

Phase transitions in lithium ammonium sulfate below room temperature: An ultrasonic study

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A detailed ultrasonic study of the elastic properties of lithium ammonium sulfate (LiNH_4SO_4) or LAS has been carried out below room temperature. The elastic constants of LAS at room temperature are reported. The discrepancy present in earlier elastic constant data associated with the different choice of axes for this orthorhombic system are clarified. The results of the temperature variation study down to 220 K confirm the ferroelastic phase transition at 285 K and establish a thermal hysteresis of about 2.5 K between the cooling and heating cycles. Results of the investigation on the suspected weak phase transition at 256 K suggest that this transition occurs at 242 K on cooling and at 256 K on heating, thus having a thermal hysteresis of about 14 K. However, since the observed elastic anomaly for this transition is very small, the nature of this transition still remains unclear. [S0163-1829(96)01046-6]

I. INTRODUCTION

Lithium ammonium sulfate, LiNH_4SO_4 , or LAS is an extensively studied crystal which is known to exhibit an interesting sequence of phase transitions like many other members of the sulfate family. A variety of experiments carried out on this material by different workers¹⁻⁴ have established the sequence of phase transitions depicted in Fig. 1. At room temperature the structure of LAS crystals belongs to a $P2_1cn$ (C_{2v}^9) (orthorhombic) space group, with four molecules per unit cell. Both the ferroelectric transition at 460 K and the ferroelastic transition at 285 K are of first order. X-ray results show that there are four molecules per unit cell in phases I and II, eight in phase III, and 16 in phase IV. Hildmann *et al.*⁵ have shown that phase III is ferroelastic making LAS an example of a ferroelastic crystal which is not simultaneously ferroelectric. The x-ray results of Simonson, Denoyer, and Moret,⁶ the infrared-absorption curves of Gerbaux *et al.*,⁷ and the dielectric constant and Raman spectroscopic measurements of Martins *et al.*⁸ have established a second-order phase transition occurring at 28 K taking LAS to a C_s^4 space group (phase IV) with a doubling of the unit-cell volume.

The elastic constants of LAS at room temperature have been measured by earlier workers using ultrasonic³ and Brillouin-scattering⁹⁻¹¹ techniques. The temperature variation of selected elastic constants near the 460 K ferroelectric

phase transition has been determined by ultrasonic¹² and Brillouin-scattering^{13,14} techniques. Also, clear evidence for the ferroelastic transition at 285 K has been obtained in the experimental results on the temperature variation of the elastic constants using Brillouin-scattering technique.¹¹ These experimental results and the Landau-type theoretical models proposed by Torgashev, Dvorak, and Smutny,¹⁵ Luspin, Hauret, and Gillet,¹⁰ Hirotsu *et al.*,¹³ and Schranz and co-workers^{16,17} have made it possible to get a clear understanding of the ferroelectric and ferroelastic phase transitions occurring in LAS.

Several questions have been raised about the polar nature of phase III. Kruglik, Simonov, and Aleksandrov⁴ claimed that this phase is polar with a monoclinic structure belonging to the $P2_1c$ (C_{2h}^5) space group. The nonpolar nature of LAS in phase III was rejected by Poulet and Mathieu¹⁸ who used Raman scattering to study the phase II→phase III transition. Their results showed that some Raman bands appearing below the transition point at 285 K is an indication of cell doubling, carrying modes from the boundary to the center of the Brillouin zone. They have described this transition as a first-order ferroelastic one but phase III was considered polar, belonging to a $P2_1$ (C_2^2) space group. They also proposed that phase III could be a modulated phase with a long modulation period. The polar nature of phase III was supported by Gerbaux *et al.*⁷ who found a weak anomaly in the dielectric constant and some pyroelectric response on both sides of the transition point. Based on their Raman studies, Torgashev *et al.*¹⁹ agreed with Poulet and Mathieu¹⁸ on the doubling of the unit cell but argued that phase III belongs to the $P2_1c$ (C_{2h}^5) space group, in accordance with Kruglik, Simonov, and Aleksandrov⁴ and Simonson, Denoyer, and Moret.⁶ Then this phase would be monoclinic and nonpolar with eight molecules per unit cell. The ambiguity is raised by a mode with frequency 24 cm^{-1} in Raman spectra at 183 K that behaves as a soft mode when the temperature approaches the transition point at 285 K. However, if phase III has a center of inversion, then polar modes would only be infrared active. This led Poulet and Mathieu¹⁸ to propose that phase III is polar, with a structure belonging to a noncentrosymmetric space group, probably C_2^2 .

