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Optical, elastic, and dielectric studies of the phase transitions in lawsonite

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Results of optical birefringence, ultralow-frequency elastic, dilatometric, and dielectric measurements of lawsonite crystals are presented in a wide temperature range including two successive phase transitions $Cmcm \rightarrow (T_1 = 273 \text{ K}) \rightarrow Pmcn \rightarrow (T_2 = 120 \text{ K}) \rightarrow P2_1 \text{cn}$. Pronounced pretransitional effects are observed in macroscopic properties in a large temperature region ($\approx 200 \text{ K}$) above $T_1$. The low-temperature transition at $T_2 = 120 \text{ K}$ is found to be proper ferroelectric. A deviation from the Curie-Weiss law appears in the temperature dependence of the dielectric susceptibility in the region of the ferroelectric transition below $T_2$. Frequency dependent measurements of the dielectric permittivity yield evidence that ferroelectric domain-wall motion is responsible for this deviation from the standard behavior.

I. INTRODUCTION

Lawsonite, $\text{CaAl}_2[(\text{Si}_2\text{O}_7)(\text{OH})_2] \cdot \text{H}_2\text{O}$, is a mineral which is a common constituent of high-$P$ and low-$T$ metamorphic environments like blueschists. Containing $\approx 11$ wt% $\text{H}_2\text{O}$, it may be responsible for carrying water down into Earth’s mantle. After several subsequent investigations by different authors, Baur$^1$ has refined the structure at room temperature at 273 K revealed that the $\text{H}$ atoms show an extremely strong anisotropic displacement parameter along [001]. This is in agreement with the $\text{H}$ dynamic disorder around the O4 atoms essentially within the (100) plane.

Below $T_2 = 120 \text{ K}$ the structure changes to the polar space group $P2_1\text{cn}$, which is characterized by a loss of the (100)-mirror plane [Fig. 1(c)]. The $\text{H}wa$ atoms of the $\text{H}_2\text{O}$ groups deviate downwards from the (100) plane, and those of the hydroxyl groups ($\text{H}ha$) deviate upwards. In this paper we report results of optical birefringence, ultralow-frequency elastic, dilatometric, and dielectric studies together with their phenomenological analysis, which is essential for under-

![FIG. 1. Structure of lawsonite projected along [100]: (a) $Cmcm$ at room temperature; (b) $Pmcn$ at 233 K; (c) $P2_1\text{cn}$ at 110 K. Numbers denote the deviation of the atom from the (100) plane ($X=0$) in $\text{Å} \cdot 10^{-2}$. Dashed lines indicate \text{H}...\text{O} bonds shorter than 2.00(2) $\text{Å}$.](image)
standing the origin of both transitions. There is not much information about the phase transition at $T_2$. Up to now, even its transition temperature has not been precisely determined. Here we present clear evidence that its origin is proper ferroelectric.

II. EXPERIMENTAL SETUP

For the present investigation we used crystals of lawsonite from Tiburon Peninsula, Marin County, California. The sample (no. G14555 of the South Australian Museum, Adelaide, Australia) was kindly given to us by Dr. Allan Pring.

The crystals were oriented according to the natural faces (morphology) and checked optically for macroscopic defects, inclusions, etc. The sample dimensions were: 0.4–0.8 $\times$ 2 $\times$ 2 mm$^3$ for birefringence, 0.5$\times$0.5$\times$3 mm$^3$ for dilatometric and elastic measurements and 0.5$\times$3$\times$3 mm$^3$ for dielectric measurements.

A polarizing microscope (Zeiss Axiophot) equipped with a Linkam hot stage was used for the optical experiments. The birefringence was measured fully automatically using the Senarmont compensation method. A variable rectangular aperture allowed selection of a part of the crystal sample free from macrodefects and natural inclusions. Oriented crystal plates (along [100] direction) with silver painted electrodes were used for measurements of the dielectric constant. The dielectric measurements were performed using an impedance analyzer manufactured by Hewlett-Packard (HP4192A) and controlled by a personal computer. The temperature of the sample chamber was regulated by a commercial temperature controller (Eurotherm 818) between 80 and 750 K. The low-frequency elastic measurements were performed by a parallel plate stress (PPS) method using a commercial dynamic mechanical analyzer (DMA-7, Perkin-Elmer). In the PPS mode this device also provides simultaneous automatical determination of the thermal expansion with an accuracy better than 2 nm.

