Phase Transitions and Water Dynamics of $[Mn(H_2O)_6](ClO_4)_2$ Studied by Differential Scanning Calorimetry and Neutron Scattering Methods

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DSC measurements performed at 95 - 290 K have shown that $[Mn(H_2O)_6](ClO_4)_2$ possesses, besides a high-temperature phase, existing above 323 K, four low-temperature solid phases. The inelastic incoherent neutron scattering (IINS) spectra and neutron powder diffraction (NPD) patterns registered at 20 - 290 K have supported the DSC results and provided evidence that the investigated substance possesses even more than five solid phases. The IINS spectra have shown that in the room-temperature phase, water molecules perform fast stochastic reorientation at the picosecond scale. The orientational disorder characteristic for the room-temperature phase can be easily overcooled and frozen. Even by relatively slow cooling at ca. 40 K/hour a metastable, orientational (protonic) glass phase is formed below ca. 160 K. Below ca. 100 K, a structural phase transition was observed by the NPD, however the IINS spectra indicate existence of the pure ordered low-temperature phase only after annealing the sample for a few hours at 100 K. On heating, a structural phase transition takes place at ca. 120 K, and at ca. 225 K water molecules begin fast reorientation.

Key words: Hexaaquamanganese(II) chlorate(VII); Phase Transitions; DSC; Neutron Scattering.

1. Introduction

Hexaaquametal(II) chlorates(VII) with the general formula $[M(H_2O)_6](ClO_4)_2$, where M = Mg, Mn, Fe, Co, Ni and Zn, form at room temperature a body-centered orthorhombic-pseudohexagonal structure (space group no. 31 = $Pmn2_1 = C^7_{2v}$) with two metal ions per unit cell [1]. Since the unit cell has three equally probable orientations, crystals of these compounds grow as three-component twins [1, 2]. West [1] has coined the term "hermaphrodite" for this type of twinning. According to Ghosh and Ray [2] there are two types of orthorhombic unit cells: a type A when the cell consists of M atoms at $^1/_4$ *c* in the corner columns and at $^3/_4$ *c* in the central column, and a type B when it is inverse. These two types of cells differ only by a shift of $^1/_2$ *c*. Because the cell can be either of the type A or B, there exists a one-dimensional disorder in the form of some mistakes repeating along the *b*-axis of the three-component twins.

Phase transitions in these compounds have been detected by many methods, however there exists considerable disagreement concerning the transition temperatures and even the number of phases [3], especially for the compounds with M = Mn, Fe, and Co. For $[Mn(H_2O)_6](ClO_4)_2$ the following transition temperatures were detected: 323, 247 and 135 K by DSC and adiabatic calorimetry [3, 4], 160 and 89 K by NMR [5], 120 K by magnetic susceptibility [6], and 341, 248 and 161 K by IR and RS [7].

The aim of this study is to clarify the polymorphism of $[Mn(H_2O)_6](ClO_4)_2$ and its connection with water dynamics as well as with changes of the crystal structure. The investigations were performed with inelastic incoherent neutron scattering (IINS), neutron powder diffraction (NPD) and differential scanning calorimetry (DSC) methods.

2. Experimental

$[Mn(H_2O)_6](ClO_4)_2$ was prepared by dissolving pure $MnCO_3$ in pure diluted $HClO_4$. The solution was concentrated by mild heating, and needle-shaped crystals obtained after cooling the solution were puri-

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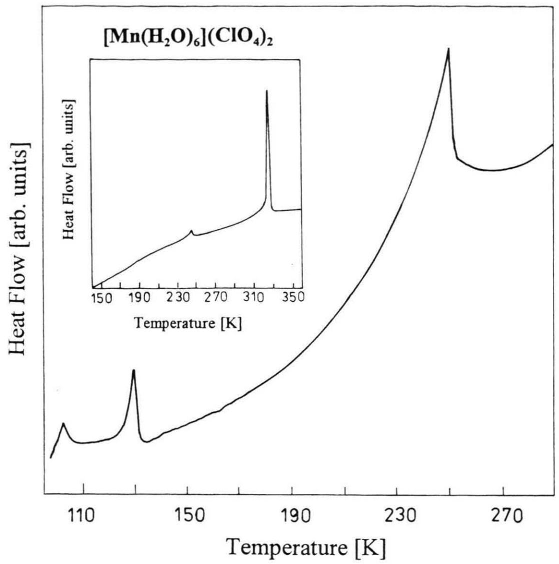

