Vol. 88 (1995) *ACTA PHYSICA POLONICA A* No. 3

CONNECTION BETWEEN REORIENTATIONAL MOTIONS OF NH_3 GROUPS AND PHASE TRANSITIONS IN $[Ni(NH_3)_6](NO_3)_2$ AND $[Mg(NH_3)_6](NO_3)_2$ COMPOUNDS

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(Received April 27, 1995)

Quasielastic neutron scattering data for $[Ni(NH_3)_6](NO_3)_2$ and $[Mg(NH_3)_6](NO_3)_2$ were subjected to a new analysis. On the basis of the excess of intensity of elastic component observed in these spectra in comparison to the intensity of this component resulting from the applied reorientational model this analysis determined temperature dependence of the new "R" parameter. This parameter gives us information concerning the number of these NH_3 groups which in the $[Me(NH_3)_6]^{2+}$ cation reorientate with the correlation time of order of 10^{-12} s. It has been ascertained that in phases I and II of both substances under study all NH_3 groups reorientate fast ($R = 6NH_3$ groups), whereas in phases III and IV only part of these groups reorientate fast ($R = 3NH_3$ groups — in the case of $[Ni(NH_3)_6](NO_3)_2$ and $R = 2NH_3$ groups — in the case of $[Mg(NH_3)_6](NO_3)_2$). Moreover, the temperature dependence of reorientational correlation time τ for these fast reorienting NH_3 groups were also determined. The remaining NH_3 groups reorientate on a much slower time scale. Both temperature dependencies: R vs. T and τ vs. T register a deep thermal hysteresis of the phase transition: phase II–phase III ($T^{h}_{C2} - T^{c}_{C2} \approx 95$ K and ≈ 35 K respectively for $[Ni(NH_3)_6](NO_3)_2$ and $[Mg(NH_3)_6](NO_3)_2$).

PACS numbers: 61.50.Ks, 64.70.Kb, 28.20.Cz, 35.20.Yh

1. Introduction

Complex compounds of the type $[Me(NH_3)_6]X_2$ (where $X = Cl^-, Br^-, ClO_4^-, BF_4^-, NO_3^-$ and $Me = Ni^{2+}, Mg^{2+}$) were the object of analysis in the previous paper [1]. Besides the temperature dependence of correlation time τ also the temperature dependence of a "p" parameter was determined. The "p" parameter was responsible for the excess of intensity of the elastic component in quasielastic neutron scattering (QNS) spectra in comparison to the intensity resulting from the reorientational model which was applied. This parameter had no physical meaning and in paper [1] for its high values we did not determine the values of the reorientational correlation times.

It was because of the specific behaviour of the "*p*" parameter, among others, that the compounds $[Ni(NH_3)_6](NO_3)_2$ and $[Mg(NH_3)_6](NO_3)_2$ occupied a separate position in the analysis. Namely, the temperature dependence of the "*p*" parameter for these compounds shaped a characteristic thermal hysteresis loop of the phase II–phase III transition. The difference in the temperature of this phase transition on heating and on cooling the sample ($T^{h}_{C2} - T^{c}_{C2}$) is large and is about 95 K for $[Ni(NH_3)_6](NO_3)_2$ and about 35 K for $[Mg(NH_3)_6](NO_3)_2$.

The hysteresis of phase II–phase III transition in these compounds was discovered using the method of adiabatic calorimetry [2, 3] and the neutron scattering methods [3–6]. Subsequently, its occurrence was confirmed by X-ray diffraction [7], proton magnetic resonance [3] and the temperature analysis of the Raman bands width [8, 9] methods.

Moreover, all the studies mentioned above have clearly pointed to a close correlation between phase II–phase III transition and reorientational motions of the NH_3 groups in these compounds. This has been unequivocally verified by measurements made for $[Ni(ND_3)_6](NO_3)_2$ using the adiabatic calorimetry and neutron diffraction methods [10], which showed the shift of the phase II–phase III transition in the direction of higher temperatures in comparison to the non-deuterated sample.

