Thermodynamic and Structural Properties of Solid and Molten Sodium Magnesium Fluoride

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The liquidus curve on both sides of the $NaMgF_3$ peak in the phase diagram $NaF - MgF_2$ has been determined by thermal analysis. The compound $NaMgF_3$ has a perovskite structure (orthorhombic) $a_0 = 5.354 \pm 0.002$ Å, $b_0 = 7.669 \pm 0.004$ Å, and $c_0 = 5.485 \pm 0.003$ Å.

The enthalpy of fusion of $NaMgF_3$ has been determined by drop calorimetry and a value 17.7 ± 0.1 kcal/mol has been obtained. This value has been used to calculate the liquidus temperature on both sides of the $NaMgF_3$-peak, from the equation

$$T = \frac{\Delta H_\mathrm{f} + \Delta \overline{H}}{\Delta H_\mathrm{f}/T_\mathrm{f} - R' \log N}$$

A "spinel model" for liquid $NaMgF_3$ has been introduced. In this model it is assumed that complex MgF_4^{2-} ions will be formed in the melt and that sodium and the additional magnesium ions are distributed in the melt according to the formula $(NaMg_{1/4})(MgF_4)_{3/4}$. Mol fractions of sodium magnesium fluoride are calculated from the equation

$$N_{NaMgF_3} = 1.870 \, N_{Na} N_{Mg}^{1/4} (N_{MgF_4^{2-}})^{3/4}$$

Good agreement between the calculated and observed freezing point depressions is obtained by allowing for a small negative enthalpy of mixing in the system, given by $H_{NaMgF_3} = (-1000 + 2000N^2_{NaF})N^2_{NaF}$ on the NaF-side or $\overline{H}_{NaMgF_3} = -1000N^2_{MgF_2}$ on the MgF_2-side of the $NaMgF_3$ peak.

I. INTRODUCTION

In the solid state the sodium magnesium fluoride compound $NaMgF_3$ has a perovskite structure, with magnesium octahedrally surrounded by six fluorine atoms while sodium is surrounded by twelve fluorine atoms. At room temperature the structure of $NaMgF_3$ is orthorhombic, according to investigations by Chao et al.[1] At temperatures above 900°C it becomes cubic. Sodium magnesium fluoride melts congruently at 1029.5°C. It has been found in nature and given the name neighbourite.

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The question of complex formation in molten binary mixtures of a monohalide, such as sodium fluoride, with a dihalide, as magnesium fluoride, has for some time attracted the attention of many investigators. The most attractive mixtures so far seem to have been the chloride mixtures KCl-$CdCl_2$ and KCl-$MgCl_2$. Both form ABX_3 compounds in the solid state.

The question has been raised whether these compounds will form complex ions of the type (a), BX_3^-, or the type (b), BX_4^{2-}, when they melt.[2] There is strong experimental evidence today, both from spectroscopic and thermodynamic data, that complex (b), BX_4^{2-}, and not complex (a), BX_3^-, is formed in melts of composition ABX_3 in the lower temperature range.

Here must be mentioned a work by Smith et al.[3] on the melting mechanism of $CsNiCl_3$. From some very elegant spectroscopic examinations they were able to conclude that tetrahedral nickel complexes, $NiCl_4^{2-}$, were formed in molten $CsNiCl_3$, while it was evident at the same time that non-complexing nickel ions could be found in the outer shell of the nickel complex. The hetero-geneous coordination equilibrium occurring at the melting point was expressed as follows:

$$CsNiCl_{3(s)} \rightleftharpoons (T|Ni^{2+}, \ Cs^+)_{(1)}$$
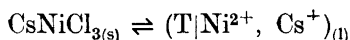
Similar ideas for the melting mechanism of $NaMgF_3$ and other compounds having the perovskite structure, or ABX_3 composition, were put forward a few years ago by the present authors. The idea was to calculate the liquidus curve on both sides of the ABX_3-peak in the phase diagram of the system AX – BX_2 by using a "spinel model" for molten ABX_3. Calculations on two compounds, $NaMgF_3$ and $KMgCl_3$, were carried out.[4] Some of these calculations will be presented in this paper, together with some calorimetric investigations of the enthalpy of fusion of $NaMgF_3$ and of the eutectic mixture, 0.712 $NaF + 0.288$ $NaMgF_3$.

