be expected from either type of ground state.[28] In contrast to the ground state, the excited state is severely flattened; hence, there is a large difference between the absorption and emission energies.

The absorption maximum of the $[Cu(mmp)_2]^+$ system is somewhat anomalous because it occurs at a higher energy than that of $[Cu(dmp)_2]^+$. However, the mmp ligand differs from the others in that it carries only one alkyl substituent, and the energies of the π^* orbitals of phenanthroline are known to vary with the degree of substitution.[29]

Thus, the evidence is convincing that geometric relaxation of the excited state is a very important factor influencing the lifetimes of the charge-transfer states of $[Cu(dmp)_2]^+$ and related systems. Previous results on mixed-ligand complexes of copper(I) can be explained in the same way.[30] In addition, essentially the same model has been used to account for fluorescence lifetimes and quantum yields for a series of stilbene derivatives.[31,32]

We should also point out that the solvent medium has an influence upon the geometric relaxation within the excited state. This effect can be demonstrated by a comparison of the data for the $[Cu(L1)_2]^+$ and $[Cu(L2)_2]^+$ systems. Locally at the metal center, the interligand steric interactions are expected to be similar for the two complexes. Nevertheless, the emission maximum occurs at higher energy for the $[Cu(L1)_2]^+$ system because flattening of the complex involves movement of the phenanthrolines against the solvent cage as well as against each other. In essence, substituents that protrude into the solvent medium experience a drag, which hinders the excited-state rearrangement. In accord with this reasoning $[Cu(dmp)_2]^+$ and $[Cu(dbp)_2]^+$ emit at almost the same wavelengths in fluid CH_2Cl_2 solution at room temperature, while they exhibit quite different emission maxima in a rigid matrix at 90 K.

Finally, it is interesting to note that, despite the high emission intensities and long lifetimes exhibited by $[Cu(L1)_2]^+$ and $[Cu(L2)_2]^+$ in a rigid glass, the same complexes give almost no detectable emission in fluid solution. The quenching can probably be attributed to another type of structural reorganization that can occur in fluid solution, namely internal exciplex formation between the copper center and one of the aniline nitrogens. As noted above, interactions with Lewis bases are very effective at quenching CT states in these copper systems.[14-17] If longer lifetimes in fluid solutions are to be obtained, bulky substituents must be designed or chosen so as to avoid internal exciplex quenching.

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Vibrational Spectra of Niobium(V) Fluoro and Oxo Fluoro Complexes Formed in Alkali-Metal Fluoride Melts

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Raman spectra of the molten system $LiF-NaF-KF-K_2NbF_7$ at 650 °C indicate the presence of NbF_7^{2-} ions with vibrational frequences at 626 (p), 371 (dp) and 290 cm^{-1} (dp). With the addition of small amounts of oxide, vibrational frequences due to a $NbOF_n^{(n-3)-}$ species are observed at 921 (p), 583 (p) and 307 cm^{-1} (dp) for oxide to niobium(V) mole ratios up to approximately 2. The most probable value of n is 5. Infrared spectra of solidified melts support the existence of a niobium-oxygen double bond in this complex. The vibrational spectrum is in accord with the band pattern of monomeric $NbOF_5^{2-}$ with a C_{4v} symmetry. Further additions of oxide lead to formation of $NbO_2F_n^{(n-1)-}$ complexes. Bands in the Raman spectrum of the melt at 878 and 815 cm^{-1} and in the infrared spectrum of the solidified melt at 879 and 809 cm^{-1} are ascribed to stretching vibrations of the NbO_2 entity. The Raman spectrum and the infrared spectra are consistent with the presence of $NbO_2F_4^{3-}$ ions of C_{2v} symmetry. Melts saturated with oxide show vibrational frequencies that are likely to be due to $[NbO_3F_n]^{(1+n)-}$-containing species which, furthermore, seem to polymerize.

Introduction

Only very few Raman spectroscopic investigations have been performed on fluoride melts. This is probably due to the experimental difficulties in handling such extremely corrosive systems at elevated temperatures. Most of the previous publications have been concerned with the species formation in the industrial important cryolite melts.[1-3] As far as we know, only one investigation concerning fluoride melts containing refractory metal fluorides (ZrF_4) has been reported in the literature.[4]

This is rather surprising since it is well-known[5-7] that refractory metals such as niobium and tantalum can be plated from metal fluorides dissolved in alkali-metal fluoride melts and in this way give very corrosion-resistant surface layers.

Solid K_2NbF_7 has been shown to contain discrete NbF_7^{2-} ions with a C_{2v} symmetry.[8] The Raman spectrum[9] of this salt has bands at 388, 630, and 782 cm^{-1}. Contrary to this, solid $CsNbF_6$, which contains octahedral NbF_6^-, shows Raman bands[9] at 280, 562, and 683 cm^{-1}. Infrared spectra[10] of solid K_2NbF_7 and spectra[10] of Nb(V) in molten KF-LiF showed bands characteristic of the NbF_7^{2-} ion.

