NQR View of Solid Phases of NOCl*,**

J. Pirnat, Z. Trontelj, and H. Borrmann[a]

Institute of Mathematics, Physics, and Mechanics, Ljubljana, Slovenia
[a] Max-Planck Institut für Festkörperforschung, Stuttgart, Germany

Z. Naturforsch. **53a,** 537–541 (1998); received March 24, 1998

Chlorine NQR studies of solid nitrosyl chloride NOCl between 110 and 212 K are reported. In the temperature dependence an order-disorder phase transition near 145 K, found by X-ray diffraction, is confirmed. Unusual hysteretic NQR signal behaviour indirectly proves also the low temperature phase transition below 100 K. In the measured temperature region fast relaxing mechanisms are present. The upper limit of the expected ^{14}N NQR frequency is estimated using the Townes-Dailey approach.

1. Introduction

At present, NOCl is not an often used chemical. At room temperature and normal pressure it is an aggressive poisonous gas that liquefies at about 267 K. It is one of the active components of *aqua regia*, which was used by alchemists and in certain crafts. It attracted our attention because of its not well known and not quite understood phase transitions. On cooling from the temperature of melting (~212 K) to that of liquid nitrogen, the polycrystalline solid gradually changes its color from ruby red to deep yellow, and finally it apparently changes its macroconstitution and disintegrates into a bright yellow microcrystalline snow. The Raman [1] and infrared [2] measurements show that the low temperature phase transition near 80 K exhibits hysteresis of more than 50 K. We thought that NQR could enlighten the NOCl structure changes and their dynamics because both Cl and N are well known quadrupolar probes and even oxygen offers a chance with its less abundant isotope ^{17}O. Clarifying the NOCl behaviour would also advance the general understanding of the N-O and N-Cl bonds. Furthermore, due to the low number of atomic constituents and their low atomic weight, the molecule is suitable for theoretical studies.

2. Structural Features from Previous Measurements

Comparison of the microwave data for the gas phase [3] with the X-ray data for the solid [4] revealed that the molecular dimensions do not change very much going from the gas phase to the solid. Already in the gas, the unusually long N-Cl bond indicates considerable ionic character [3, 5], and that is even more expressed in the solid, where this distances lengthened and increases with cooling. On the other hand, in the gas state the N-O bond is short for a double bond and shows partial triple character. On solidifying, the N-O distance becomes still shorter, but with further cooling it starts increasing (Figure 1). The last fact does not fit into the scheme of two competing structures in the case of NOCl: covalent O=N--Cl and ionic $O\equiv N^+\ Cl^-$. According to this scheme, the higher admixture of the longer ionic N-Cl bond should be always accompanied by higher occupancy of the triple N-O bond, which means shorter bond. However, one should not overlook the molecular interactions in the crystal which are more difficult to estimate.

The crystal structure was studied recently by X-ray diffraction [4] at different temperatures above 100 K (Figure 2). The high temperature structure Cmcm incorporates four-molecular unit cell. Each molecule can occupy two mirror symmetric orientations with 50% probability. Near 145 K the X-ray diffraction revealed a new,

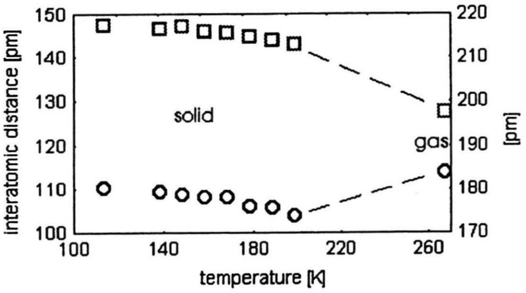

Fig. 1. Temperature dependence of the interatomic distances N-O (○, left scale) and N-Cl (□, right scale) [4].

---

* Presented at the XIVth International Symposium on Nuclear Quadrupole Interactions, Pisa, Italy, July 20–25, 1997.
** Supported in part by the Ministry of Science and Technology of the Republic of Slovenia.

