Phase Transitions and Water Dynamics of $[Co(H_2O)_6](ClO_4)_2$ and $[Mn(H_2O)_6](BF_4)_2$ Studied by Neutron Scattering Methods

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Inelastic incoherent neutron scattering (IINS) spectra and neutron powder diffraction (NPD) patterns, registered for $[Co(H_2O)_6](ClO_4)_2$ at 18 - 270 K and for $[Mn(H_2O)_6](BF_4)_2$ at 18 - 230 K, provided evidence that these crystals possess three solid phases in these ranges of temperatures. In both compounds the phase transition occurring at T_{C3} is connected with a change of the crystal structure, and that occurring at T_{C2} with a change in the rate of the reorientational motions of H_2O ligands.

Key words: Hexaaquacobalt(II) chlorate(VII) and Hexaaquamanganese(II) tetrafluoroborate; Phase Transitions; Structural Changes; Water Reorientation; Neutron Scattering.

1. Introduction

Hexaaquametal(II) chlorates(VII) and hexaaquametal(II) tetrafluoroborates with the general formula $[M(H_2O)_6](XY_4)_2$, where M = Mg, Mn, Fe, Co, Ni, Zn and XY_4 = ClO_4 and BF_4, form a body-centered orthorhombic-pseudohexagonal structure (space group no. 31 = $Pmn2_1$ = $C_{2v}{}^7$) with two molecules per unit cell at room temperature [1, 2]. More details about the crystal structure of these compounds were presented in [3].

Phase transitions in these compounds have been studied by many methods, however there is a considerable disagreement concerning the transition temperatures and even the number of phases, especially in the case of compounds with M = Mn, Fe, and Co [3, 4]. For $[Co(H_2O)_6](ClO_4)_2$ we detected by DSC [3] phase transitions at the temperatures: T_{C1} = 348 K, T_{C2} = 241 K, and T_{C3} = 156 K. However, the temperatures of the phase transitions were also ascribed to 263 K and 215 K by adiabatic calorimetry [5], to 354 K, 243 K, and 155 K by EPR [6, 7], to 156 K by the Mössbauer effect [8], to 160 K by NMR [9], to 166 K by magnetic susceptibility [10, 11], to 333 K, 240 K and 166 K by IR and RS [12], and to 344 K, 295 K, 243 K, 182 K, 155 K, 136 K and 121 K by X-ray and dielectric permittivity [13]. For $[Mn(H_2O)_6](BF_4)_2$ we detected by DSC [4] the phase transitions at the following temperatures: T_{C1} = 250 K, T_{C2} = 223 K and T_{C3} = 162 K.

So far, the connection between phase transitions and reorientational motions of anions and cations has only been proposed for $[Ni(H_2O)_6](ClO_4)_2$ and $[Mg(H_2O)_6](ClO_4)_2$. The high temperature phase of these compounds has been interpreted as a disordered phase where $ClO_4{}^-$ tetrahedral anions and H_2O ligands perform fast stochastic reorientations with correlation times of the order of 10^{-12} s [14 - 16], and $[M(H_2O)_6]^{2+}$ cations perform “tumbling” motions with a correlation time of the order of 10^{-6} s [15]. The relatively large motions of $ClO_4{}^-$ anions stop at the T_{C1} phase transition [16]. In the first intermediate phase there is still a disorder connected with the H_2O groups. The second intermediate phase is fully orientationally ordered, which was suggested on the basis of the lower value of the T_{C2} temperature for $[Ni(D_2O)_6](ClO_4)_2$ in comparison with a non-deuterated sample [17]. The crystal structure probably changes at the T_{C3} phase transition.

