Solubility and Raman spectra of Nb(V) in LiF–NaF–KF–Na$_2$O melts

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Abstract

The solubility of Nb(V) as a function of O^{2-} composition in the ternary eutectic LiF–NaF–KF (FLiNaK) melt at 700°C has been determined. Raman spectra at different oxide concentrations and temperatures were recorded. Based on chemical analysis of melt samples and bands in the spectra suggestions related to the Nb–O–F complex formation are given. The addition of Na$_2$O to FLiNaK containing 0.22 mole kg^{-1} K$_2$NbF$_7$, show that at: $n_O/n_{Nb}<2$; there is no precipitation of Nb(V) compounds. The Raman spectra of the melt indicated the presence of monomeric NbF$_7^{2-}$ at low oxide concentrations, which reacted with oxide to form monomeric NbOF$_5^{2-}$ when r was increasing. Further additions of Na$_2$O formed the NbO$_2$F$_4^{3-}$ species having a maximum concentration at $n_O/n_{Nb}=2$; when $2<n_O/n_{Nb}<3$, a solid of the type AlkNbO$_3$ was formed. At $n_O/n_{Nb}=3$, a minimum in the Nb(V) and O^{2-} solubilities were observed, but the structure of the species in the melt were uncertain. At higher oxide content, $3<n_O/n_{Nb}<4$, the AlkNbO$_3$(s) previously formed was dissolved, possibly with the formation of both corner and edge sharing distorted NbO$_6$ octahedra. The solubility of Nb$_2$O$_5$ in FLiNaK was measured as a function of temperature (550–800°C), and the dissolution mechanism seems to be given by the reaction: Alk$^+$+Nb$_2$O$_5$(s)+ 4F$^-$=NbO$_2$F$_4^{3-}$+AlkNbO$_3$(s). ΔH_{sol}^0 for the reaction (based on concentrations in mole kg^{-1}) was found to be ≈90 kJ mol^{-1} K^{-1}. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Niobium belongs to the V-A group of elements and is a refractory metal with attractive chemical properties. Even though it is thermodynamically very reactive, it shows a high resistance to corrosion due to the Nb$_2$O$_5$ layer formed on the surface under oxidising conditions. Together with metals like tantalum, molybdenum and tungsten, niobium has been used under conditions where regular materials like steel and steel alloys will have insufficient corrosion properties. The refractory metals are unfortunately rather expensive, and it is rarely affordable to build larger structures from these metals alone. An important motivation for a continued investigation of the refractory metals originates from their potentials as protective surface layers made by electroplating or other techniques, on cheaper and less corrosive-resistant base materials. The first successful production of coherent coatings of refractory metals was

performed by Mellors and Senderhoff [1] by electroplating from a molten fluoride solvent. The eutectic LiF–NaF–KF (FLiNaK) liquid is a convenient molten salt solvent, and has been given a lot of attention due to its relatively low melting point, 459°C, and good electroplating characteristics. During electrochemical plating, the main problem is often the production of an insufficiently coherent surface of the metals used, which mainly arises when the electrolyte has too high oxide concentrations. Christensen et al. [2] and Matthiesen et al. [3] proposed that the ideal condition for obtaining a coherent layer of Nb in FLiNaK is achieved at $n_O/n_{Nb}<1.0$.

Matthiesen et al. [4] measured the solubility of Nb(IV,V) as a function of the O^{2-} composition in FLiNaK at 700°C. SrO was used as a source for oxygen in the experiments with Nb(V) while Na$_2$O was chosen for the Nb(IV) system due to difficulties dissolving SrO at high oxygen concentrations. The results for Nb(V) indicate a minimum solubility at $n_O/n_{Nb}=3$ due to precipitation of AlkNbO$_3$, and a tendency of dissolution of this oxide upon further additions of SrO. For the Nb(IV) system, precipitation of the solid compound Alk$_x$NbOF$_{2+x}$ seemed to occur when

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$1 < n_O/n_{Nb} < 2$, while further addition of oxide lead to precipitation of Alk_2NbO_3, and a minimum solubility at $n_O/n_{Nb} = 3$. The solid dissolved completely upon further addition of oxide. The solubility of Nb_2O_5 in FLiNaK at 700°C was found ~0.5 mole kg^{-1} and the following dissolution mechanism was proposed:

$$Alk^+ + Nb_2O_5 + xF^- = NbO_2F_x^{(x-1)-} + AlkNbO_3(s) \quad (1)$$
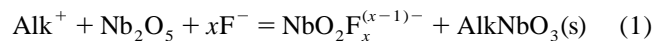
Recent vibrational spectroscopic studies have been reported for LiF–NaF–KF–K_2NbF_7 melts at different n_O/n_{Nb} ratios [5]. In pure melts (without oxide) the presence of NbF_7^{2-} was established. New bands were observed with addition of small amounts of oxide. These bands were assigned to the existence of $NbOF_5^{2-}$ ions. Furthermore, $NbO_2F_4^{3-}$ complexes were proposed to be formed with increasing ratios n_O/n_{Nb} up to ~2. For melts 'saturated' in oxide ($n_O/n_{Nb} > 3$) the [NbO_3F_n] type complexes as well as distorted NbO_6 octahedra were suggested to exist.

This work concerns the systematic investigation of the solubility of Nb(V) in FLiNaK melts at ratios $0 < n_O/n_{Nb} < 8.7$. Complementary Raman spectra of melts at different ratios and temperatures, and Raman and IR spectra of solidified melts were recorded. The results are interpreted and discussed in terms of the structural properties of the species formed.

2. Experimental

2.1. Chemicals and materials

K_2NbF_7 was prepared by precipitation and re-crystallisation from a hydrogen fluoride (HF) solution, and analysed for oxide by a carbothermal reduction method (LECO TC-436). The salt contained ~$5 \cdot 10^{-2}$ mole % oxygen.

Na_2O was made by decomposing Na_2O_2 in an Al_2O_3 crucible at 600°C under a vacuum of 10^{-3} mbar, for 12 h. The oxide was then mortared thoroughly, and the procedure repeated. By dissolving the oxide in water and titration with HCl, it was possible to find the purity of the compound. Assuming the reaction $Na_2O + H_2O = 2$ NaOH, the solution was titrated until neutrality. A typical result after double decomposition showed a purity of 98% compared to pure Na_2O. This is however a simplified way of calculating the purity, as it is assumed that deviation from 100% is due to the presence of unreacted Na_2O_2. The latter will also react with water: $Na_2O_2 + H_2O = H_2O_2 + 2$ NaOH; forming the monoprotic acid hydrogen peroxide in addition to sodium hydroxide. Hydrogen peroxide, that has a $pK_a = 11.65$ is not dissociated at pH 7 (titration end point) and will not have any effect on the titration. The increased molar weight of Na_2O_2 compared to that of Na_2O will however affect the results. Taking this into account the following will be valid: 1 g oxide contains x g

Na_2O_2 and y g Na_2O, or rather $x/78$ mole of Na_2O_2 and $y/62$ mole of Na_2O. If the oxide had been perfectly pure ($x = 0$) the titration endpoint would be reached after addition of ($2y/62$) mole of HCl since each mole of Na_2O produces 2 moles of NaOH. Instead, neutrality is reached after addition of $(2x/78) + (2y/62)$ mole of HCl. Thus, when a purity of 98% is reported one gets: $(2x/78) + (2y/62) = 0.98(2y/62)$ giving $x = 0.0975$ and $y = 0.9025$ (since $x + y = 1$). More generally $(2x/78) + (2y/62) = p(2y/62) \Rightarrow x = 78(1-p)/16$ and $y = (78p - 62)/16$, where p is the purity as a number from 0 to 1. By adding 1 g of an oxide with a reported purity of 98% to a melt, one actually adds 0.00125 mole of Na_2O_2 (7.9 mole %) and 0.0146 mole of Na_2O (92.1 mol %). Knowing that Na_2O_2 is stable in FLiNaK up to at least 600°C [6], the presence of the sodium peroxide should be taken into account when using the compound. This has not been emphasized in the literature up to now. Analysis of the oxide that were used in the present experiments, indicated a purity $> 96.5\%$ Na_2O (series 1) and $> 98\%$ Na_2O (series 2).

The analytical grade Nb_2O_5 (Alfa 99.99%) was dried in a glassy carbon crucible at 150°C for 24 h, before use. NbO_2 and NbO were prepared by electrodeposition from an aqueous solution, dried at room temperature and stored in black containers before use. The alkali fluorides (analytical-reagent grade; Alfa) were re-crystallised twice by slow cooling (3°C h^{-1}) in a platinum crucible under Ar(g). All graphite and glassy carbon materials (Carbone-Loraine) were heated to 840°C for 16 h at 10^{-3} mbar.

2.2. Procedures

The equilibrium studies at different oxide to niobium ratios were carried out in a furnace mounted vertically under an argon filled glove box, making it possible to access the experimental cell from inside without introducing moisture to the cell. The water and oxygen content in the box were 1 and 3 ppm, respectively. All handling of purified salts and samples were performed in the box. The cell and furnace assembly is shown in Fig. 1. A graphite lid was put on top of a glassy carbon crucible, and eight graphite radiation shields were mounted on top of the lid at a regular distance to decrease the vertical temperature gradient. A glassy carbon tube surrounded the radiation shields to reduce the corrosive actions of fluorides on the quartz cell. The lid and the shields had holes for samples extraction and feeding of salts, stirring unit and thermocouple. Melt samples for chemical analysis were extracted using graphite ladles, while stirring was performed with a graphite blade connected to an electrical motor via a steel rod. The whole set-up was placed inside a quartz container lowered into a Kanthal cell heated by the external furnace. A brass lid, with holes similar to the graphite lid and the radiation shields, was put on top of the quartz tube to prevent impurities falling into the melt from the glove box.
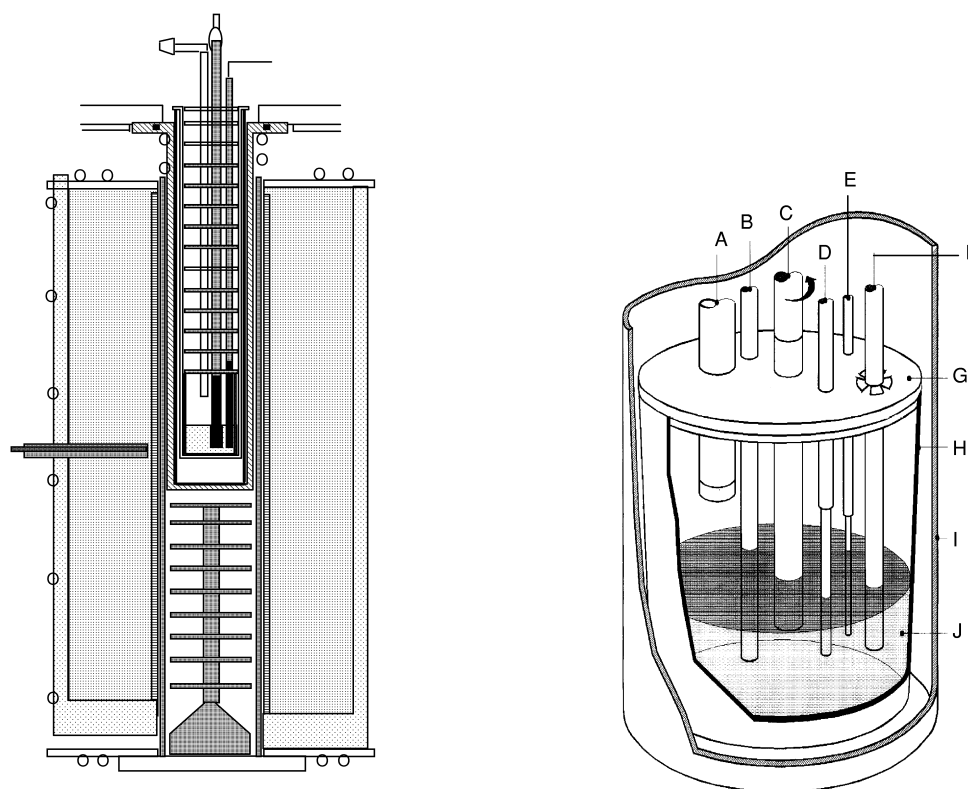
Fig. 1. Experimental cell and furnace mounted to glovebox: (A) quartz sampling tube; (B) electrode, not in use; (C) stirrer; (D) electrode, not in use; (E) electrode, not in use; (F) thermocouple; (G) graphite lid; (H) glassy carbon crucible; (I) quartz container; (J) melt.