Fig. 1. DSC curves of $[Mn(H_2O)_6](ClO_4)_2$, registered on heating the sample at a rate of 10 K/min. The insertion shows the results from [3].

fied by repeated crystallization in specially distilled, twice in a silver vessel and twice in a quartz one, water. Then the crystals were dried for several days in a desiccator over BaO and stored in a hygrostat, because they are very hygroscopic. The composition of the substance was established on the basis of chemical and thermal analyses. The infrared and Raman spectra have certified the purity of the sample.

The DSC measurements at 95 - 290 K were performed with a Perkin-Elmer PYRIS 1 DSC apparatus at the M. Smoluchowski Institute of Physics of the Jagiellonian University. The experimental details were the same as published in [8].

The IINS and NPD studies were performed at eight temperatures: 20, 100, 120, 130, 150, 170, 225, and 290 K. The NPD and IINS spectra were measured simultaneously by the time-of-flight method in the NERA spectrometer [9] at the high flux pulsed reactor IBR-2 at Dubna. The sample was mounted into a thin-wall aluminum container ($140 \times 60 \times 1$ mm^3). The sample holder was then placed in the top-loaded neutron cryostat with a cold finger cooled with a helium refrigerator. The temperature of the sample could be changed within the range 20 - 300 K and stabilized with an accuracy ± 5 K at any chosen value. The energy resolution of the NERA spectrometer for the IINS spectra in the range 100 - 800 cm^{-1} amounts to 5 - 3%. The spectral width of the elastic peak at 4.3 Å equals to ca. 5 cm^{-1}. Both types of measurements were made for many scattering angles. The final IINS spectra were obtained by summing the data taken from all 15 detectors, whereas in the case of NPD, the different angles were used to record the chosen ranges of the lattice spacing d_{hkl} with appropriate resolution. It should be stressed that because the sample contains many hydrogen atoms, the NPD spectra were recorded on a highly incoherent background. Due to that, no detailed analysis of the diffraction patterns for the not deuterated sample could be made. So, the interpretation of the diffraction patterns was only qualitative, but it was very useful for the identification of particular phases. The different thermal treatment of the sample (like fast and slow cooling and/or annealing) was used in order to obtain, if possible, full information concerning the polymorphism of $[Mn(H_2O)_6](ClO_4)_2$.

Table 1. Thermodynamic Parameters of the Phase Transitions in $[Mn(H_2O)_6](ClO_4)_2$.

Temperature [K]	ΔH [kJ·mol^{-1}]	ΔS [J·mol^{-1}·K^{-1}]
$T_{C1} = 323.5$	7.5	23
$T_{C2} = 238.8$	3.5	14
$T_{C3} = 126.0$	0.2	2
$T_{C4} = 97.7$	0.1	1

3. Results and Discussion

Figure 1 shows the temperature dependence of the heat flow (DSC curve) for $[Mn(H_2O)_6](ClO_4)_2$ between 95 and 290 K obtained, during heating the sample. At first the sample was cooled slowly down from room temperature to liquid nitrogen temperature, with a rate of 1 K/min, and annealed at this temperature during 1 hour. Then the DSC scans were performed during heating the sample with a constant rate of 10 K/min. As can be seen in Fig. 1, three well-marked peaks of the DSC curve were detected, so the substance possesses four solid phases in that temperature range. Mind that the substance has also a high-temperature phase above T_{C1} = 323 K [3], which is shown in Fig. 1 as an insertion. The thermodynamic parameters of the detected phase transitions are presented in Table 1.