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The complex formation of Nb(V) dissolved in aqueous hydrogen fluoride depends on the HF concentration.[9] Raman spectra of solutions with high HF contents (>25%) indicated the presence of NbF_6^- complexes whereas oxo fluoro complexes of composition $NbOF_5^{2-}$ were formed in solutions with low HF concentrations (<25%). The oxo fluoro complex showed a polarized band at 920 cm^{-1} characteristic of a niobium–oxygen double-bond vibration. Raman and infrared spectra of $NbOF_5^{2-}$ in solutions and solids were consistent with six-coordination of C_{4v} symmetry.[9]

A vibration of 920 cm^{-1} also appeared in the infrared spectrum of hydrolyzed Nb(V) in LiF–KF melts.[10] X-ray diffraction patterns of the solidified melt compared well with the one of solid[11] K_3NbOF_6, and $NbOF_6^{3-}$ was therefore believed to be present even in the melt.[10]

Solid dioxofluorides of the type $Alk_3(NbO_2F_4)$ (Alk = Na, K, Rb) are also known to exist.[12] The $(NbO_2F_4)^{3-}$ ion has a six-coordinate arrangement of the ligands with the two oxygen atoms in cis position to each other (C_{2v} symmetry).[12]

The aim of the present work is to investigate the formation of Nb(V) fluoro and oxofluoro complexes in eutectic LiF–NaF–KF melts (FLINAK) as a function of the oxide contents. Possible structures for the complexes will be discussed on the basis of Raman spectra of the melts and infrared spectra of solidified melts.

Experimental Section

All weighings and handling of chemicals were performed in nitrogen- or argon-filled gloveboxes with very low water contents (dew point approximately −45 °C).

The alkali-metal fluorides that made up the FLINAK solvent were analytical grade chemicals (Merck) purified by recrystallization in the following way: 100 g of the salt was placed in a platinum crucible and subjected to a vacuum treatment at 400 °C for approximately 8 h in order to remove moisture. The salts were then heated to a temperature 20 °C above the melting point under an argon atmosphere. After being melted, the samples were slowly cooled (4 °C/h) to a temperature 20 °C below the melting point. From this temperature down to room temperature, a more rapid cooling was applied (elapsed time 10 h). By this treatment, the impurities were concentrated in the central part of the solidified lump. After careful crushing, the impure part of the lump could be manually divided from the rest. In the case of LiF, this procedure was repeated one more time.

K_2NbF_7 was obtained from Alfa Chemicals Inc. The salt was analyzed for potassium and niobium by atomic absorption and for fluoride by potentiometric measurements with fluoride ion selective electrodes (from Radiometer). Anal. Found: Nb, 30.4 ± 0.1; K, 26.8 ± 0.3; F, 42.9 ± 0.8. Calcd: Nb, 30.6; K, 25.7; F, 43.7. The X-ray powder diffraction pattern only showed lines characteristic of K_2NbF_7.[8]

Na_2O and Nb_2O_5 were obtained from Aldrich (98%) and CERAC (optical grade, 99.95%) respectively. The samples for the Raman spectroscopic measurements were premelted in glassy-carbon crucibles at 700 °C under an argon atmosphere. K_3NbOF_6 was prepared by mixing of K_2NbF_7 and KF dissolved in aqueous HF solution. The K_3NbOF_6 precipitate was washed with distilled water and dried.

Since no transparent material, except diamond, which can withstand the corrosion from FLINAK is known, windowless cells of high-temperature resistant (spectroscopic grade) graphite were employed as containers for the Raman spectroscopic measurements. These cells were filled with 220–240 mg of the samples and placed in quartz tubes under an argon atmosphere (0.5 atm pressure).

The whole setup was placed in a homemade furnace[13] provided with an Inconel insert and Kanthal wire heating element allowing temperatures up to 1200 °C. The design of the furnace is intended rather to maximize the light gathering and reject the blackbody radiation than to obtain the best temperature homogeneity. Accordingly, the temperature could only be adjusted within ±5 °C.

The Raman spectra were excited by using the 4880 Å radiation (300 mW) from an argon ion laser (Coherent Radiation Type 52B). The spectra were recorded with a modified Cary 81 spectrometer, provided with an EMI 9558A photomultiplier.[14] The spectrometer has been interfaced with a microcomputer (IBM PS/2 30) for the acquisition and manipulation of the spectra. The spectrum of a single component was obtained from mixed spectra by computer subtraction. The time constant was kept as low as possible (0.2 s) to avoid distortion of the spectra, especially when high scan rates were used. The slit widths were between 4 and 6 cm^{-1} depending on the sample. The scan rates were typically 125 cm^{-1}/min, but faster scan rates (500 cm^{-1}/min) had to be used on samples that were evaporating. Indeed, samples only containing low amounts of oxides (less than one oxide for each Nb) were very difficult to run because of evaporation of niobium fluoride, causing cloudiness of the windows. The samples for the infrared spectra were prepared by mixing the solidified melt with KBr in the glovebox. The mixture was pressed into pellets which were placed in the sample compartment under vacuum. The spectra were recorded with a Bomem Type DA3-26 instrument.