The cell was kept in the glove box furnace at 500°C for 24 h in order to remove adsorbed water, before the LiF, NaF, KF and K_2NbF_7 were added to the glassy carbon crucible in given amounts. Equilibrium was established at 700°C by careful stirring of the melt. A sample was then extracted and pellets of Na_2O were added to the melt to obtain a given n_O/n_{Nb} ratio. This was repeated in order to cover the range of oxygen to niobium ratios from 0 to 8.7. Two series of solubility experiments were performed; series 1 covering the compositions $0 < n_O/n_{Nb} < 4.6$, and series 2 covering $2 < n_O/n_{Nb} < 8.7$. In series 2, the first addition of Na_2O was done directly into the crucible before it was lowered into the cell for further additions of fluorides and Na_2O. The saturation experiments with the three oxides Nb_2O_5, Nb_2O and NbO were performed by adding a certain amount of the oxide to the melt (pure FLiNaK), and by extraction of samples at a regular basis until two samples contained the same concentration of oxygen. For Nb_2O_5, the saturation levels were also measured at different temperatures.

The oxide content of the extracted samples was determined by carbothermal method using LECO TC-436, as described by Mediaas et al. [7]. Four parallels were analysed for each composition, and results are given as a mean value using a standard deviation based on a normal distribution. The four parallels were chosen from different parts of the solidified samples, to avoid any systematic error due to inhomogeneity in the quenched melts. Niobium analysis of the extracted samples was performed by ICP (inductively coupled plasma emission spectroscopy). The samples, 0.2 g each, were dissolved in 10 ml HF (40%) and 1 ml HNO_3 (68%), and distilled water was added to a volume of 100 ml. In order to dissolve the samples completely, it was necessary to keep the solutions at 50°C, and this temperature was also kept during analysis to avoid precipitation.

2.3. Raman analysis

The 488 nm line of an argon ion laser (Spectra Physics, Model 2017, power: 600 mW) was used for exciting the spectra. For analysing and collecting the spectra the T-64000 (Jobin Yvon) Raman system, equipped with a Spectraview-20 $2D^{™}$ liquid N_2-cooled charge coupled device (CCD) detector, was used in the triple configuration. The spectral resolution was 5–6 cm^{-1} and the integration time was 5–15 s. The spectral window centred at 450 and 850 cm^{-1} in the Stokes region in order to record a spectrum from 50 up to 1200 cm^{-1}. Before each experiment two liquid samples were used for adjusting the optics and the polarisation characteristics of the spectra; CCl_4 at room temperature and a mixture of $0.3ZnCl_2$–$0.7CsCl$ at 800°C. The system was interfaced with a personal computer and the spectra were saved in digital

form. Two different polarisation directions were used for recording the spectra namely VV and HV. Due to the high corrosivity of FLiNaK melts, the windowless graphite cell technique was used for recording the spectra. The cell design [8] and the high-temperature furnace [9] are described elsewhere. The cells were degassed at 1000°C for 10 h before use.

3. Results and discussion

3.1. Solubility of Nb(V) and O^{2-} in FLiNaK with variations in oxygen content

The influence of Na_2O concentration on the oxide and Nb(V) solubility, and Nb(V)–F–O complexation in FLiNaK melts containing a given amount of K_2NbF_7, was studied as a function of the n_O/n_{Nb} molar ratio at 700°C. The oxide concentration in the melt is plotted versus the molar ratio n_O/n_{Nb} in Fig. 2 (series 1) and Fig. 3 (series 2), where the content of oxygen and niobium in both the melt and in the possible solid Nb–O-containing compounds are included in the ratio.

The measured oxide content in samples with $n_O/n_{Nb} > 4$ has a rather high standard deviation, and this is probably due to inhomogeneity of the quenched melts. The mean value of the analysed data is, however, fairly accurate, since most of the sample was used for analysis or the samples for analysis were taken from representative parts of the quenched melt in order to compensate for the

gradient in concentration through the salt. It is possible to give an evaluation of the stoichiometry of the precipitating species as well as the complexes formed from the observations below. The n_O/n_{Nb} data are based on added amounts of Na_2O and K_2NbF_7 (0.22 mole kg^{-1} melt). Corrections are made for the measured oxygen and niobium content in the salt withdrawn for analysis.

3.1.1. $0 < n_O/n_{Nb} < 2$

The niobium concentration in the melt is constant, and the oxygen concentration increases linearly as the ratio n_O/n_{Nb} increases (Figs. 2 and 3). All the added oxide goes into solution. In fact, a higher concentration is observed than that corresponding to the added amounts of Na_2O. A similar effect was reported by Christensen et al. [2] also that in a K_2NbF_7–Na_2O–FLiNaK melt, and was attributed to 'experimental difficulties'. The oxide that was used in series 1 indicated a purity of about 96.5 mole % Na_2O by titration with HCl. As already mentioned, the enhanced oxide concentration is probably due to Na_2O_2. An addition of the 96.5 mole % Na_2O will indeed produce a too high oxygen concentration due to the Na_2O_2 content. A 1-g amount of Na_2O will give $1/62 = 0.0161$ mole of oxygen while addition of 1 g Na_2O_2 will give $2/78 = 0.0256$ mole of oxygen to the melt. A purity 96.5 mole % means that the oxide contains 17.1 wt. % of Na_2O_2 and 82.9 wt. % of Na_2O. A 1-g amount of this oxide will therefore contain 0.0178 mole of oxygen; about 10% more than the oxygen content in 1 g of pure Na_2O.
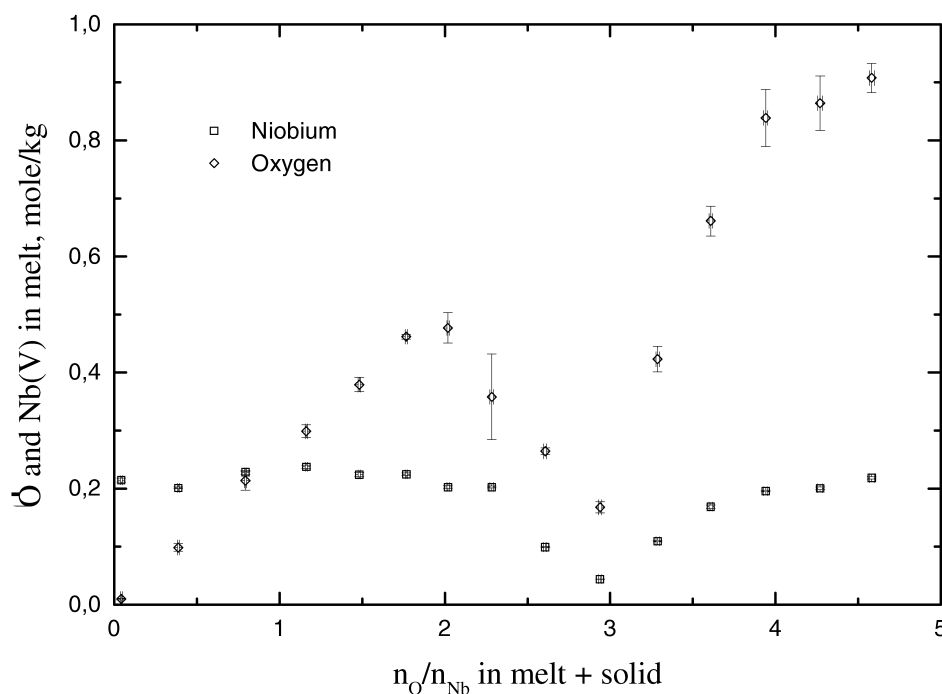
In series 2 an oxide with a measured purity of 98.5 mole

Fig. 2. Oxide (Na_2O) and Nb(V) concentrations in the liquid LiF–NaF–KF eutectic at 700°C versus the molar ratio of the total amount of oxide and niobium in the melt and in the solid phases. Series 1: $0 < n_O/n_{Nb} < 4.7$.

Fig. 3. Oxide (Na$_2$O) and Nb(V) concentrations in the liquid LiF–NaF–KF eutectic at 700°C versus the molar ratio of the total amount of oxide and niobium in the melt and in the solid phases. Series 2: $2 < n_O/n_{Nb} < 8.7$.
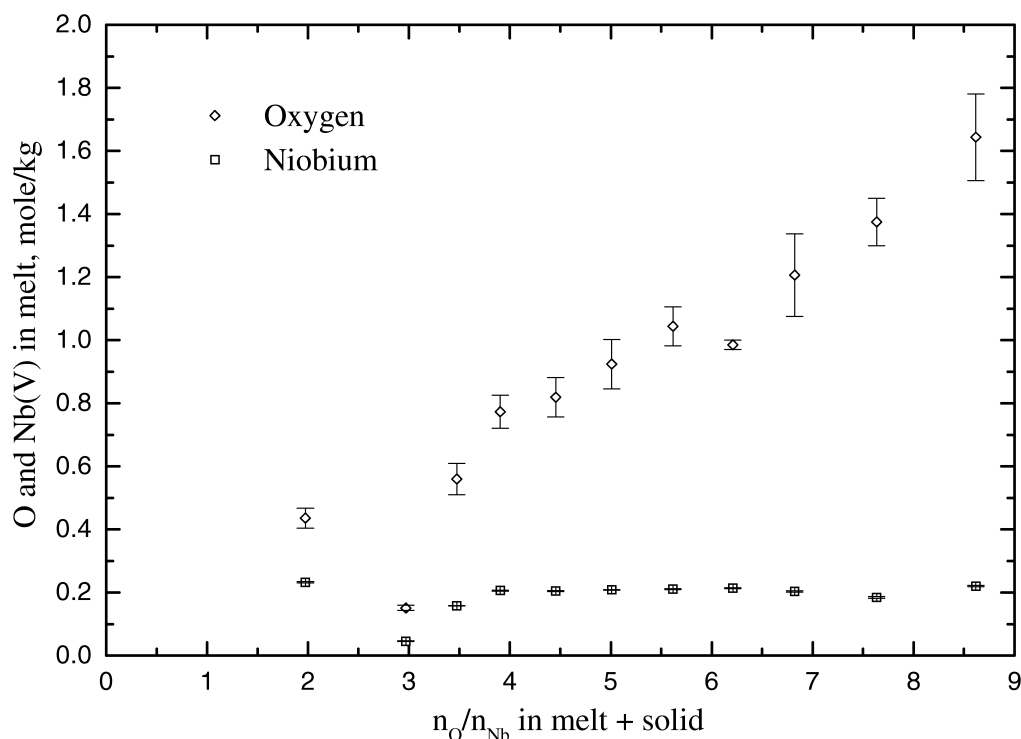
% was used; an oxide containing about 4.3 mole % more oxygen than pure Na$_2$O (comparing on equal weight).