The time-of-flight IINS spectra of $[Mn(H_2O)_6]$-$(ClO_4)_2$ against the neutron wavelength for six temperatures are presented in Figure 2. All of them were obtained during heating the sample, but first the sample was cooled to 20 K and then annealed at ca. 100 K

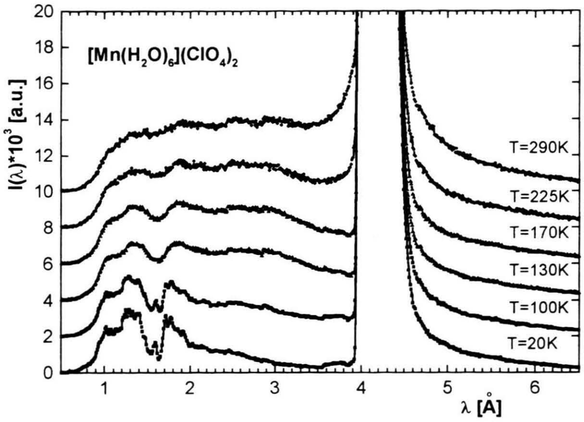

Fig. 2. IINS spectra of $[Mn(H_2O)_6](ClO_4)_2$, registered at six temperatures.

(for more details of such treatment of the sample, see below). A very sharp change in the character of the IINS spectra, especially for the low wavelengths, can be seen between 100 and 130 K. One can link this with the existence of phase transitions. We believe that there are the phase transitions detected by DSC at T_{C4} = 98 K and at T_{C3} = 126 K. Two upper IINS spectra (i. e. for temperatures of 225 and 290 K) show a broadening of the elastic peak characteristic for orientationaly-disordered crystals. Particularly, a very clear quasielastic component can be seen left to the elastic peak. Taking the energy resolution of the NERA spectrometer into account, this indicates the existence of fast stochastic molecular motions, most probably the picosecond reorientational jumps of water molecules around their axis of symmetry. Such a motion of the $M(H_2O)_6{}^{2+}$ complex has been already observed in another $[M(H_2O)_6](ClO_4)_2$ compounds [5, 10]. The quasielastic broadening does not exist in the IINS spectra of $[Mn(H_2O)_6](ClO_4)_2$ at lower temperatures. This can be explained as evidence of an orientational order-disorder phase transition, which occurs probably between 170 and 225 K. It should be added that Nöldeke [11] has noticed a little bit slower stochastic H_2O-flip motions even below 150 K. However, this is not consistent with our DSC measurements, which did not indicate any phase transition in that temperature range.

As was mentioned above, the phase transitions noticeable in the IINS spectra were also observed by the NPD measurements. Typical diffraction patterns registered at chosen temperatures for two scattering angles are presented in Figure 3. Very sharp changes