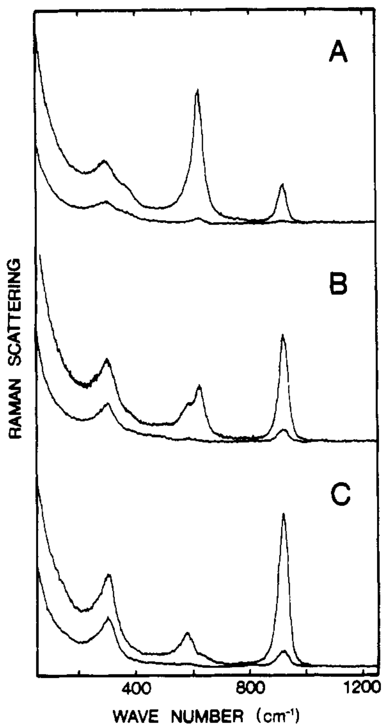

Figure 1. Raman spectra of 2.7 mol % Nb(V) in eutectic LiF–NaF–KF melts at 650 °C with low oxide contents. Ratios of oxide to niobium (mol/mol) corrected for oxide in the solvent were as follows: (a) 0.26; (B) 0.76; (C) 0.93.

Results

Variation of the Spectra with the Oxide Content. Figure 1 shows Raman spectra of Nb(V) dissolved in a FLINAK melt at 650 °C. The concentration of niobium (2.7 mol %) has been kept constant and the amounts of oxide added to the melt are increased when going from spectrum 1A to 1C.

Since some oxide is formed during the handling of the solvent, none of the spectra represent pure niobium–fluoride species (as we shall see later, the affinity of oxide to Nb(V) is large, resulting in an almost quantitative reaction between oxide and niobium).

A Raman spectrum of Nb(V) dissolved in FLINAK without addition of oxide is shown in Figure 1A. Due to the previously mentioned oxide impurities, a mole ratio of oxide to niobium of 0.26 is obtained. Bands are observed at 290 (broad), 371 (shoulder), 583, 626, and 921 cm^{-1}. With addition of oxide up to a O^{2-}/Nb ratio of 0.92 (Figure 1C), the bands at 365 and 626 cm^{-1} decrease while the bands at 583 and 921 cm^{-1} increase and the band at 290 cm^{-1} is shifted toward higher frequencies (310 cm^{-1}).

Figure 2A shows a Raman spectrum of a Nb(V)–FLINAK melt where the ratio of oxide to niobium(V) is greater than one (O^{2-}/Nb = 1.27). It is clear that new bands appear in the Raman spectrum. From a comparison of Figure 2A with Figure 1C, it is evident that the bands at 921 and 583 cm^{-1} are diminishing with increasing oxide ratio, while a new strong polarized band appears at 878 cm^{-1} together with a depolarized band at 815 cm^{-1}.

In Figure 2B is shown a spectrum where the oxide to niobium(V) ratio has also been further increased (O^{2-}/Nb = 2.4). The 921-cm^{-1} vibration appears only as a weak shoulder on the now

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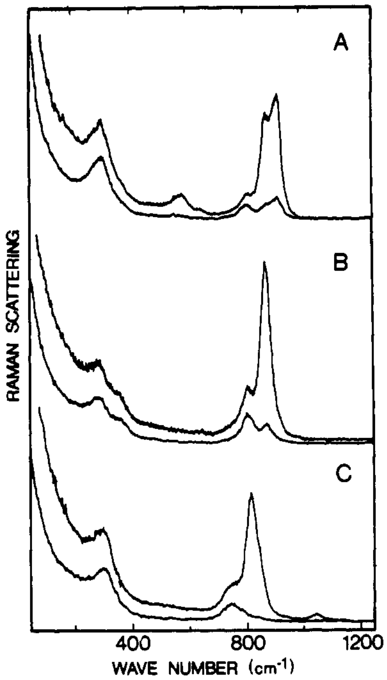

Figure 2. Raman spectra of 2.7 mol % Nb(V) in LiF–NaF–KF melts with high oxide contents. Ratios of oxide to niobium (mol/mol) corrected for oxide in the solvent were as follows: (A) 1.27; (B) 2.38; (C) saturated with oxide. Temperatures were 650 °C.

very strong band at 878 cm^{-1}; furthermore, the band at 583 cm^{-1} has completely vanished. Also two depolarized bands at 284 and at 360 cm^{-1} are now observed.

Finally, when the melt is saturated with oxide, a band pattern like the one in Figure 2C is seen. In comparison with Figure 2B, the vibrations at 284, 360, 815, and 878 cm^{-1} have vanished and a new set of bands appears at 300 (dp), 820 (p), 750 (dp), and 1044 (p) cm^{-1}.

Temperature Variations. The melts that give rise to the Raman spectra shown in Figures 1C and 2A have been subjected to a study of the temperature influence on the Raman spectra. The spectra of the Figure 2A composition were invariant in the 650–775 °C temperature range, whereas the Figure 1C composition gave temperature-dependent Raman spectra as shown in Figure 3 (the Raman spectrum at 653 °C is identical with that in Figure 1C).

