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Structural Phase Transition Study of NiX,GNH, (X = NO, BF, ancl ClO, 1 with IR and Raman Spectra

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The IR and Raman spectra of NiX26NH3 (*X* = NO3, BF4 and CROk) crystals were obtained at room and liquid Np temperatures. The structural change which comes with the well known ammonia cooperative phase transition is analysed by symmetry considerations. The hexammine metal complexes with molecular anions (*X* = NO3, BF4, CRO4 and PF~) are classified in a series II which, below *Tc,* undergoes the A type deformation of the Bates and Stevens classification. For the halogen anions (*X* = CR, Br and I) crystals (series I) the *B* type deformation is assigned. Discussions which leads to the conclusion that hydrogen-bonds are largerin series II, being responsible for the **low** deformation and higherTc,when compared to series I, are presented.

Foram obtidos os espectros IR e Raman dos cristais NiX26NH3 (*X* = NO3, BF„ e C!LO4) ás temperaturas ambientes de **N2** liquido. Mudança de estrutura oriunda da bem conhecida transição de fase cooperativa das amônias é analisada por considerações de simetria. Complexos hexamoniacais de metais com anions moleculares (X = NOg, BFh, Cio4, e PFâ) são classificados em uma série denominada **I1** que,abaixo de $T_{C'}$ sofre uma deformação do tipo A da classificação de Bates e Stevens. Para cristais com anions halogêneos (série I) foi assinalada uma deformação do tipoB. São apresentadas discussões que levaram á conclusão de que pontes de hidrognio são maiores na série **II**, sendo responsáveis pela baixa deformação e alto $T_{C'}$ quando comparadas com **a** série 1.

1. INTRODUCTION

In this paper we report IR and Raman spectra measurements of NiX_26NH_3 (X = NO_3, BF_4 and $C\ell O_4$) crystals attempting to describe a structural change which comes with the cooperative phase-transition observed in these salts. We attempt also to explain high T_c values of these crystals, as compared to those observed in halogen hexammine complexes. In the previous reports we discussed several known properties about this transition and reported (I) IR spectra[1] of $Ni(NO_3)_26NH_3$ and (II) EPR spectra[2] of $Me(NO_3)_26NH_3$ (Me = Ni, Zn and Cd) crystals.

The cooperative phase transition in nickel hexammine complexes has been subject of large interest. It was discovered from EPR studies of nickel halogen complexes (X = CR, Br and I) and recent studies show similar transition in (X = NO_3, BF_4, $C\ell O_4$ and PF_6) and in other isomorphous transition metal complexes. It is accepted that in all these salts the cooperative transition is related to the decreasing of degrees of rotation of ammonia molecules. At high enough temperatures, the ammonia molecules are rotating with a frequency greater than 4×10^{10} Hz around the Ni - N (nitrogen of NH_3) axis giving a time averaged cubic crystal field symmetry at the Ni^{++} site. If the temperature is lowered, the rotation of ammonia molecules are freezed cooperatively at a characteristic temperature T_c. Consequently the triangular shaped charge distribution of the NH3 protons gives a non cubic crystal field at the Ni^{++} site. This phenomenon produces a sudden change in some physical properties which have been measured by EPR, NMR, IR, Specific Heat, Mössbauer, X-Ray, Dielectric Constant and Volumetric Change.

A theory to explain this phase transition was developed by Bates and Stevens[3] and Bates[4]. This theory was extended by Aiello and Palma-Vittorely[5] and was improved by Bates *et al.*[6]. Bates[4] showed that two kinds of structural changes are expected: A, where one cubic cell gives a rhombohedral unit cell, and *B*, where two cubic unit cells give one monoclinic or triclinic cell. *B* type transformation of structure was observed in $FeC\ell_26NH_3$ by X-Ray diffraction[7]. This was the first confirmation of the structural change predicted in the Bates-Stevens model.

2. CRYSTAL STRUCTURE AND KNOWN PROPERTIES

The $NiX_2 6NH_3$ (X = NO_3, BF_4 and $C\ell O_4$) crystals have cubic structure at rom temperature. The Ni atoms form a *fcc* lattice[8] with a_0 = 10.98, 11.22 and 11.41 Å, respectively for X = NO_3, BF_4 and $C\ell O_4$. Each Ni^{++} is at the center of six NH_3 molecules disposed octahedrally forming a cluster $|Ni(NH_3)_6|^{++}$. This cluster is localized at the center of a cube of edge $a_0/2$, whose vertices are occupied by the X anions.

