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Optical properties of the ferroelastic phase transition in $(NH_4)_4LiH_3(SO_4)_4$

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Abstract. The ferroelastic phase transition in $(NH_4)_4LiH_3(SO_4)_4$ at 232 K has been studied by birefringence measurements in the temperature range 190–300 K. The temperature dependence of the birefringence can be well described by the Landau theory for a proper ferroelastic phase transition of second order. The domain structure is compatible with the symmetry reduction from the tetragonal to the monoclinic phase.

1. Introduction

The existence of the following solid compounds at 30 °C in the system $(NH_4)_2SO_4$–Li_2SO_4–H_2SO_4–H_2O has been reported in the literature (Gmelin (1936), and references therein): Li_2SO_4, $Li_2SO_4.H_2O$, $Li_2SO_4.\frac{1}{3}H_2O$, $LiHSO_4$, $(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, NH_4LiSO_4, $NH_4LiH_2(SO_4)_2$, $NH_4Li_3H_2(SO_4)_4$, $(NH_4)_3LiH_4SO_4$, $(NH_4)_3LiH(SO_4)_4$, $(NH_4)_4LiH_3(SO_4)_4$, $(NH_4)_4Li_3H(SO_4)_4$. Of these $(NH_4)_2SO_4$, NH_4HSO_4, NH_4LiSO_4 and $(NH_4)_3H(SO_4)_2$ have been intensively studied because of their interesting phase transitions (Landolt–Börnstein 1990) and Li_2SO_4 because it is an interesting superionic conductor. Little is known about the other compounds. Very recently, the structure of $(NH_4)_4LiH_3(SO_4)_4$ (ALHS) has been determined (Pietrasko *et al* 1991, Polomska *et al* 1993). At room temperature, ALHS has the tetragonal space group $P4_1$ with the lattice parameters $a = 7.642$ Å and $c = 29.566$ Å. At 232.5 K a phase transition takes place, changing the crystal to the ferroelastic monoclinic phase with the space group $P2_1$, similar to the isomorphous Rb salts $Rb_4LiH_3(BO_4)_4 (B \equiv S$ on Se) (Polomska and Smutny 1988, Wolejko *et al* 1988, Piskunowicz *et al* 1989, Pietrasko *et al* 1991). To obtain a deeper insight into the nature of the phase transition, we have performed optical investigations on ALHS. In particular the measurement of the birefringence gives valuable information on the variation in the order parameter with temperature (Fousek and Petzelt 1979).

2. Experimental details

The crystals have been grown from a stoichiometric aqueous solution of Li_2SO_4, $(NH_4)_2SO_4$ and H_2SO_4 at room temperature by slow evaporation of the water. Sometimes, when the supersaturation was too high, different crystals appeared prior to ALHS, which did not show a phase transition at 232 K. No systematic study was made to check the chemical composition

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and the conditions of nucleation of these crystals. ALHS crystalizes in two main shapes: firstly thin, rectangular and almost quadratic plates, several millimetres thick and up to 40 mm broad with the crystallographic [001] axis perpendicular to the plates, and secondly in the form of truncated pyramids, several centimetres in dimension with the [001] axis perpendicular to the basis of the pyramids. The crystals were of good optical quality. Although ALHS is highly hygroscopic, it was possible during the winter-time to cut out and polish proper plates for optical investigations when, because the rooms were heated, the humidity of the air was low. The orientations of the *a* and *c* plates were determined by their conoscopic pictures.

A polarizing microscope (Zeiss Axiophot) equipped with a Linkam hot stage was used for the experiments. A small home-made pressure clamp fixed on the hot stage made it possible to apply various uniaxial stresses to the samples. The birefringence was measured fully automatically using Senarmont compensation (Zimmerman and Schranz 1993). A variable rectangular aperture allowed selection of a single-domain part of the crystal.

3. Results and discussion

A typical pattern of ferroelastic domains of ALHS observed at about 223 K is shown in figures 1(*b*) and 1(*c*). The domain boundaries are planar and the two stripe systems are mutually perpendicular. However, the domain walls are not oriented at an angle $\alpha = 45^\circ$ with respect to the [100] axis of the high-temperature tetragonal phase, but at $\alpha = 57^\circ \pm 2^\circ$. In addition, the orientation of the domain wall slightly rotates with changing temperature (about 0.02° K^{-1}). This result is consistent with a symmetry reduction from a tetragonal symmetry 4 to the monoclinic symmetry 2. Unlike the symmetry reduction from 4 mm to 2, where the orientation of the domain walls is fixed by the lost mirror plane, this is not the case for symmetry reduction from 4 to 2. Although the two permissible domain wall directions are mutually perpendicular, fulfilling the compatibility condition of Sapriel (1975), their orientations are not fixed with respect to the axis of the high-symmetry phase. Similar results have been found for ALHS (Polomska *et al* 1993) and for $RbLiH_3(SO_4)_4$ (Polomska and Smutny 1990).