Certainly all these changes in band patterns point in the direction of the formation of a number of species as functions of the oxide to niobium ratio and temperature. It seems that at least three different species are formed with increasing oxide contents. The nature of these species will be discussed in the following section.

Discussion of the Nb(V) Complex Formation. Nb(V) Fluoro Complexes. Since the intensities of the bands at 371 and 626 cm^{-1} are diminishing with increasing oxide contents of the melt, these bands are ascribed to vibrations from a niobium fluoro complex. The broad band at 290 cm^{-1} (Figure 1A) probably consists of two vibrations, of which the low-frequency component is due to a niobium fluoro complex and the other vibration (~310 cm^{-1}) to an oxofluoro complex (vide infra). As previously mentioned both NbF_7^{2-} and NbF_6^- complexes are known to exist in solid compounds.[8,9] In order to clarify which of these niobium (V) complexes are present in FLINAK, we found it useful to reexamine the Raman spectrum of solid K_2NbF_7. In Table I the Raman frequencies of this compound are listed together with the frequences of other six-, seven-, and eight-coordinated metal fluoro complexes known from the solid state and in aqueous HF and molten salt solutions. Our Raman spectrum of solid K_2NbF_7 (not shown) is in accordance with previous results[9] except for the appearance of additional weak bands at 275 and 239 cm^{-1}.

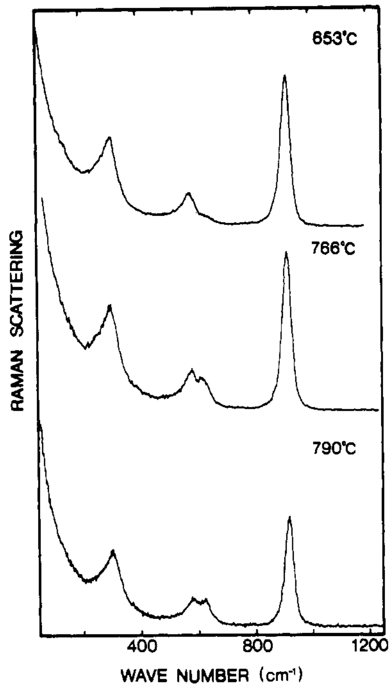

Figure 3. Raman spectra of 2.7 mol % Nb(V) in LiF–NaF–KF melts with a oxygen to niobium ratio of 0.93 at different temperatures (shown on the figure).

Table I. Raman Frequencies of Niobium(V) and Zirconium(IV) Fluoride Complexes in Solutions, Melts, and the Solid State[a]

A. Six-Coordinated Metal Atoms

complex	medium	vibrations, cm^{-1} ν_5	ν_2	ν_1	ref
NbF_6^-	HF, aqueous	280		685	9
NbF_6^-	$CsNbF_6$, solid	280	562	683	9
ZrF_6^{2-}	Li_2ZrF_6, solid	251	303	585	4
ZrF_6^{2-}	LiF–NaF, melt	250[b]		577	4

B. Seven- and Eight-Coordinated Metal Atoms

complex	medium	vibrations,[c] cm^{-1} ν_{M-F}	$\nu_{M-F,as}$	$\nu_{M-F,ss}$		ref
ZrF_7^{3-}	Na_3ZrF_7, solid	250	363	556		4
$ZrF_x^{(x-4)-}$	LiF–NaF, melt	258		555		4
NbF_7^{2-}	K_2NbF_7, solid		388	630	782	9
NbF_7^{2-}	K_2NbF_7, solid	275	388	631	791	this work

C. Niobium(V) in LiF–NaF–KF Melts

complex	medium	vibration, cm^{-1} ν_{M-F}	$\nu_{M-F,as}$	$\nu_{M-F,ss}$	ref
$NbF_n^{(n-5)-}$	LiF–NaF–KF, melt	290	371	626	this work

[a] Key: ss = symmetric stretch; as = antisymmetric stretch. [b] Suggested to be a T_{2g} mode collapsed into one band.[4]

From Table I, several important trends can be observed. The strongest bands (ν_1 in the case of octahedral coordination) show only minor changes in frequency when going from the solid state to aqueous HF or molten salt solutions. It can further be seen, in the case of both Nb(V) and Zr(IV), that this band is shifted toward lower frequencies with increasing coordination number of the metal.

Rather drastic frequency changes are observed for the lower frequency bands as a function of the coordination number. E.g., when the ν_2 vibration of NbF_6^- is compared to the corresponding vibration of NbF_7^{2-}, a decrease (from 562 to 388 cm^{-1}) is evident in the solid-state Raman spectrum.[8] Finally a low-frequency band around 280 cm^{-1} is observed in the spectrum of both NbF_6^- and NbF_7^{2-} complexes.