Several known properties of $Ni(NO_3)_2 6NH_3$ crystals were mentioned in I and II. Recently it was reported a EPR study of this crystal under high hydrostatic pressure[9]. The cooperative phase-transition was observed at a critical pressure p_c with hystheresis in T_c. In the $Ni(BF_4)_2 6NH_3$ a sharpe peak in specific heat[10] was observed at T_c = 140 K, the EPR line broadening[11] at T_c = 135 K and a X-Ray (111) reflexion splitting[12] at T_c = 132 K. The EPR spectra[13] of $(Ni:Cd)(BF_4)_2 6NH_3$ shows a sudden appearing of the crystal field distortion at T_c = 147 K. Differential magnetization measurements at liquid[14] ^{4}He temperatures of $Ni(BF_4)_2 6NH_3$ and $Ni(C\ell O_4) 6NH_3$ were also reported. In the $Ni(C\ell O_4)_2 6NH_3$ the EPR line[15,16] shows the sudden line broadening at T_c = 168 K, NMR line also shows the line broadening around T_c[17,18] and the specific heat (Ref.19) shows a sharpe peak at T_c = 173 K. The magnetic susceptibility of the $Ni(C\ell O_4)_2 6NH_3$ was also reported[20]. The Raman and part of the IR spectra were reported recently for (X = Cl, Br, I, $C\ell O_4$ and BF_4) including ammonia deuterated samples[21,22].

3. EXPERIMENTAL

The $NiX_2 6NH_3$ (X = NO_3, BF_4 and $C\ell O_4$) crystals were prepared by reaction of $NiCO_3$ with solutions of nitric, fluoroboric and perchloric acids respectively and adding concentrated NH_4OH in excess.

The Raman spectra were recorded in a Raman Laser JEOL 400T spectrometer using an exciting line of 4880 Å from an Ar laser. The low temperature spectra were recorded in a cylindrical cell in a liquid N_2 bath. The lines below 200 cm^{-1} were not observed at low temperatures, due to the increasing of the scattered exciting line width, and the resolution of the observed lines was generally poor in these temperatures. The IR spectra were recorded in a Hitachi IR FIS-3 spectrometer (80 to 400 cm^{-1}) and in a Hitachi IR 285 spectrometer (400 to 4000 cm^{-1}). The samples were mulled in nujol. Polyethylen and KBr windows were used. The low temperature spectra were recorded in a Hitachi IR FIS-3 spectrometer using a liquid N_2 cell.

4. RAMAN AND IR SPECTRA OF $NiX_2 6NH_3$

The experimental data of $NiX_2 6NH_3$ (X = NO_3, BF_4 and $C\ell O_4$) are shown in Table 1. The Raman and the IR spectra of these crystals are at room and liquid N_2 temperatures. The Raman and part of the IR spectra of the $Ni(BF_4)_2 6NH_3$ and the $Ni(C\ell O_4)_2 6NH_3$ were reported recently[21,22] using spectrometers of other manufactures. Our data agree very well with these measurements which are indicated in parenthesis. We assumed similar vibrational assignment[21,22] for $Ni(BF_4)_2 6NH_3$ and $Ni(C\ell O_4)_2 6NH_3$. The IR spectra of the $Ni(NO_3)_2 6NH_3$ between 200 - 4000 cm^{-1} were reported by us in (I). In the present work we report IR spectra between 80 - 4000 cm^{-1} of the above crystals and Raman scattering of $Ni(NO_3)_2 6NH_3$ not yet published.