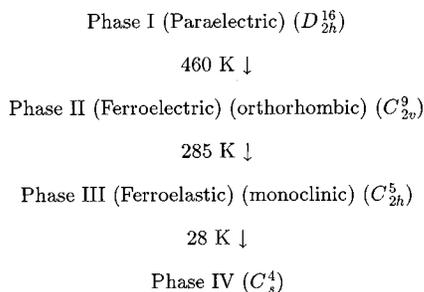


FIG. 1. Sequence of phase transitions in LAS.

Some of these discrepancies have been addressed by Martins *et al.*⁸ who undertook dielectric constant and polarized Raman-scattering measurements on LAS below room temperature. They detected a phase transition taking place at 256 K. Infrared absorption and dielectric measurements by Gerbaux *et al.*⁷ also have indicated a transition taking place at this temperature. Specific-heat measurements²⁰ also have shown an anomaly near 256 K. Martins *et al.*⁸ have suggested that the transition at 256 K is second order, order-disorder type, and reversible. Their results were not sufficient to decide whether LAS goes from C_{2h}^5 to a new symmetry belonging to the C_s^1 or C_s^2 space group at 256 K.

In order to throw more light on the nature of the transitions at 285 and 256 K, we have carried out a detailed ultrasonic study of the temperature dependence of the elastic constants of LAS below room temperature. Present work is the first ultrasonic study in LAS in this temperature range. The only elastic data available for LAS below room temperature is from a Brillouin-scattering study¹¹ near the 285 K transition over a limited temperature range without investigating the thermal hysteresis of this transition. There are no elastic data available in literature near the 256 K transition. In present work both the temperature variations during heating and cooling have been investigated. The details of the experimental technique used and the results obtained are described in the following sections. A detailed discussion of the results is given in the last section.

II. EXPERIMENTAL TECHNIQUE

A. Sample preparation

Single crystals of LAS, LiNH_4SO_4 , are grown by evaporation of an equimolar solution of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$ at a constant temperature of 311 K. A large single crystal of LAS, measuring about 5 cm in the c -axis direction is obtained after a period of 60 days. LAS usually grows in two different forms, one is the prismatic form and the other is the pseudo-hexagonal form. The pseudo-hexagonal form is a twined crystal and is usually obtained from spontaneously nucleated seeds at room temperature. The untwined prismatic form of LAS has been grown for the present studies. The crystallographic directions of the grown crystal is determined by comparing the measured interfacial angles with the calculated values of interfacial angles using the lattice parameters, $a = 8.78 \text{ \AA}$, $b = 9.131 \text{ \AA}$, $c = 5.282 \text{ \AA}$.²¹ The good agreement between the calculated and measured values of interfacial angles prove that our direction identification is correct.

The grown crystals of LAS have been cut using a slow speed diamond wheel saw so as to have propagation direction along a , b , and c axes as well as $[101]$, $[110]$, and $[011]$ directions. The cut samples in different directions have thickness in the range 0.8–to 1.2 cm. The samples are polished carefully using cerium oxide to optical reflection level. The misorientations of the cut samples are less than 1° .