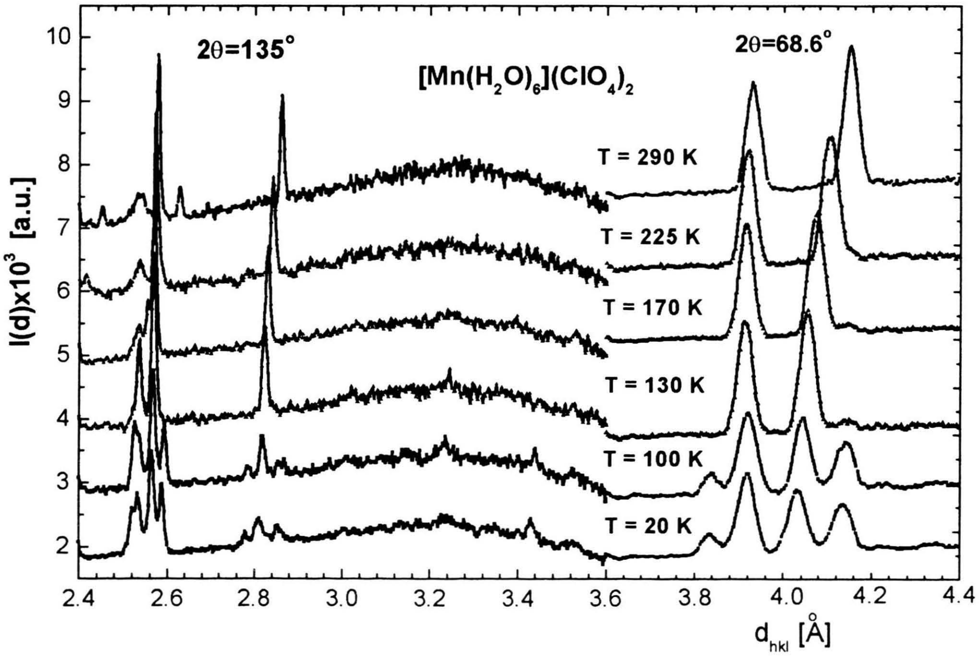

Fig. 3. NPD patterns of $[Mn(H_2O)_6](ClO_4)_2$, registered for two scattering angles at six temperatures on heating the annealed sample.

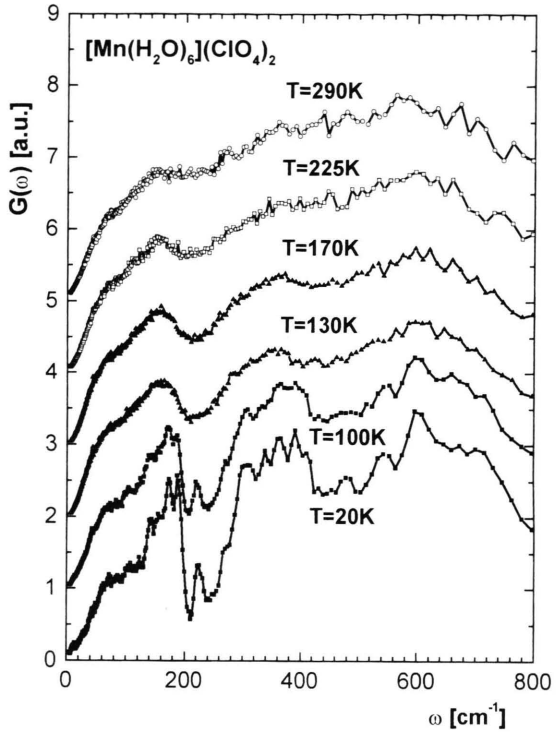

Fig. 4. $G(\omega)$ functions of $[Mn(H_2O)_6](ClO_4)_2$ in the range 10 - 800 cm^{-1} for six chosen temperatures on heating the annealed sample.

of the spectra can be seen between 100 and 130 K, and between 225 and 290 K. A very good correlation with the T_{C4} = 98 K and T_{C2} = 239 K phase transition temperatures registered in the DSC experiment is obvious and gives evidence of their structural character. Additionally, a very careful examination of the diffraction patterns for all temperatures (including also those not shown in Fig. 3, especially that of 150 K) allows us to suspect also some (but very fine-drawn) changes of the peak sequences in patterns for 130 and 170 K. They are seen well enough in the range of d_{hkl} spacing between 2.40 and 2.65 Å. It can be a result of the phase transitions – the first one occurring at ca. 130 K (in the DSC experiment registered at T_{C3} = 126 K) and the second one occurring at ca. 160 K (not observed by us in the DSC experiment but registered by NMR [5] and IR, RS spectroscopy [7]). Some very small differences between diffraction patterns at 170 and 225 K can be also observed and can be related to orientational disorder of H_2O groups above 250 K which is very clearly seen in the IINS spectra (see Fig. 2) and has already been discussed.