In the IR spectra from 80 to 200 cm^{-1} we observed a lattice vibration mode around 110 cm^{-1}. We distinguish this mode from the others by noting that it has a smaller temperature dependence when compared to $|Ni(NH_3)_6|^{++}$ skeletal vibrations, the $\nu(F_{1u})$ and the $\delta(F_{1u})$ modes. Due to limitations of the low temperature cell used it was not possible to observe if NO_3^- internal modes split. We assigned the observed internal vibrations of NO_3^- group and $|Ni(NH_3)_6|^{++}$ skeletal using free molecular approximation. In this approximation the $|Ni(NH_3)_6|^{++}$ skeletal vibrations have two Raman active vibrations, $\delta(F_{2g})$ $\sim$ N-Ni-N bending and $\nu(A_{1g})$ Ni-N stretching. The IR active vibrations are $\delta(F_{1u})$ $\sim$ N-Ni-N bending and $\nu(F_{1u})$ $\sim$ Ni-N stretching. The NO_3^- group has four Raman and IR active vibrations, δ_e, ν_e, ν_{a1} and ν_{a2}. The ν_{a2} is usually a weak line and was not observed. The observed NO_3^- group vibrations are in agreement with the reported assignments for NO_3^- in different matrices[23].

Table 1. Observed Spectra of $Ni(NO_3)_2 6NH_3$ Complexes.

assignment	Raman		IR	
	RT	LNT	RT	LNT
$\nu_{lattice}$		98	113	120
band A		190		
$\delta(F_{2g})$	230	235		
$\delta(F_{1u})$			223	228
$\nu(F_{1u})$			325	335
$\nu(A_{1g})$	370	380		
$\delta_e(NO_3)$	715	715		
$\nu_e(NO_3)$	1380	1385	1355	1355
$\nu_{a2}(NO_3)$			830	835
$\nu_{a1}(NO_3)$	1050	1050		
$\rho(NH_3)$			660	670
$\sigma_s(NH_3)$			1210	1195
$\sigma_d(NH_3)$			1620	1620
$\nu_s(NH_3)$			3280	3280
$\nu_a(NH_3)$			3365	3360
				3375

In Figure 1 we show the correlation between the lattice mode ν_L and the lattice parameter a_0. The halogen series and the series formed by (X = NO_3, BF_4 and $C\ell O_4$) form two distinct groups. These distinct groups are also observed when we plot $o_d(NH_3)$ and $\sigma_s(NH_3)$ versus a_0 (Figure 2). The fundamentals σ_d and σ_s of $NiX_2 6NH_3$, (X = halogen), are linear functions of the lattice parameters a_0, so that a straightline can be fitted within ± 2 cm^{-1}. The evaluated values for $X = NO_3$, BF_4 and $C\ell O_4$, using these lines are given in parenthesis in Table 3, showing that they are out of halogen group.

Table 2. Observed Spectra of $Ni(BF_4)_2 6NH_3$ and $Ni(ClO_4)_2 6NH_3$ Complexes*.

X (anion)	BF_4				ClO_4			
assignment	Raman		IR		Raman		IR	
	RT	LT	RT	LNT	RT	LNT	RT	LNT
$\nu_{lattice}$					55(58)	(60,74)		
			93(96)	100(104)			92(94)	98(109)
			113	113			113	113
			175	175			175	175
band *A*				(196)				
$\delta(F_{2g})$	240(232)	240 250(240)			230(230)	240(240)		
$\delta(F_{1u})$			222(224)	230(230)			224(224)	228(230)
$\nu(F_{1u})$			320(322)	326(328)			320	328
$\nu(A_{1g})$	360(360)	365(367)			360(360)	360(366)		
δ_e (anion)			358(354)	358(359)	460	460	470	
δ_{f2}(anion)	525	525			620	625		
ν_{f2}(anion)	1205	1205			1100	1100	1090	
ν_{a1}(anion)	770	770			935	935		
$\rho(NH_3)$			650				625	
$\sigma_s(NH_3)$			1235				1235	
$\sigma_d(NH_3)$			1630				1620	
$\nu_s(NH_3)$			3330				3320	
$\nu_a(NH_3)$			3410				3400	

* Values between parenthesis are from references 21 and 22.