The thermal hysteresis for $[Ni(NH_3)_6](NO_3)_2$ was also observed by Lesiak et al. [11] using the EPR and dilatometric methods, by Piekara-Sady et al. [12] using dilatometric method, by Fimland et al. [13] using the dielectric method, by Trybuła and Stankowski [14] using also dielectric method and by Czaplicki et al. [15] using the nuclear magnetic resonance method.

In the present paper we have attempted to determine the relation between the reorientation of the NH_3 groups and the phase II–phase III transition for the two substances mentioned in the title of this paper by means of analysis of the temperature dependence of reorientational correlation time τ and the number of fast reorientating NH_3 groups in the $[Me(NH_3)_6]^{2+}$ cation — i.e. "*R*" parameter.

In Sec. 2 we discuss the principles of our new analysis. In Sec. 3 results of this analysis together with their discussion are presented. Finally in Sec. 4 we offer our conclusions.

2. The principle of the analysis based on quasielastic and elastic neutron scattering

In the present paper we have assumed that the elasticity excess of the elastic component seen in the QNS spectra for the compounds under study occurs when the selected reorientational model takes into account too many reorientational motions. This situation can take place when part of the NH_3 groups reorientates in a given phase of the substance under study much more slowly than other NH_3 groups. This part of the NH_3 groups will then be treated as "stationary" from the point of view of the QNS method, i.e. these groups will contribute only to the elastic component of the QNS spectrum.

If, then, the number of fast reorientating NH_3 groups in $[Me(NH_3)_6]^{2+}$ cation is denoted as "R", the neutron scattering function $S^{\rm inc}(\kappa,\omega)$ can be separated in the following way:

$$S^{\rm inc}(\kappa,\omega)=\left(1-\frac{R}{6}\right)\delta(\omega)+\frac{R}{6}S_R^{\rm inc}(\kappa,\omega), \tag{1}$$

where $S_R^{\rm inc}(\kappa,\omega)$ refers only to this part of the NH_3 groups which reorientates fast.

In such a case the model function of neutron scattering, which we have fitted to the QNS spectra for substances under study, assumes the following shape:

$$F^m(\kappa,\omega)=C\left\{[6-R(1-s)]\delta(\omega)+[R(1-s)]S_R^{\rm inc}(\kappa,\omega)\right\}*G(\omega), \tag{2}$$

where $C=[1/24\pi(k_{\rm f}/k_{\rm i})]\,\sigma^{\rm inc}\exp(\hbar\omega/k_{\rm B}T)$, $\sigma^{\rm inc}$ is the cross-section of incoherent neutron scattering, $\hbar\omega=E_{\rm f}-E_{\rm i}$ and $\hbar\kappa=\hbar(k_{\rm f}-k_{\rm i})$ are neutron energy and neutron momentum transfers respectively, R is a parameter defining the number of the NH_3 groups which in $[Me(NH_3)_6]^{2+}$ cation perform fast (picoseconds) reorientation, s is the intensity component (expressed in percentages) of elastic neutron scattering caused by the sample holder. The value of "s" is determined experimentally. This value is from several to a dozen or so percent and decreases with the increase in the momentum transfer k. $G(\omega)$ is the instrumental function which can be expressed by the following formula:

$$G(\omega)=A[1+B(\omega-\omega_0)]\exp[-(\omega-\omega_0)^2/(\Delta\omega)^2], \tag{3}$$

where A is a normalizing constant, B is a small parameter of the asymmetry of this function, ω_0 is the position of the function maximum expressed in meV, and $\Delta\omega$ is the resolution power of the spectrometer (half width at half maximum). The $\Delta\omega$ value is determined for each given scattering angle and a given measured series by fitting the formula (3) to experimental QNS points in such measuring temperature which ensures that quasielastic broadening no longer takes place.

As a reorientational model we have chosen such a model of motions where hydrogen atoms in the NH_3 group perform instantaneous uniaxial 120° jumps around the Me–N axis. The scattering function in the formula (2) has, then, the following shape:

$$S_R^{\rm inc}(\kappa,\omega)=\frac{1}{3}\left(1+\frac{2\sin\sqrt{3}\kappa r}{\sqrt{3}\kappa r}\right)\delta(\omega)+\frac{2}{3\pi}\left(1-\frac{\sin\sqrt{3}\kappa r}{\sqrt{3}\kappa r}\right)\frac{\Gamma}{\Gamma^2+(\hbar\omega)^2}, \tag{4}$$

where $r=0.0954$ nm is the rotation radius of hydrogen atoms in the NH_3 group, $\Gamma=3\hbar/2\tau$, τ is the mean time between instantaneous 120° jumps.

