Comment on `X-ray structural characterization, Raman and thermal analysis of LiNH$_4$SO$_4$ above room temperature'

COMMENT

Comment on 'X-ray structural characterization, Raman and thermal analysis of LiNH$_4$SO$_4$ above room temperature'

Paweł E Tomaszewski

Institute of Low Temperature and Structure Research, Polish Academy of Sciences,
50–950 Wrocław 2, Poland

Abstract. In a recent paper (1999 *J. Phys.: Condens. Matter* **11** 8995) Solans *et al* observed a new phase transition and solved the structure of high-temperature phases. We believe that the results commented on can be explained by the mixture of two different components (α and β modifications or ferroic domains) in the sample and not by introducing the two new intermediate phases supposed by Solans *et al*.

In a recent publication Solans *et al* [1] present results of their x-ray and Raman studies of LiNH$_4$SO$_4$ above room temperature. This crystal has been well known since 1868 [2, 3]. Its structure and physical properties were extensively studied by various methods especially in the period 1974–1983. Now, the LiNH$_4$SO$_4$ bibliography contains about 200 papers. Thus, it seems that each new paper about this compound should present better and more reliable data than the previously published ones. Unfortunately, the paper commented on here does not present such a case. The authors published the rather poor data obtained, as it seems, on mixed and/or multidomain samples and presented in a unconventional manner, and without critical review of the main previously published results. Below some of the questioned statements will be discussed. The results of the Raman studies are out of the scope of this comment.

1. Phase situation

The phase situation in the title crystal is clearly indicated in the corresponding entry of the phase transition database [4]. The main result is that LiNH$_4$SO$_4$ exists in *two* different polymorphic modifications called α and β [2, 5]. Each of them has its *own* phase diagram. The first modification (α) has a phase transition at about 255 K [6] from $Pmc2_1$ symmetry at room temperature to unknown symmetry below. The second modification (β) has phase transitions at about 285 K and 460 K [7–9]. The symmetry changes from $Pmcn$ for the high-temperature phase, to $P2_1cn$ for the room-temperature phase to $P2_1/c$ for the low-temperature phase. Below 27 K another phase exists with Cc symmetry. The α modification can be transformed to the β modification by using temperature. This transition occurs at about 350 K [8, 9] and has an irreversible character. Thus, the reverse transition is impossible and, when lowering the temperature, the β modification is the only stable phase in the whole temperature region in the subsequent temperature cycling; the phase transitions observed are from the β modification only. Furthermore, depending on the growth conditions (mainly of temperature), both modifications could *coexist* in the same sample [2, 8, 9]. Next, only one of these phases (β) has a *ferroelectric* behaviour (which involves the existence of ferroelectric *domains*) and

a peak in the dielectric permittivity curve against temperature [10, 11]. Last, but not at least, the α modification may exist in three *polytypes* [5, 12].

Taking into account all the above properties, the analysis of all experimental data should be made very carefully. Without, at least, reference by the authors to the complicated situation described above, all their further statements may be without significant scientific value.

It is not sufficient to write the temperature of sample growth. The studied crystals were grown at 333 K, thus in the region where the phase transition from α to β modification occurs (the onset for this transition is about 325 K and the peak of DTA spectrum is at 350 K [8]). The pH of water solution was also unknown, thus we could not exclude the growth of the α modification as an intergrowth in the large crystals of β modification or as separate crystals. The well known latter possibility could affect the powder experiments when the sample was prepared by milling as-grown crystals. This needs detailed further studies or, at least, detailed author comment.

It should be noted that the cited paper by Połomska [9] is related to the phase transition from the α to β modification and not from phase I to II within the β modification, as wrongly stated in the paper commented on!

Nevertheless, the results presented in the paper commented on strongly indicate that the studied sample is a *mixture* of two different modifications (α and β). This leads to the experimental data showing a phase transition from both modifications as in the reported data. Moreover, the vanishing of the transition at about 335 K is a proof of the initial presence of the α modification in the sample [8, 9]; the subsequent thermal cycles do not show the existence of the α modification. The same results were observed by Chhor *et al* [13] but without satisfactory explanation. Now, it is well established that the α modification transforms *irreversibly* with slow kinetics to the β modification at this temperature [8, 9]. Samples believed to be pure single phase have turned out to be mixtures.