II. EXPERIMENTAL

1. *Chemicals.* Sodium fluoride, NaF, analytical reagent grade, Merck, Germany, was melted before use and clear crystals were selected. Magnesium fluoride, MgF_2, "For the Surface Treatment of Lenses", British Drug Houses, England, was dried in a vacuum furnace at 400°C before use.

Sodium magnesium fluoride, $NaMgF_3$, was prepared by fusing stoichiometric amounts of sodium fluoride and magnesium fluoride in a Pt-crucible in a purified nitrogen atmos-phere. The material was checked by X-ray investigation (Table 3).

2. *Thermal analysis.* The equipment used in the present work for the cooling curve stud-ies was the same as described in a previous paper.[5]

A graphite crucible, 55 mm in diameter and of 120 mm height, containing $50 - 100$ g of salt, was placed inside a thermal gradient free furnace. The temperature was recorded by a Pt/Pt 10 % Rh thermocouple calibrated at the melting points of silver, 960.5 °C, and aluminium, 559.7°C. Supercooling of the melt was prevented by stirring and by seeding with small crystals of sodium fluoride or sodium magnesium fluoride. An accuracy in the determination of temperature of about ± 0.2°C is obtained by using this method.

3. *X-Ray investigations.* X-Ray investigations of the $NaMgF_3$ sample were carried out with a Philips diffractometer (Goniometer PW 1050/25 and Electronic circuit panel) equipped with a scintillation counter.

4. *Drop calorimetry.* The sample was put into a weighed platinum capsule. The air was removed completely by evacuating the capsule, which then was filled with purified argon. A lid was then welded on the capsule, and the filled capsule was weighed. The

weight of the sample was taken as the difference between that of the filled and the empty capsule. All handling of the sample was done inside a dry-box filled with purified nitrogen.

The enthalpy of fusion was measured by drop calorimetry. The sample was equilibrated in a vertical laboratory furnace and lifted into the calorimeter, which was placed above the furnace. The calorimeter proper was a silver calorimeter with adiabatic shields. The furnace temperature was measured by a Pt/Pt 10 % Rh thermocouple and the calorimeter temperature by a quartz thermometer. The calorimetric set-up will be described in detail elsewhere.[6]

III. RESULTS

1. *Thermal analysis.* Results obtained by thermal analysis (cooling curve method) are listed in Table 1 and plotted in a phase diagram in Fig. 1 together with the freezing point depressions obtained by Cantor.[11]
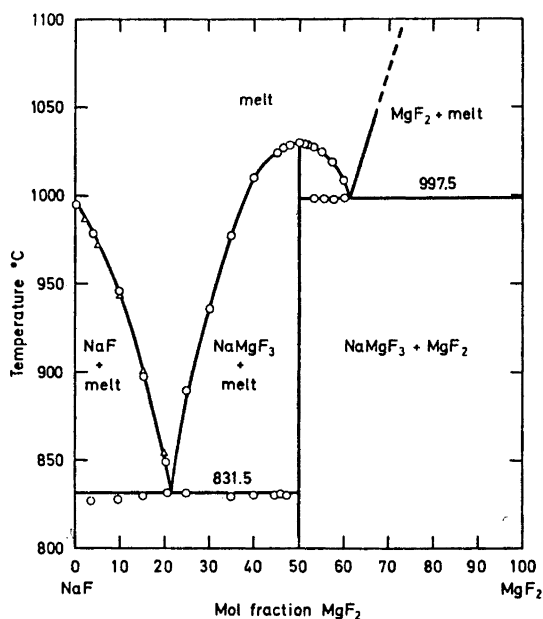

Fig. 1. The phase diagram of the system NaF − MgF₂. ○, experimental points, this work. △, experimental points, Cantor.[11]

2. *X-Ray examinations.* The results from the X-ray examination of NaMgF₃ are summarized in Table 2. Good agreement with the X-ray data for natural and synthetic NaMgF₃ given by Chao *et al.*[1] was obtained. No trace of sodium fluoride was detected.

3. *The enthalpy of fusion of NaMgF₃ and (NaF + NaMgF₃).* The results from the calorimetric experiments are given in Tables 3 and 4, and plotted in Figs. 2 and 3. In the case of NaMgF₃, the specific heat at 315 K $C_p = 26.35$ cal mol⁻¹

Table 1. The system $NaF-MgF_2$. Results from thermal analysis. T_1 = temperature of first crystallization. T_2 = second thermal arrest (eutectic temperature).