B. Elastic constant measurements

Velocities of longitudinal and transverse ultrasonic waves of frequency 10 MHz propagating along the different crystallographic directions have been measured accurately (with

bond correction) by the pulse-echo overlap method²² using a MATEC ultrasonic system. The relevant expressions for isolating the elastic constants from velocity data for an orthorhombic crystal have been given earlier by us.²³ Velocities of a total of 12 modes have been measured to isolate and cross-check the nine elastic constants of LAS at room temperature.

Temperature variation of all the diagonal elastic constants of LAS in orthorhombic pure mode directions below room temperature have been measured in the range 310–220 K. This range includes the well-known phase transition near 285 K and the recently proposed⁸ phase transition near 256 K. The temperature variation measurements have been carried out in a liquid-nitrogen cryostat with the sample mounted in an accurately controlled constant temperature environment. Silicone grease (RS Components, UK. No. 555-083) has been used as the bond between the sample and transducer. Temperature variation measurements are carried out in temperature intervals of 1 K and in intervals of 0.1 K near the transition points. Measurements have been carried out during cooling and heating cycles with the rate of temperature change in the range of 0.1 to 0.5 K per minute.

One major difficulty with ultrasonic measurements in LAS below room temperature is the sudden development of cracks in the crystal near the 285 K phase transition. This often happens even at extremely slow cooling rates. We have found that ultrasonic measurements are still possible below the transition temperature, in the presence of cracks in the crystal, with considerably reduced echo amplitudes. This is achieved by careful tuning and sensitive adjustments of the measuring system. Attenuation measurements are often found to be difficult to perform due to the deviation of the echo pattern from exponential decay below the transition temperature.

III. RESULTS

A. Elastic constants of LAS at room temperature

On examination of the previous measurements, it can be found that there are wide disagreements between the values of elastic constants reported by various workers. We have resolved these disagreements to some extent by identifying the fact that different workers have taken a different choice of axes for this orthorhombic crystal. Mróz *et al.*,¹¹ who have recently compared their values with the previous measurements, do not seem to have noticed this point. Using the tensor notation of the elastic constants, all the elastic constants can be transformed from one choice of axes to another and it can be seen that there are six possible choices for selecting the three lattice parameters a , b , and c . The conversion scheme for all the elastic constants of LAS under a different choice of axes are tabulated in Table I.

In Table II we give the values of all the nine elastic constants of LAS measured at 300 K. The McSkimin Δt criterion²⁴ has been applied to account for phase differences due to reflection of ultrasonic waves at various interfaces while estimating the travel time in the sample. The accuracy of the values reported in Table II is better than $\pm 2\%$. The value of density used for calculating elastic constant from velocity is $\rho = 1.902 \text{ gm cm}^{-3}$.^{10,11} The values of elastic constants reported by earlier workers are also given for comparison. We have compared the previous measurements after re-

TABLE I. Conversion table for elastic constants of orthorhombic LAS under different choice of crystallographic axes.

| Lattice parameters | Axes choice (1) ^a | Axes choice (2) ^b | Axes choice (3) | Axes choice (4) | Axes choice (5) | Axes choice (6) |
|--------------------|------------------------------|------------------------------|-----------------|-----------------|-----------------|-----------------|
| 5.282 Å= | <i>a</i> | <i>c</i> | <i>b</i> | <i>c</i> | <i>b</i> | <i>a</i> |
| 9.131 Å= | <i>b</i> | <i>b</i> | <i>a</i> | <i>a</i> | <i>c</i> | <i>c</i> |
| 8.780 Å= | <i>c</i> | <i>a</i> | <i>c</i> | <i>b</i> | <i>a</i> | <i>b</i> |
| C_{11} | C_{11} | C_{33} | C_{22} | C_{33} | C_{22} | C_{11} |
| C_{22} | C_{22} | C_{22} | C_{11} | C_{11} | C_{33} | C_{33} |
| C_{33} | C_{33} | C_{11} | C_{33} | C_{22} | C_{11} | C_{22} |
| C_{44} | C_{44} | C_{66} | C_{55} | C_{66} | C_{55} | C_{44} |
| C_{55} | C_{55} | C_{55} | C_{44} | C_{44} | C_{66} | C_{66} |
| C_{66} | C_{66} | C_{44} | C_{66} | C_{55} | C_{44} | C_{55} |
| C_{12} | C_{12} | C_{23} | C_{12} | C_{13} | C_{23} | C_{13} |
| C_{13} | C_{13} | C_{13} | C_{23} | C_{23} | C_{12} | C_{12} |
| C_{23} | C_{23} | C_{12} | C_{13} | C_{12} | C_{13} | C_{23} |

^aChoice by recent x-ray work (Ref. 21).