The band patterns obtained in this work for niobium(V) dissolved in FLINAK (not considering the oxide bands) are very close to the one for the NbF_7^{2-} anion in solid K_2NbF_7. Although it is not always correct to draw conclusions from comparison of band positions in the solid state and in the melt, we feel it is safe to

Table II. Raman and Infrared Vibrational Frequences of $NbOX_n$ Species (X = F, Cl)

		vibrations, cm^{-1}					
species	medium	$\nu_{Nb=O}$	ν_{Nb-X}			method	ref
$NbOF_5^{2-}$	HF solutions	920–935	595	290		Raman	9
$NbOF_5^{2-}$	$K_2NbOF_5 \cdot H_2O$ solid	935	600	295		Raman	9
$NbOF_5^{2-}$	$K_2NbOF_5 \cdot H_2O$ solid	932	*a*			infrared	9
$NbOCl_5^{2-}$	Cs_2NbOCl_5 solid	922		319		infrared	15
$NbOF_n^{(n-3)-}$	KF–LiF melt	920	*a*			infrared	10
$NbOF_n^{(n-3)-}$	LiF–NaF–KF melt	921 (p)[b]	583 (p)	307 (dp)	266	Raman	this work
$NbOF_6^{3-}$	K_3NbOF_6 solid	910	545	295		Raman	this work
$NbOF_n^{(n-3)-}$	LiF–NaF–KF melt solidified	912	540			infrared	this work

[a] Range not measured. [b] Key: (p) polarized; (dp) depolarized.

conclude that the NbF_7^{2-} ion is also present in the melt since the two strongest bands of this species in the solid compound (631 and 388 cm^{-1}) are also observed in the Raman spectrum of the melt, at very near the same frequencies (626 and 371 cm^{-1}). The absence of the strongest band of NbF_6^- (683 cm^{-1}) in the melt spectrum further supports this explanation.

Monooxo Fluoro Complexes of Niobium(V). The bands at 583 and 921 cm^{-1}, which increase with addition of oxide (Figure 1B,C), must be due to a niobium oxo fluoro species. From Table II, it can be seen that a niobium(V)–oxygen double bond causes a vibration in the 920–935-cm^{-1} region (both Raman and infrared active) as well in the case of niobium oxo fluoro[9,10] as in niobium oxo chloro[15] species. Bridging oxygen–niobium bonds also have one vibration that is both Raman and infrared active, but at much lower frequencies (e.g. 770 cm^{-1} for $NbOCl_3$ solid[16]).

It is interesting to note that the highest metal–fluoride vibration decreases in frequency by approximately 40 cm^{-1} when two fluorides are substituted with one oxide in the case of both tungsten and molybdenum[17,18] (i.e. $WF_6 \rightarrow WOF_4$ or $MoF_6 \rightarrow MoOF_4$). This trend is also seen in the case of niobium(V) where band positions are observed at 630 and 600 cm^{-1} for solids that contain the complex ions NbF_7^{2-} and $NbOF_5^{2-}$ respectively.[9] (See Tables I and II.) If only one fluorine atom is substituted (i.e. $NbOF_6^{3-}$), a greater decrease in frequency of this niobium–fluoro stretching vibration is observed (~85 cm^{-1}).

In the case of bridging fluoride, bands with a lower frequency than the bridging oxide are observed (e.g. at 520 cm^{-1} in liquid WOF_4[18]).

The frequencies of the lower niobium fluoride vibrations are rather independent of the number of fluorine atoms in the niobium oxo fluoro complexes. We found a vibration at 295 cm^{-1} for $NbOF_6^{3-}$ in solid K_3NbOF_6 identical with the 295-cm^{-1} vibration observed by Keller[9] for $NbOF_5^{2-}$ in the $K_2NbOF_5 \cdot H_2O$ compound.

From what has been said above, it seems obvious that the 921-cm^{-1} vibration observed in our Raman experiments is due to a terminal niobium–oxygen double bond.

We also measured the infrared spectrum of the solidified melt that was previously used to record the Raman spectrum shown in Figure 1C. Observation of a band at 912 cm^{-1} in the infrared spectrum further supports the assignment of the 921-cm^{-1} vibration to a niobium–oxygen double bond. We ascribe the Raman bands at 583 and 307 cm^{-1} to niobium–fluoro vibrations in accordance with previous assignments of bands in monooxofluoroniobium(V) complexes.[9]

Since no bands are observed with frequencies between 307 and 583 cm^{-1}, it is not likely that fluoride bridging takes place. Oxide bridging also does not seem reasonable, since no bands are observed in the 600–800-cm^{-1} region. The niobium oxo fluoro species is therefore probably monomeric of the type $NbOF_n^{(n-3)-}$. It is a question whether *n* is equal to 5 or 6, but although neither of these possibilities can be excluded, we find a value of 5 most likely, since the vibration at 583 cm^{-1} observed in our Raman spectrum is not very far from the niobium–fluoro vibration at 595 cm^{-1} of the $NbOF_5^{2-}$ complex ion in aqueous HF solutions at room temperature.[9] The Raman band pattern is consistent with a C_{4v} symmetry of the $NbOF_5^{2-}$ ion with a stretch vibration (A_1) due to Nb=O (921 cm^{-1}), a stretch vibration (A_1) from Nb—F (583 cm^{-1}), and a Nb–F vibration at 307 cm^{-1}, which could be due to B_2 and/or E. The 583-cm^{-1} vibration is probably of an origin similar to that for the ν_2 vibration found for $ReOF_5$.[19]