The aim of this study is to clarify the polymorphism of $[Co(H_2O)_6](ClO_4)_2$ and $[Mn(H_2O)_6](BF_4)_2$ and to find its connection with reorientational motions

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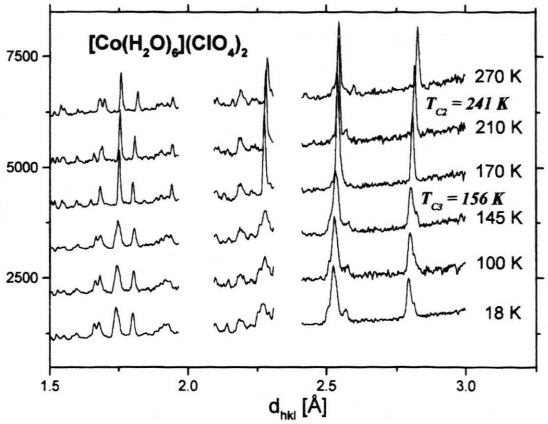

Fig. 1. The NPD patterns of $[Co(H_2O)_6](ClO_4)_2$ for six chosen temperatures of measurement, registered on heating of the sample. The reflexes, arising from neutron scattering on the two walls of the aluminum sample holder, were cut off from the patterns.

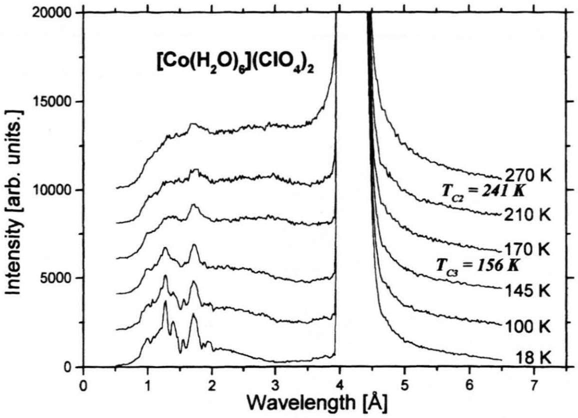

Fig. 2. The IINS spectra of $[Co(H_2O)_6](ClO_4)_2$ for six chosen temperatures of measurement, registered on heating the sample.

of water molecules as well as with changes in the crystal structure. The investigations were performed with inelastic incoherent neutron scattering (IINS) and with neutron powder diffraction (NPD). A comparison with the results obtained by us earlier with DSC [3, 4] was also made.

2. Experimental

$[Co(H_2O)_6](ClO_4)_2$ and $[Mn(H_2O)_6](BF_4)_2$ were prepared by dissolving the corresponding carbonates in diluted $HClO_4$ and HBF_4, respectively. The solutions were concentrated by mild heating, and needle-shaped crystals obtained after cooling the solutions were purified 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 were later stored in a hygrostat, because they are highly 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 samples.

The NPD and IINS spectra were measured simultaneously, using the time-of-flight method in the NERA spectrometer [18] in the high flux pulsed reactor IBR-2 in Dubna (Russia). The sample was mounted in a thin-wall aluminum container ($140 \times 60 \times 1$ mm^3) at room temperature. The sample holder was then placed in the top-loaded neutron cryostat, the temperature beeing held constant by 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 ± 5 K accuracy at any chosen value. The energy resolution of the NERA spectrometer amounts to 5 - 3% for the IINS spectra in the range 100 - 800 cm^{-1}. The spectral width of the elastic peak at 4.3 Å equals to ca. 5 cm^{-1}. Both types of measurements were made at several scattering angles. The final IINS spectra were obtained by summing data taken from all 15 detectors, whereas in the case of the NPD, different angles were used to record the chosen ranges of the lattice spacing d_{hkl} with an appropriate resolution. It should be stressed that, because the sample contains many hydrogen atoms, the NPD spectra were recorded on a highly incoherent background. For this reason, their interpretation has only a qualitative character.