III. EXPERIMENTAL RESULTS

Figure 2 shows the temperature dependences of the optical birefringence along the principal crystallographic directions of lawsonite. In the inset the temperature dependence of the derivative $d(\Delta n_{xy})/dT$ is shown.
271 K. In the low-temperature region additional anomalies of the optical birefringence are observed at \( T_2 \approx 120 \) K along all crystallographic directions, but the most pronounced one occurs along the [100] direction. These anomalies are attributed to the low-temperature transformation \( Pmcn \rightarrow P2_1cn \).

Figure 3 shows the temperature dependence of the lattice parameters of lawsonite calculated from our thermal expansion data, using the room-temperature values of the lattice parameters as reference points. They show anomalous changes at the same temperature as the optical birefringence data. The most pronounced anomalies occur for the \( a \) parameter, where the behavior of thermal expansion clearly shows a kink at \( T_2 \) and a rounded smeared anomaly near \( T_1 \) in agreement with the optical birefringence data. It is emphasized that the thermal-expansion coefficient along this direction changes the sign in the vicinity of the transition point. This indicates a strong coupling between the ordering process \( \sim \) and the strain tensor component \( U_{xx} \). Such a strong coupling should also influence the temperature dependence of the Young’s modulus. Indeed, Fig. 4 shows that the most pronounced softening near \( T_1 \) occurs again along the [100] direction.

In Fig. 5 the temperature dependence of the dielectric constant \( \varepsilon_a \) (measured) (a) and inverse value \( \varepsilon_a^{-1} \) (calculated from the data) (b) of lawsonite measured along [100] direction for different frequencies. The dashed line indicates Curie-Weiss behavior.

IV. DISCUSSION

A. Free energy

Let us denote by \( 2 \tau_x, 2 \tau_y, 2 \tau_z \), the length of the conventional \( Cmcm \) base-centered unit cell \( \Gamma_0 \). According to Ref. 8 the primitive unit cell vectors \( \mathbf{a}_1, \mathbf{a}_2, \) and \( \mathbf{a}_3 \) are

\[
\mathbf{a}_1 = (\tau_x, \tau_y, 0), \quad \mathbf{a}_2 = (-\tau_x, \tau_y, 0), \quad \mathbf{a}_3 = (0, 0, 2\tau_z)
\]

and the reciprocal-lattice vectors are

\[
\mathbf{b}_1 = \left(\frac{\pi}{\tau_x}, \frac{\pi}{\tau_y}, 0\right); \quad \mathbf{b}_2 = \left(\frac{-\pi}{\tau_x}, \frac{\pi}{\tau_y}, 0\right); \quad \mathbf{b}_3 = \left(0, 0, \frac{\pi}{\tau_z}\right).
\]

The intermediate phase \( Pmcn \) belongs to the primitive orthorhombic Bravais-lattice-type \( \Gamma_0 \), the unit cell of which coincides with the conventional \( Cmcm \) unit cell. The transition \( Cmcm \rightarrow Pmcn \) is associated with an instability at the wave vector \( \mathbf{k}_{15} = (\mathbf{b}_1 + \mathbf{b}_2)/2 \) (here and below in Kovalev’s notation

\( ^9 \)). The star of the wave vector consists of a single
vector and all space-group irreducible representations in this point of the Brillouin zone are real and one dimensional. The order parameter $Q_1$ for this transition transforms according to the irreducible representation $T_3$. The low-temperature phase transition $P m c n \rightarrow P 2_1 c n$ can be described in the simplest case as a distortion $P_1 (k=0)$ (where $P_1$ is the $x$ component of the polarization vector) of the intermediate phase, where the soft mode instability appears in the center of the Brillouin zone ($k_{19}=0$) associated with the one-dimensional representation $T_4$ of the space group $P m c n$.

Following the standard prescription of, e.g., Ref. 9, the free-energy expansion for the two phase transitions can be written as

$$F=F_{Q_1, U, D}+F_{P_1, U, D}+F_U+F_D,$$  

$$F_{Q_1, U, D} = \frac{A_1}{2} Q_1^2 + \frac{B_1}{4} Q_1^4 + \frac{C_1}{6} Q_1^6 + (a_1 U_1 + a_2 U_2) + a_3 U_3) Q_1^2 + \frac{1}{2} (b_4 U_2^2 + b_4 U_2^2 + b_6 U_6^2) Q_1^2 + \frac{1}{2} (c_1 D_1^2 + c_2 D_2^2 + c_3 D_3^2) Q_1^2,$$