It is difficult to say how the presence of Na$_2$O$_2$ will affect the chemistry of the system, but it seems to be a reasonable explanation for the high oxygen content in the melt. The values for n_O/n_{Nb} in Figs. 2 and 3 are based on the assumption that the added oxide is pure Na$_2$O, and still the minimum in solubility is found close to the ratio $n_O/n_{Nb} = 3$, and not at a lower ratio. This solubility minimum is probably due to the precipitation of a solid with a ratio of oxygen to niobium equal to 3, and the minimum is expected where the total ratio n_O/n_{Nb} in the system is 3.

The solubility data do not provide information about the species in the melt, but clearly specifies that there is no solid salts are present in the system. The results are consistent with reaction (2) and the formation of NbOF$_5^{2-}$ and NbO$_2$F$_4^{3-}$ complexes in the melt as suggested by von Barner et al. [5]:

$$yO^{2-} + NbF_7^{2-} = NbO_yF_x^{(2y+x-5)-} + (7-x)F^- \qquad (2)$$
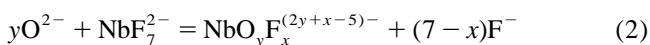
3.1.2. $2 < n_O/n_{Nb} < 3$

As shown in Fig. 2, the concentration of both oxygen and niobium decreases as the ratio n_O/n_{Nb} increases, and reaches a solubility minimum at $n_O/n_{Nb} = 3$. Precipitation of a solid compound AlkNbO$_3$ seems to occur as indicated by reaction (3); similar to the one presented by Matthiesen et al. [3]:

$$NbO_2F_4^{3-} + O^{2-} + Alk^+ = AlkNbO_3 + 4F^- \qquad (3)$$

Rosenkilde et al. [10] measured the solubility of KNbO$_3$ in FLiNaK by using cyclic voltammetry, and found a solubility 0.032 mole kg^{-1} at 700°C. This is in reasonable agreement with the data in Figs. 2 and 3.

According to Eq. (3), the slopes of the lines for the decreasing Nb(V) and O^{2-} concentrations in the melt should be close to -1 and -2, respectively. The lines in Fig. 2 show slopes of about -0.75 and -1.3, respectively. The results indicate that probably another reaction takes place simultaneously, possibly the formation of a soluble Nb–O–F complex with $n_O/n_{Nb} = 3$. It is, however strange that precipitation of AlkNbO$_3$(s) should occur simultaneously as the formation of the dissolved species NbO$_3$F$_x^{(1+x)-}$. Fig. 4 is a close-up of Fig. 2 and shows the four measured oxide concentrations in the range $1.8 < n_O/n_{Nb} < 3.2$. It is expected that precipitation will started as soon as the dissolved species reaches a critically high concentration, and that this concentration would remain constant as long as the precipitated solid was present in the system. If the solid oxide was totally insoluble in the melt, the oxygen concentration would be expected to follow the dashed line in Fig. 4. Precipitation starts immediately as the ratio n_O/n_{Nb} exceeds 2, and the oxygen concentration is given by the line with slope $= -2$. If the solid oxide has a solubility corresponding to the measured oxygen concentration at the ratio $n_O/n_{Nb} = 3$, the solubility should follow the dotted line in Fig. 2. Precipitation does not start
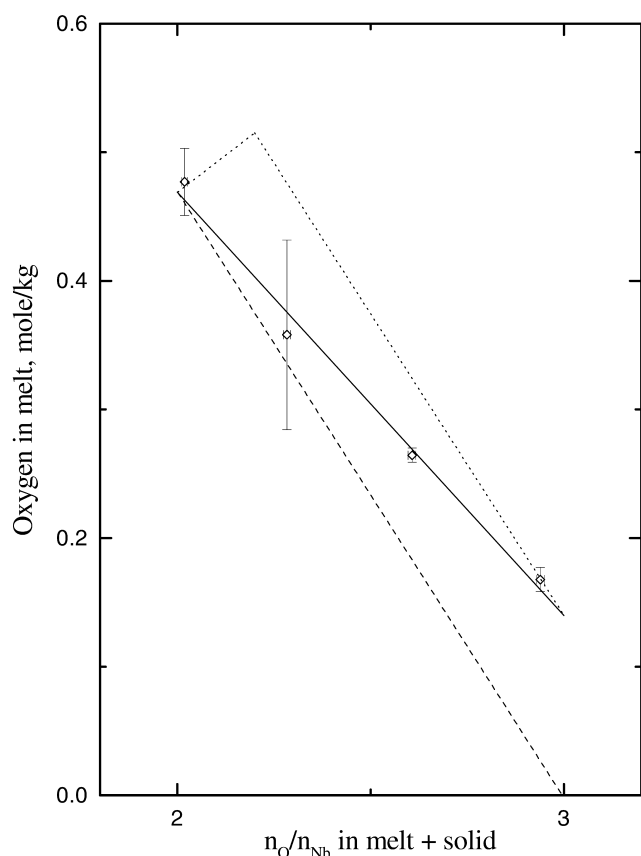
Fig. 4. Close-up of Fig. 2 in the range $1.8 < n_O/n_{Nb} < 3.2$. The solid line is a regression line based on the four data points, while the dotted and dashed lines are theoretical lines given by reaction XX.

before a limiting concentration of the dissolved species is reached, but once the melt is saturated, the oxygen concentration descends along the line with slope $= -2$. Neither of these options fits with what is actually being observed.
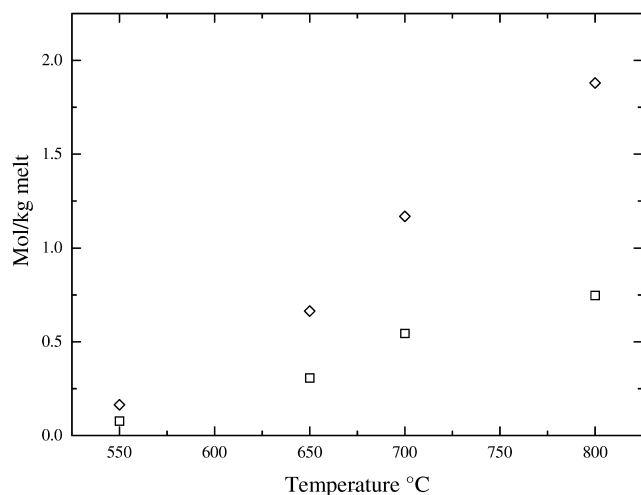
Matthiesen et al. [3] performed a similar experiment

Fig. 5. Niobium (V) and oxygen concentrations as a function of temperature in LiF–NaF–KF eutectic saturated with Nb_2O_5.

when they studied the influence of SrO in K_2NbF_7 containing FLiNaK melts. As previously mentioned they reported a precipitation of a solid compound $AlkNbO_3$ for $2 < n_{SrO}/n_{Nb(V)} < 3$, but more importantly; the oxygen concentrations followed a trend similar to the dotted line in Fig. 4. It is therefore likely that the above observation is due to the presence of Na_2O_2 in the melt. It is however difficult to understand why Na_2O_2 has this effect on the system.

3.1.3. $3 < n_O/n_{Nb} < 8.7$

Dissolution of the solid $AlkNbO_3$ occurs. The concentration of both oxygen and niobium increases up to the ratio $n_O/n_{Nb} = 4$, indicating that all the added compounds are dissolved in the melt at this point. Matthiesen et al. [4] propose formation of a $NbO_yF_x^{(2y+x-5)-}$ complex, probably with $y = 4$. It is not possible to draw any further conclusions based only on the solubility data. When the ratio n_O/n_{Nb} exceeds 4, the niobium concentration remains more or less constant while the oxygen composition in the melt increases only slightly. This indicates a formation of a solid compound with a high n_O/n_{Nb} ratio since this will mainly influence the oxide concentration in the melt.

3.2. Solubility of Nb_2O_5, NbO_2 and NbO in FLiNaK

Matthiesen et al. [4] studied the solubility of Nb_2O_5 in FLiNaK at 700°C, and argued that the $NbO_2F_x^{(x-1)-}$ complex was responsible for the measured solubility (see Eq. (1)). It is important to note that, even with very low additions of Nb_2O_5 there seemed to be a precipitation of $AlkNbO_3$, and that the concentrations of niobium and oxygen increased linearly as a function of the added amounts until saturation was reached. From their data, the n_O/n_{Nb} ratio in the melt seemed to be 2.2. Unable to determine the structure of the soluble species, Matthiesen et al. [4] assumed the presence of $NbO_2F_4^{3-}$ and Nb_2O_5(dissolved) to account for the n_O/n_{Nb} ratio in the melt. Based on the present spectroscopic data it is unlikely that Nb_2O_5 is present as a dissolved species. It is more appropriate to assume that $NbO_2F_x^{(x-1)-}$ and $NbO_3F_x^{(1+x)-}$ are present. It is reasonable to assume that all the added oxide goes into solution until $AlkNbO_3$ saturation is reached. Reaction (4) will be dominating before saturation:

$$Nb_2O_5(s) + 2xF^- = NbO_2F_x^{(x-1)-} + NbO_3F_x^{(1+x)-} \qquad (4)$$
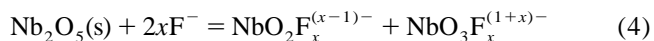
On the other hand when the saturation limit of $AlkNbO_3$ is reached, reaction (5) will be dominating:

$$Nb_2O_5(s) + xF^- + Alk^+ = NbO_2F_x^{(x-1)-} + AlkNbO_3 \qquad (5)$$

The solubility of Nb_2O_5 in FLiNaK has been measured as a function of temperature, and samples at different temperature levels have been withdrawn and analysed for oxygen and niobium. The results are shown in Fig. 5.