2. Lattice parameters

The authors published data of insufficient quality on the changes of the lattice parameters calculated from the powder diffraction data, and do not compare them with the precise results (of the accuracy of 10^{-5}) obtained by the x-ray Bond method [7]. Peculiarities in the thermal dependence of lattice parameters obtained from a single crystal experiment which could suggests supplementary phase transitions in $LiNH_4SO_4$ were not found. Similar good data were published several times [14–16].

3. Crystal structure analysis

The structure of both $LiNH_4SO_4$ modifications (α [5]) and β [17–19]) are totally different, thus it is not possible to make a common structure analysis by the only supposition about the twinning of β modification. It seems that the structure of all phases of β-$LiNH_4SO_4$ were solved and refined (with hydrogens; e.g. [6, 18–20]) with sufficiently high accuracy that new analysis is not needed, especially without finding the positions of hydrogen atoms. NB: the authors of [1] wrongly think that the paper by Pietraszko and Łukaszewicz [5] concerns the β modification while it reports the crystal structure of the α modification!

The x-ray measurements using automatic CAD diffractometer procedures (as used by the authors of the paper commented on) allow us to omit several Bragg reflections not corresponding to the cell chosen for measurements. Thus, the collected data corresponding to the one modification (i.e. β) might be affected in several reflections by the intensity from

another modification (i.e. α). The 'average' structure could be wrong!

A second source of errors could be related to the existence of domain structure in the β modification [10, 11, 21]. When solving the crystal structure of the ferroelectric phase (as in our case of the phase II and II') it is necessary to take into account the obvious presence of ferroelectric domain structure, which disturbs the final results of studies leading to the 'average structure'. If the amount of both types of domain is not equal, the 'average structure' has a symmetry lower than the truly average structure observed as high-temperature phase I Misinterpretation of such data may occur in the case of the paper commented on.

4. New phase transition

The 'new' phase transition at 335 K introduced by Solans *et al* has a reasonable explanation by a mixture of two different components. Both types of such components, polymorphic modifications or ferroic domains, give a more significant description than the simple existence of a new phase transition.

(a) The first interpretation is based on the coexistence of α and β modifications within the studied sample. The phase transition in the smaller component α in the sample should affect the data by changing the intensity of some of the reflections. Such a change in the intensity distribution may be interpreted as a change due to the phase transition in the main component of the sample.

(b) The second possible interpretation is based on the domain structure of the β modification. The phase transition at about 335 K from phase II to new phase II' seems to be an artefact due to the accidental change in domain structure at that temperature. The amount of 'right-oriented' domains contained in the sample investigated was changed with the temperature with respect to the amount of 'left-oriented' domains (like in $LiCsSO_4$ reported by Pietraszko *et al* [22]). When domains move in the sample the apparent 'switch' from 'left' to 'right' domain may occur at an arbitrary temperature, here it appears accidentally at about 335 K. This changes the intensities of some Bragg reflections and results in the 'average' structure of different degree of averaging of the 'left-' and 'right-oriented' domains. The search for the basic structure of one domain (single domain sample) is then difficult. The authors of [1] have seen this effect when they wrote that the new phase (phase II' above 335 K) is close to the enantiomeric phase II.

5. Other remarks

In the paper commented on some other wrong or uncertain results should be noticed.

(a) The $P2_1nb$ space group is *polar* and not 'non-polar' as was wrongly stated by the authors! The high-temperature phase is non-polar as regards the physical properties (such as ferroelectricity or the existence of spontaneous polarization) and then centrosymmetric with regard to the symmetry of the structure and physical properties.

(b) The choice of polar space group $P2_1nb$ for the high-temperature phase is in contradiction with the physical properties of this phase. The vanishing of spontaneous polarization in the ferroelectric–paraelectric phase transition (on heating) indicates non-polar symmetry and the subsequent structure refinement should be made in the highest possible non-polar space group (in our case in $Pmcn$ like in [20, 23]).

(c) Several authors have stated that the decomposition of $LiNH_4SO_4$ occurs at a temperature well below those given in the paper commented on as a melting temperature [7, 16, 24, 25]. What then really happens at 601 K?