^bThe choice of axes for present work; also adopted by workers in Refs. 3 and 10.

arranging the elastic constants according to Table I and this shows much better agreement between the constants reported by previous workers. Present measurements clarify the confusion in literature regarding elastic constants of LAS.

B. Variation of elastic constants below room temperature

The temperature variation of the elastic constants C_{11} , C_{66} , C_{33} , C_{44} , and C_{55} below room temperature, in the range 310 to 220 K, are shown in Figs. 2–5. Some measurements could not be obtained over the full temperature range due to the loss of echo pattern. The phase transition occurring at 285 K is clearly visible in all the figures. The longitudinal

constants C_{11} and C_{33} undergo abrupt changes at this temperature whereas the transverse constants C_{44} , C_{55} , and C_{66} exhibit more of a continuous increase below this temperature. There is a clear thermal hysteresis of ≈ 2.5 K between the cooling and heating cycles for this transition. Present measurements establish that on cooling the transition takes place at 285.5 K and on heating the transition takes place at 288 K.

The phase transition at 285 K changes the symmetry of the crystal. The crystal goes from the room-temperature (phase II) orthorhombic $mm2$ (C_{2v}) point group to monoclinic $2/m$ (C_{2h}) point group below the phase transition temperature (phase III). Many of the pure modes in orthorhom-

TABLE II. Elastic constants of LAS in comparison with previously measured values (after rearrangement according to the axes choice defined in Table I). All values are in GPa.

| Elastic constant | Ref. 3 ^{a,c,e} | Ref. 13 ^{b,d,f} | Ref. 10 ^{b,d,g} | Ref. 12 ^{a,d,h} | Ref. 11 ^{b,c,i} | Present work ^{a,j} |
|------------------|-------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-----------------------------|
| C_{11} | 41.59 | 44.5 | | 39.3 | 43.8 | 43.57±0.6 |
| C_{22} | 44.10 | 46.2 | | 40.3 | 52.2 | 46.66±0.6 |
| C_{33} | 49.73 | 54.5 | | 50.2 | 55.2 | 55.11±0.6 |
| C_{44} | 15.40 | | 16.1 | 15.7 | 13.1 | 16.29±0.2 |
| C_{55} | 9.88 | | 10.6 | 10.0 | 10.8 | 10.41±0.2 |
| C_{66} | 15.73 | | 16.4 | 15.5 | 15.1 | 16.96±0.2 |
| C_{12} | 19.7 | | | 21.5 | 23.6 | 19.67±1.5 |
| C_{13} | 26.1 | | | 24.7 | 27.7 | 28.88±1.5 |
| C_{23} | 22.8 | | | 21.0 | 34.1 | 26.26±1.5 |

^aUltrasonic measurements.

^bBrillouin-scattering measurements.

^cValues from tabulated data.

^dValues from temperature variation curves.

^eAt 300 K, axes chosen is (2).

^fAt 300 K, axes chosen is (1).

^gAt 300 K, axes chosen is (2).

^hAt 300 K, axes chosen is (3).

ⁱAt 293 K, axes chosen is (1).

^jAt 300 K, axes chosen is (2).