This explanation is in contrast to the one given by Fordyce and Baum[10] for the oxo fluoro complex formation of Nb(V) in LiF–KF melts. On the basis of observation of an infrared vibration at 920 cm^{-1} and a X-ray diffraction recording of a solidified melt, they claimed[10] that $NbOF_6^{3-}$ exists in molten KF–LiF. It should however be kept in mind that a vibration around 920 cm^{-1} is typical for both $NbOF_6^{3-}$ and $NbOF_5^{2-}$ and that dissociation (in this case $NbOF_6^{3-} \rightarrow NbOF_5^{2-} + F^-$) often takes place with increasing temperature (solid → melt).

Finally it can be seen from Figure 3 that a temperature-dependent equilibrium exists between NbF_7^- and $NbOF_5^{2-}$:

$$NbF_7^{2-} + O^{2-} \rightleftharpoons NbOF_5^{2-} + 2F^- \tag{1}$$

Since the 626-cm^{-1} band increases with temperature, this equilibrium is clearly shifted to the left with increasing temperature.

Dioxo Fluoro Species of Niobium(V). When the oxide to niobium ratio exceeds 1, a new species characterized by bands at 878 (p), 815 (dp), 360 (dp), and 284 cm^{-1} (dp) appears. These bands have a maximum intensity at an oxide to niobium ratio of approximately 2 (Figure 2B). The 878- and 815-cm^{-1} bands lie in the region of niobium–oxygen stretching vibrations. The highest frequency that is normally due to a symmetric M=O stretch vibration (A_1) is somewhat lower than that observed (920 cm^{-1}) for a niobium–oxygen double bond of $NbOX_n$ (X = F, Cl) species.[9,10,16]

It seems to be a general trend that introduction of a second oxygen atom in oxo halides of vanadium, niobium, molybdenum, and tungsten lower the frequency of the symmetric metal–oxygen stretch vibration. In going from a MOX_4 (M = V, Nb, Mo, W; X = F, Cl) to a MO_2X_n (*n* = 3, 4) species, this frequency is diminished by approximately 100 cm^{-1} (e.g. VOF_4^- in $CsVOF_4$[20] and $VO_2F_4^{3-}$ in $K_3VO_2F_4$[21] give a decrease of 103 cm^{-1}). This decrease is somewhat less when MOX_5 species are compared with MO_2X_4 species, typically around 30–50 cm^{-1}. Thus for Cs_2MoOCl_5[15] and $Cs_2MoO_2Cl_4$[21] the difference is 32 cm^{-1}, and for $NbOF_5^{2-}$ and $NbO_2F_4^{3-}$ in potassium salts, the difference is 45 cm^{-1} (see Tables II and III).

When we compare our highest Raman frequency of $NbOF_5^{2-}$ in FLINAK melts (921 cm^{-1}) to the one found for the $NbO_2F_n^{(n-1)-}$ complex in the melt (878 cm^{-1}), a decrease of 43 cm^{-1} is evident. This 878-cm^{-1} vibration is still due to a symmetric Nb=O stretch vibration, but it has been lowered because of the presence of another oxygen. The appearance of a vibration at 879 cm^{-1} in our infrared spectrum of the solidified melt (Figure 4) further

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Table III. Raman and Infrared Spectral Data of MO_yF_n Species (y = 2, 3)

		vibrations,[f] cm^{-1}				
species	medium	$\nu_{MO_2,ss}$	$\nu_{MO_2,as}$	other bands	method	ref
$(NH_4)_2[MoO_2F_3]$	solid	965	916		Raman	21
		951	898	747[a]	IR	21
$Na_2[MoO_2F_4]$	aqueous solution	951 (p)	920 (dp)		Raman	21
		948	912		IR	21
$K_2[MoO_3F_2]$	aqueous solution	903		295[d] 722[b]	Raman	21
		904	850	295[d] 714[b]	IR	21
$(NH_4)_3[MoO_3F_3]$	solid	900	824	652	Raman	21
		902	813	460	IR	21
$K_3[VO_2F_4]$	solid	928	890	546[c]	Raman	21
		920	883	362	IR	21
		905	871		IR	12
$K_2[VO_2F_3]$	solid	922	898	550[c] 345[a]	IR	22
$K_3[NbO_2F_4]$	solid	890	811		IR	12
$NbO_2F_x^{(x-1)-}$	LiF-NaF-KF melt	878 (p)	815 (dp)	360 (dp) 284 (dp)	Raman	this work
	solidified melt	879	809		IR	this work
$NbO_3F_n^{(6+n-5)-}$	LiF-NaF-KF	820 (p)	750 (dp)	300 (dp)	Raman	this work

[a] Mo-F-Mo bridging vibration. [b] Mo-O-Mo bridging vibration. [c] V-F stretching vibration. [d] Mo-F vibration. [e] V-F-V vibration. [f] Key: ss = symmetric stretch; as = antisymmetric stretch; p = polarized; dp = depolarized.