3. Results and Discussion

Typical diffraction patterns for $[Co(H_2O)_6](ClO_4)_2$, registered at six temperatures, are presented on Figure 1. All of them were obtained during heating of the sample. Very sharp changes of the NPD spectra can be seen between 145 and 170 K. A good correlation with the T_{C3} = 156 K phase transition as registered in the DSC experiment [3] is obvious and gives evidence of its structural character. Some very small differences between diffraction patterns at 210 and 270 K can also be observed. They can be related to the orientational disorder of H_2O groups above T_{C2} = 241 K, what is

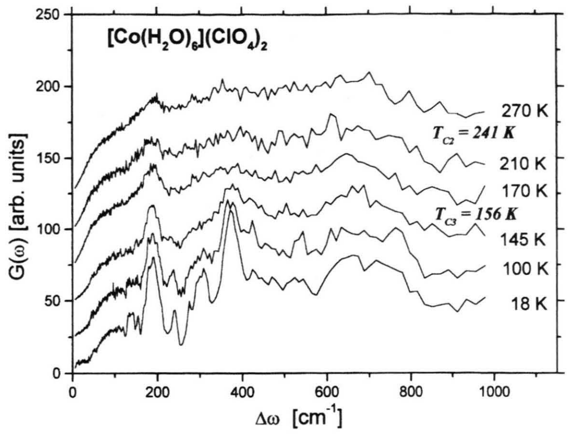

Fig. 3. The $G(\omega)$ functions of $[Co(H_2O)_6](ClO_4)_2$ in the range 10 - 800 cm^{-1} calculated from the IINS spectra.

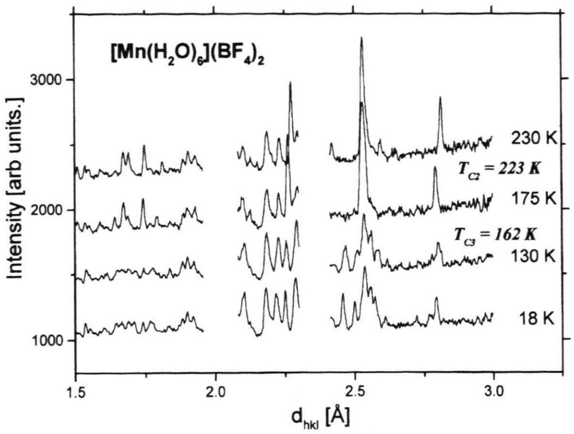

Fig. 4. The NPD patterns of $[Mn(H_2O)_6](BF_4)_2$ for six chosen temperatures of measurement, registered on heating of the sample. The reflexes, arising from neutron scattering on the two walls of the aluminum sample holder, were cut off from the patterns.

very clearly seen in the IINS spectra discussed below (see Figure 2).

The time-of-flight IINS spectra of $[Co(H_2O)_6]$-$(ClO_4)_2$ against the neutron wavelength scale for six chosen temperatures of measurements are presented on Figure 2. All of them were obtained during heating of the sample. A very sharp change in the character of the IINS spectra, especially for low wavelengths, can be seen between the spectra at temperatures of 145 and 170 K, and can be linked to the occurrence of a phase transition in the sample. We believe that there is a phase transition detected by DSC at T_{C3} = 156 K. There are also some differences between the IINS spectra at 210 and 270 K. Namely, the spectrum at 270 K shows a broadening of the elastic peak characteristic for orientationally disordered crystals. Particularly, a very clear quasielastic component can be seen to the left of the quasielastic neutron scattering (QNS) peak. Taking the energy resolution of the NERA spectrometer into account, this implies the occurrence of fast stochastic molecular motions, most probably the picosecond reorientational jumps of water molecules around their axis of symmetry. Such a type of motion has already been observed in $[Ni(H_2O)_6](ClO_4)_2$ and $[Mg(H_2O)_6](ClO_4)_2$ [14, 15]. The quasielastic broadening does not exist in the IINS spectra of $[Co(H_2O)_6](ClO_4)_2$ at lower temperatures of measurement. This can be considered as an evidence of the orientational order-disorder phase transition at T_{C2} = 241 K.