Except for the sample withdrawn at 800°C, the n_O/n_{Nb} ratio in the melt varies between 2.11 (at 550°C) and 2.14 (at 705°C), while the n_O/n_{Nb} ratio at 800°C is close to 2.5. The results from the latter could indicate a complete dissolution of Nb_2O_5. However, this is not reasonable due to the low solubility of $AlkNbO_3$ at the other temperatures. The measured melt composition at 800°C is probably not correct, and it is not included in the calculations of ΔH^0_{sol} of Nb_2O_5 in FLiNaK. The activity of Nb_2O_5 and $AlkNbO_3$ is set equal to one (present as solids in the melt), and the concentrations of $NbO_2F_x^{(x-1)-}$ and the possible $NbO_3F_x^{(1+x)-}$ complexes are calculated from the n_O/n_{Nb} ratio in the melt. These data are then used to calculate the equilibrium constant K for Eq. (4) at the different temperatures. The values of K are based on molar concentrations assuming ideality for all dissolved species. By plotting $-(\ln K) \times R$ as a function of $1/T$ the molar enthalpy ΔH^0_{sol} can be found as the slope of the curve. By assuming temperature independent ΔH^0_{sol} and ΔS^0_{sol}, the ΔH^0_{sol} was estimated to be 90 kJ mol^{-1} K^{-1}.

The attempts to measure the solubility of NbO and NbO_2 in FLiNaK failed due to decomposition of the two oxides during the experiment. The dissolution of the oxides proceeded very slowly, and a stable level of oxygen was never reached in the melts. The solidified melts had a dark blue colour, indicating the presence of niobium with oxidation state less than 5. In both cases a metallic film was found on the crucible after the experiment was finished. A black crystalline solid was also found on the stirring rod. Elemental analysis with scanning electron microscopy (SEM) indicated that the metallic film was pure niobium, while the black solid from one rod seemed to be an alloy of potassium and niobium. Neither oxygen nor carbon was found in any of the deposits. These observations indicate a decomposition of the niobium ions to Nb(0) and Nb(V). It is know that the reaction:

$$4Nb^{5+} + Nb^0 = 5Nb^{4+} \tag{6}$$

is nearly completely shifted to the right for niobium in FLiNaK with low oxide content [2]. Rosenkilde et al. [10] studied the electrochemistry of Nb(IV)–O–F complexes in FLiNaK at different n_O/n_{Nb} ratios, and found very low anodic limiting currents in melts with $n_O/n_{Nb} = 1.6$. They therefore concluded that Nb(IV)–O–F complexes decompose to form elementary niobium and niobium(V) dioxo fluoride complexes when the ratio n_O/n_{Nb} exceed 1. This result fits well with the decomposition that was observed in the present experiment, but does not fit with the results of Matthiesen et al. [3]. It is not yet clearly understood why the dissolution of NbO_2 in FLiNaK lead to decomposition and formation of elementary niobium. One early explanation was that the presence of carbon in the system allowed formation of NbC (or another niobium carbide), in a reaction like:

$$5Nb^{4+} + C(s) = NbC(s) + 4Nb^{5+} \tag{7}$$

This reaction has been reported by Kutznetzov et al. [11] to take place in FLiNaK between carbon and four-valent niobium. There was, however, no carbon in our deposits, and reaction (7) cannot explain the data. It is likely that the niobium(IV) dioxo fluoride complex is thermodynamically unstable, and that its decomposition reaction is kinetically controlled, leading to the different results reported by Matthiesen et al. [3] and Rosenkilde et al. [10].

The failure to obtain NbO solubilities can simply be explained by the fact that Nb(II) is not stable in FLiNaK. It probably decomposes to the more stable Nb(0), Nb(IV) and Nb(V) states.

3.3. Raman spectroscopic analysis of Nb(V) in molten FLiNaK with variations in oxygen content

Table 1 list the main observed frequencies at different ratios and temperatures of all the fluoride mixtures observed in Raman spectra. No fluorescence background was detected in the measured spectra. A large number of spectra were recorded but only a part of them are presented here in order to give an overall picture of the liquid systems. Figs. 6–10 show representative Raman spectra obtained for a series of FLiNaK–K_2NbF_7–NaO_2 liquid mixtures at different n_O/n_{Nb} ratios. From this study the following general observations can be made:

(1) $0 < n_O/n_{Nb} < 0.5$: in this range the Raman spectra are characterised by four main bands; three polarised at 922, 630 and 585 cm^{-1} and one depolarised at 304 cm^{-1} (Fig. 6). As the oxide content increases the intensity of 922 and 585 cm^{-1} bands increases, while the band at 630 cm^{-1} decreases.

(2) $0.5 < n_O/n_{Nb} < 1.5$: the intensity of the 630 cm^{-1} band is continuously decreasing, and disappears at ratios above 1.2. The intensity of the bands at 922 and 585 cm^{-1} increases up to $n_O/n_{Nb} = 1$ and decreases with further addition of oxide. At $n_O/n_{Nb} \sim 0.8$–1.2 four new bands are observed in the spectra; one polarised at 878 and three depolarised at 815, 368 and 290 cm^{-1} (Fig. 6). The intensity of the 878 and 815 cm^{-1} bands increases as the ratio n_O/n_{Nb} increases.

(3) $1.5 < n_O/n_{Nb} < 2.5$: the Raman spectra are dominated by four bands; the three depolarised at ~290, 370 and ~812 cm^{-1} and one polarised at ~877 cm^{-1} (Fig. 7). Above ratio 2 the overall intensity of the spectra decreases as the ratio n_O/n_{Nb} increases. The last observation fits very well with the solubility measurements, in which both oxide and niobium concentrations were found to decrease in the liquid.

(4) $3 < n_O/n_{Nb} < 8.7$: new bands are observed in the Raman spectra at $n_O/n_{Nb} \sim 3$; two polarised at 840 and 820 cm^{-1} and two depolarised at 750 and 300 cm^{-1}. The intensity of the 840 cm^{-1} band decreases as the oxide content increases and disappears at ratios above 4. Furthermore, with increasing temperature and a given composition, the intensity of the 840 cm^{-1} band increases relative

Table 1
Observed Raman bands in K_2NbF_7–FLiNaK–Na_2O mixtures at different n_O/n_{Nb} ratios and temperatures

n_O/n_{Nb}	T (°C)	Main frequencies								
0.04	750	303[a]			630				922	
0.39	610	302		(588)[b]	630				923	
0.80	750	305		585	(631)		881	817	922	
1.16	670	(296)	(368)	585	(633)		878	815	921	
1.48	670	291	(360)				878	815	(922)	
1.76	700	289	(364)				877	815		
2.02	720	292	(368)				880	816		
2.28	700	(277)	(355)				877	(808)		
2.60	740	(277)	(355)				877	(810)		
2.98	840	(304)				(756)	844	(818)		
3.28	750	306				(751)	841	826		(1045)
3.61	760	300				(749)	(841)	820		(1045)
	820	300				(749)	(841)	820		(1045)
	850	300				(749)	(841)	820		
3.94	780	300				(745)	(840)	820		1045
4.27	750	302				745		820		1045
4.58	740	300				745		820		1045
5.03	780	310				745		824		1052
5.64	780	310				748		824		1051
6.24	780	310				749		824		1052
6.83	860	309				748		822		1050
7.64	830	310				747		822		1049
8.65	860	310				746		822		1049

[a] Frequencies with an estimated error of 1 cm^{-1}.
[b] Numbers in parentheses indicate shoulder bands and frequencies with an estimated error of ± 5 cm^{-1}.

to the corresponding 820 cm^{-1} band (Fig. 10). The three remaining bands have constant frequency for ratios up to $n_O/n_{Nb}=8.7$. At ratios close to 4 a new polarised band is observed at ~1045 cm^{-1}, and its intensity increases as n_O/n_{Nb} increases.

3.4. Raman and IR spectroscopy of solidified melts in the FLiNaK–K_2NbF_7–Na_2O system

Some of the solidified melts were analysed by means of IR spectroscopy, to better distinguish between possible symmetries of the niobium oxo fluoro complexes. The results are presented in Fig. 11, where the transmittance spectrum of pure FLiNaK is added to show the 'background' of the analysis. To be able to compare the spectra from molten salt solutions with solid samples, one has to be certain that the structural properties are preserved upon quenching of the melts. The Raman spectra of some of the solidified samples were therefore recorded to prove this, and the results are shown in Fig. 12.

The sample with a ratio of oxygen to niobium $n_O/n_{Nb}=$ 0.8 has a band at around 920 cm^{-1} that is both IR and Raman active, while none of the other bands appear in both the IR and the Raman spectrum. The broad shoulder from 550 to 650 cm^{-1} in the IR analysis is difficult to assign to a specific band. For the sample with $n_O/n_{Nb}=$ 2.02 there is at least two vibrations at around 880 and 600 cm^{-1}, and possibly one at 810 cm^{-1} that is present in both the IR and the Raman spectra of the solidified melt. At the ratio $n_O/n_{Nb}=2.98$, the IR signal is very weak, and no bands can be clearly identified in the spectrum under 1000 cm^{-1}. The Raman spectrum, however, shows a weak band at around 830 cm^{-1}, possibly with the same origin as the 840 cm^{-1} band in the molten salt (Fig. 8). For the most oxide rich sample with $n_O/n_{Nb}=8.7$, a sharp peak at around 1060 cm^{-1} is found to be both Raman and IR
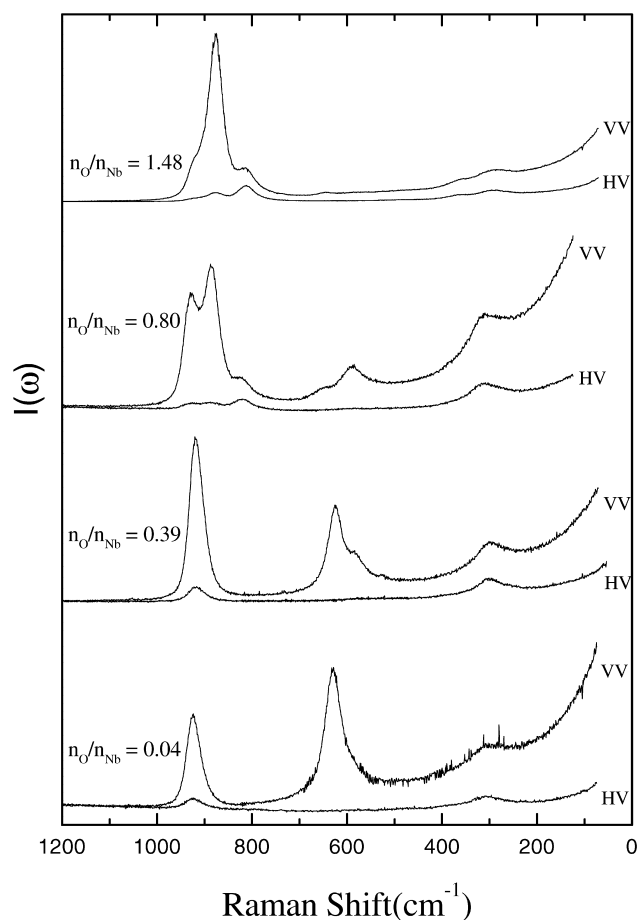
Fig. 6. Raman spectra of 0.22 mole kg^{-1} Nb(V) in LiF–NaF–KF eutectic melt with n_O/n_{Nb} ratio varying between 0.04 and 1.48.