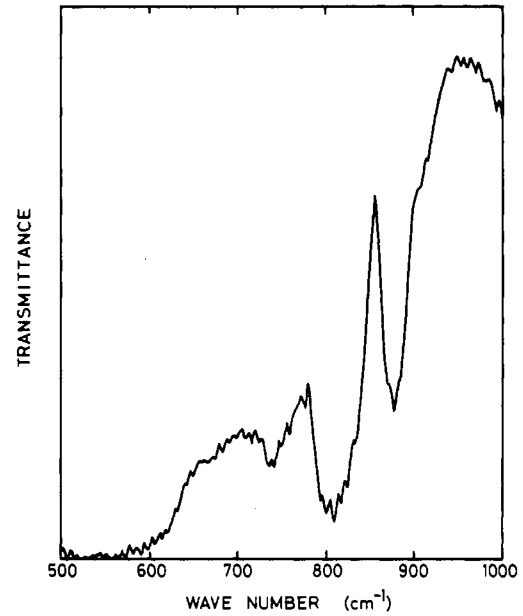

Figure 4. Infrared spectrum of 2.7 mol % Nb(V) in solidified melt (the same as in Figure 2B). Ratio of oxide to niobium was 2.38.

supports this assignment. This band is probably due to the same vibration as the 890-cm^{-1} Raman band[12] when one takes into consideration that small differences in the positions of the Raman and infrared frequencies of the same mode are very likely (especially when melt spectra are compared with solid-state spectra).

We ascribe the depolarized band at 815 cm^{-1} observed in our Raman spectrum of the melt to an antisymmetric stretch vibration of the NbO_2^+ entity. There are several reasons to do so. One could imagine that the band was due to a bridging Nb-O-Nb vibration. However, such a vibration is found at a considerably lower frequency (770 cm^{-1}) in solid $NbOCl_3$, which contains six-coordinated niobium[16] (distorted octahedral symmetry). In the case of molybdenum oxo fluoro species the metal-oxygen bridging frequencies are more than 150 cm^{-1} lower than the Mo=O symmetric stretching frequency of the MoO_2 group. In our case, the difference in frequencies between the Nb=O stretch vibration and the 815-cm^{-1} vibration is only 63 cm^{-1}, which makes an assignment to a bridging oxygen vibration unlikely.

Furthermore, it should be noted that an infrared band[12] is observed at 811 cm^{-1} in the spectrum of solid $K_3NbO_2F_4$, and a band at very near the same frequency (809 cm^{-1}) is observed in our infrared spectrum of the solidified melt (see Table III). These frequencies are not far from the 815-cm^{-1} Raman band of the melt and probably have the same origin.

The nature of the two depolarized bands at 360 and 284 cm^{-1} are more uncertain. They are probably not due to Nb-F symmetric stretch vibrations because of their low frequency, and the same argument excludes Nb-O-Nb bridging vibrations. Antisymmetric vibrations from Nb-F bonds is a possibility. Another possibility is a low-frequency vibration of the NbO_2 group, which would be likely to be found around 350 cm^{-1}. Infrared spectra of the melt would be of great help in order to clarify the origin of these bands.

From Table III, it can be seen that a band pattern with two M-O frequencies in the 800-950-cm^{-1} region, which are both infrared and Raman active, is typical of MO_2F_n type complexes of C_{2v} symmetry (with the two oxygen atoms in cis position). A trans position of the oxygen atoms would give a D_{4h} symmetry, which can be excluded since such a symmetry will not give corresponding IR and Raman bands because of the presence of a center of symmetry.

Since our Raman spectrum shows no band in the oxygen bridging region, we find it likely that $NbO_2F_4^{3-}$ complexes are present in FLINAK melts. Our infrared spectrum of the solidified melt seems to support this explanation since the two high-frequency Nb=O stretching modes are also observed here as they should be for such a complex (the 735-cm^{-1} band frequency is only observed in the infrared solid-state spectrum (Figure 4) and not in the Raman spectrum of the melt (Figure 2B)). Finally it should be remarked that our frequencies are very near the ones observed in the infrared spectrum of solid $K_3NbO_2F_4$, which is known to contain discrete $NbO_2F_4^{3-}$ anions.[12]

Trioxofluoro Species. Nb(V) dissolved in FLINAK saturated with oxide has a Raman spectrum as shown in Figure 2C.