$$F_{P_1, U, D} = \frac{A_2}{2} P_1^2 + \frac{B_2}{4} P_1^4 + \frac{C_2}{6} P_1^6 + (a_1' U_1 + a_2' U_2) + a_3' U_3) P_1^2 + \frac{1}{2} (b_4' U_2^2 + b_4' U_2^2 + b_6' U_6^2) P_1^2 + \frac{1}{2} (c_1' D_1^2 + c_2' D_2^2 + c_3' D_3^2) P_1^2,$$

$$F_U = \frac{1}{2} C_{\mu \nu} U_{\mu} U_{\nu},$$

$$F_D = \frac{1}{2} \alpha_{i}^{-1} D_i^2.$$  

Here $\mu, \nu = 1, \ldots, 6$ (Voigt notation) and $i = 1, 2, 3$.

$A_1 = A_{10}(T-T_1)$ and $A_2 = A_{20}(T-T_2)$; $A_{10}, A_{20}, B_1, B_2, C_1, C_2$ are assumed to be positive; $C_{\mu \nu}$ and $\alpha_0$ are the bare values (at $T \gg T_1$) of the elastic constants and optical polarizabilities, respectively. The coupling parts of the free energy responsible for the interactions between the order parameters and static deformations $U_{\mu}$ or electrical displacements $D_i$ at high ("optical") frequencies are also included. It should be noted that only the basic interactions are included in these parts of the above free-energy expansion Eq. (1).

B. Optical birefringence, thermal expansion, and elastic anomalies

In the mean-field approximation, the anomalies observed in the optical, thermal, and elastic properties are easily obtained using the free-energy expansion Eq. (1). In particular, for the refractive indices and thermal expansion one obtains a qualitatively similar behavior:

$T_2 < T < T_1$:

$$\frac{\partial^2 F}{\partial P \partial P}.$$  

One obtains for $T > T > T_2$

$$\epsilon_{11} = \frac{1}{A_{20}(T-T_2)}.$$  

while for $T < T_2$

FIG. 6. Temperature dependence of the squared spontaneous strain.

$$\delta n_i = n_o (\alpha_i^{-1} - \alpha_i^{-1}) = n_o \frac{\partial^2 F}{\partial D_i^2} = \frac{n_o^2}{2} c_i Q_1^2,$$  

$$\delta U_\mu = S_{\mu \nu} a_\nu Q_1^2, \quad \mu, \nu = 1, 2, 3,$$

where $Q_{10}$ is the equilibrium order parameter.

$T < T_2$:

$$\delta n_i = \frac{n_o^3}{2} (c_1 Q_1^2 + c_1^2 P_1^2),$$

$$\delta U_\mu = S_{\mu \nu} a_\nu Q_1^2 + S_{\mu \nu} a_\nu P_{10}^2, \quad \mu, \nu = 1, 2, 3,$$

where $P_{10}$ is the equilibrium order parameter in the ferroelectric phase; $\delta n_i$ and $\delta U_\mu$ are the anomalous changes of the refractive index and spontaneous deformation, respectively; $n_o$ is the average refractive index; $S_{\mu \nu} = C_{\mu \nu}^{-1}$ is the bare elastic compliance tensor. One realizes that the anomalous changes of birefringence and the deformation in the mean-field approximation are both proportional to the square of the order parameters. Indeed, in a plot of $\delta n_i$ versus $\delta n_j$ or $\delta U_\mu$ versus $\delta U_{\nu}$, straight lines are obtained in accordance with Eqs. (2) and (3). As an example, Fig. 6 illustrates the temperature dependences of $\delta U_\mu^2 \propto Q_{10}^2$. The straight lines suggest that the phase transition at $T_1 = 273$ K in lawsonite is at least very near to a tricritical point, i.e., $Q_{10} \propto (T_1 - T)^{3/4}$. However, due to the large contribution of order parameter fluctuations no definite conclusion can yet be drawn about this point.