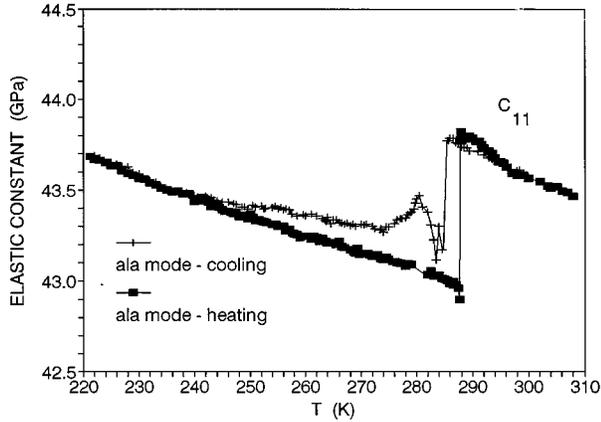


FIG. 2. Temperature variation of elastic constant for the cooling and heating cycle of the *ala* mode in LAS.

bic phase are no longer pure modes in the monoclinic phase and combination constants of monoclinic symmetry are only applicable in phase III. With our choice of axes [see choice (2) in Table I] the *c* axis coincides with the twofold *y* axis in the monoclinic phase. Cell doubling upon transition takes place along orthorhombic *a* axis⁴ which is also made to correspond with monoclinic *x* axis. The orthorhombic *b* axis is made to correspond with monoclinic *z* axis.

The involved constants in both phases for different propagation modes are tabulated in Table III with our choice of axes. We indicate different modes with a three letter notation; the first letter (*a*, *b* or *c*) indicates the direction of wave propagation, the second letter (*l* or *t*) indicates whether the waves are longitudinal or transverse, the third letter (*a*, *b* or *c*) indicates the direction of polarization. We find some errors and inconsistencies in a similar table given earlier by Mróz *et al.*¹¹

In the monoclinic phase, some minor elastic anomalies can be noticed. For the combination constant in *atb* mode there appears a dip at 242 K on cooling and a slope change at 256 K on heating (Fig. 3). Similarly for the *clc* mode there is a weak anomaly at 242 K on cooling and at about 256 K on

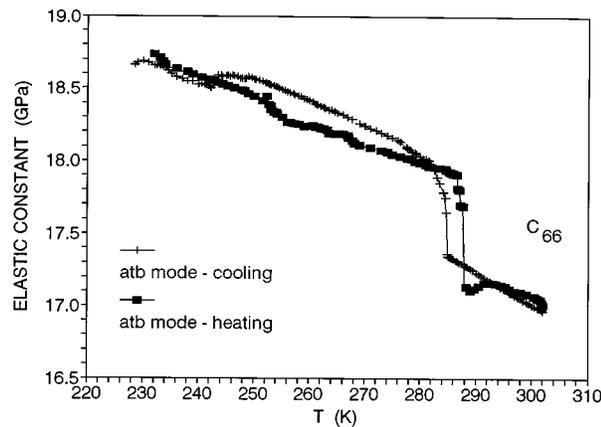


FIG. 3. Temperature variation of elastic constant for the cooling and heating cycle of the *atb* mode in LAS.

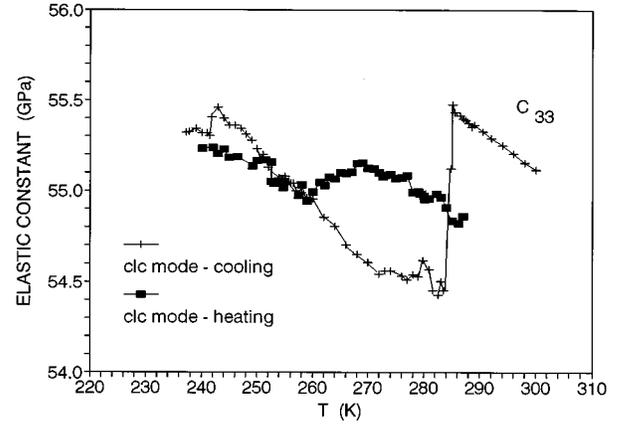


FIG. 4. Temperature variation of elastic constant for the cooling and heating cycle of the *clc* mode in LAS.

heating (Fig. 4). These anomalies are indicative of a weak phase transition occurring in LAS with a thermal hysteresis of about 14 K between the cooling and heating cycles.