Mol % MgF_2	Mol % $NaMgF_3$	T_1 °C	T_2 °C
0		995.0	
3.84		977.9	827.2
9.37		946.2	828.2
15.41		897.0	830.0
20.13		848.7	831.4
26.22		890.8	831.8
30.04		936.2	831.8
34.67	53.06	977.3	829.0
40.00	66.67	1010.3	830.4
45.00	81.80	1023.8	830.5
45.55		1025.0	831.0
46.00	85.20	1025.7	831.0
47.00	88.70	1027.5	830.0
48.00	92.30	1028.5	
49.00	96.10	1029.3	
50.00	100.00	1029.5	
51.00	96.10	1029.2	
52.00	92.30	1028.6	
53.00	88.70	1027.6	997.0
54.00	85.20	1026.4	997.5
55.00	81.80	1024.9	
57.50	73.90	1018.6	997.6
60.00	66.60	1008.1	998.1

Table 2. X-Ray data for $NaM F_3$, ($\lambda_{CuK\alpha} = 1.5405$ Å). Orthorhombic: $a_0 = 5.3542 \pm 0.0024$ Å, $b_0 = 7.6696 \pm 0.0038$ Å, $c_0 = 5.4850 \pm 0.0026$ Å.

hkl	Int.	$\sin^2 \theta_{obs} \times 10^4$	$\sin^2 \theta_{calc} \times 10^4$	$d_{hkl(obs)}$	$d_{hkl \, (lit.)}$[1]
020	s	403	403	3.837	3.85
111	w	505	505	3.428	3.44
002	m	793	789	2.735	2.75
121	s	807	808	2.711	2.71
200	m	829	828	2.675	2.68
120	w	994	996	2.443	2.44
201	m	1024	1025	2.507	2.41
112	m	1096	1097	2.327	2.33
130	s	1114	1115	2.308	2.305
211	s	1123	1126	2.799	2.297
022	m	1193	1192	2.230	2.232
220	m	1135	1131	2.186	—
131	w	1314	1312	2.125	2.128
122	m	1401	1399	2.058	2.060
221	w	1427	1428	2.039	2.040
040	vs	1611	1613	1.920	1.918
032	vw	1698	1697	1.869	1.872
212	vw	1719	1717	1.858	1.862
132	vw	1904	1904	1.765	1.765

Table 2. Continued.

231	vw	1933	1933	1.752	1.755
310	w	1960	1963	1.740	1.743
103	w	1984	1982	1.729	1.733
222	w	2019	2020	1.714	1.716
113	vw	2079	2083	1.689	1.692
311	vw	2161	2161	1.657	1.664
123	m	2383	2385	1.578	1.583
042	m	2405	2403	1.571	1.575
240	m	2442	2442	1.559	1.561
321	s	2466	2463	1.551	1.553

vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

degree^{-1} was calculated from the C_p's of the component fluorides at 315 K, the last temperature being a mean of the calorimeter temperature for all drops.
The data were fitted by a lest squares treatment to equations of the type

$$\text{NaMgF}_3(\text{s}): H_T - H_{298.15} = -16404 + 37.72T$$
$$\text{NaMgF}_3(\text{l}): H_T - H_{298.15} = -1059 + 39.47T$$

Table 3. Enthalpy increments, $H°_T - H°_{298.15}$, for NaMgF₃.

	Temp. K	$H°_T - H°_{298.15}$ cal/mol
1	1223.2	29 741
2	1244.3	30 573
3	1258.9	31 025
4	1282.9	32 016
5	1318.9	50 911
6	1323.8	51 267
7	1331.6	51 436
8	1339.1	51 730

Table 4. Enthalpy increments, $H°_T - H°_{298.15}$, for the eutectic mixture 0.282 NaF + 0.718 NaMgF₃.