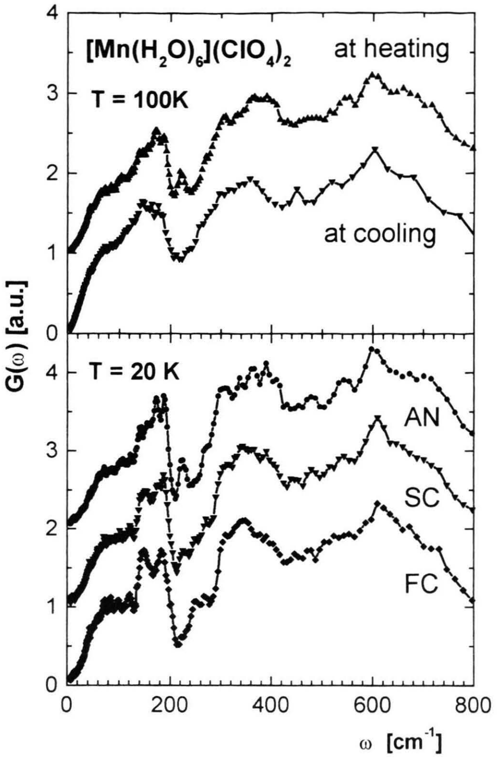

Fig. 5. $G(\omega)$ functions in the range 10 - 800 cm^{-1} on heating and cooling the $[Mn(H_2O)_6](ClO_4)_2$ sample. The lower part shows $G(\omega)$ at 20 K obtained after fast cooling (FC), slow cooling (SC), and after annealing (AN) the sample for a few hours at 100 K. The upper part shows the $G(\omega)$ at 100 K obtained on slow cooling and on heating the sample from 20 K.

Figure 4 presents generalized phonon density of state (frequency distribution) functions $G(\omega)$ between 10 and 800 cm^{-1}, calculated in one-phonon harmonic approximation from the IINS spectra shown in Figure 2. The rich structure of the two lowest temperature $G(\omega)$ curves and the energy gap between lattice and internal modes, seen very well just above 220 cm^{-1}, indicate that the low-temperature phase, existing below 100 K, has an ordered structure. It can be obtained only by annealing the sample for a few hours at about 100 K. Distinct differences between the $G(\omega)$ spectra at 100 and 130 K are also clearly seen.

The differences in $G(\omega)$ spectra associated with the annealing (AN), and also with the fast (FC) and slow cooling (SC) of the sample can be seen in Figure 5. The most important ones are associated with the appearance of a sharp peak at ca. 220 cm^{-1} and with some fine structures of the spectra between 300 and

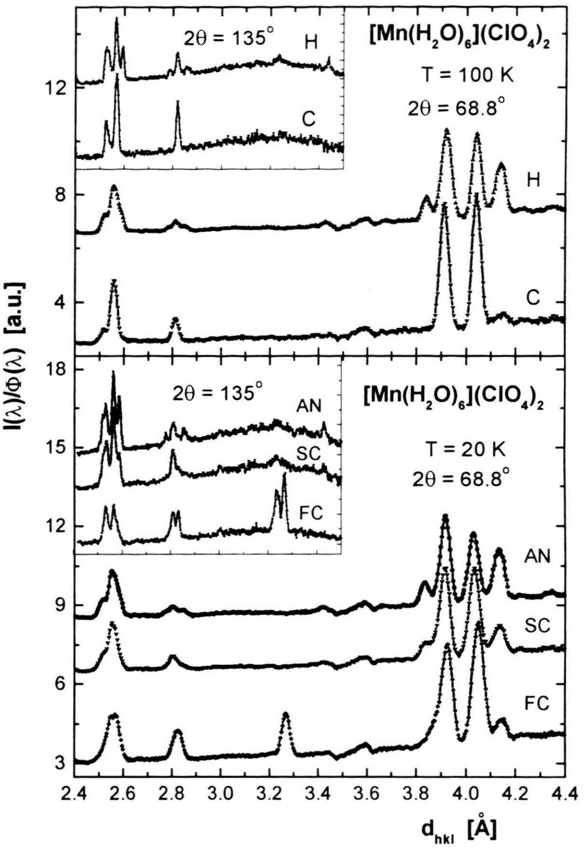

Fig. 6. NPD patterns on heating and cooling the $[Mn(H_2O)_6](ClO_4)_2$ sample. The upper part shows the results obtained at 100 K on slow cooling (C) and on heating (H) of the sample. The lower part shows the results obtained at 20 K after fast cooling (FC), slow cooling (SC), and after annealing (AN) the sample for a few hours at 100 K. Insertions show NDP patterns registered at a high scattering angle (better resolution).

