

Kinetic effects associated with the low-temperature phase transitions in lawsonite

STUART A. HAYWARD^{1*}, RAMON BURRIEL², STEFAN MARION³, HINRICH-WILHELM MEYER⁴
and MICHAEL A. CARPENTER⁴

¹Departamento de Física de la Materia Condensada, Universidad de Sevilla, Apartado 1065, E-41080 Sevilla, Spain

²Instituto de Ciencia de Materiales de Aragon, CSIC - Universidad de Zaragoza, Pza. San Francisco, E-50009 Zaragoza, Spain

³Center for Materials Science, University of Oslo, N-0349 Oslo, Norway

⁴Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, United Kingdom

Abstract: The specific heat of natural and deuterated lawsonite, $\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$, has been measured in the temperature ranges 77 K-310 K, using ac calorimetry, and 230 K-320 K, using differential scanning calorimetry. Anomalies due to the $Cmcm-Pm\bar{c}n$ ($T_C = 273$ K) and $Pm\bar{c}n-P2_1cn$ ($T_C = 130$ K in natural lawsonite, 143 K in deuterated lawsonite) transitions have been observed and analysed. By comparing these data with the results of earlier conduction calorimetry experiments, the kinetic behaviour of these two transitions was studied.

For the $Cmcm-Pm\bar{c}n$ transition, the excess entropy only correlates with other measures of the order parameter ($\Delta S \propto Q^2$) in the situation where an ordered lawsonite is heated very slowly. However, the total excess entropy associated with the phase transition does not appear to vary significantly with the rate or direction of the temperature ramp. Extrapolation of the entropy vs. temperature curves to absolute zero implies a maximum excess entropy of $6 \text{ J K}^{-1} \text{ mol}^{-1}$, consistent with the configurational entropy of a two-site mixing model, with a small excess.

For the $Pm\bar{c}n-P2_1cn$ transition, the various experiments give mutually consistent results, implying that the transition behaviour is limiting second order without kinetic anomalies.

Key-words: lawsonite, phase transitions, H ordering, calorimetry, kinetics.

Introduction

The crystal structure of lawsonite, as refined by Baur (1978), consists of a framework of SiO_4 tetrahedra and AlO_6 octahedra. The octahedra form edge-sharing chains, cross-linked by pairs of tetrahedra (Si_2O_7 groups). The cavities in this relatively dense framework contain Ca cations, H_2O groups, and protons.

Two phase transitions have been observed in lawsonite on cooling from room temperature (Libowitzky & Armbruster, 1995; Libowitzky & Rossman, 1996). At 273 K, the symmetry is reduced from $Cmcm$ to $Pm\bar{c}n$. Below approximately 130 K, the space group is further reduced to $P2_1cn$. In both of these transitions, the orientational order-disorder of the water and hydroxyl groups appears to play an important role.

Following these studies by Libowitzky and co-workers, a number of investigations have been performed, in order to understand the thermodynamic nature and atomic-scale

mechanisms of these transitions. Studies of these transitions provide insights into the behaviour of hydrogen and water within aluminosilicate frameworks, which may be more generally applicable.

The temperature dependencies of the order parameters for these transitions have been measured by a number of different experimental methods, including studies of birefringence and macroscopic thermal expansion (Sondergeld *et al.*, 2000), X-ray lattice refinements and infrared spectroscopy (Meyer *et al.*, 2000), and neutron diffraction (Meyer *et al.*, 2001). The results of these studies are consistent in indicating that the $Cmcm-Pm\bar{c}n$ transition is thermodynamically close to the Landau tricritical point (that is, $Q^4 \propto T_C - T$, where Q is the order parameter of the transition, and T_C the transition temperature). The lower-temperature transition ($Pm\bar{c}n-P2_1cn$) is second order, according to X-ray diffraction measurements (Sondergeld, pers. comm.).

As well as fixing the energy scale of a phase transition, calorimetric experiments also provide an alternative tech-

*e-mail: sah21@esc.cam.ac.uk.

Present address: Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, United Kingdom.