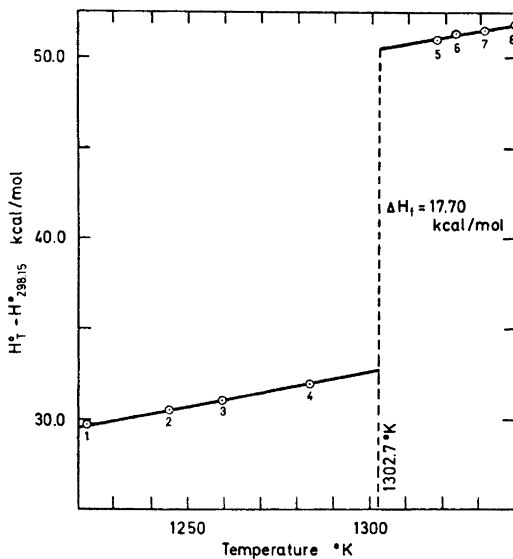|	Temp. K	$H°_T - H°_{298.15}$, cal/mol
1	999.6	13 173
2	1045.6	13 820
3	1059.7	14 379
4	1085.8	14 751
5	1099.9	14 764
6	1121.7	24 187
7	1141.9	24 852
8	1158.6	25 321
9	1174.3	25 736

Fig. 2. Enthalpy curve, $H°_T - H°_{298.15}$, in kcal/mol, for NaMgF$_3$.

An enthalpy of fusion for NaMgF$_3$ at the melting point 1029.5°C of $\Delta H_f = 17.7 \pm 0.1$ kcal/mol was obtained from the drops. For the eutectic mixture (0.718 NaF + 0.282 NaMgF$_3$) an enthalpy of fusion of 8.7 ± 0.10 kcal/mol was obtained at the melting point of the mixture, 820°C.

4. *The enthalpy of mixing of liquid NaF and NaMgF$_3$ and of liquid NaF and MgF$_2$.* At 1105 K the enthalpy of fusion of the eutectic mixture is found to be
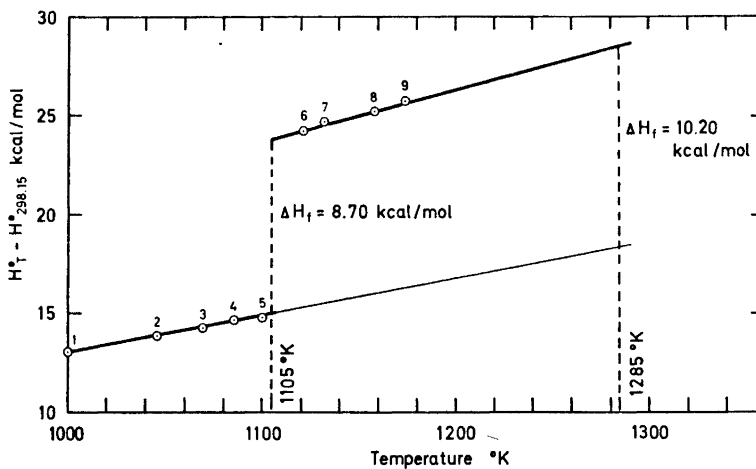
Fig. 3. Enthalpy curve, $H°_T - H°_{298.15}$, in kcal/mol, for
(0.782 NaF + 0.218 MgF$_2$).

8.70 kcal/mol. This corresponds to a value of $\Delta H_f = 10.20$ kcal/mol at 1285 K, as can be seen from Fig. 3.

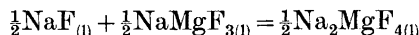The enthalpy of mixing of molten NaF and NaMgF$_3$ can be calculated from eqn. (1)

$$\Delta H^M = \Delta H_{f(\text{eut. mix})} - [N_{\text{NaF}} \, \Delta H_{f(\text{NaF})} + N_{\text{NaMgF}_3} \, \Delta H_{f(\text{NaMgF}_3)}] \qquad (1)$$

or

$$\Delta H^M = 10.20 - (0.782 \times 8.20 + 0.218 \times 17.70) \text{ kcal}$$

Hence, the enthalpy of mixing is $\Delta H^M = -0.1 \pm 0.1$ kcal/mol.

Assuming that the stable complex anion species in the melt is MgF$_4^{2-}$, the enthalpy of the reaction

$$\tfrac{1}{2}\text{NaF}_{(1)} + \tfrac{1}{2}\text{NaMgF}_{3(1)} = \tfrac{1}{2}\text{Na}_2\text{MgF}_{4(1)}$$

would roughly be $\Delta H_r = -0.25$ kcal/mol, with an estimated uncertainty of ± 0.15 kcal/mol. This value will be used in the discussion.

