$

provided that the temperature is not too close to the critical value. Figure 5 illustrates an attempt to fit the expression to the experimental anomalous heat capacity. The parameter T_k was so chosen as to yield the widest linear portion in the plot. Actually, the experimental points fit closely to the linear plot up to the onset of the first order effect. This means that we are not in the critical region even at the transition temperature. The large value of the isothermally absorbed entropy is in line with this observation. A conclusion drawn from the favorable comparison with the Landau theory as shown in Fig. 5 is that a restriction is placed on the crystal symmetry of the low temperature phase: the space group of the low temperature phase is a subgroup of the space group of the cubic phase. This is not particularly informative for the present crystal because the high temperature phase involved has the highest symmetry Fm3m.

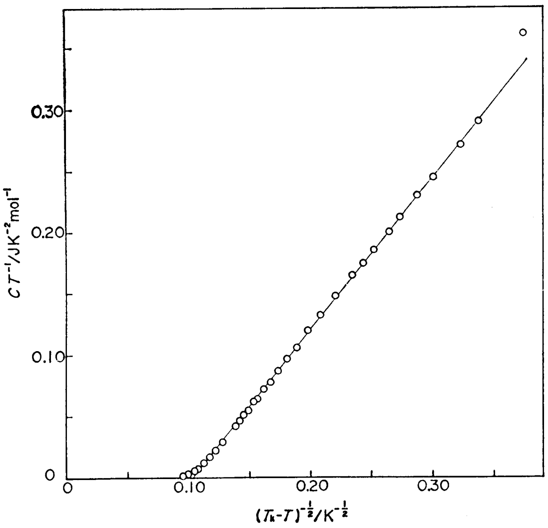

Fig. 5. C_p/T plotted against $(T_k-T)^{-1/2}$ with T_k= 272.8 K. Linearity of the plot implies conformity of the anomalous heat capacity to the Landau theory.

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26) Recently, W. von der Ohe (*J. Chem. Phys.*, **65**, 3575 (1976)) reported a Raman study of the trigonal $(NH_4)_2$-$[TiF_6]$ single crystal in which the $[TiF_6]^{2-}$ ion has a similar octahedral configuration but is situated at a trigonal site. The $\nu_5(F_{2g})$ mode of the complex ion is site-group-split by 1 cm^{-1} at the room temperature. The overall width of the ν_5 spectrum is reported to be 20 cm^{-1}. This is considerably smaller than the width ($\approx$38 cm^{-1}) of the corresponding mode of the $[FeF_6]^{3-}$ ion in the cubic phase of the $(NH_4)_3[FeF]_6$ crystal, suggesting that the latter is composed of overlapping modes. This, in turn, implies that local environment of the $[FeF_6]^{3-}$ ion has a trigonal or lower symmetry when observed in such a short time as is relevant to the Raman scattering, even though the diffraction symmetry of the site is O_h. The orientational disorder model considered in the text is thus consistent with the spectroscopic observation.