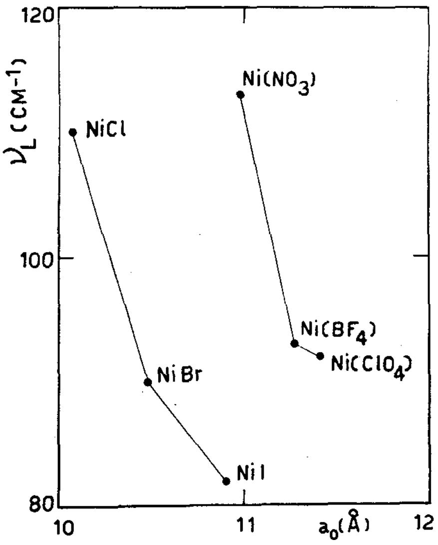

Fig.1 - Lattice vibration versus a_0 of $NiX_2 6NH_3$. This figure shows two groups of $NiX_2 6NH_3$ complexes, namely series I (halogen complexes) and series II (molecular complexes).

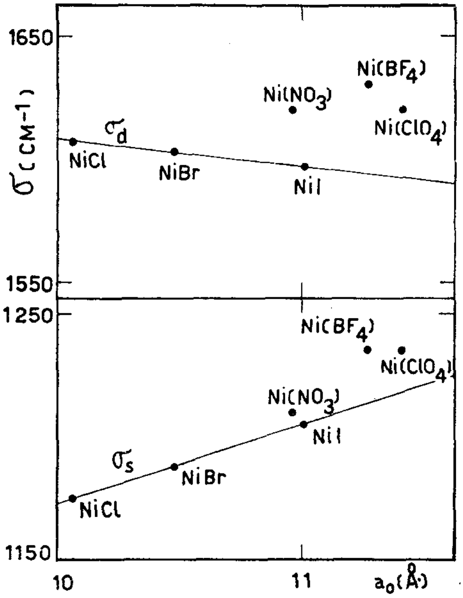

Fig.2 - σ_d and σ versus a_0 of $NiX_2 6NH_3$. The straight lines correspond to a linear fit for series I The series II complexes data are out of this linear fit.

Table 3. Observed values of σ_s, σ_d, ν_s, ν_a and ρ for some $NiX_2 6NH_3$ crystals.

X	σ_s(cm^{-1})	σ_d(cm^{-1})	ν_s(cm^{-1})	ν_a(cm^{-1})	ρ
Cℓ	1175$^+$	1607$^+$	3240	3340	680$^+$
Br	1188$^+$	1603$^+$	3250	3330	672$^+$
I	1205$^+$	1597$^+$	3260	3330	654$^+$
NO_3	1210 (1203)	1620 (1598)	3280	3365	660
BF_4	1235 (1212)	1630 (1595)	3330	3410	650
$C\ell O_4$	1235 (1218)	1620 (1593)	3320	3400	625

The values between parenthesis were obtained using a linear extrapolation from halogen crystals frequencies.

+ From references 24, 25 and 26.

The strength of the ν_L mode reflects the interaction between $|Ni(NH_3)_6|^{++}$ clusters and X anions. From the above results, we can say that this interaction is considerably different in the two series of anions (X = halogen) and (X = NO_3, BF_4 and $C\ell O_4$). We define crystals with (X = halogen) as series I and (X = NO_3, BF_4 and $C\ell O_4$) as series II. The existence of these two distinct series is the most important subject of our conclusions.

5. DISCUSSION

In the section 4 it was shown that experimental IR and Raman results of ν_L, $\sigma_d(NH_3)$ and $\sigma_s(NH_3)$ vibrations are larger in series II than in series I, when these frequencies were correlated with a_0. The strength of the lattice mode comes from the interaction between the $|Ni(NH_3)_6|^{++}$ cluster and the X anion, which depends on the charge distribution and the hydrogen-bond. If we suppose that the major contribution is the charge distrihution, the ν_L dependence with a_0 is expected to decrease with increasing of a_0. From the experimental ν_L versus a_0 (Figure 1), this behavior is observed. However, the curve of the series II is dislocated toward higher values than the series I. This observation suggests that the $|Ni(NH_3)_6|^{++}...X^-$ hydrogen-bond interaction is larger in series II. This result is consistent with the correlation of a_d and a_s with a_0 (Figure 2).

