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DISORDER IN $(ND_4)_3ZnCl_5$ AT LOW TEMPERATURES

NIKOLA TJAPKIN
"Boris Kidrič" Institute of Nuclear Sciences-Vinča, 11001 Belgrade, Yugoslavia
and
GERARD PEPY
Laboratoire Léon Brillouin, CEN Saclay, 91191 Gif sur Yvette, France

Regarding its known physical properties, $(NH_4)_3ZnCl_5$ is not a particularly interesting material and only a small number of papers have been published about it, dealing mainly with determination of its structure by X-rays, and its crystallization. In Ref. 1 the structure is determined (except for the positions of hydrogen atoms) at room temperature and it has been shown that it should be regarded as packing of NH_4^+, Cl^- and $ZnCl_4^=$ ions, and that the structure is more correct to be written as $(NH_4)_2ZnCl_4 \cdot NH_4Cl$. In Ref. 2 this structure is refined (orthorhombic, Pnma, a = 9.887, b = 12.625, c = 8.716 Å, z = 4). In Ref. 3 the structure is determined at 120 K and it has been established that there is no phase transition. Only a slightly aspherical charge distribution around the Zn^{2+} ion was observed.

Investigation of $(ND_4)_3ZnCl_5$ was not in our programme. We obtained single crystal of this compound while trying to crystallize deuterated $(NH_4)_2ZnCl_4$ at room temperature by slow evaporation from D_2O solution of NH_4Cl and $ZnCl_2$ in the molar ratio 2:1. Namely, this recipe is given in most of the papers dealing with $(NH_4)_2ZnCl_4$, a very interesting ferroelectric of the A_2BX_4 type, characterized by a large number of phase transitions, although it was shown earlier in Ref. 4 that with the ratio 2:1 only $(NH_4)_3ZnCl_5$ crystallizes, as we obtained. But soon we observed unusual temperature behaviour of $(ND_4)_3ZnCl_5$ (calculated deuteration is 96%), described in this paper, so we decided to study the compound more thoroughly.

By elastic scattering of slow neutrons on a triple axis spectrometer we found the unit cell parameters of our $(ND_4)_3ZnCl_5$ single crystal (a = 9.886, b = 12.635, c = 8.718 Å) to be in excellent agreement with those given in Ref.2. While the temperature was being decreased to about 10 K we did not notice unusual behaviour of Bragg's peaks which correspond to the structure at room temperature. However, we have noticed that from about 240 K, with decreasing of

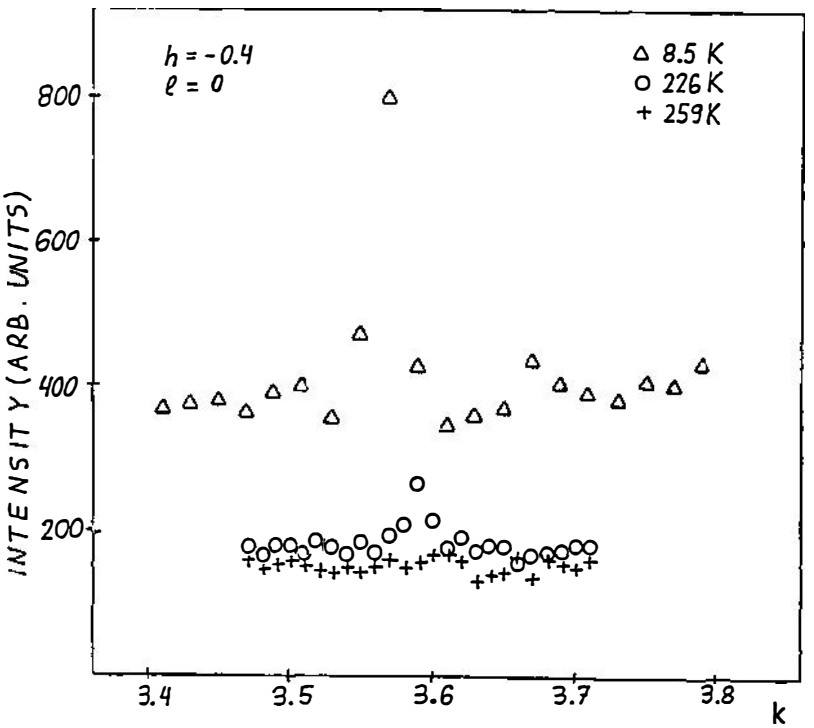

Fig. 1. Neutron scattering elastic (spectrometer set to $\omega = 0$) intensity of the scan (-0.4, $3.4 < k < 3.9$, 0) at different temperatures.