C. Dielectric susceptibility

The dielectric susceptibility is readily calculated using the free-energy expansion (1) and the relation

$$\epsilon_{ij} = \left( \frac{\partial^2 F}{\partial P \partial P} \right)^{-1}.$$

One obtains for $T > T > T_2$

$$\epsilon_{11} = \frac{1}{A_{20}(T-T_2)}.$$  

while for $T < T_2$
where $B_2$ results from a renormalization of the coefficient $B_2$ due to strain coupling. In case of a second-order phase transition, assuming $B_2 > C_2 P_{10}^2$, one can neglect the sixth-order term, leading for $T < T_2$ to

$$\epsilon_{11} = \frac{1}{A_{2o}(T - T_2) + 3 B_2 P_{10}^2 + 5 C_2 P_{10}^4},$$

(8)

Indeed, Fig. 5 clearly displays a linear temperature dependence of $\epsilon_{11}$ also below $T_2$. But the ratio of slopes $\epsilon_{11}(T > T_2)/\epsilon_{11}(T < T_2) = 1:1.25$ (at $f = 20$ kHz) is quite different from the expected behavior 1:2. One possible explanation of this discrepancy is to assume a contribution of ferroelectric domain-wall motion to the dielectric response. In that case the dielectric permittivity would be enhanced below $T_2$.

In the simplest form, the dielectric permittivity in presence of domains can be written as

$$\epsilon_{ij}(\omega, T) = \left(\frac{\partial^2 F}{\partial P_i \partial P_j}\right)^{-1} \frac{1}{1 + i \omega \tau_{p1}} + \frac{\Delta \epsilon_P}{1 + i \omega \tau_E}.$$  (10)

The last part corresponds to the contribution of domain-wall motion, which we have written as a Debye response for simplicity, while usually a distribution of relaxation times is more appropriate. $\Delta \epsilon_P$ can in principle be calculated for a simple arrangement of ferroelectric domains, but for the present discussion we use only the fact that $\Delta \epsilon_P (T < T_2) > 0$, while, of course, $\Delta \epsilon_P (T > T_2) = 0$. For $\omega \tau_{p1} \ll 1$ one obtains a domain wall contribution to $\epsilon_{11}$ below $T_2$ in agreement with experiment, whereas for $\omega \tau_{E} \approx 1$ this contribution vanishes.

Figure 5 shows measurements of $\epsilon_{11}$ at three different frequencies. With increasing frequency one observes a clear tendency towards monodomain response. Nevertheless, a significant domain-wall contribution still exists at $f = 2$ MHz, implying $\tau_{p1} > 10^{-7}$ s. It should be stressed that no dispersion is found above $T_2$, i.e., $\tau_{p1} < \tau_{D} < 10^{-7}$ s, where $\tau_{p1}$ is the order parameter relaxation time.

V. SUMMARY

We have presented results of optical birefringence, ultralow-frequency elastic, dilatometric, and dielectric measurements of lawsonite single crystals performed in a wide temperature range (80–700 K). We found anomalies in agreement with two continuous phase transitions $Cmcm - T_1 = 273$ K $\rightarrow$ $Pmcn - T_2 = 120$ K $\rightarrow$ $P2_1 cn$. The phase transition at $T_1$ is accompanied by enormous birefringence tails starting about 200 K above $T_1$. The tail is most pronounced in $\Delta n_{xy}$. A theory for the description of the large fluctuation tails in lawsonite is in preparation.

Below $T_2 = 120$ K we have detected $D-E$ hysteresis loops, implying that the low-temperature phase is proper ferroelectric. Consistently, the dielectric permittivity $\epsilon_{11}$ increases (by a factor of 7) when approaching $T_2$ from both sides. The inverse dielectric permittivity yields a linear temperature dependence above and below $T_2$ with a ratio of slopes 1:1.25 instead of 1:2 as expected from a simple Curie-Weiss law. This deviation can be explained in terms of a contribution of ferroelectric domain-wall motion to the permittivity below $T_2$. The characteristic relaxation time of the domain-wall motion is $\tau_D \approx 10^{-4}$ s. This value may be compared to the one in $\mathrm{KD}_2 \mathrm{AsO}_4$, where domain-wall contributions to $\epsilon$ have been identified. In this material, just below the transition temperature $T_c = 162.5$ K, one finds a relaxation time $\tau_D \approx 10^{-8}$ s, shifting to higher values on lowering the temperature. Around $T_c = 143$ K, domain freezing occurs in $\mathrm{KD}_2 \mathrm{AsO}_4$. In lawsonite the domain walls are mobile down to the lowest measured temperatures $T = 80$ K. Further work to study the domain-wall motion in lawsonite at low temperatures and high frequencies (GHz region) is in progress.

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12Below $T_1$, both bulk and fluctuation contributions of the equilibrium order parameter enter into any theoretical description of measured birefringence and thermal expansion. Of course, individual isolation of these contributions depends in a crucial way on the underlying model used. Work on this problem is in progress.