Fig. 7. Raman spectra of 0.22 mole kg^{-1} Nb(V) in LiF–NaF–KF eutectic melt with n_O/n_{Nb} ratio varying between 1.7 and 2.6.

active. The remaining bands either do not appear in both the spectra, or are too diffuse or weak to be determined.

3.5. The niobium(V) fluoride complex in molten FLiNaK

The spectra of the samples containing very small amounts of oxide were very difficult to obtain due to a reaction between niobium fluoride and fused silica envelope of the experimental cell. The spectrum shown in Fig. 6 is therefore of a rather mediocre quality, but it is shown to better understand the trends when the niobium fluoride complex is the dominating Raman active species in the system. The spectral behaviour of the band at 630 cm^{-1} in Fig. 6 is associated with the niobium fluoride complex in these melts, while all the other bands are due to some niobium oxo-fluoride complexes that will be described later. This is in agreement with the previous measurements by von Barner et al. [5].

To determine the symmetry of the niobium(V) fluoride complex in FLiNaK, it is reasonable to compare the measured spectra with bands in related systems. This was done properly by von Barner et al. [5], and will only be 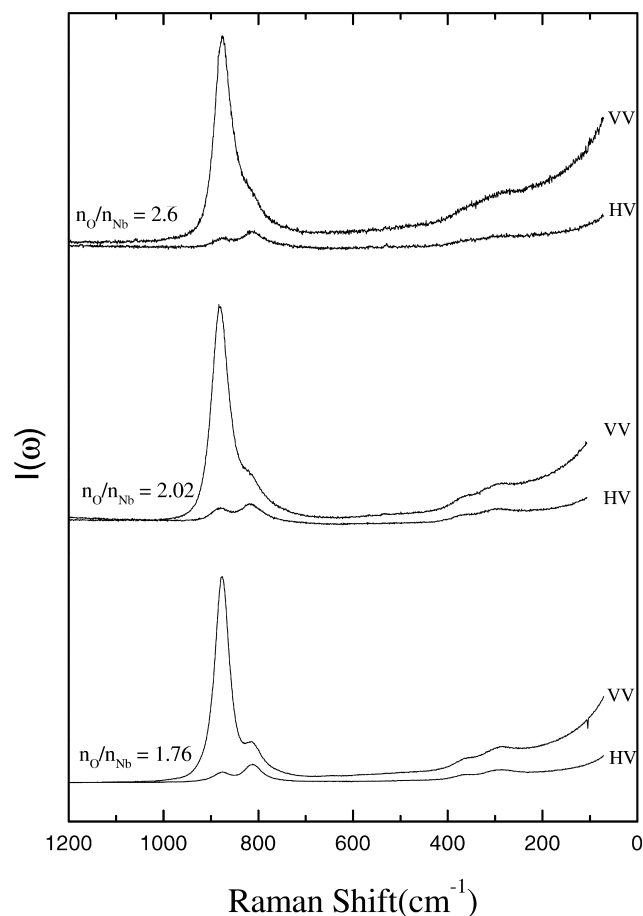covered briefly here. Keller [12] recorded the Raman spectra of K$_2$NbF$_7$ dissolved in concentrated HF, and found bands at 685 and 280 cm^{-1} that by comparison with the spectra of solid CsNbF$_6$, was ascribed to the presence of a NbF$_6^-$ complex in these solutions. The presence of octahedral NbF$_6^-$ units in CsNbF$_6$ was explained by a comparison with other molecules of symmetry O$_h$, like the isoelectronic MoF$_6$. Keller further examined solid K$_2$NbF$_7$, and found a sharp and strong band at 630 cm^{-1}, and two weaker bands at 388 and 782 cm^{-1}, and this was later confirmed by von Barner et al. [5] who in addition found a band at 275 cm^{-1}. Solid K$_2$NbF$_7$ was early studied with X-ray diffraction by Hoard [13], and was shown to possess a monoclinic structure with discrete NbF$_7^{2-}$ anions of C$_{2v}$ symmetry. Neutron diffraction studies of the same compound indicate that the NbF$_7^{2-}$ ion has a lower symmetry [14]. Such structure of the NbF$_7^{2-}$ ion consists of a four member fluorine square put on top of a three-member fluorine triangle, with the central niobium atom placed between them.

Since the band at 630 cm^{-1} in Fig. 6 is also found in solid K$_2$NbF$_7$, it is reasonable to assume that NbF$_7^{2-}$ is present in the melts with low oxide content, with a similar symmetry as in the solid. Barner et al. [5] who also
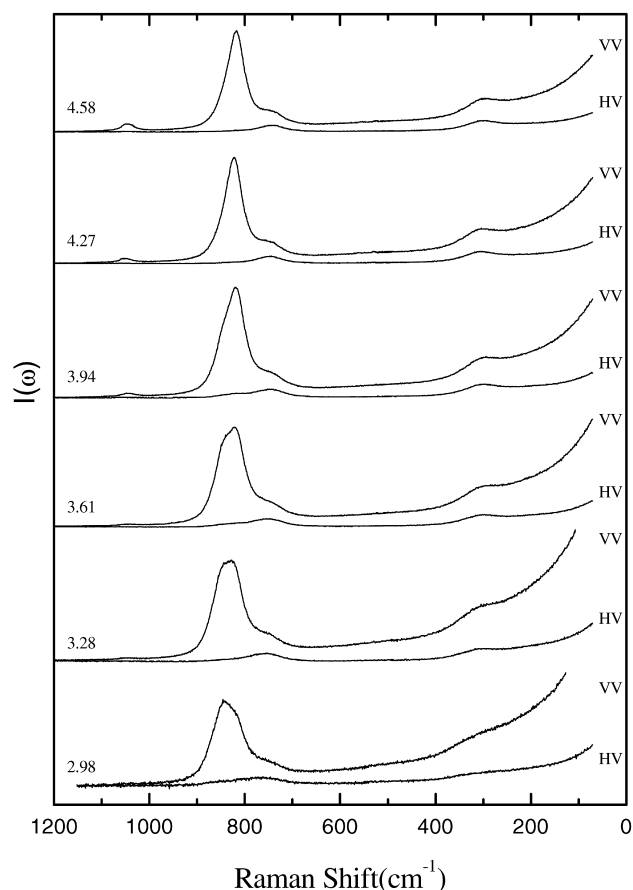
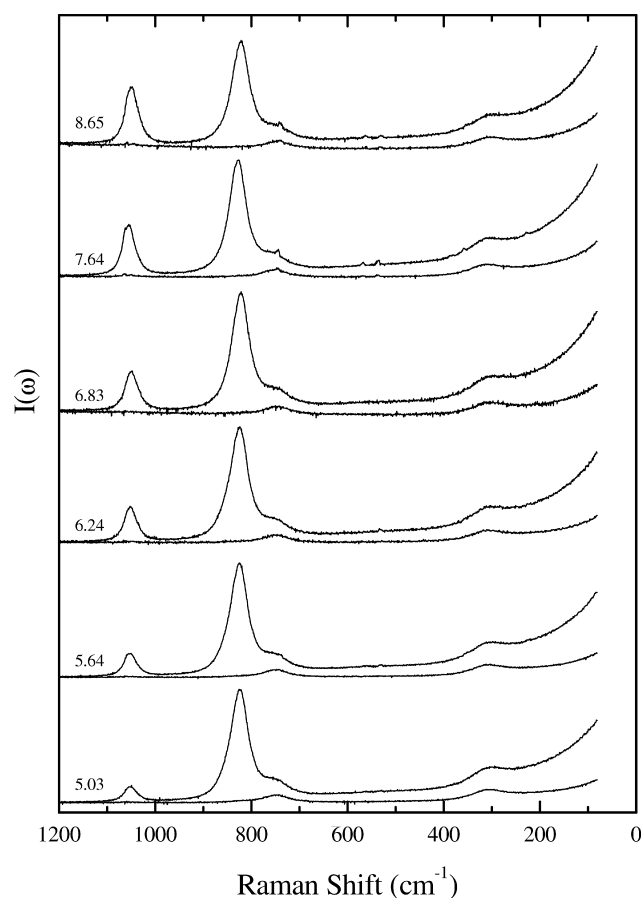Fig. 8. Raman spectra of 0.22 mole kg^{-1} Nb(V) in LiF–NaF–KF eutectic melt with n_O/n_{Nb} ratio varying between 2.98 and 4.6.

Fig. 9. Raman spectra of 0.22 mole kg^{-1} Nb(V) in LiF–NaF–KF eutectic melt with n_O/n_{Nb} ratio varying between 5.03 and 8.65.

measured bands at 290 and 371 cm^{-1} made a similar conclusion, and stated the absence of the strongest band of NbF_6^- at 683 cm^{-1} as a further support for their explanation. It is however difficult to distinguish whether the symmetry of the NbF_7^{2-} anion in molten FLiNaK is C_s or C_{2v}; none of the symmetries can be completely ruled out due to the broadness of the 630 cm^{-1} band. The presence of NbF_7^{2-} in molten FLiNaK is further supported by Fordyce and Baum [15] who found the anion in the LiF–KF binary by using IR-reflection spectroscopy.

3.6. The niobium(V) mono oxo fluoride complex in molten FLiNaK

When oxygen is added to the melt the band at 630 cm^{-1} fades away and the observed intensity of the bands at 304, 585 and 922 cm^{-1} becomes stronger. The spectra features indicate the presence of oxo fluoro complexes in these melts. The 922 cm^{-1} polarized band is in close agreement with recent studies in molten fluorides [5] as well as with earlier vibrational studies in $K_2NbOF_5 \cdot H_2O$ [12] and A_2NbOF_5 (A: Rb, Cs) [16] solids and is assigned to the Nb=O symmetric stretching vibration. The A_2NbOF_5 solid compounds are isostructural to the K_2GeF_6 [17–19] con-

taining isolated $NbOF_5^{2-}$ species having an ideal C_{4v} molecular symmetry. In both IR and Raman spectra of these solids, the Nb–F stretching frequency was found at 577 cm^{-1} in the caesium compound and at 586 cm^{-1} for the Rb_2NbOF_5 solid [16]. The polarised band at 585 cm^{-1}
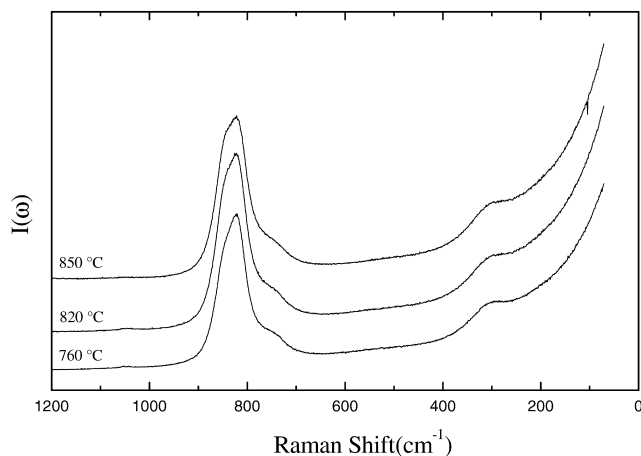

Fig. 10. Raman spectra of 0.22 mole kg^{-1} Nb(V) in LiF–NaF–KF eutectic melt with n_O/n_{Nb} ratio=3.61 at different temperatures.