Figure 3 presents generalized phonon density of state (frequency distribution) functions $G(\omega)$ in the range of 10 - 800 cm^{-1}, calculated in one-phonon harmonic approximation from the IINS spectra shown on Figure 2. Differences between the $G(\omega)$ spectra at 145 and 170 K are clearly visible. This indicates the occurrence of a T_{C3} = 156 K phase transition. The presence of intensity peaks in the three lowest $G(\omega)$ curves, and the energy gap between lattice and internal modes, seen well just above 250 cm^{-1}, indicate that, contrary to both intermediate phases, the low-temperature-phase, existing below 156 K, has an ordered structure.

Typical diffraction patterns for $[Mn(H_2O)_6](BF_4)_2$, registered at four temperatures, are presented on Figure 4. Very sharp changes of the spectra can be seen between 130 and 175 K. A quite good correlation with the T_{C3} = 162 K phase transition, registered in the DSC experiment [4], is obvious and gives evidence of its structural character. Some very small differences between the diffraction patterns at 175 and 230 K can also be observed and can be related to the orientational disorder of H_2O groups above T_{C2} = 223 K. This is very clearly seen in the IINS spectra (see Fig. 5) and will be discussed below.

The time-of-flight IINS spectra of $[Mn(H_2O)_6]$-$(BF_4)_2$ against the neutron wavelength scale for four chosen temperatures are presented on Figure 5. All of them were obtained during heating of the sample. A sharp change in the character of the IINS spectra, especially for low wavelengths, can be seen between 130 and 175 K and can be linked to the occurrence

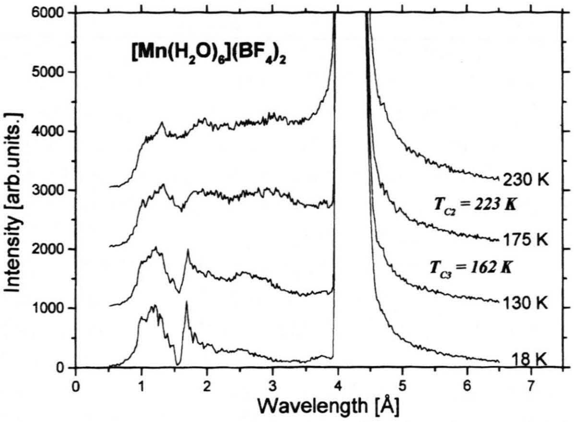

Fig. 5. The IINS spectra of $[Mn(H_2O)_6](BF_4)_2$ for six chosen temperatures of measurement, registered on heating of the sample.

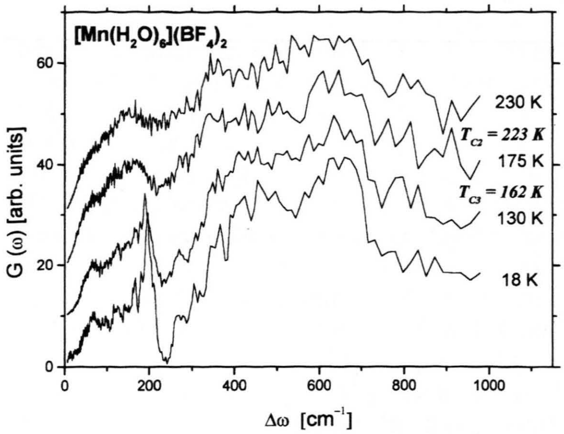

Fig. 6. The $G(\omega)$ functions of $[Mn(H_2O)_6](BF_4)_2$ in the range 10 - 800 cm^{-1} calculated from the IINS spectra.

of a phase transition. We believe that there is a phase transition detected by DSC at T_{C3} = 162 K. There are also some differences between the IINS spectra at 175 and 230 K. Specifically, the spectrum at 230 K shows a broadening of the elastic peak, characteristic for orientationally disordered crystals. Particularly, a very clear quasielastic component can be seen to the left of the QNS peak. Taking the energy resolution of the NERA spectrometer into account, this implies the occurrence of fast stochastic molecular motions, most probably the picosecond reorientational jumps of water molecules around their axis of symmetry. The quasielastic broadening does not exist in the IINS spectra of $[Mn(H_2O)_6](BF_4)_2$ for lower temperatures. This can be explained as an evidence of the orientational order-disorder phase transition at T_{C2} = 223 K.