The enthalpy of mixing in the system NaF $-$ MgF$_2$ is not known, it can, however, be calculated from available thermodynamic data by use of the following cycle
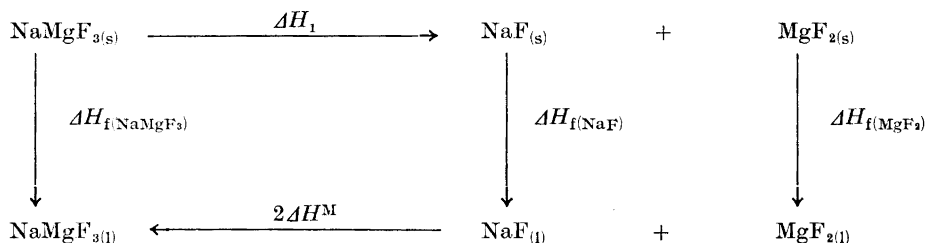
From the cycle:

$$\Delta H_1 + \Delta H_{f(\text{NaF})} + \Delta H_{f(\text{MgF}_2)} + 2\Delta H_M = \Delta H_{f(\text{NaMgF}_3)} \qquad (2)$$

By inserting the enthalpies:

ΔH_1 $\quad = 7.7$ kcal/mol (Sokolov and Belyaev[7])
$\Delta H_{f(\text{NaF})}$ $\quad = 8.1$ kcal/mol (Grønvold and Jenssen Holm[8])
$\Delta H_{f(\text{MgF}_2)}$ $\quad = 13.4$ kcal/mol (Naylor [9] and Holm [10])
$\Delta H_{f(\text{NaMgF}_3)}$ $\quad = 17.70$ kcal/mol (this work)

one obtains

$$2\Delta H^M = 17.7 - 7.7 - 8.1 - 13.1 = -10.8 \text{ kcal/mol}$$

or

$$\Delta H^M = -5.40 \text{ kcal/mol}$$

IV. DISCUSSION

1. *The spinel model.* In the spinel structure, AB$_2$O$_4$, the B atoms occupy half of the octahedral positions while the A atoms fill a quarter of the tetrahedral interstices. NaMgF$_3$ can be transferred from the original perovskite formula to the spinel formula by multiplication by 4/3.

$$4/3 \ NaMgF_3 = (Na_{4/3}Mg_{1/3} \square_{1/3})MgF_4$$
$$\text{perovskite} \qquad\qquad \text{spinel}$$
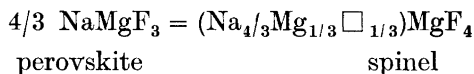
Here it is assumed that magnesium will take the tetrahedral A positions while 4/3 Na, 1/3 Mg and 1/3 $\square$ (vacancies) will be distributed over the octahedral B positions. However, in the molten phase it seems more realistic to omit the vacancies and express $NaMgF_3$ only as

$$[Na, \ Mg_{1/4}] \quad [(MgF_4)_{3/4}]$$
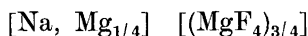
The sodium and the magnesium ions in the first bracket will be distributed statistically over the same type of positions while the rest of the Mg ions, in the last bracket, are tetrahedrally bonded as complex ions and will not be distributed among the other cations.

The mol fraction of $NaMgF_3$ can then be expressed as

$$N_{NaMgF_3} = k N_{Na} N_{Mg}^{1/4}(N_{MgF_4^{2-}})^{3/4} \tag{3}$$

To fulfil the requirement $N_{NaMgF_3} = 1$ for pure $NaMgF_3$ we have to set

$$1 = k\left(\frac{1}{1+1/4}\right)\left(\frac{1/4}{1+1/4}\right)^{1/4}$$

or $k = 1.870$, and the mol fraction of $NaMgF_3$ becomes

$$N_{NaMg_3} = 1.870 N_{Na} N_{Mg}^{1/4}(N_{MgF_4^{-}})^{3/4} \tag{4}$$

This spinel model was first introduced for molten salt mixtures by Flood and Hagemark [12] when discussing the structural properties in molten mixtures of MgO and Al_2O_3.

2. *The NaF-side of the NaMgF_3-peak.* In a mixture containing n_0 mol $NaMgF_3$ and n_1 mol NaF, the number of mol of sodium, n_{Na^+}, magnesium, $n_{Mg^{2+}}$, and complexed magnesium, $n_{MgF_4^{2-}}$, will be given by

$$n_{Na^+} = n_0 + n_1, \ n_{Mg^{2+}} = \tfrac{1}{4}n_0 - \tfrac{1}{4}n_1, \ \text{and} \ n_{MgF_4^{2-}} = \tfrac{3}{4}n_0 + \tfrac{1}{4}n_1$$

(Here it is assumed that Mg^{2+} reacts with the added F^- to form MgF_4^{2-}.)