By applying unaxial pressure along the *a* or *b* directions of a *c* plate, it was possible to transform the crystals into a single-domain state. The process of disappearance of ferroelastic domain walls under the action of a compressive unaxial stress σ_1 is illustrated in figure 1, where figure 1(*a*) shows the initial multidomain state and figure 1(*c*) the single-domain state.

In figures 2 and 3 the temperature dependences of the linear birefringence Δn_c and $(\Delta n_c)^2$ respectively, are presented. Δn_c is the morphic birefringence which is zero in the parent phase and is induced below T_c by the structural phase transition. Unlike the situation for $Rb_4LiH_3(SO_4)_4$ (Przeslawski *et al* 1990), $(\Delta n_c)^2$ is not linearly proportional to the temperature below T_c in the case of ALHS. This behaviour suggests the influence of higher-order terms in the thermodynamic potential Φ. The symmetry reduction from 4 to 2 can occur in two different ways which are described by the order parameters $\frac{1}{2}(\epsilon_1 - \epsilon_2)$ or ϵ_6, respectively. In analogy to $Rb_4LiH_3(SO_4)_4$ (Hempel *et al* 1988) we describe the present phase transition by the order parameter $\eta = \frac{1}{2}(\epsilon_1 - \epsilon_2)$. Then the simplified version of the thermodynamic potential Φ can be written as

$$\Phi = \tfrac{1}{2}\alpha(T - T_c)\eta^2 + \tfrac{1}{4}\beta\eta^4 + \tfrac{1}{6}\gamma\eta^6 \qquad (1)$$

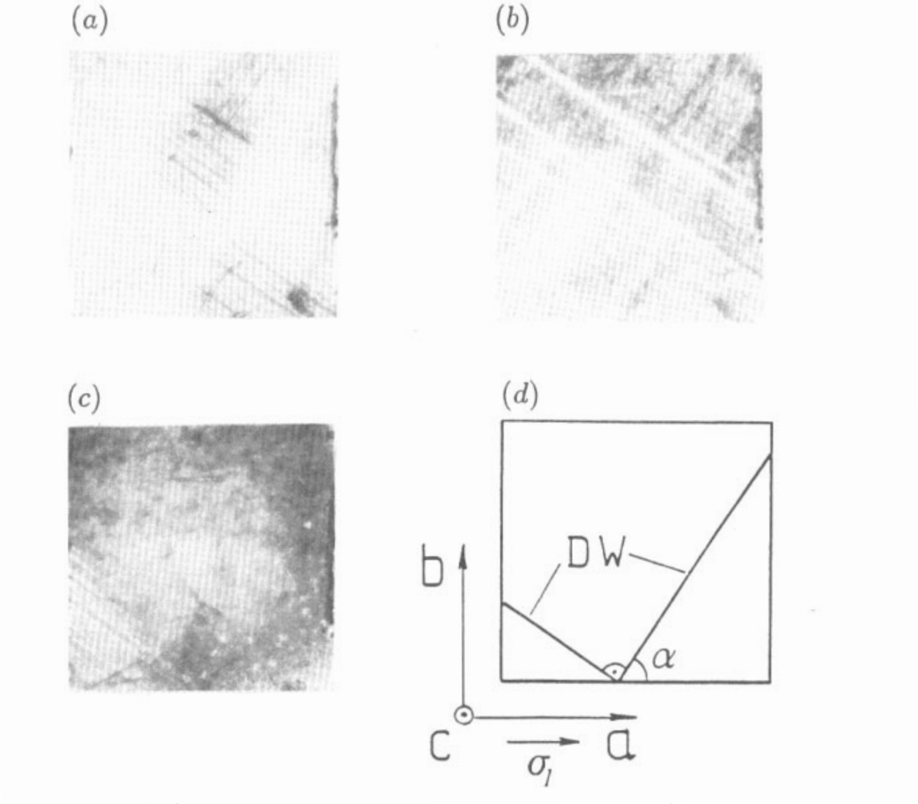

Figure 1. Changes in the domain structure induced by a compressive unaxial stress σ_1: (*a*) $\sigma_1 = 0$; (*b*) $\sigma_1 = 0.45$ MPa; (*c*) $\sigma_1 = 0$ (after application of $\sigma_1 = 1$ MPa), $T = 223$ K; (*d*) schematic picture of the ferroelastic domain structure (DW, domain walls; a, b, c, tetragonal notation).

where α, β and γ are the renormalized coefficients, i.e. after elimination of the strains. As usual γ has to be positive to stabilize Φ.