400 cm^{-1} for the (AN) sample. Comparison with the Raman scattering spectra [7] let us to relate that sharp peak at 220 cm^{-1} to the Raman active internal mode ν_2 (E_g) at 214 cm^{-1}, and the group of peaks in the range 300 - 400 cm^{-1} – to the other modes assigned to metal-oxygen vibrations in a $Mn(H_2O)_6^{2+}$ octahedral cation distorted by hydrogen bonding. Because the different thermal treatment of the sample is also associated with the changes in the diffraction patterns (see Fig. 6, discussed below), one can suppose that the additional structural phase transition occurs in the vicinity of 100 K. This phase transition corresponds very well to the T_{C4} = 98 K phase transition detected by DSC.

Figure 6 presents the diffraction patterns, registered at 100 K of the slowly cooled (C) and heated (H) sample, at 20 K of the fast cooled (FC) and slowly cooled (SC) one and at 100 K of one annealed (AN) for a few hours after fast cooling. During slow cooling the sample at 100 and 20 K a similar pattern was obtained. Interestingly, after heating the sample from 20 K to 100 K quite a different pattern was registered. After repeated cooling from 100 K to 20 K the (AN) pattern was registered, which is very similar to the (H) pattern at 100 K obtained during the heating. Afterwards, the sample was heated up to 290 K. Next it was fast cooled, by putting it into liquid nitrogen, and after loading into a cryostat it was cooled down to 20 K. Now, the pattern registered at 20 K (FC) is similar to the (C) pattern registered at 100 K. However, differences can be seen in the patterns, especially in the low d_{hkl} value region for the better resolution (the highest scattering angle), shown in Fig. 6 as an insertion. All of the facts presented above implicate that the fast and even the relatively slow cooling (from 290 K to 100 K with the rate of ca. 40 K/hour as occurred in our experiment) freezes orientational disorder existing in the high-temperature phases and leads most probably to the orientational (protonic) glass state below ca. 160 K.

4. Conclusions

$[Mn(H_2O)_6](ClO_4)_2$ exhibits an interesting and rich polymorphism. The substance exhibits, besides the high-temperature phase above 323 K, four intermediate- and one low-temperature phases. Five structural phase transitions were observed in the neutron scattering measurements during heating the sample. They take place between: 100 - 130 K, 130 - 170 K, 170 - 225 K and 225 - 290 K. The phase transition temperatures detected by DSC at T_{C4} = 98 K, T_{C3} = 126 K and T_{C2} = 239 K are in quite a good agreement with those predicted by neutron scattering methods. The phase transitions observed in neutron scattering spectra at ca. 160 K and ca. 225 K, which have not been observed in the DSC curve, are probably connected with starting-up or stopping of the slow and fast reorientations of water molecules, respectively.

At room temperature, water molecules perform fast stochastic reorientations with a characteristic correlation time of the order of picoseconds. Orientational disorder, characteristic for the room-temperature phase can easily be overcooled and frozen. Even relatively slow cooling leads probably to an orientational (protonic) glass below ca. 160 K. Both the NPD and the IINS spectra indicate that the pure ordered low-temperature phase can be obtained below ca. 100 K only after annealing the sample at about 100 K over a few hours. During the heating, H_2O molecules start-up to reorient progressively between 170 and 225 K. Just above 225 K all water groups perform a fast reorientation (i. e. in the neutron spectrometer "detection window").

Acknowledgements

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