

DIELECTRIC and ELASTIC PROPERTIES OF
(NH₄)₄LiH₃(SO₄)₄(ALHS)¹M. Zimmermann², W. Schranz*Institute of Experimental Physics, University of Vienna, Strudlhofgasse 4,
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We present measurements of the electrical permittivity of (NH₄)₄LiH₃(SO₄)₄(ALHS) in the range between 40 K and 410 K. Above $T_c = 233$ K the frequency dependences of ϵ' and ϵ'' show the behaviour of a crystal with proton conductivity. At about 405 K a noticeable change of the specific conductivity is observed. In addition measurements of the thermal expansion coefficients have been performed. Measurements of the low frequency elastic compliance along the tetragonal a -axis in the frequency region of 1-50 Hz and in the temperature region between 95 K and 420 K revealed a frequency dependent temperature shift of a damping maximum in the ferroelastic phase which could be connected to domain freezing. Also an elastic behaviour which is dependent on the "history" of the crystal was observed.

1. Introduction

ALHS belongs to a family of ferroelastic crystals A₄LiH₃(XO₄)₄ (A = K, Rb, NH₄; X = S, Se) attracting attention in the last years (e.g. [1-7]). It undergoes a ferroelastic phase transition at about 233 K which was first reported by Pietraszko et al. [8]. The crystal structure changes from tetragonal symmetry P₄ down to monoclinic symmetry P2₁ [9, 10] where a ferroelastic domain pattern is observed [11].

2. Samples

The crystals were grown at room temperature from a non-stoichiometric acid aqueous solution of Li₂SO₄, (NH₄)₂SO₄ and H₂SO₄ by slow evaporation of water. Clear crystals mostly in the form of truncated pyramids with a side length between 5 and 10 mm were obtained. Using conoscopy we found the direction perpendicular to the basis of the pyramids to be [001]. As the crystals are hygroscopic care has been taken to avoid damage of the surface by humidity. Besides, the state of the crystals has been checked with a polarizing microscope (compare also [12]). The typical size of the prepared samples was about 2 × 2 × 3 mm. To check composition and structure of the samples X-ray powder diffraction was performed at room temperature and could be described well by the lattice parameters published in the literature [8, 10].

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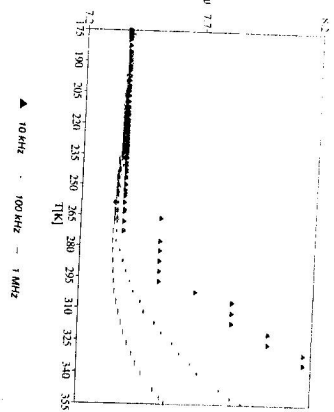


Fig. 1: Real part of the dielectric constant ϵ_{11} in ALHS around T_c

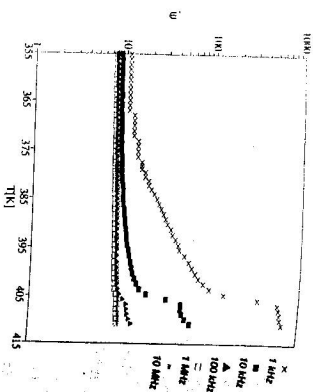


Fig. 2: Real part of the dielectric constant ϵ_{11} in ALHS above room temperature