In Figure 3 we show a_0 vs T_c diagram. We extended here the definition of series II to (X = NO_3, BF_4, $C\ell O_4$ and PF_6, and $Me \equiv$ metais) because they form the same group (see Figure 3). Also, we extended here the definition of series I to (X = $C\ell$, Br and I, and $Me \equiv$ metals). Similar diagram was reported by Stankowski[27]. The salts of the series II have larger T_c than in the series I, although their larger a_0 values. However, as discussed above, if the hydrogen-bond interaction $|Ni(NH_3)_6|^{++}...X^-$ is greater because X^- are molecules in all the members of series II, it explainswhy T_c is larger. This observation indicates that the hydrogen-bonds give important contribution to the properties of phase-transition. Two consequences of the larger magnitude of the hydrogen-bonds in the series II result: (a) larger rotational bar-

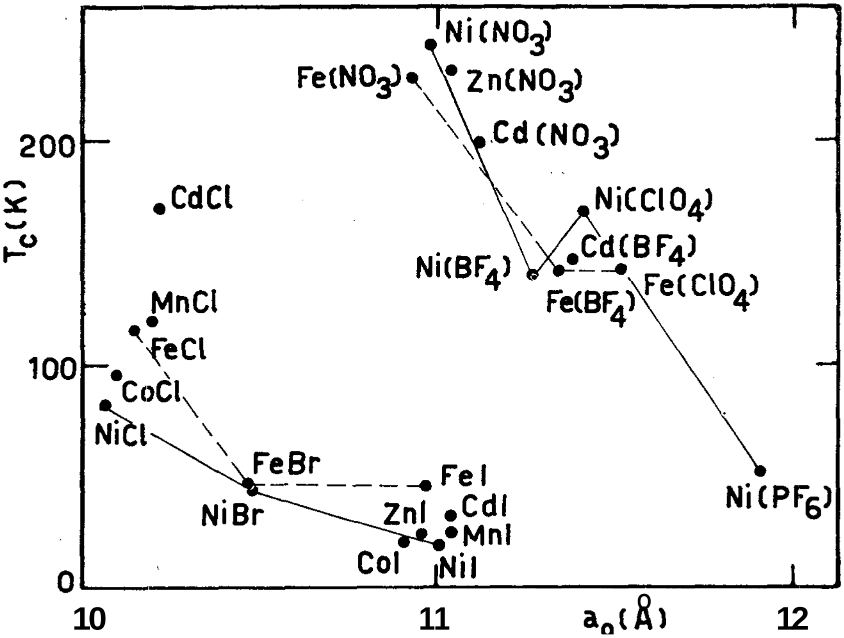

Fig.3 - Critical temperature versus a, of MeX_26NH_3. This diagram shows two groups of complexes, namely series I (halogen complexes) and series II (molecular complexes).

rier of the ammonia molecules; and/or (b) larger Ni-N bond distance or larger $|Ni(NH_3)_6|^{++}$ radius.

Structural changes consequently can be different in series I and II. The split of the vibration assigned to the stretching of the CRO, $\nu(T_2)$ vibration in the $Ni(C\ell O_4)_2 6NH_3$ and in the $Ni(C\ell O_4)_6 ND_3$ [21], shows the appearing of a trigonal C_{3v} or tetragonal D_{2d} crystal field symmetry below T_c. As the $|Ni(NH_3)_6|^{++}$ skeletal vibrations do not split, the probable symmetry is trigonal C_{3v}. The trigonal symmetry indicates an A type deformation of the Bates-Stevens classification. Also, in $Ni(BF_4)_2 6NH_3$ and $Ni(NO_3)_2 6NH_3$ the skeletal vibrations do not split, suggesting a trigonal C_{3v} crystal field synnnetry at the Ni^{++} site, which correspond to the A type deformation. We believe that all the members of the series II give the same type of deformation and to the series I we can assign the B type deforrnation. Several experimental techniques seem to comprove this assumption as discussed below.

The $\nu(F_{1u})\sim$ Ni-N stretching vibration does not split in series II, contrarily to the splitting observed in $CoC\ell_2 6NH_3$ below T_c, as reported by Matsuo et *al.* [28]. This fact suggests that $CoC\ell_2 6NH_3$, which belongs to series I of our classification, has a larger deformation than crystals of series II, as expected.