Reprint requests to Dr. J. Pirnat; Fax: +386 61 21 72 81.

0932-0784 / 98 / 0600-0537 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72027 Tübingen

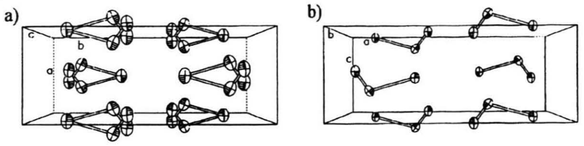

Fig. 2. Disordered (a) and ordered crystal structure (b) of NOCl [4].

probably 2^{nd} order phase transition, where the occupation of the two allowed molecular orientations begins to lean to one side and the crystal symmetry lowers to Pnma. From 145 to 113 K, the molecular ordering gradually increases from 50% to 97%.

The Raman measurements [1] revealed two solid phases: the "ionic" phase I below 80 K and (disregarding the hysteresis) the "covalent" phase II above 80 K. According to the X-ray diffraction measurements [4], phase I remains but the previous "covalent" phase should be split into an ordered phase below 145 K (new phase II) and the disordered phase III above that temperature up to the melting point. In the temperature dependence of the Raman spectra between 90 K and 200 K one notes the disappearance of some Raman lines with increasing temperature at temperatures not far form the II-III transition. We think that the disappearance of the "dephasing torsion" [1] frequency at 117 cm^{-1} and the N-O stretch frequency near 1900 cm^{-1} could be connected with a loss of preference in the NOCl orientation and with decoordination of molecular reorientations.

The least known phase of NOCl is phase I. The Raman spectrum [1] is distinctly different from the spectra at higher temperatures. The authors [1, 2] claim that the strongest peak of the low temperature Raman spectrum at 2086 cm^{-1} belongs to the stretching frequency of the NO^+ group, a representative of the ionic phase. However, they suspect that the ionic and the covalent phase are likely to coexist below 80 K in different proportions, each one contributing to the spectrum. Infrared studies of solid nitrosyl chloride [2] opened some new questions about the influence of the sample shape (thin film) on the low temperature phase transition.

The X-ray scattering measurements were done on single crystals spontaneously grown within a polycrystalline sample. In the low temperature phase, no sufficiently big crystals remain because of disintegration of the crystals. Only powder patterns could be recorded which confirm the alteration of the lattice but do not suffice to determine its structure [6].

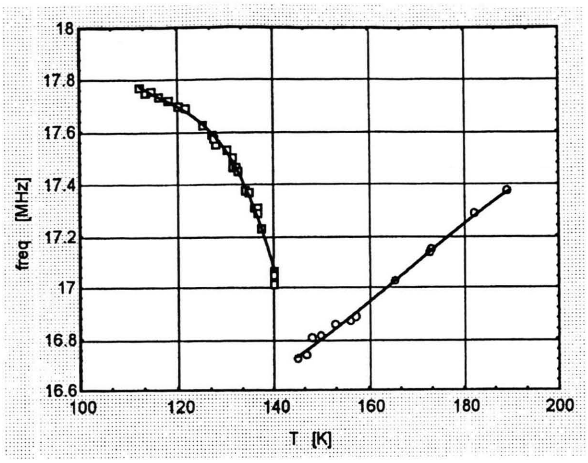

Fig. 3. Temperature dependence of the ^{35}Cl NQR line in NOCl.

3. NQR View

Chlorine pure NQR is usually easiest to detect but gives the fewest data in powders because of one transition frequency per isotope only. Nitrogen pure NQR exhibits poorer s/n ratio because of typically lower NQR frequencies but powder measurements already offer two independent EFG tensor parmeters: the principal value and the asymmetry parameter. ^{17}O NQR is used less frequently because of the low abundance of the isotope.