All the modes investigated (Table III) exhibit clear anomaly near 285 K with a temperature hysteresis of 2.5 K between cooling and heating cycles. The *ctb* and *cta* modes do not exhibit any significant anomalies below 285 K, so only their cooling curves are plotted. Since the *blb* mode also shows no significant anomaly below 285 K, its temperature variation is not reproduced here.

IV. DISCUSSION

A. Phase transition at 285 K

As has been reported by earlier workers, the phase transition at 285 K is clearly a first-order ferroelastic one. Even though the continuous increase of the shear elastic constants below 285 K carry signatures of a second-order phase transition, there is no other evidence in support of this. So we think that the transition is first order itself. In the temperature dependence of elastic constants shown in Figs. 2 and 3, one can notice a clear thermal hysteresis of ≈ 2.5 K between the

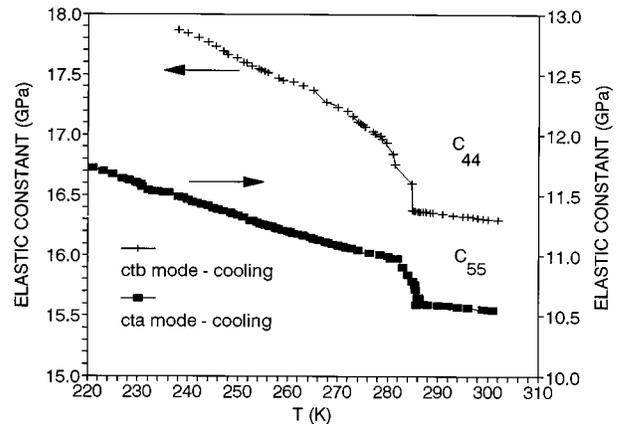


FIG. 5. Temperature variation of elastic constant for the cooling cycle of the *ctb* and *cta* modes in LAS.

TABLE III. The involved elastic constants in orthorhombic $mm2$ and monoclinic $2/m$ phase of LAS for different modes of propagation.

| Modes | $mm2$ phase | $2/m$ phase |
|---------|-------------|--|
| ala^a | C_{11} | $\frac{1}{2}\{C_{11} + C_{55} + [(C_{11} - C_{55})^2 + 4C_{15}^2]^{1/2}\}$ |
| atc | C_{55} | C_{66} |
| atb^a | C_{66} | $\frac{1}{2}\{C_{11} + C_{55} - [(C_{11} - C_{55})^2 + 4C_{15}^2]^{1/2}\}$ |
| clc^a | C_{33} | C_{22} |
| ctb^a | C_{44} | $\frac{1}{2}\{C_{44} + C_{66} + [(C_{44} - C_{66})^2 + 4C_{46}^2]^{1/2}\}$ |
| cta^a | C_{55} | $\frac{1}{2}\{C_{44} + C_{66} - [(C_{44} - C_{66})^2 + 4C_{46}^2]^{1/2}\}$ |
| blb^a | C_{22} | $\frac{1}{2}\{C_{33} + C_{55} + [(C_{33} - C_{55})^2 + 4C_{35}^2]^{1/2}\}$ |
| bta | C_{66} | $\frac{1}{2}\{C_{33} + C_{55} - [(C_{33} - C_{55})^2 + 4C_{35}^2]^{1/2}\}$ |
| btc | C_{44} | C_{44} |

^aModes which have been investigated in this work.