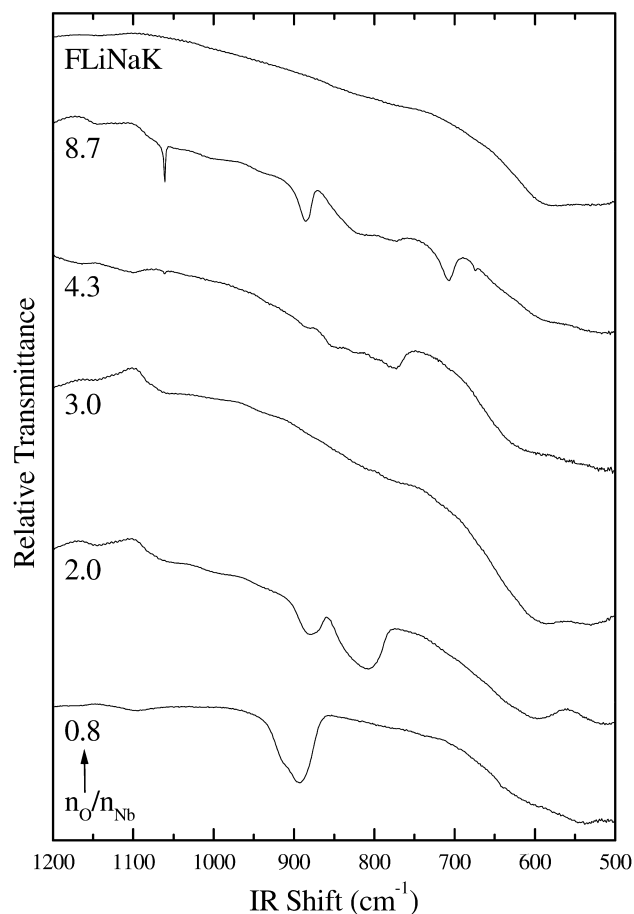Fig. 11. FT-IR spectra of solidified samples of 0.22 mole kg^{-1} Nb(V) in LiF–NaF–KF eutectic melt with n_O/n_{Nb} ratio varying between 0.8 and 8.7. The spectrum of pure FLiNaK is included for comparison.

Fig. 12. Raman spectra of solidified samples of of 0.22 mole kg^{-1} Nb(V) in LiF–NaF–KF eutectic melt with n_O/n_{Nb} ratio varying between 0.8 and 8.7.

(Fig. 6) is very close to these bands and thus could be associated with the Nb–F stretching frequency of $NbOF_5^{2-}$ species in our melts. This is further supported by early Raman studies of tungsten and molybdenum fluoride [20] and mono oxo fluoride [21] melts, where the substitution of two fluoride ions by one oxygen lead to a red shift of about 40 cm^{-1} of the symmetric stretching vibration of the metal–fluorine band in the metal–mono-oxo-fluoro complexes. A similar trend is also observed here by a decrease of 45 cm^{-1} in the Nb–F stretching frequency when comparing NbF_7^{2-} with $NbOF_5^{2-}$.

The origin of the depolarised band at 304 cm^{-1} is more difficult to explain. In previous Raman spectroscopic studies in molten fluoride media [5] as well as in the $K_2NbOF_5 \cdot H_2O$ [12] solid, this band was attributed to the Nb–F vibration due to E and/or B_2 vibrational modes of the C_{4v} $NbOF_5^{2-}$ complex. For such C_{4v} molecules we expect eleven fundamental modes; eight of them are both Raman and IR active ($4A_1$, 4E) while the rest three modes ($2B_1$, B_2) are Raman active only. According to the description of the vibrational modes of such C_{4v} molecules [22], these modes are the result of either NbF_4 scissoring

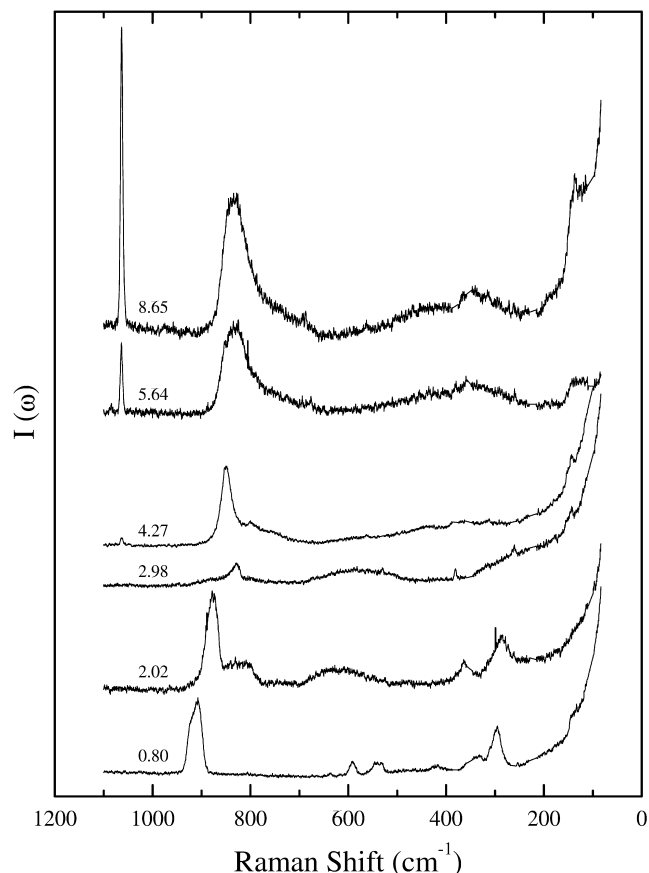type of vibration [$\nu_7(B_2)$] or NbOF bending mode [$\nu_9(E)$] of the $NbOF_5^{2-}$ species. In the Cs_2NbOF_5 solid a band at ~300 cm^{-1} present in both the Raman and IR spectra and was assigned to the NbOF bending mode of the $NbOF_5^{2-}$ isolated complexes in that crystal [16]. This in turn indicates that our band at 304 cm^{-1} could be associated with the NbOF bending mode of the same species.

Since there are no bands observed in the frequency region between 304 and 585 cm^{-1} a possible fluoride bridging is unlikely. Such bands were observed in the gas-phase Raman spectrum of $NbOCl_3$ by Beattie et al. [23] where double chains of Nb–Cl–Nb produce a strong polarised band at 395 cm^{-1}. The same goes for the absence of bands between 600 and 800 cm^{-1}; thus no oxygen bridging takes place in these liquids, which implies that the $NbOF_5^{2-}$ species is probably a monomer.

The above suggestions are close to that of a recent study in similar fluoride melts [5]. The difference on the assignment of the low frequency band could be resolved by further Raman measurements on Cs_2NbOF_5 single crystal at elevated temperatures. Also the spectral changes upon melting of the later compound as well as an IR study

in this low frequency region of the solidified melt and the compound would help in resolving this discrepancy.

3.7. The niobium(V) dioxo fluoride complex in molten FLiNaK

From the observations in Fig. 7, the appearance of four new bands in the spectra could be associated to the existence of new oxo fluoro complexes in the melt. The present spectra (Figs. 7 and 8) are in good agreement with previously reported data where the bands were assigned to the existence of $NbO_2F_4^-$ monomers in the liquid [5]. The band at 290 cm^{-1} is ascribed to an asymmetric Nb–F vibration in the dioxo fluoro complex, while the symmetric band at 880 cm^{-1} and the asymmetric bands at 815 and 370 cm^{-1} are ascribed to Nb–O stretching. The arguments for this are as follows.

As for the niobium mono oxo fluoride complex, the strongest symmetric band is assigned to a Nb–O vibration where the high frequency reflects the character of a strong double bond. Replacing a fluorine atom with a second oxide atom in the complex causes a decrease in this frequency, indicating that the bond becomes weaker. This is because the electron density around the central niobium atom increases, and this leads to a reduction in the attractive forces between the central and the surrounding atoms. In this case, the reduction in bond strength causes a decrease in frequency of 42 cm^{-1}. This is a trend that can be observed in other refractory metal oxo halides (like vanadium, niobium, molybdenum and tungsten oxo halides), when a second oxide is introduced into the complex. When a second oxide is introduced into a MOX_4 complex to form MO_2X_n ($n = 3$, 4) a shift of about 100 cm^{-1} is observed in the symmetrical stretch frequency (comparing for example VOF_4^- and $VO_2F_4^{3-}$ [24,25]). For species with an octahedral structure, MOX_5, the effect is smaller and the frequency normally drops about 30–50 cm^{-1} when going to MO_2X_4 (in the niobium complexes, the frequency drop is about 45 cm^{-1}) [5].

The other high frequency band at 815 cm^{-1} that was observed in the Raman of the melt and the IR spectra of the corresponding solidified melt, is also likely to be due to a niobium–oxygen vibration. As suggested by von Barner et al. [5], the band is ascribed to an asymmetric stretch vibration of the NbO_2^+ entity. The band does not appear in the mono oxo complex, and is therefore probably due to a vibration involving two oxide in addition to the central niobium atom. An important feature of the vibration is that it is both IR and Raman active, and the niobium dioxo fluoro complex can therefore not have a centre of symmetry.

The band at 290 cm^{-1} is probably due to an asymmetric Nb–O–F vibration in the dioxo fluoro complex. In accordance with the reduction in the symmetrical stretching frequency that was observed when a second oxide was introduced to the complex, it is also possible that the

frequency of the asymmetric Nb–O–F vibration is reduced. As the electron density around the central atom is increased the bonds to the surrounding atoms will weaken, and result in a red shift of the vibrations. In the case of the depolarised Nb–O–F band, a reduction of about 15 cm^{-1} is observed.