Minimizing (1) we obtain the well known formula

$$\eta^2 = A_1\{-1 + [1 - A_2(T - T_c)]^{0.5}\} \qquad (2)$$

where $A_1 = \beta/2\gamma$ and $A_2 = 4\alpha\gamma/\beta^2$.

Because of the photoelastic effect a spontaneous birefringence appears below T_c (Fousek and Petzelt 1979). This spontaneous part $\delta(\Delta n_i)$ of the birefringence, derived after subtracting the background, is linearly proportional to the order parameter in the case of $\delta(\Delta n_c)$, while in the cases of $\delta(\Delta n_a)$ and $\delta(\Delta n_b)$ a quadratic term in the order parameter has also to be taken into account (see, e.g., Wood and Glazer 1980):

$$\delta(\Delta n_c) = \Delta n_c = K_c\eta \qquad (3a)$$

$$\delta(\Delta n_a) = \delta(\Delta n_b) = K_{a,b}\eta + \ell_{a,b}\eta^2 \qquad (3b)$$

Fitting the data for Δn_c (figure 3) according to equations (3*a*) and (2) we find that $K_c^2 A_1 = 57 \pm 11$, $A_2 = (1.88 \pm 0.3) \times 10^{-2}$ and $T_c = 232.53 \pm 0.2$ K. From the positive

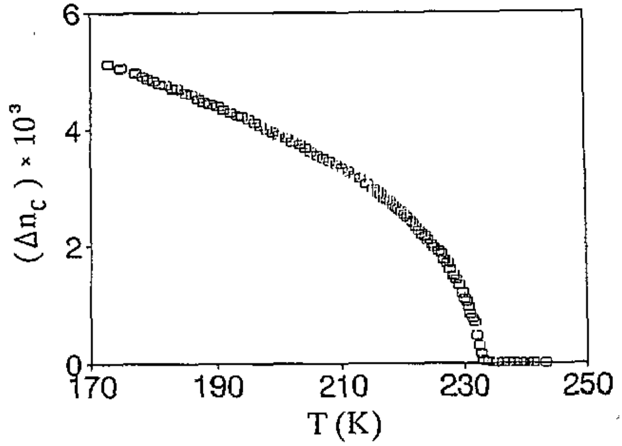

Figure 2. Plot of Δn_c against temperature for an ALHS crystal ($\sigma_a = 0$).

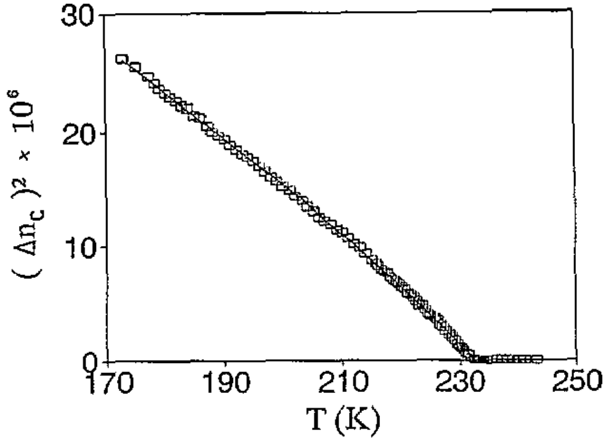

Figure 3. Plot of $(\Delta n_c)^2$ against temperature for an ALHS crystal ($\sigma_a = 0$); □, experimental; ——, fit according to equation (2).

signs of $K_c^2 A_1$ and γ it follows that $\beta > 0$, which implies the phase transition in ALHS to be of second order.

In figure 4 the linear birefringence Δn_a versus temperature is presented. In the paraelastic phase, Δn_a is independent of temperature.