cooling and heating cycles. One expects this kind of a hysteresis in elastic constant values when a crystal undergoes a first-order ferroelastic phase transition.²⁵ This small hysteresis can be attributed to the pinning of the ferroelastic domains when the sample is cycled through the transition. The elastic constant data obtained from Brillouin-scattering experiments¹¹ do not show this hysteresis, probably because the authors did not make the measurements during cooling as well as heating cycles. Further the Brillouin data¹¹ show steplike changes for all the constants while the present ultrasonic data show some continuous variation for the shear mode constants below 285 K. It is interesting to note that this kind of discrepancy between ultrasonic and Brillouin experiment is also present in LAS for the 460 K transition for the elastic constant C_{44} . Schranz *et al.*¹⁷ have argued that this difference in behavior of the elastic constant under Brillouin scattering ($f=10$ GHz) and ultrasonic ($f=10$ MHz) experiment is due to the presence of a soft relaxational mode that couples only to the low-frequency shear mode. Present results indicate the presence of a similar mechanism in LAS below the 285 K transition.

A Landau model describing the sequence of phase transitions occurring in LAS has been put forward by Torgashev, Dvorak, and Smutny.¹⁵ Schranz and co-workers^{16,17} have theoretically analyzed the possible couplings between strains and the order parameter involved. Mróz *et al.*¹¹ have put forward a theoretical model for the ferroelastic phase transition in LAS focusing attention on the vicinity of the transition. After writing down the free-energy expression and considering the strain e_5 , one can show that the order parameter η is given by

$$\eta = \left[\frac{(C_{55}^0 + 2G_5 P^2)}{l} \right] e_5, \quad (1)$$

where P is the polarization. The coupling between e_5 and P shifts the transition temperature by a constant value. With the transition to the ferroelastic phase, the polarization of the sample vanishes leading to a destabilization of the polarized phase. The effective second-order elastic coefficients experience a discontinuity at $T=T_c$ which is increased by the si-

multaneous disappearance of polarization. In the paraelastic phase (P), $e \approx 0$ (not exactly zero due to coupling with polarization) and

$$C_{55}^P \approx 2(b_2 + \mu P_s^2), \quad (2)$$

whereas in the ferroelastic phase (F), the relevant combination constant is

$$C_{55}^F \approx 17b_2, \quad (3)$$

such that

$$\Delta C = C_{55}^F - C_{55}^P \approx 15b_2 - 2\mu P_s^2. \quad (4)$$

Owing to the associated metastability of the phases, thermal hysteresis can be expected to occur. Similar theoretical formulations and arguments apply to the discontinuities exhibited by other strains. These discontinuities and thermal hysteresis are clearly seen in our elastic constant results shown in Figs. 2–5. In our results, the thermal hysteresis is observed both for the transition temperature and for the elastic constants. The thermal hysteresis effect of elastic constants is more evident in longitudinal mode constants.

B. Phase transition at 256 K

The small anomalies seen in our elastic constant curves shown in Figs. 3 and 4 are indicative of a transition taking place between 240 and 260 K. During the cooling cycle the anomaly is seen at 242 K and during the heating cycle it appears at 256 K indicating that there is a thermal hysteresis of ≈ 14 K for this transition between the cooling and heating cycles. A thermal hysteresis for this transition have not been reported earlier. Both Gerbaux *et al.*⁷ and Martins *et al.*⁸ have reported that the transition is occurring at 256 K, while Chhor, Abello, and Pommier²⁰ have interpreted the transition temperature as 248 K which in fact is near the mean value of 242 and 256 K. Since the observed elastic anomalies for this transition are very small, no clear conclusions can be derived presently, regarding the nature of this transition.

V. CONCLUSIONS

Our detailed ultrasonic studies on LAS give a final set of elastic constant values reported in Table II. The confusion in literature regarding the elastic constants, as a result of the different choice of axes for LAS adopted by different workers, is clarified with the use of a conversion table. Our measurements establish a ferroelastic phase transition at 285 K which is characterized by a thermal hysteresis in elastic constants in accordance with the predictions of the Landau theory. Finally, our experimental results indicate a weak

phase transition occurring in LAS at 242 K during the cooling cycle and at 256 K during the heating cycle. These results indicate that LAS is another interesting member of the sulfate family exhibiting a sequence of phase transitions as the temperature is varied.

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