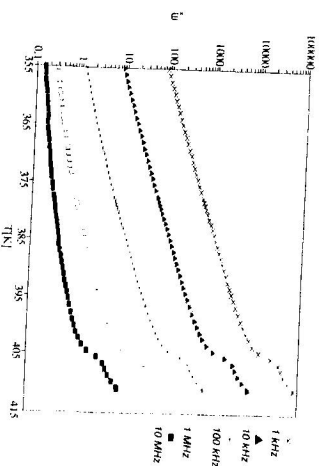


Fig. 3: Imaginary part of the dielectric constant ϵ_{33} in ALHS around T_c

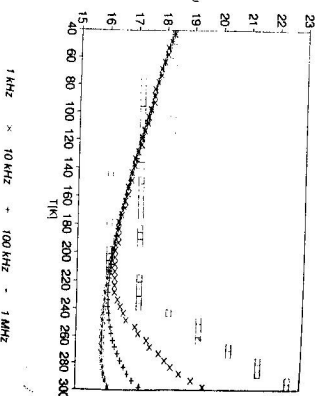


Fig. 4: Real part of the dielectric constant ϵ_{33} in ALHS around T_c

3. Dielectric measurements

Recently measurements of the permittivity of ALHS between 220 K and 300 K have been published [10] and superionic behaviour in $A_4LiH_3(XO_4)_4$ crystals has been reported [13]. In order to get more insight into the processes we performed measurements of the dielectric constants along the tetragonal a - and c -direction between 40 K and 410 K. Measurements were performed with a Hewlett-Packard 4192A LF Impedance Analyzer in the frequency range between 1 kHz and 10 MHz. Above T_c , ϵ' shows a large dispersion while there is almost no dispersion below T_c (see Figures 1 and 4). In the a -direction as well as the in c -direction there is a "shoulder" in the temperature dependence of the dielectric constant at about 405K (see Figures 2 and 5). ϵ'' revealed a behaviour which is comparable to that of $Rb_4LiH_3(SO_4)_4$ [14] (see Figures 3 and 6). Extrapolating from our data we found the dc conductivity σ to be about $0.5 \times 10^{-9} S/m$ at 400K for both the a - and the c -direction. The activation energy E_a in a -direction obtained from an Arrhenius law fit is about 1.3 eV below 405 K, about 6 eV around

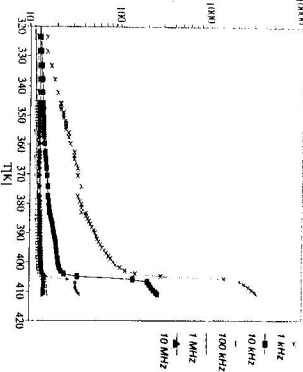


Fig. 5: Real part of the dielectric constant ϵ_{11} in ALHS above room temperature

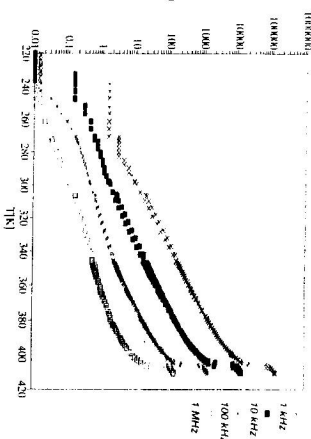


Fig. 6: Imaginary part of the dielectric constant ϵ_{33} in ALHS

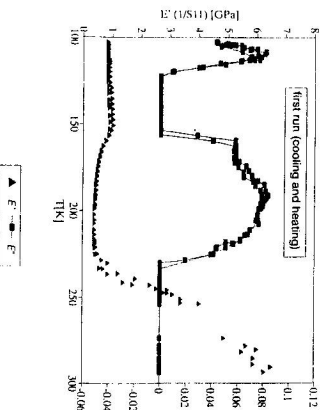


Fig. 7: Inverse value of the elastic compliance S_{11} at 10 Hz in a 'fresh' ALHS-crystal

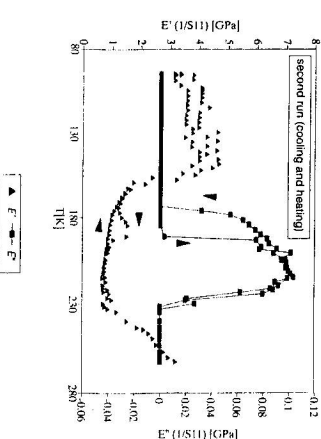


Fig. 8: Inverse value of the elastic compliance S_{11} at 10 Hz in an 'old' ALHS-crystal

405K and about 2.8 eV above 405K. In c -direction E_a is about 1 eV below 405 K, it then increases up to several eV around 405 K and is about 1.8 eV above 405K.