The origin of the band at 370 cm^{-1} is more uncertain. Because of its low frequency and depolarised nature, it is probably not due to a Nb–F symmetric stretch like the bands at 630 and 585 cm^{-1} in the niobium fluoro and oxo fluoro complexes. The same argument further excludes Nb–O–Nb bridging vibrations, as these are expected to be polarised and at a higher frequency. The most likely possibilities are an asymmetric Nb–F vibration, a low frequent deformation mode of the NbO_2^+ entity or a bridging fluorine mode like in WOF_4 [20]. As for the latter, the bridging fluorine vibration was almost invisible in the Raman spectra while it appeared clearly in the IR spectrum of solid WOF_4. Since this bridging frequency is as high as 555 cm^{-1} it is unlikely that the band at 370 cm^{-1} has the same origin. Griffith and Wickins [25] investigated a series of *cis* dioxo fluorides of molybdenum and tungsten and found in general three bands in the Raman spectra; one strong polarised near 950 cm^{-1}, one moderately intense and depolarised near 900 cm^{-1}, and finally one weakly polarised band at 370 cm^{-1} with moderate intensity. All the bands further appeared as strong absorptions in the IR spectra of the solid complexes. The low frequency band was ascribed to the deformation $\delta(MO_2)$, an A_1 mode in the dioxo complex. Even though none of the three possibilities can be excluded, it is assumed that the latter is the most probable due to the many similarities between the trends and structures in the molybdenum and niobium oxo fluorides.

Having a possible assignment of the bands of the niobium dioxo fluoride does not mean that the molecular formula of the dioxo fluoride is given. There is always an uncertainty of the number of fluorine atoms, but the most probable answer fits with the suggestion that was presented by von Barner et al. [5]; $NbO_2F_4^{3-}$. This fits well with the above mentioned trend of replacing one fluorine with one oxide to achieve a red shift in the symmetric Nb–O stretch of about 40 cm^{-1}. The measured high frequency bands at 880 and 815 cm^{-1} further fits well with the observed bands in solid $Rb_2KNbO_2F_4$ [26]. Such a complex will be an octahedral molecule with a C_{2v} symmetry where the two oxides are in the *cis* position, and thus having no centre of symmetry.

Any oxygen bridging in the form of a Nb–O–Nb band seems unlikely in this case, due to the absence of visible vibrations in the Raman spectra between 815 and 600 cm^{-1}. This does not go for the possible fluorine bridges since the band intensity from this mode is expected to be weak in the Raman spectra. In the IR spectrum (Fig. 11), there might be a weak band at around 520 cm^{-1}, which is not found in the corresponding solid state Raman spec-

trum. IR spectra of the molten samples would in this case give valuable information regarding possible fluorine bridges, but such measurements are faced with extreme experimental difficulties.

3.8. The niobium(V) trioxo fluoride complex in molten FLiNaK

When approaching the ratio of $n_O/n_{Nb} = 3$, the intensity of the bands at 290, 370, 812 and 880 cm^{-1} decreases. As the minimum in solubility is reached, all these bands are gone, and peaks at around 310, (750), 822 and 840 cm^{-1} appear. From these observations it seems that new structural entities are present in the melt. In their work, von Barner et al. [5], assumed that the melt was saturated with oxide and found four bands at 300, 745, 820 and 1044 cm^{-1}. The solubility data presented in this paper show that no absolute saturation exists above ratios $n_O/n_{Nb} = 3$; on the contrary the solubility increases with further addition of Na$_2$O. The first three bands were assigned [5] to the possible existence of NbO$_3$F$_3^{4-}$ species in the melts and the high frequency band at 1044 cm^{-1} to edge sharing NbO$_6$ octahedra. It was also claimed [5] that another hidden band located at the wing of 820 cm^{-1} band could be associated to the presence of corner sharing octahedral NbO$_6$ units in that molten media. This hidden band is probably the ~841 cm^{-1} polarised band which is clearly observed in the present data. The spectra at $n_O/n_{Nb} = 4.28$ looks like the one reported by von Barner et al. [5] for their 'saturated' melt.

Since the bands at 822(p), 750(dp) and 310(dp) cm^{-1} are present in the liquid spectra at ratios $n_O/n_{Nb} > 4$, the species that could be associated to these bands are probably complexes with four oxygens for each niobium. The origin of the polarised band at 840 cm^{-1} must be different since this band no longer is present at $n_O/n_{Nb} = 4.27$, and it seems likely that the band is due to a complex with an oxide to niobium ratio of 3. The polarised character of the band, and the fact that it appears at a high frequency indicates that it is an Nb–O symmetric stretch; similar to the bands at 920 and 880 cm^{-1} that was found for complexes at lower n_O/n_{Nb} ratios. For the mono and dioxo fluoro complexes it was observed that a replacement of one fluorine with one oxygen atom caused the symmetric stretch frequency to drop by approximately 40 cm^{-1}. If the same phenomenon is valid also for further substitution of fluoride by oxide, a frequency of about 840 cm^{-1} would be expected for the complex NbO$_3$F$_3^{4-}$. By introducing a third oxygen, the electron density around the central niobium atom increases, and the strength of the bonds decreases due to a lower electron affinity.

Griffith and Wickins [25] measured IR spectra of the related molybdenum oxo fluoro complexes, and found a decrease in the symmetrical v^s(MoO$_2$) frequency of 49 cm^{-1} when going from K$_2$[MoO$_2$F$_4$]·H$_2$O to K$_3$[MoO$_3$F$_3$]. A similar trend was observed in the Raman

spectra, but there with different cations in the two solids compared. The observations made by Griffith and Wickins [25] fit well with the shift that was found in the present work, and it is therefore likely that the band at 840 cm^{-1} is due to a NbO$_3$F$_x^{(1+x)-}$ complex. As for the number of fluorines that is attached to the complex, a value of 3 seems most likely due to the previously mentioned trend; substitution of one fluorine by one oxygen causes a decrease in the symmetric stretch frequency of about 40 cm^{-1}. It should however be stated that this is just an assumption that seems more likely than other possibilities, and since no bands are associated to Nb–F vibrations in this complex, the value of x will be uncertain.

The complex NbO$_3$F$_x^{(1+x)-}$ will not contain a centre of symmetry, no matter what the value of x is, and it should therefore be possible to find the vibration at 840 cm^{-1} in both the IR and the Raman spectrum. As already mentioned, the concentrations of niobium and oxygen were very low in the sample that was analysed by means of IR, and the spectrum shows more or less only the characteristics of solidified FLiNaK. If x is set to 3, there are two possible configurations for the complex: The *trans*-1,2,6- and the *cis*-1,2,3-trioxo complex. It is not possible to distinguish between these from the spectroscopic results, but according to Griffth and Wickins [25] the *cis* configuration is preferred over the *trans* in d^0-complexes; complexes where the central atom lacks d-electrons. This is the case for Nb(V), and it is therefore assumed that the band at 840 cm^{-1} is due to the complex *cis*-1,2,3 NbO$_3$F$_3$ with a C$_{3v}$ symmetry. Any oxygen or fluoride bridging is impossible to determine due to the lack of bands that can be attributed to the complex.

It should also be mentioned that the solid precipitate that is formed at the ratio $n_O/n_{Nb} = 3$ has a typical perovskite structure, build up by corner sharing NbO$_6$ octahedra with the alkali ion placed in the cavity between eight octahedra [27]. This is a very stable structure, and any dissolved species cannot possess a similar structure without having several terminal oxygens (this would require a ratio n_O/n_{Nb} above 3). The actual solubility of the oxide in FLiNaK is instead due to the above mentioned species that seems to be a lot less stable than the perovskite solid.

3.9. Niobium(V) oxo fluoride complexes with a ratio of n_O/n_{Nb} above 3 in molten FLiNaK

As already mentioned, the bands at 820(p), 750(dp) and 310(dp) cm^{-1} are ascribed to a complex with $n_O/n_{Nb} > 3$. As the solid oxide starts to dissolve, with increasing n_O/n_{Nb} ratio above 3, all these bands become more intense due to the increasing concentration of species in the melt. In addition, a new and very high frequent band appears at around 1045. The polarised band at 820 cm^{-1} and the depolarised band at 750 cm^{-1} are probably of a similar origin as the two bands 880 and 815 cm^{-1} that were observed for the dioxo fluoro complex. The bands appear as a pair, and are due to symmetric and asymmetric Nb–O

vibrations, in this case probably in the NbO_4^{3-} entity. The intensity of one band relative to the other remains constant regardless of the n_O/n_{Nb} and the temperature of the melt. The bands furthermore seems to be present in both the IR and the Raman spectra of the solidified melts, which excludes a centre of symmetry in the species they originate from.

It is tempting to ascribe the band at 310 cm^{-1} to a Nb–O–F vibration in the new complex, since this band appears at a similar frequency, with similar characteristics as the band at 305 cm^{-1} that was connected to such a vibration in the niobium mono oxofluoride complex. In that case it is possible to compare the vibration with known assignments in solid compounds like A_2NbOF_5 (A: Cs, Rb) but now this becomes more difficult. No literature data are available on solid niobium oxofluoro compounds with a sufficiently high oxygen to niobium ratio, and that makes the origin of the band at 310 cm^{-1} uncertain.

Again, any possible oxygen bridging in the form of an Nb–O–Nb band seems unlikely due to the absence of bands in the Raman spectra between 750 and 600 cm^{-1}. As already stated previously, bands due to fluorine bridging modes is expected at lower frequencies, but they might be weak in the Raman spectra. By comparing the IR spectra of solidified FLiNaK with the solidified samples at ratios of $n_O/n_{Nb}=4.3$ and 8.7, there seems be a broad band at around 500 cm^{-1}. This could possibly indicate that these very oxygen rich species contain bridging fluoride, but in the absence of IR spectra of the molten samples no definite conclusion can be made.

Rosenkilde et al. [10] investigated these very oxide rich melts of Nb(V) in molten FLiNaK by means of electrochemistry, and found evidence for the existence of at least two different species in the melts for $n_O/n_{Nb}>4$. The first species appears at $n_O/n_{Nb}>3.8$, while the other species appears at slightly higher ratios. This fits well with the present results, where the bands at 820, 750 and 310 cm^{-1} are ascribed to the first species they observed, and the very high frequency band at around 1045 cm^{-1} to the second species. The fact that the intensity of the high frequency band increases relative to the others as the oxide content is increased, does indeed indicate the presence of two species. It further implies that this latter species is a more oxide rich complex than the first, and the symmetrical high frequency band is ascribed to an Nb=O vibration.

It has been shown earlier in this paper that NbF_7^{2-}, $NbOF_5^{2-}$, $NbO_2F_4^{3-}$ and possibly $NbO_3F_3^{4-}$ are present in the melts for $0=n_O/n_{Nb}=4$. When new bands are found at even higher ratios, it seems likely that new species with an even higher ratio of oxygen to niobium are stable in such melts. Such species have, as far as we know, never been identified in any solvent. An attempt is therefore made to determine the stoichiometry of these complexes. Let us consider the first species, $NbO_4F_x^{(3+x)-}$ that obviously is the reason for the increased solubility in the melts as the ratio $n_O/n_{Nb}>3$. If the number of x is set to 0, one obtains an NbO_4^{3-} complex very similar to the other MO_4^{n-}

complexes that are formed by most other elements in group III A, IV A, V A and VI A. These tetrahedral complexes are stable in both solids and different solvents, except that they are extremely rare for the case of niobium and tantalum. In fact, $YNbO_4$ and $YTaO_4$ are exceptional examples for the two latter elements. In all the different polymorphs of solid Nb_2O_5, the tetrahedral configuration is in clear minority versus the dominating octahedral groups of distorted NbO_6 units [28]. It is therefore highly unlikely that the very rare NbO_4^{3-} tetrahedron is present in molten FLiNaK, and the value of x is thus more likely to be higher than 0.