To avoid the influence of domains and to see whether the results in figure 2 are influenced by the presence of ferroelastic domains, we have measured the temperature dependence of the birefringence under an applied unaxial stress. In this case it was possible to measure a single-domain sample. Figure 5 shows $\Delta n_c(T)$ with an applied stress $\sigma_1 = 0.45$ MPa. In a similar way to previously, we have fitted the data using equation (2). Now the fitted parameters turned out to be $K_c^2 A_1^\sigma = 40.6 \pm 9$, $A_2^\sigma = (2 \pm 0.4) \times 10^{-2}$ and $T_c^\sigma = 233.57 \pm 0.2$ K. As expected for a proper ferroelastic phase transition, T_c^σ shifted to significantly higher temperatures when a stress was applied (figure 6). In addition, a birefringence tail is observed in the tetragonal phase of ALHS (figure 5). This smearing

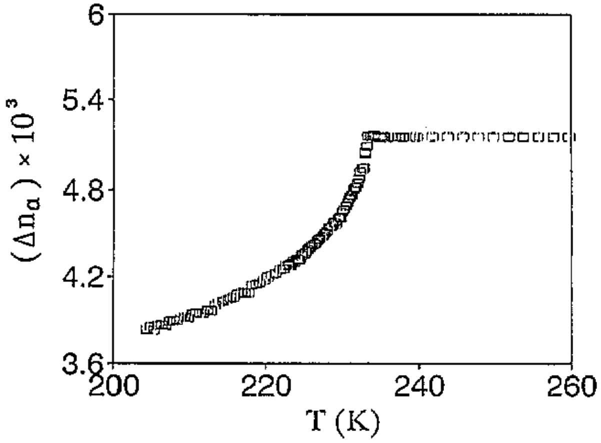

Figure 4. Plot of (Δn_a) against temperature for an ALHS crystal ($\sigma_a = 0$).

of the phase transition is caused by application of the symmetry-breaking stress σ_1 (see, e.g., Lines and Glass, 1977), which makes the crystal of a single-domain nature.

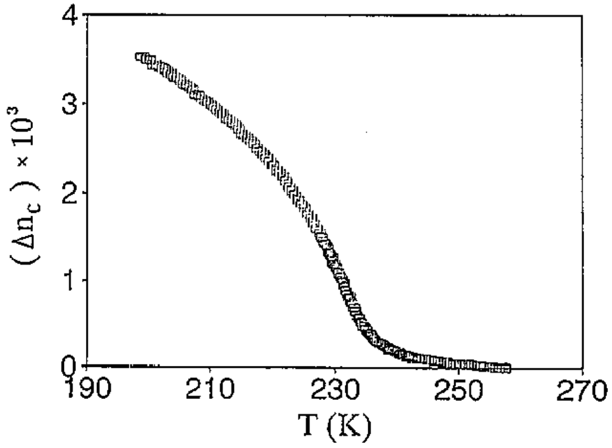

Figure 5. Plot of Δn_c against temperature for an ALHS crystal ($\sigma_a = 0.45$ MPa).

4. Conclusions

ALHS single crystals were grown and optically investigated. ALHS undergoes a ferroelastic phase transition at $T_c = 232.5$ K. Investigations of the ferroelastic domain structure are consistent with a structural phase transition from the tetragonal symmetry 4 to the monoclinic symmetry 2, in agreement with recent x-ray structure investigations (Polomska *et al* 1992). The temperature dependence of the spontaneous birefringence can be well described by the Landau theory for a second-order phase transition including terms up to the sixth order in the thermodynamic potential.

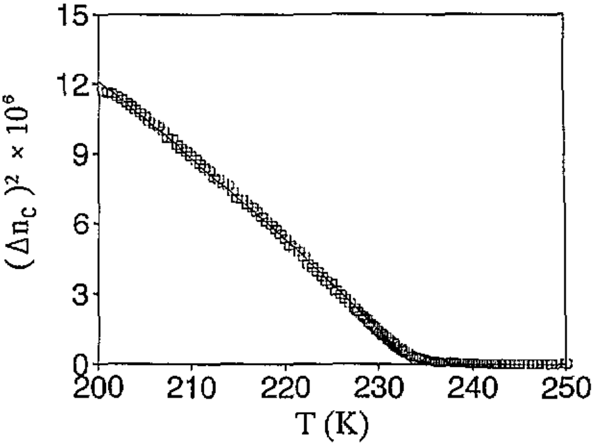

Figure 6. Plot of $(\Delta n_c)^2$ against temperature for an ALHS crystal ($\sigma_a = 0.45$ MPa): □, experimental; ——, fit according to equation (2).

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