DSC measurements on a Perkin Elmer Differential Scanning Calorimeter (DSC7) yielded the melting point to be at about 430 K. Another shoulder in the specific heat was found about 15K below the melting point (compare [15]). Its possible origin is referred to in the conclusion.

4. Elastic measurements

The ferroelastic phase transition 4 \rightarrow 2 is described by an order parameter $\gamma(e_1 - e_2) + \delta e_6$ [16] thus inducing elastic instabilities in the plane perpendicular to the tetragonal c -axis. Therefore we investigated the static and low-frequency elastic behaviour of ALHS with a Perkin Elmer Dynamic Mechanical Analyzer (DMA7) along the tetragonal a -direction. In this apparatus the sample is located between parallel plates and a chosen static pressure is applied which is modulated by a dynamic pressure of chosen amplitude and frequency. The amplitude and phase shift of the elastic response of chosen sample allows to determine the real and the imaginary part of the elastic compliance S . Our measurements have been performed with a static pressure between 0.1 - 0.3 MPa to ensure an elastic response of the sample which is significantly above the resolution of the mentioned apparatus. The determination of the relative change of the elastic compliance is more precise than that of the absolute values. The measured absolute value of $E'_{11} \equiv 1/S_{11}$ at room temperature was found to be at about 6×10^9 Pa which is in good agreement with already published results (measurements of elastic constants with Brillouin scattering [16]). Above room temperature E'_{11} , the real part of E'_{11} , shows a decrease especially at temperatures between 390 K and 420 K. Measurements showed that the elastic behaviour of the crystal depended on whether it was the first run or the second time that the crystal was cooled below T_c within a few hours. In the first run E'_{11} remains rather small but shows the same qualitative behaviour as in later runs (see Figure 7): A large decrease when approaching T_c from above, then a V-shaped minimum at T_c ; when cooling further E'_{11} increases at about 158 K to reach a plateau; besides, E'_{11} shows a small maximum at about 188 K which only appears in the heating curve. For an 'old' crystal (i.e. after the first run within the same experiment - see Figure 8) E'_{11} remains higher than in the first run and the increase of E'_{11} at 158 K is much larger than in a 'fresh' crystal. Sometimes even the room temperature value of E'_{11} is reached. E''_{11} , the imaginary part of E'_{11} , reveals a maximum in the first run which is almost never reproduced in later runs. This maximum shifts to lower temperatures with decreasing frequency. In the region between 158 K and T_c E''_{11} exhibits a second maximum which is rather broad and sometimes consists of more than one peak. In general E''_{11} is smaller where E'_{11} takes larger values. After leaving the sample in the apparatus under small static pressure for one night the crystal again behaved like a fresh one. The measured elastic behaviour along the a -direction was reproducible also with different samples cut from different crystals. Measurements along the tetragonal c -direction did not reveal the damping peaks mentioned above.

The linear thermal expansion coefficient α has been measured between 100 K and 295 K by Mróz et al. [15]. We measured α above room temperature and found it to be constant at 3×10^{-5} for the a - and the c -direction up to 423 K.

5. Conclusions

The appearance of a strong frequency dispersion of the dielectric constant (above $T_c = 233$ K) is consistent with the assumption of superionic conducting behaviour of ALHS. The change in the activation energy at 405 K may be due to a change in the

mechanism of conducting and to pre-melting effects. This matches with the observation of an additional shoulder in the DSC results.

Distinct anomalies have been found in the imaginary part of the complex elastic compliance below the ferroelastic phase transition. The results along the a -direction lead to the hypothesis that there are domain processes which can be held responsible. As the results are similar to those in ferroelastic KDP-like crystals [17, 18] we suggest the occurrence of domain freezing in ALHS. More detailed investigations are in progress to clarify the mentioned problems.

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