The corresponding mol fractions

$$N_{Na^+} = \frac{n_0 + n_1}{\tfrac{5}{4}n_0 + \tfrac{3}{4}n_1}$$

$$N_{Mg^{2+}} = \frac{\tfrac{1}{4}n_0 - \tfrac{1}{4}n_1}{\tfrac{5}{4}n_0 + \tfrac{3}{4}n_1}$$

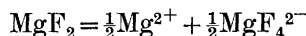$$N_{MgF_4^{2-}} = \frac{\tfrac{3}{4}n_0 + \tfrac{1}{4}n_1}{\tfrac{3}{4}n_0 + \tfrac{1}{4}n_1} = 1$$

The mol fraction of $NaMgF_3$ can be calculated from

$$N_{NaMgF_3} = 1.870\left(\frac{n_0 + n_1}{\tfrac{5}{4}n_0 + \tfrac{3}{4}n_1}\right)\left(\frac{\tfrac{1}{4}n_0 - \tfrac{1}{4}n_1}{\tfrac{5}{4}n_0 + \tfrac{3}{4}n_1}\right)^{1/4} \tag{5}$$

3. *The MgF$_2$-side of the NaMgF$_3$-peak.* If the mixture contains n_0 mol NaMgF$_3$ and n_2 mol MgF$_2$ we will have the following numbers of mol for the ions present

$$n_{\text{Na}^+} = n_0, \quad n_{\text{MgF}_4{}^{2-}} = \tfrac{3}{4}n_0 + \tfrac{1}{2}n_2, \text{ and } n_{\text{Mg}^{2+}} = \tfrac{1}{4}n_0 + \tfrac{1}{2}n_2$$

Here it is assumed that

$$\text{MgF}_2 = \tfrac{1}{2}\text{Mg}^{2+} + \tfrac{1}{2}\text{MgF}_4{}^{2-}$$

giving $\tfrac{1}{2}n_2$ mol of Mg^{2+} and $\tfrac{1}{2}n_2$ mol of MgF$_4{}^{2-}$ per n_2 mol MgF$_2$ added.

The mol fractions are given by

$$N_{\text{Na}^+} = \frac{n_0}{\tfrac{5}{4}n_0 + \tfrac{1}{2}n_2}$$

$$N_{\text{Mg}^{2+}} = \frac{\tfrac{1}{4}n_0 + \tfrac{1}{2}n_2}{\tfrac{5}{4}n_0 + \tfrac{1}{4}n_2}$$

$$N_{\text{MgF}_4{}^{2-}} = \frac{\tfrac{3}{4}n_0 + \tfrac{1}{2}n_2}{\tfrac{3}{4}n_0 + \tfrac{1}{2}n_2} = 1$$

In this case the mol fraction of NaMgF$_3$ will be expressed by

$$N_{\text{NaMgF}_3} = 1.870 \left[\frac{n_0}{\tfrac{5}{4}n_0 + \tfrac{1}{2}n_2} \right] \left[\frac{\tfrac{1}{4}n_0 + \tfrac{1}{2}n_2}{\tfrac{5}{4}n_0 + \tfrac{1}{2}n_2} \right]^{\tfrac{1}{4}} \tag{6}$$

4. *Calculations of the NaMgF$_3$-peak.* Since solid solutions have not been observed on either side of the NaMgF$_3$-peak in the system, the following well-known expression for the activity is valid.

$$\log a_{\text{NaMgF}_3} = -\frac{\Delta H_f}{R'} \left(\frac{1}{T} - \frac{1}{T_f} \right) \tag{7}$$

or

$$\log N_{\text{NaMgF}_3} = -\frac{\Delta H_f}{R'} \left(\frac{1}{T} - \frac{1}{T_f} \right) + \frac{\overline{H}_{\text{NaMg}_3}}{T} \tag{8}$$

Here ΔH_f is the enthalpy of fusion of NaMgF$_3$, T_f is the melting temperature, 1302.7 K, and $\overline{H}_{\text{NaMgF}_3}$ is the partial enthalpy of mixing.