Figure 6 presents a generalized phonon density of state functions $G(\omega)$ in the range of 10 - 800 cm^{-1} calculated in one-phonon harmonic approximation from the IINS spectra shown on Figure 5. Distinct differences between the $G(\omega)$ spectra at 130 and 175 K are also clearly visible. This indicates the occurrence of a T_{C3} = 162 K phase transition. The presence of intensity peaks in the two lowest $G(\omega)$ curves, and the energy gap between lattice and internal modes seen very well just above 250 cm^{-1}, indicate that, contrary to both intermediate phases, the low-temperature phase below 162 K has an ordered structure.

As shown above, the polymorphisms of $[Co(H_2O)_6](ClO_4)_2$ and $[Mn(H_2O)_6](BF_4)_2$, as well as their connection with changes of the crystal structure and water dynamics, are very similar. However, it should be stressed that there is no such similarity between the polymorphisms of $[Mn(H_2O)_6](ClO_4)_2$ and $[Mn(H_2O)_6](BF_4)_2$ (see [19]). The difference consists largely in that $[Mn(H_2O)_6](ClO_4)_2$ has not four, but five or even seven solid phases. Moreover, the orientational disorder of H_2O ligands, typical for the room temperature phase of $[Mn(H_2O)_6](ClO_4)_2$, can be easily overcooled and frozen. The pure ordered low temperature phase can be obtained below ca. 100 K only after annealing the sample at about 100 K for a few hours. During the heating of the sample, H_2O groups start to reorient progressively between 170 and 225 K [19].

4. Conclusions

- $[Co(H_2O)_6](ClO_4)_2$ has, apart from the high-temperature phase above 348 K, two intermediate-temperature phases and one low-temperature phase. One structural and one orientational order-disorder phase transition was observed in the neutron scattering measurements during heating of the sample. They take place within 145 - 170 K and 210 - 270 K. The phase transition temperatures detected by DSC [3] at T_{C3} = 156 K and at T_{C2} = 241 K are consistent with those predicted by the neutron scattering methods. According to the NPD measurements, the phase transition at T_{C3} = 156 K is connected with a change of the crystal structure. The IINS and QNS measurements indicate that the phase transition at T_{C2} = 241 K is connected with fast reorientations of water molecules initiated during heating. Therefore, at the room-temperature phase and the high-temperature phase, water molecules perform fast stochastic reorientations with a characteristic correlation time of the order of several dozens and several picoseconds, respectively.

- $[Mn(H_2O)_6](BF_4)_2$ has, apart from the high-temperature phase above 250 K, two intermediate-temperature phases and one low-temperature phase. One structural and one orientational order-disorder phase transition was observed in the neutron scattering measurements during heating of the sample. They take place within 130 - 175 K and 175 - 230 K. The phase transition temperatures detected by DSC [4] at T_{C3} = 162 K and at T_{C2} = 223 K are consistent with those predicted by neutron scattering. The phase transition at T_{C3} = 162 K is connected with a change in the crystal structure, and the one at T_{C2} = 223 K with fast reorientations of water molecules initiated during heating of the sample. Therefore, in the first intermediate-temperature phase and the high-temperature (room-temperature) phase, water molecules perform fast stochastic reorientations with a characteristic correlation time of the order of several dozens and several picoseconds, respectively.

- The polymorphisms of $[Co(H_2O)_6](ClO_4)_2$ and $[Mn(H_2O)_6](BF_4)_2$, as well as their connection with changes of the crystal structure and the dynamics of H_2O molecules, are very similar. However, it should be noticed here that there is no such similarity between the polymorphisms of $[Mn(H_2O)_6](BF_4)_2$ and $[Mn(H_2O)_6](ClO_4)_2$ [19].

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