Fittings were performed using the standard method of the least squares, namely the χ^2 function, which was an indicator of the quality of fittings, was minimized in relation to the fitted parameters.

3. Results and discussion

Figures 1a and 2a show the temperature dependence of the number of NH_3 groups which in the $[Me(NH_3)_6]^{2+}$ cation perform fast reorientation (i.e. the "R" parameter) when the sample was cooled (filled-in circles) and heated (empty circles) for $[Ni(NH_3)_6](NO_3)_2$ and $[Mg(NH_3)_6](NO_3)_2$ respectively.

On the basis of changes in the value of R parameter in the function of temperature for $[Ni(NH_3)_6](NO_3)_2$ (see Fig. 1a) it can be seen that:

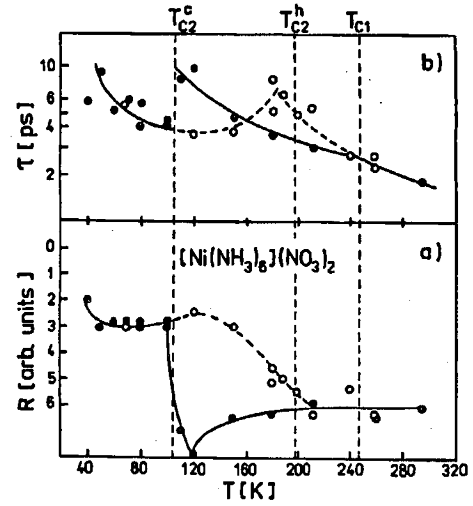

Fig. 1. Temperature dependence of the "R" parameter (a) and the reorientational correlation time $\tau(120°)$ (b) for $[Ni(NH_3)_6](NO_3)_2$. Empty circles — heating of the substance, filled-in circles — cooling of the substance. Vertical broken lines indicate temperatures of phase transitions: T_{C1} and T^h_{C2} — determined by calorimetry [2] and T^c_{C2} — determined on the basis of the present analysis. Note that values of $\tau(120°)$ are given in the logarithmic scale.

On cooling the sample — in phase I and phase II *all* the NH_3 groups perform fast reorientation ($R = 6NH_3$ groups), whereas in phase III (and in phase IV too) only 50% of the NH_3 groups ($R = 3NH_3$ groups) reorientates fast and the remaining 50% of the NH_3 groups is "stationary" in terms of the QNS method. Below $\approx$ 40 K fast reorientation occurs only for *circa* 33% of the NH_3 groups ($R = 2NH_3$ groups);

On heating the sample — in phase III at first only 50% of the NH_3 groups performs fast reorientation. Subsequently, just before the phase III—phase II transition a gradual setting in motion of the remaining, freezed — so far — NH_3 groups, takes place so that following this phase transition, in phase II and then in phase I, all the NH_3 groups perform fast reorientation.

On the basis of changes in the value of R parameter in the function of temperature for $[Mg(NH_3)_6](NO_3)_2$ (see Fig. 2a) it can be seen that:

On cooling the sample — in phase I and phase II *all* the NH_3 groups perform fast reorientation ($R = 6NH_3$ groups), whereas in phase III only *circa* 33% of the NH_3 groups ($R = 2NH_3$ groups) reorientates fast and the remaining 66% of the NH_3 groups is "stationary" in terms of the QNS method. Below 50 K fast reorientation occurs only for *circa* 16% of the NH_3 groups ($R = 1NH_3$ group);

On heating the sample — in phase III at first only 33% of the NH_3 groups performs fast reorientation. Subsequently, just before the phase III–phase II transition a gradual setting in motion of the remaining, freezed — so far — NH_3 groups, takes place so that following this phase transition, in phase II and then in phase I, all the NH_3 groups perform fast reorientation.