We have found a single NQR line of ^{35}Cl and one of ^{37}Cl in frozen NOCl and followed them down to 110 K (Figure 3). For the high temperature phase, the single line spectrum is consistent with the average crystal structure as determined by X-rays. The line-width near the melting point (~7 kHz) indicates that NQR detects the time average of the EFG tensor between the two molecular orientations in average surroundings. In the case of static disorder, the expected line-breadth would be more like 100 kHz (depending on the effective atomic charges). The supposition of fast flipping between the two orientations is supported by the NQR relaxation measurement. Both the relaxation times T_1 and T_2 are too short to be measured accurately (<50 μs). With cooling the relaxation times remain below 50 μs, whereas the line-width begins to increase slowly (Figure 4) [7].

In part the ^{35}Cl NQR temperature dependence in Fig. 3, shows an almost linear decreasing of the NQR frequency with cooling down from the melting point

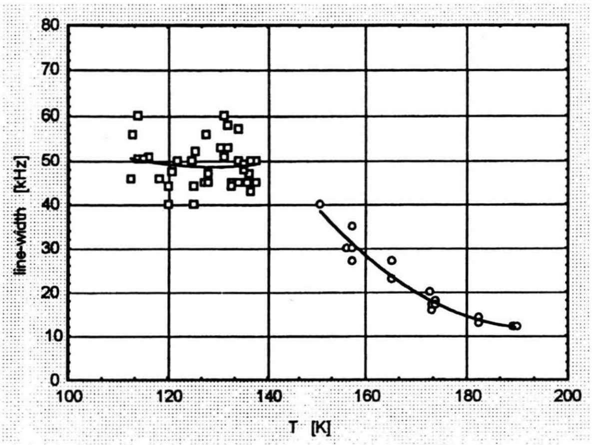

Fig. 4. Temperature dependence of the ^{35}Cl line-width.

(phase III). This is consistent with the increasing N-Cl distance as measured by X-rays. It also means increasing ionicity of the bond. The increased line-width when approaching 145 K might be a consequence of the further increase of the relaxation rate (life-time broadening) with slowing down the molecular flipping or some additional disorder in the crystal lattice (defects, ions).

At the phase transition III-II near 145 K the Cl NQR temperature dependence changes its slope but the line remains single and retains its width. Relaxation slowing down is also not noticed. We suppose that the chlorine NQR frequency dependence below the phase transition reflects the increasing ordering of molecular orientation. The molecular flipping must still be so fast that the NQR probe feels the time average of the EFG tensor. With prolonged occupation of one orientation, the average tensor components approach their limiting values, which leads to increased principal values. The frequency shift obtained from the simple point charge model, employing variable molecular orientation, was normalized to the experimental data. As a result, Fig. 5 shows the temperature dependence of the occupation probability of preferential molecular orientation, calculated from the measured chlorine NQR temperature dependence.

Below 100 K, the Cl NQR signal disappears in the noise. Further cooling of the sample results in disappearance of the signal even when returning to higher temperatures up to 145 K. The sample obviously transforms to phase I, where the Cl NQR signal has not been found yet, although in expectation of a highly ionic N-Cl bond the search was done down to 1.7 MHz.

^{14}N NQR would be a helpful supplementary method of studying processes in NOCl. With its powder spectrum, consisting generally of 3 lines (one is just the difference between the ν^+ and ν^- frequencies), it offers more information on the crystal electric field than Cl NQR. The nitrogen NQR frequency is not as sensitive to the ionicity of the N-Cl bond as the chlorine NQR. The spectrum of phase I probably would not differ too much from the phases II and III. But until now we could not detect the ^{14}N NQR in NOCl. In order to estimate more accurately the frequency region where to search, a