(d) The presentation of data is rather unconventional with the large empty space in figures 1(a) and 1(c). In this case the best solution is to show all data in the same diagram. All possible correlation will be then seen without any problems.

(e) There is a lack of error bars in the figure 1. One could suppose that the standard deviations for the presented data are at least about 10^{-3} A, thus 'hiding' all anomalies on the curves (see remark (b)).

(f) The authors of [1] present their data in an unconventional manner. What are the mean data for the multicomponent sample written in a single column in table 1 under the caption indicating both names of components (phase II + II$'$)? The presented data should correspond either to phase II or to phase II$'$. The average data are without any physical meaning.

(g) Finally, the assumption of non-disordered structure of high-temperature phase I leads to the wrong interpretation of the character of phase transition. The correct, and well described in the literature, mechanism is of order–disorder type (e.g. [16, 26–28]).

The situation in LiNH$_4$SO$_4$ is still far from being clear and the commented paper does not bring us closer to the desired understanding of the nature of structure and phase transitions.

References

[1] Solans X, Mata J, Calvet M T and Font-Bardia M 1999 *J. Phys.: Condens. Matter* **11** 8995
[2] Scacchi A 1868 *Atti R. Accad. Napoli, Sci. Fis. Mat.* **3** 1
[3] Wyrouboff G 1880 *Bull. Soc. Min. France* **3** 198
[4] Tomaszewski P E 1992 *Phase Transitions* **38** 127
[5] Pietraszko A and Łukaszewicz K 1992 *Pol. J. Chem.* **66** 2057
[6] Hildmann B O 1980 *PhD Thesis* Aachen
[7] Tomaszewski P E and Pietraszko A 1979 *Phys. Status Solidi* a **56** 467
[8] Sosnowska I, Hilczer B and Piskunowicz P 1990 *Solid State Commun.* **74** 1249
[9] Połomska M, Hilczer B and Baran J 1994 *J. Mol. Struct.* **325** 105
[10] Hilczer B, Meyer K-P and Szcześniak L 1984 *Ferroelectrics* **55** 201
[11] Połomska M, Wolak J and Szcześniak L 1994 *Ferroelectrics* **159** 179
[12] Tomaszewski P E 1992 *Solid State Commun.* **81** 333
[13] Chhor K, Abello L and Pommier C 1989 *J. Phys. Chem. Solids* **50** 423
[14] Gierlotka S, Przedmojski J and Pura B 1986 *Fiz. Dielektr. Radiospektroskop.* **12** 161
[15] Hirotsu S *et al* 1981 *J. Phys. Soc. Japan* **50** 3392
[16] Iskornev I M and Flerov I N 1977 *Fiz. Tverd. Tela* **19** 1040 (Engl. transl. *Sov. Phys. Solid State* **19** 605)
[17] Dollase A 1969 *Acta Crystallogr.* B **25** 2298
[18] Hildmann B O, Hahn Th, Heger G, Kurtz W and Arnold H 1978 *KfK-Bericht* **2719** 19
[19] Mashiyama H and Kasano H 1993 *J. Phys. Soc. Japan* **62** 155
[20] Hildmann B O, Hahn Th, Kurtz W and Heger G 1979 *KfK-Bericht* **2911** 17
[21] Połomska M and Tikhomirova N A 1982 *Ferroelectr. Lett.* **44** 205
[22] Pietraszko A, Tomaszewski P E and Łukaszewicz K 1981 *Phase Transitions* **2** 141
[23] Itoh K, Ishikura H and Nakamura E 1981 *Acta Crystallogr.* B **37** 664
[24] Loiacono G M *et al* 1980 *Ferroelectrics* **23** 89
[25] Mitsui T *et al* 1975 *J. Phys. Soc. Japan* **39** 845
[26] Aleksandrova I P, Blat D Kh, Zinenko V I and Kruglik A I 1981 *Kristallografiya* **26** 531 (Engl. transl. *Sov. Phys.–Crystallogr.* **26** 301)
[27] Rozanov O V, Aleksandrova I P and Rosenberger H 1982 *J. Mol. Struct.* **83** 399
[28] Yamamoto I, Hiroe A and Hirotsu S 1983 *J. Phys. Soc. Japan* **52** 920