The liquidus temperatures have been calculated from eqn. (8) by setting $\overline{H} = 0$

$$T = \frac{\Delta H_f}{\Delta S_f - R' \log N_{\text{NaMgF}_3}} \tag{9}$$

Here $\Delta S_f = \Delta H_f / T_f$, the entropy of melting has been introduced. The mol fraction N_{NaMgF_3} has been calculated from eqn. (5) on the NaF-side and eqn. (6) on the MgF$_2$-side. The results are plotted as Curve I in Fig. 4.

As can be seen eqn. (8) gives freezing point depressions which do not fully explain the experimental results, when $\overline{H}_{\text{NaMgF}_3}$ is set equal to zero.

However, by introducing a small negative enthalpy of mixing

$$\overline{H}_{\text{NaMgF}_3} = (-1000 + 2000 N_{\text{NaF}}) N^2_{\text{NaF}} \tag{10}$$
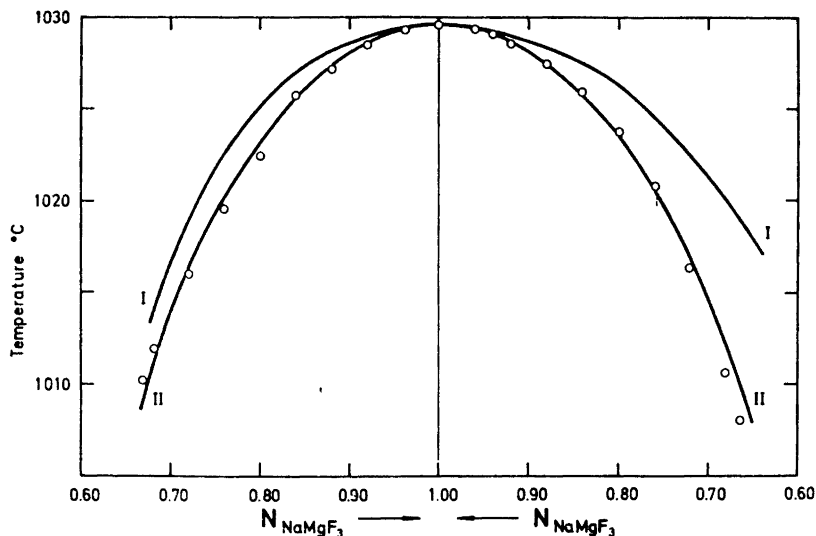
Fig. 4. Experimental and calculated liquidus curves on the NaF-side and the MgF$_2$-side of the NaMgF$_3$-peak. Curve I: Calculated curve assuming $\overline{H}_{\text{NaMgF}_3} = 0$. Curve II: Calculated curve assuming $\overline{H}_{\text{NaMgF}_3} = -1000N^2_{\text{MgF}_2}$ on the MgF$_2$-side, and $\overline{H}_{\text{NaMgF}_3} = -(1000 + 2000N_{\text{NaF}})N^2_{\text{NaF}}$ on the NaF-side.

on the NaF-side, and

$$H_{\text{NaMgF}_3} = -1000N_{\text{MgF}_2} \qquad (11)$$

on the MgF$_2$-side in eqn. (12)

$$T = \frac{\Delta H_\text{f} + \Delta \overline{H}}{\Delta S_\text{f} - R' \log N_{\text{NaMgF}_3}} \qquad (12)$$

Good agreement is obtained between the experimental and the calculated freezing point depressions (Curve II).

The following can be said in favour of the suggested enthalpies of mixing. The interaction parameters correspond to an enthalpy of mixing in the system NaF$-$NaMgF$_3$ of $(-1000 \times 0.25) = -250$ cal/mol. This value is within the limits of the measured value, -250 ± 150 cal/mol. The reason for the small enthalpy of mixing is that the measured value includes an enthalpy of reaction due to a shift in the dissociation equilibrium,
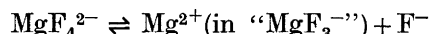
$$\text{MgF}_4{}^{2-} \rightleftharpoons \text{Mg}^{2+}(\text{in ``MgF}_3{}^{-}\text{''}) + \text{F}^-$$

where the Mg^{2+}-ions in the outer shell, Mg^{2+} in "MgF$_3$$^-$", are in equilibrium with the Mg^{2+}-ions in the MgF$_4$$^{2-}$-complex. When sodium fluoride or magnesium fluoride is added to the melt, this equilibrium will be shifted to the left. The energy release observed will be proportional to the amount of MgF$_4$$^{2-}$ formed in the melt by this reaction.

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