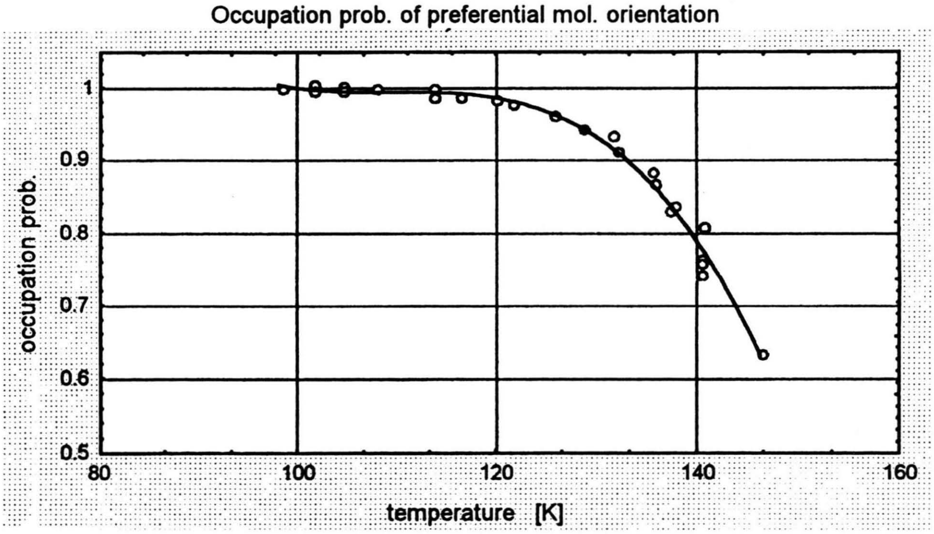

Fig. 5. Temperature dependence of the preferential molecular orientation in NOCl.

Townes-Dailey analysis [8] of the expected EFG tensors has been made.

Assuming that the structure of NOCl can be described as a combination of covalent O=N--Cl and ionic $O{\equiv}N^+Cl^-$, their proportion is first estimated from the ratio of ^{35}Cl NQR frequencies in NOCl and in a typical covalent N-Cl bond. Then the EFG tensor at the N site is obtained as a weighted average of the EFG tensors corresponding to the double and the triple bond in the previously estimated proportion.

For the nitrogen EFG in the covalent form of NOCl the same s-character is used for the N-O and N-Cl bonding orbitals. The following orthonormalized set of approximate molecular orbitals near N is assumed:

bond	occup.	
N-O$_\sigma$	1	$\psi_1 = \frac{1}{\sqrt{2}}\left(\sqrt{1-\mathrm{ctg}^2\,\vartheta}\cdot s - \mathrm{ctg}\,\vartheta\cdot p_y - p_x\right),$
N-O$_\pi$	1	$\psi_2 = p_z,$
N-Cl$_\sigma$	1	$\psi_3 = \frac{1}{\sqrt{2}}\left(\sqrt{1-\mathrm{ctg}^2\,\vartheta}\cdot s - \mathrm{ctg}\,\vartheta\cdot p_y + p_x\right),$
lone p.	2	$\psi_4 = \mathrm{ctg}\,\vartheta\cdot s + \sqrt{1-\mathrm{ctg}^2\,\vartheta}\cdot p_y,$

where the coordinate system is chosen to have its y-axis parallel to the symmetry axis of the O-N-Cl angle (Figure 6a). This angle equals 2ϑ. With these assumptions, and axially symmetric EFG tensor along the symmetry axis of the O-N-Cl angle is obtained:

$$q_{yy} = q_{\mathrm{at.}}\,(1-\mathrm{ctg}^2\,\vartheta), \quad q_{zz} = q_{xx} = -q_{yy}/2,$$

where $q_{\mathrm{at.}}$ is the principal value of the EFG caused by a single electron at the atomic *p* orbital.