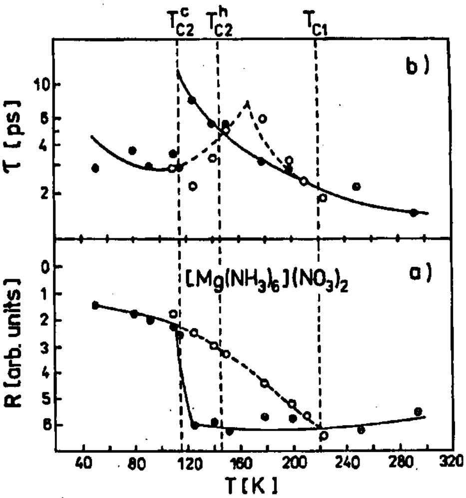

Fig. 2. Temperature dependence of the "*R*" parameter (a) and the reorientational correlation time $\tau(120°)$ (b) for $[Mg(NH_3)_6](NO_3)_2$. Empty circles — heating of the substance, filled-in circles — cooling of the substance. Vertical broken lines indicate temperatures of phase transitions: T_{C1} and T^h_{C2} — determined by calorimetry [3] and T^c_{C2} — determined on the basis of the present analysis. Note that values of $\tau(120°)$ are given in the logarithmic scale.

Figures 1b and 2b show the temperature dependence of the correlation time $\tau(120°)$ for $[Ni(NH_3)_6](NO_3)_2$ and $[Mg(NH_3)_6](NO_3)_2$, respectively. The figures show two different temperature dependencies — filled-in circles — on cooling the sample, empty circles — on heating the sample.

On cooling $[Ni(NH_3)_6](NO_3)_2$ a sharp decrease in the $\tau(120°)$ value at the temperature of the phase II–phase III transition takes place ($T^c_{C2} = 105$ K) whereas *on heating* the increase in the $\tau(120°)$ occurs at a much higher temperature approaching the phase transition: phase III–phase II determined exactly by adiabatic calorimetry [2] ($T^h_{C2} = 197$ K).

On cooling $[Mg(NH_3)_6](NO_3)_2$ a sharp decrease in the $\tau(120°)$ value at the temperature of the phase II–phase III transition takes place ($T^c_{C2} = 115$ K) whereas *on heating* the increase in the $\tau(120°)$ occurs at a much higher temperature approaching the phase transition: phase III–phase II determined exactly by adiabatic calorimetry [3] ($T^h_{C2} = 145$ K).

The picture of the reorientational dynamics of the NH_3 groups in the substances under study obtained in this work is in agreement with the information obtained earlier by us and co-workers using the NMR method [3] and the neutron scattering methods [5, 6].

It is worth adding that the studies of inelastic and quasielastic neutron scattering carried out for $[Ni(NH_3)_6(NO_3)_2$ by Kearley and Blank [16] suggest, similarly to our studies, that in phase III only 50% of the NH_3 groups performs fast reorientation.

4. Conclusions

1. In phases I and II of $[Ni(NH_3)_6](NO_3)_2$ and $[Mg(NH_3)_6](NO_3)_2$ all NH_3 groups in the complex cation perform fast reorientation around the Me–N axis. At the transition point to phase III the reorientation of part of the NH_3 groups undergoes sharp freezing so that in phases III and IV for $[Ni(NH_3)_6](NO_3)_2$ only half of the NH_3 groups performs fast reorientation, and in phase III for $[Mg(NH_3)_6](NO_3)_2$ only one third of them performs fast reorientation. A possibility cannot be excluded that besides slow reorientation also strongly damped librations of these groups can occur.

2. On heating, setting in motion of the freezed reorientation of the above-mentioned part of the NH_3 groups starts gradually just before the phase transition: phase III–phase II. After the transition to phase II, which, on heating the substances under the study, takes place at a much higher temperature (T^{h}_{C2}) than on cooling (T^{c}_{C2}), all the NH_3 groups reorientate fast. The difference ($T^{h}_{C2} - T^{c}_{C2}$) defines the width of thermal hysteresis loop of the phase II–phase III transition. For $[Ni(NH_3)_6](NO_3)_2$ this width is ≈ 90 K, and for $[Mg(NH_3)_6](NO_3)_2$ it is ≈ 35 K.

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