Adopting the above arguments, it now remains to determine how many fluorine atoms are present in the $NbO_4F_x^{(3+x)-}$ species. It might be the dimer $Nb_2O_8F_2^{8-}$ with two bridging fluorine bands since the IR measurements not could exclude such bridges. The complex would possess a D_{2h} symmetry, much similar to the dimeric Nb_2Cl_{10} that was investigated by Edwards and Ward [29]. This is however just a speculation. There might be several possible answers to what the structure of $NbO_4F_x^{(x-3)-}$ looks like. All the other complexes that have been observed at lower n_O/n_{Nb} ratios have turned out to be monomeric, and the new species is therefore assumed to be the same since there is no clear evidence for bridging bands. The most probable solution then seems to be an $NbO_4F_2^{5-}$ with the two fluorines in the *cis* position to avoid a centre of symmetry. The complex then has a C_{2v} symmetry, and the band at 310 cm^{-1} is probably due to a bending vibration of the Nb–O–F entity. It further has a remarkably high charge; a good example of the extreme complexing abilities of the heavy metals like niobium, tantalum, tungsten and molybdenum. Going from $NbO_3F_3^{4-}$ to $NbO_4F_2^{5-}$ a reduction in the symmetrical Nb=O stretch of about 20 cm^{-1} is observed, which is only half of what has been observed earlier in substitution of one fluorine with one oxygen. This might be explained by the fact that the electron density around the central niobium atom is already rather large, and that the substitution now has a smaller effect.

The temperature dependence of the melt with $n_O/n_{Nb}=3.6$ (Fig. 10), showed that the band at 840 cm^{-1} became stronger relative to the band at around 822 cm^{-1} at higher temperatures. The following equilibrium seems to be established for the two species:

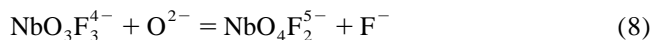$$NbO_3F_3^{4-} + O^{2-} = NbO_4F_2^{5-} + F^- \qquad (8)$$

Fig. 10 indicates that the equilibrium shifts towards the left side of Eq. (8) when the temperature increases, and the standard enthalpy ΔH^0 must be negative for the reaction. The standard entropy is somewhat more difficult to determine, but the value is probably not large since there is no change in the number of species. The negative enthalpy is therefore the driving force of the reaction, and causes any free oxide to react with the niobium trioxo complex until the concentration of this is negligible. This seems to occur when $n_O/n_{Nb}>4$.

The very high frequency band at around 1045 cm^{-1} has already been assigned to an even more oxide rich species in the melts, but the structure of this complex is yet to be determined. It is believed to be an NbO_6 polyhedra, but not necessarily with a O_h symmetry. The high frequency indicates the presence of a strong Nb=O band, and the other Nb–O bands must be weaker in order to stabilise the unit. The polyhedra is thus a distorted octahedra, and probably consist of one or two terminal oxygens while the remaining oxygen forms bridges to similar units. The presence of this high frequency band in the IR and Raman spectra of the solidified melts supports the existence of non-centro-symmetric species in the melt. Spectra of the high temperature solid Nb_2O_5 showed that the vibration corresponding to edge sharing NbO_6 units appeared at 992 cm^{-1} [30], and it is probably a related structure that causes the band at around 1045 cm^{-1}. It should be emphasised that the distorted octahedra is not an ion like NbO_6^{7-}, but rather an oxide bridged network of loosely bonded NbO or NbO_2 units, with an overall ratio of oxide to niobium at 6. This network like structure of NbO_6 is consistent with recent Raman spectroscopic studies in Nb_2O_5–$K_2S_2O_7$ system [31].

Rosenkilde et al. [10] analysed pure FLiNaK with additions of Na_2O by means of electrochemistry, and found that the oxidation/reduction peaks for the oxide ion appeared at a similar potential as the peaks in melts with $n_O/n_{Nb} \sim 6$. This further indicates that the bridging oxygen is not bonded to the niobium like the Nb–O bands that were found in complexes for melts with a lower ratio of oxide to niobium. Neither is it a bridging oxygen like those in $NbOCl_3$ [23] since no bands were found in the range 600–800 cm^{-1}. The oxygen atoms are probably loosely bonded and thus appear to be almost free oxide ions as indicated by the electrochemical study [10].

3.10. Raman spectroscopic analysis of Nb$_2$O$_5$ dissolved in FLiNaK

All the samples from the solubility experiment of Nb_2O_5 in FLiNaK were used to measure the Raman spectra in the molten state. The spectra had same shape and showed the same peaks and relative intensities as the samples with a n_O/n_{Nb} ratio between 2 and 3 (see Fig. 7). This is in agreement with the solubility data, indicating formation of a $NbO_2F_x^{(x-1)-}$ complex together with a solid compound, $AlkNbO_3$.

4. Conclusions

Raman spectroscopy and oxide and Nb solubility measurements of Na_2O–FLiNaK–K_2NbF_7 melts show that at least four different niobium oxo fluoro species are formed. The solubility data are indicating the formation of different $NbO_yF_x^{(2y+x-5)-}$ species where y and x take values depending on the n_O/n_{Nb} ratio in the melt. From the Raman measurements, the existence of NbF_7^{2-} (C_{2v}), $NbOF_5^{2-}$ (C_{4v}) and $NbO_2F_4^{3-}$ (C_{2v}) at n_O/n_{Nb} ratios up to 2 are well established. At $n_O/n_{Nb} = 3$ the solubility data indicate the precipitation of a solid compound such as $AlkNbO_3$. At this ratio the spectral features implies that formation of trio-oxo fluoro complexes in the melt is possible. At $n_O/n_{Nb} > 3$ the solubility data are consistent with a dissolution of the $AlkNbO_3$ solid, and formation of a $NbO_4F_x^{(x-3)-}$ species. At $n_O/n_{Nb} > 4$ a oxygen rich solid seems to precipitate. The Raman spectra indicate the existence of $NbO_4F_2^{5-}$ species as well as $(NbO_6)_n$ network structures in these melts.

References

[1] G.W. Mellors, S.J. Senderhoff, J. Electrochem. Soc. 112 (1965) 266.

[2] E. Christensen, X. Wang, J.H. von Barner, T. Østvold, N.J. Bjerrum, J. Electrochem. Soc. 141 (1994) 1212.

[3] F. Matthiesen, E. Christensen, J.H. von Barner, N.J. Bjerrum, J. Electrochem. Soc. 143 (1996) 1793.

[4] F. Matthiesen, P.T. Jensen, T. Østvold, Acta Chem. Scand. 52 (1998) 1000.

[5] J.H. von Barner, E. Christensen, N.J. Bjerrum, B. Gilbert, Inorg. Chem. 30 (1991) 561, and references therein.

[6] S. Pizzini, R. Morlotti, Electrochim. Acta 26 (1965) 1033.

[7] H. Mediaas, J.E. Vindstad, T. Østvold, Light Metals (1996) 1129.

[8] B. Gilbert, T. Materne, Appl. Spectrosc. 44 (1990) 299, and references therein.

[9] V. Dracopoulos, G.N. Papatheodorou, in: H.C. Delong, S. Deki, P.C. Trulove, R.W. Bradshaw, G.R. Stafford (Eds.), Proceedings of the 11th International Symposium on Molten Salts, The Electrochemical Society Proceeding Series, Electrochemical Society, Pennington, NJ, 1998.

[10] C. Rosenkilde, Aa.F. Vik, T. Østvold, E. Christensen, N.J. Bjerrum, J. Electrochem. Soc., manuscript in preparation.

[11] S.A. Kuznetsov, A.L. Glagolevskaya, S.V. Kuznetsova, A.T. Belyaevskii, P.T. Stangrit, Plenum Press, 1991, p. 1920, translated from Zhurnal Prikladnoi Khimii 63 (1990) 2078.

[12] O.J. Keller, J. Inorg. Chem. 2 (1963) 783.

[13] J.L. Hoard, J. Am. Chem. Soc. 2 (1939) 1252.

[14] G.M. Brown, L.A. Walker, Acta Crystallogr. 20 (1966) 220.

[15] J.S. Fordyce, R.L. Baum, J. Chem. Phys. 44 (1966) 1166.

[16] G. Pausewang, R. Schmitt, K. Dehnicke, Z. Anorg. Allg. Chem. 408 (1974) 1.

[17] G. Pausewang, Z. Naturforsch. 26b (1971) 1218.

[18] G. Pausewang, Z. Naturforsch. 29b (1971) 49.

[19] A.M. Srivastava, A.F. Ackerman, Mater. Res. Bull. 26 (1991) 443.

[20] T.G. Burke, D.F. Smith, A.H. Nielsen, J. Chem. Phys. 20 (1952) 447.

[21] L.E. Alexander, I.R. Beattie, A. Bukovszky, P.J. Jones, C.J. Marsden, C.J. Van Schalkwyk, J. Chem. Soc., Dalton Trans. 81 (1974).

[22] J.H. Holloway, H. Selig, H.H. Claasen, J. Chem. Phys. 54 (1971) 4305.

[23] I.R. Beattie, K.M.S. Livingston, D.J. Reynolds, G.A. Ozin, J. Chem. Soc. A 8 (1970) 1210.

[24] J.A.S. Howell, K.C. Moss, J. Chem. Soc. A 9 (1971) 270.

[25] W.P. Griffith, T.D.J. Wickins, J. Chem. Soc. A 6 (1968) 400.

[26] G. Pausewang, W. Rudorf, Z. Anorg. Allg. Chem. 69 (1969) 364.

[27] M.D. Fontana, G.E. Kugel, G. Metrat, C. Carabatos, Phys. Stat. Sol. (b) 103 (1981) 211, and references therein.

[28] A.A. McConnell, J.S. Anderson, C.N.R. Rao, Spectrochim. Acta 32A (1976) 1067.

[29] D.A. Edwards, R.T. Ward, J. Chem. Soc. A 8 (1970) 1617.

[30] U. Balachandran, N.G. Eror, J. Mater. Sci. Lett. 1 (1982) 374.

[31] S. Boghosian, F. Borup, R.W. Berg, in: P.C. Trulove, H.C. DeLong, G.R. Stafford, S. Deki (Eds.), Molten Salts XI, The Electrochemical Society Proceeding Series, Vol. 98-11, Electrochemical Society, Pennington, NJ, 1998, p. 536.