For the nitrogen EFG in ionic case, a coordinate system with the *x*-axis along the triple N-O bond was chosen because of simplicity (Figure 6b). The following set of approximate orthonormalized molecular orbitals near N is assumed:

bond	occup.	
N-O$_\sigma$	1	$\psi_1 = \alpha\cdot s + \sqrt{1-\alpha^2}\cdot p_x,$
N-O$_\pi$	1	$\psi_2 = p_y,$
N-Cl$_\sigma$	1	$\psi_3 = p_z,$
lone p.	2	$\psi_4 = \sqrt{1-\alpha^2}\cdot s - \alpha\cdot p_x.$

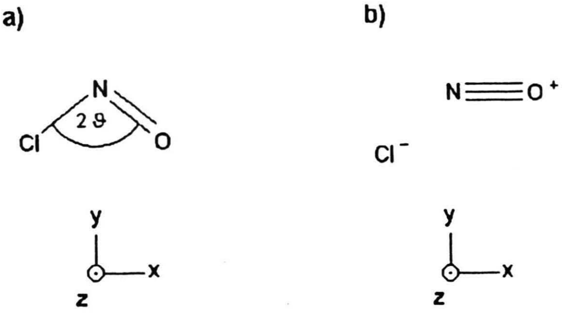

Fig. 6. Choice of the coordinate system: a) covalent case, b) ionic case.

If we assume the same ratio (*s*-character)/(*p*-character) in ψ_1 (N-O sigma bond) in the covalent and in the ionic case, then $\alpha = \sqrt{\frac{1}{2}(1-\mathrm{ctg}^2\,\vartheta)}$ and an axially symmetric EFG tensor is obtained, which is two times smaller in this case and directed along the N-O bond (*x*-axis):

$$q_{xx} = q_{\mathrm{at.}}\,(1-\mathrm{ctg}^2\vartheta)/2, \quad q_{yy} = q_{zz} = -q_{xx}/2;$$

2ϑ is again the O-N-Cl angle. The symmetry axes of the EFG tensors in the covalent and ionic case then differ by the angle ϑ, and their principal values are in the ratio 2:1.

If one obtains the weights of the ionic and the covalent form from the Cl quadrupole coupling constants (about 60% and 40%, respectively), one can estimate the expected EFG tensor at the N site as a weighted average of the ionic and the covalent case tensor in the above ratio. Taking for the O-N-Cl angle $2\vartheta = 110^0$ and for nitrogen $q_{\mathrm{at.}} \sim 10$ MHz, one estimates the nitrogen quadrupole coupling constant in NOCl as 2.46 MHz and the asymmetry parameter as ~0.451. This estimation is valid for a lattice of mostly ordered molecules in phase II. In the disordered phase III and in the upper region of phase II the averaging because of fast flipping between the two molecular orientations lowers the quadrupole coupling constant. In phase I the coupling constant is probably lowered as well because of the ionic form and the triple bond N-O.

4. Conclusions

NOCl deserves attention from the chemical and physical point of view. Three different phases have been found in the solid region of its phase diagram. In two crystal structures previously determined by x-ray diffraction, one above and one below 145 K, the temperature dependence of chlorine NQR has been measured. The phase transition results in a drastic slope change. From 110 to 212 K, the flipping of NOCl molecules is faster than the Cl NQR frequencies, but very efficient in NQR relaxation. The expected frequency region for nitrogen NQR in the solid phases is below 2 MHz. Little is known about low temperature phase below 100 K, which remains for future investigations.

[1] P. M. Killough, B. I. Swanson, and S. F. Agnew, J. Phys. Chem. **93**, 7953 (1989).
[2] L. H. Jones and B. I. Swanson, J. Phys. Chem. **95**, 86 (1991).
[3] G. Cazzoli, C. Degli Esposti, P. Palmissi, and S. J. Simenone, J. Mol. Spectrosc **97**, 165 (1983).
[4] A. Obermayer, H. Borrmann, and A. Simon, J. Amer. Chem. Soc. **117**, 7887 (1995).
[5] M. A. Roehring and S. G. Kukolich, Mol. Phys. (UK) **76**, 221 (1992).
[6] H. Borrmann, private communication.
[7] J. Pirnat, Z. Trontelj, and H. Borrmann, Z. Naturforsch. **51a**, 736 (1996).
[8] G. K. Semin, T. A. Babushkina, and G. G. Yakobson, Primenenie jadernogo kvadrupolnogo rezonansa v himii, Izd. Himia, Leningrad 1972.