temperature, in the whole reciprocal space there is an increase of the background of the elastic neutron scattering. This background is about three times higher at 10 K than at room temperature (Fig. 1). It points to the appearing of a disorder at low temperatures. As this has not been observed by X-rays at 120 K, and as in NH_4Cl, where the distances NH_4-Cl are nearly the same as in our compound, at about 240 K a rearrangement of NH_4^+ tetrahedra occurs, it is probable that we are dealing here with ND_4^+ tetrahedra, too, i.e. with deuterium (hydrogen). Simultaneously with the background increase, there appear and grow small but sharp peaks (Fig. 1), spherical in the reciprocal space, i.e. as on a powder sample. We have measured only three such peaks, at 1.61, 1.715 and 1.825 $Å^{-1}$. Their quasielastic broadening has not been noticed. These peaks speak in favour of a certain ordering within the disordering, perhaps some clusters formation. To our knowledge, no such behaviour of scattered neutrons had ever been noticed before on any material. There is a question: are we dealing with a real powder,

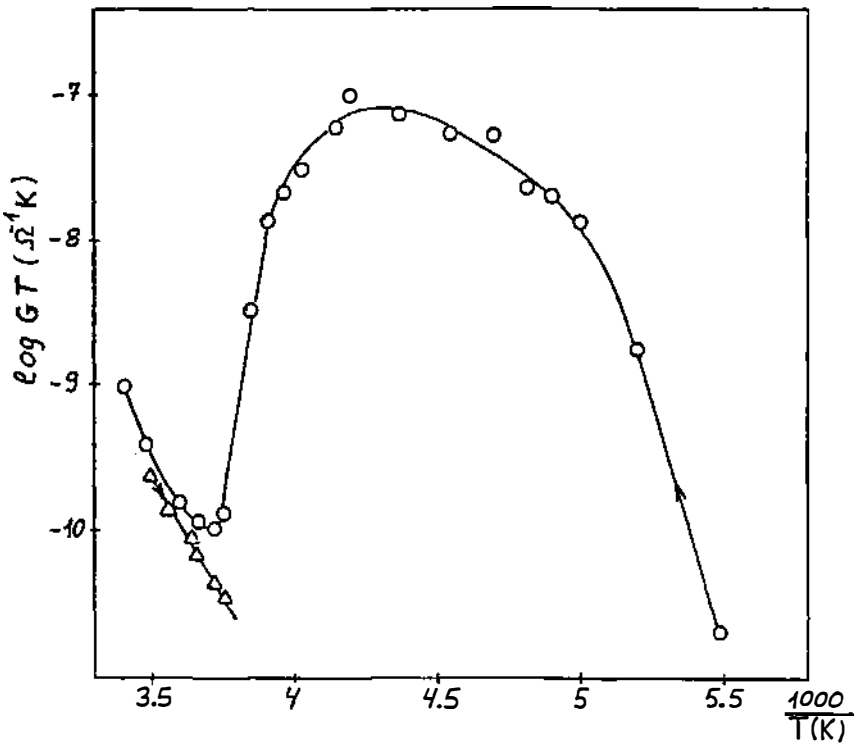

Fig. 2. Temperature dependence of d.c. conductivity G in the b-axis direction obtained on heating (O) and cooling (Δ).

i.e. is there a crystallization taking place? Visually, a liquid phase has not been noticed on the surface or inside the crystal. Thermogravimetric measurements as well as the measurements of specific heat have not detected water in the crystal. If it really was a crystallization, what would be the explanation for the increase of the background?

In order to confirm the existence of this strange phase transformation and to throw more light on it, we have done some macroscopic measurements on several samples. No anomalous behaviour in the temperature dependence of specific heat on DSC and dielectric permitivity in the (010) and (111) direction has been noticed. On the contrary, in both directions the anomalous temperature change of electric conductivity (G) was seen. However, the results are not quite reproducible for measurements on different samples as well as for measurements repeated several times on one sample. Anomalous behaviour is

sometimes very poorly manifested, especially on cooling, and the temperature region in which it appears is somewhere narrower, somewhere wider. Typical results are given in Fig. 2. For the conductivity values less than 10^{-13} Ω^{-1} the results are not reliable. A big decrease of conductivity on heating occurs at about 240 K. Such a behaviour seems to be rather in agreement with the assumption of a disorder than a crystallization.

These results should be considered as preliminar. At the moment, we are trying to find out how the history of the sample is reflected on its properties and whether the mechanism of electric conductivity is similar to that in NH_4Cl, where the formation of vacancies and proton transfer occur[5]. More light to this unusual behaviour will be given by additional neutron and NMR measurements.

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