From Table III, it can be seen that MO_3-type oxo fluoro species of molybdenum have a symmetrical Mo-O stretch vibration (both Raman and infrared active) which is approximately 50 cm^{-1} lower than the one for the dioxo fluoro complex ($MoO_2F_4^{3-}$) with six ligands. This trend is also observed for the corresponding tungsten species.[12,21]

When the highest frequency band of $NbO_2F_4^{3-}$ (Figure 2B) is compared with the one found in the Raman spectrum of the saturated melt (Figure 2C), we observe a decrease in the frequency of 58 cm^{-1}. This is quite similar to the one found for molybdenum and tungsten oxo fluoro complexes, and we therefore ascribe the 820-cm^{-1} polarized Raman band found in the spectrum of the

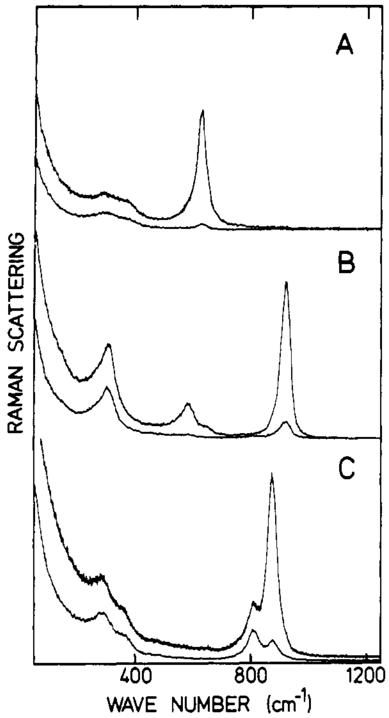

Figure 5. Raman spectra of pure Nb(V) fluoro and oxo fluoro species (see text) formed in LiF–NaF–KF melts. Most probable species: (A) NbF_7^{2-}; (B) $NbOF_5^{2-}$; (C) $NbO_2F_4^{3-}$.

saturated melt to a niobium–oxygen symmetrical stretching mode.

The origin of the depolarized band at 750 cm^{-1} is more uncertain. One would, for example, expect a band due to a Nb–O–Nb bridge to be polarized. However the 750-cm^{-1} vibration could be caused by a M–O antisymmetric stretch vibration of a species with a C_{2v} symmetry. If the broad band at 300 cm^{-1} is supposed also to be due to niobium–oxygen vibrations, the observed Raman bands at 820, 750, and 300 cm^{-1} could fit into the band pattern known for $[MO_3F_3]^{3-}$ (M = Mo, W) complexes of C_{2v} symmetry.[12,21] In such complexes, the MO_3 group has a local C_{3v} symmetry.[21] Consequently, four modes are expected for the MO_3 group, all of which should be both infrared and Raman active. The highest frequency is due to the symmetric stretching vibration (polarized); the second arises from the antisymmetric stretching vibration (depolarized) and is on the order of 70 cm^{-1} lower in frequency. The two low-frequency vibrations (one is polarized and one depolarized) are often overlapping into one broad band. Besides the metal–oxygen vibrational modes, a $[MO_3F_3]^{n-}$ complex should give rise to metal–fluorine vibrations. These are only seen as weak bands in the Raman spectrum of the molybdenum trioxo fluoro species[21] and are therefore not likely to be observed in Raman spectra of species dissolved in fluoride melts (it is well-known that often only the stronger Raman bands appear in molten salt solutions).

It should be noted that the above outlined explanations do not account for the weak polarized Raman band at 1044 cm^{-1} in the Raman spectrum shown in Figure 2C.

In this connection, it can be mentioned that edge-sheared and corner-sheared NbO_6 distorted octahedra in solid niobium oxide compounds give rise to Raman bands in the 1000- and 800-cm^{-1} regions, respectively.[23] The 1044-cm^{-1} band may well be of the former origin, and a band in the 800-cm^{-1} region could be hidden under the rather broad vibration at 820 cm^{-1} observed in the Raman spectrum (Figure 2C). A careful examination of this spectrum reveals that a shoulder may be present at the high-frequency wing of the 820 cm^{-1} band. This may indicate that we are dealing with a situation where two species are present in the melt: a complex of the $[MO_3F_n]$ type and a polymeric structure consisting of distorted NbO_6 octahedrons.

Conclusions

Depending on the value of the oxygen to niobium(V) ratio, at least four different species are formed in LiF–NaF–KF melts. In the range 0 < mol of O^{2-}/mol of Nb(V) < 1, NbF_7^{2-} is formed with a C_{2v} symmetry as previously suggested for solid K_2NbF_7.[8] When oxide is added to the melt, complexes with the general formula $NbOF_n^{(n-3)-}$ are formed. The most probable value of n is 5, giving rise to a monomeric $NbOF_5^{2-}$. The Raman spectra of the melts are in accord with the formation of such a complex of C_{4v} symmetry.

The nature of the species that are formed at high oxide to niobium ratios are more uncertain, but it seems likely that the first of them has a niobium to oxygen ratio of 1/2 (i.e $[NbO_2F_n^{(n-1)-}]_n$). The vibrational spectra (Raman of the melt and infrared of the solidified melt) are consistent with the formation of $NbO_2F_4^{2-}$ ions of C_{2v} symmetry.

In melts saturated with oxide, structures of the $[NbO_3F_n]^{(1+n)-}$ type probably exist. Furthermore, some kind of polymerization is likely to occur in this melt, since frequencies typical of vibrations of distorted NbO_6 octahedra with edge shearing are observed.[23]

By means of computer programs, it has been possible to obtain the Raman spectra of the three pure complexes believed to be NbF_7^{2-}, $NbOF_5^{2-}$, and $NbO_2F_4^{3-}$. The resulting spectra are shown in Figure 5.

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