X-Ray mezsurements, below T_c, of the $FeC\ell_2 6NH_3$ crystal, of series I, show that the (111) reflection split into three reflections of relative intensities 1, 1 and 2, showing a monoclinic deformation[7]. In the $Ni(BF_4)_2 6NH_3$, of series II, the (111) reflection is split into two reflections of equal intensities[12]. The highest symmetry compatible with this observation is a trigonal deformation. Then $FeC\ell_2 6NH_3$ shows a B type deformation while $Ni(BF_4)_2 6NH_3$ an A type deformation, in agreement to our assumption.

It is known that all the complexes $NiX_2 6NH_3$ (X = CR, Br, I, NO_3, $C\ell O_4$ and BF_4) are antiferromagnetic at low temperatures. The transition temperatures T_N are at liquid Helium temperatures, below 4K. It is possible to obtain some information about structure changes by analysing antiferromagnetic behavior, particularly when high magnetic field is applied and their phase diagram (H vs T_N) is obtained. The phase diagram of the crystals belonging to series II are nicely according to theoretical prevision of uniaxial antiferromagnetic[14,29]. This observation shows that the C_3 axis is conserved at liquid He temperatures. The phase diagram of halides which belongs to series I are more complex[30]. In the X = Br salt, the four lines of the diagram are possible indication rhombic symmetry similar to that of $MnC\ell_4 4H_2O$ (Ref.31). In the X=$C\ell$ salt complete phase diagram was not obtained but it seems like to Br salt[30], which comprove our insight again.

A significant difference is expected in EPR spectra if a rhombic comporient of the crystal field distortion is present. We evaluated D values of $NiX_2 6NH_3$ (X = CR, Br, I, BF_4 and $C\ell O_4$) and compared with other reported D values of metal hexammine complexes[32]. These values are nearly the same in these complexes and $E=O$ in all cases. In the $MeX_2 6NH_3$ crystals information about the rhombic $E(S_x^2 - S_y^2)$ term is probably averaged out by the tilting of the NH3 molecules at the measured temperatures. The tilting of the NH_3 molecules averages out the crystal field around the axis passing through the Ni and the center of the proton triangle of the ammonia molecules. This is a possible explanation for the nearly equal values for the D parameter obtained by EPR spectra in both series I and II.

Additional confirmation of our assumption could be made by the entropy of the transition. If structural phase transition occurs, an amount of latent heat and corresponding entropy variation appear at T . The hexammine iodide crystals of Ni, Co, Zn, Fe, Mn, Cd and Ca where studied by Klaaijsen[33] in this aspect. The Bates and Stevens theoretical entropy value of ammonia phase transition alone is $R\ \ell n\ 8$, for all the substances independent of the metal. Experimental entropy however varies from $R\ \ell n\ 3$ for Ni to $R\ \ell n\ 32$ for Ca. Structural phase transition, although its first order character, certainly can not give a principal contribution to explain above entropies, because the cristallographic change observed is not great. There are other possible contribution, as the variation of the potential of the hindered rotation of ammonias at T_c considered by Klaaijsen[33], which would contribute to explain experimental values. Experimental known entropies of series II are $\Delta S(NO_3) = = R\ \ell n\ 47$, $\Delta S(BF_4) = R\ \ell n\ 8$ and $\Delta S(C\ell O_4) = R\ \ell n\ 51$. Also in this series these entropy values indicate that we cannot obtain additional information about structural phase transition. In this series the high values of T_c can give another difficulty to obtain entropy variation. The lattice contribution at high temperatures is not easily estimated and ΔS is not obtained accurately.

6. CONCLUSION

The $MeX_2 6NH_3$ crystals can be grouped into two series, I with (X = halogen) and II with (X = NO_3, BF_4, $C\ell O_4$ and PF_6). Our experimental evidences suggest that hydrogen bonds are larger in series II, forming consequently distinct series with different behaviors. The structural deformations below T_c are of lower symmetry in the series I than in the series II. The crystals of series II are stabilized by an additional number of hydrogen bonds due to the molecular character of X^- anions. We suggest therefore that the series I crystals have a B type deformation of Bates and Stevens classification. In one member of this series, $FeC\ell_2 6NH_3$, this type of deformation was comproved directly by X-Ray diffraction[7]. We believe that this type of deformation can be extended to other crystals belonging to this series. To the members of the series II our experimental vibration frequencies data indicate that the A type of deformation can be assigned. In the series II the high transition temperature can be also explained as a consequence of the additional number of hydrogen bonds.

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