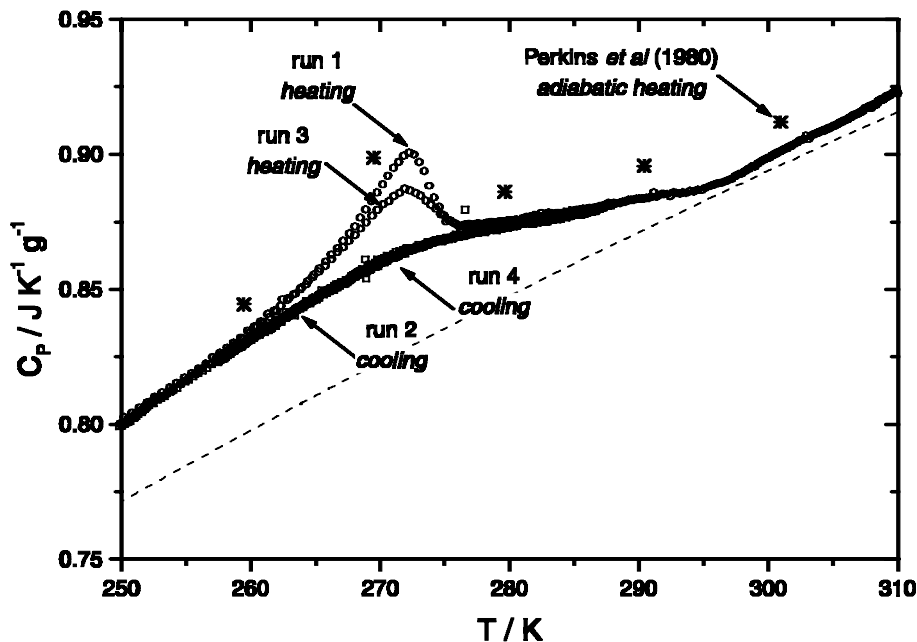


Fig. 1. Specific-heat anomalies associated with the $Cmcm$ – $Pm\bar{c}n$ phase transition in lawsonite, measured using conduction calorimetry by Martín-Olalla *et al.* (2001). The data from the two cooling experiments (runs 2 and 4) coincide fully. Data from adiabatic calorimetry experiments (Perkins *et al.*, 1980) are included for comparison.

nique to follow the temperature evolution of the order parameter. In the specific case of a Landau tricritical phase transition, the form of the C_p anomaly is

$$\Delta C_p = \frac{AT}{4(T_C)^{1/2}(T_C - T)^{1/2}} \text{ for } T \leq T_C \quad (1),$$

where A is the scaling constant between the excess entropy and the order parameter; $\Delta S = (A/2) Q^2$. Equation (1) leads to the lambda peak which is characteristic of a near-tricritical phase transition. Martín-Olalla *et al.* (2001) used a conduction calorimeter to measure the specific heat of lawsonite in the temperature range 125 K to 325 K. The results near the 273 K transition are reproduced in Fig. 1.

The data for heating the sample show the expected lambda anomaly. There is a significant tail in C_p above the transition temperature, which corresponds to similar tails seen in the results of other experiments performed on this sample (Meyer *et al.*, 2000; Sondergeld *et al.*, 2000). These tails could be due to the persistence of short-range order above T_C , or possibly dynamical effects. Due to this tail, the measured specific heat C_p , and the baseline C_{p0} do not coincide, even above 273 K. The form of the baseline in Fig. 1 is chosen so that the shape of the ΔC_p anomaly has the lambda form predicted by Equation 1; this method was described and justified fully in Martín-Olalla *et al.* (2001). For this study, we have simply applied this baseline to our new experimental data.

The difference in the C_p values in the immediate vicinity of the transition for the two heating runs does not affect the entropy calculation greatly. However, the data in Fig. 1 also show a significant hysteresis between heating and cooling cycles. This effect is not seen in other experiments, implying that a simple model of the transition, with a single displacive order parameter, does not completely describe the transition behaviour. A more complete model

needs to explain two main qualitative questions – firstly, why hysteresis is observed at all; secondly, why hysteresis is seen in calorimetric experiments, but not in (say) spontaneous strain measurements.

The observed hysteresis could have one of two main origins. One possibility is that defect microstructures are present in the high-temperature phase, and that these interact with the ordering process. This mechanism might be expected to act, since the sample used by Martín-Olalla *et al.* (2001) was a relatively large disc (0.9 g mass) cut from a natural vein, and therefore possibly quite defect-rich. An alternative hypothesis is that the hysteresis in the specific-heat data reflects irreversibility in the atomic mechanisms of ordering and disordering. Both these possibilities leave open the question of why hysteresis is seen only in the C_p data, and not in other experiments.

In order to investigate this question further, and thus to better understand the mechanisms of ordering and disordering in lawsonite, several additional calorimetric experiments have been carried out. To look for possible kinetic effects, C_p measurements at faster heating and cooling rates have been performed using ac calorimetry and differential scanning calorimetry. Differential scanning calorimetry (dsc) allows data to be collected at a temperature ramp rate (heating or cooling) approximately 1000 times faster than conduction calorimetry. On the other hand, the quantitative precision of conduction calorimetry is far superior; typically, the relative error in C_p measured by conduction calorimetry is of the order of 0.01 %, whereas for dsc, the relative error is nearer 0.5 %.

The possibility of microstructural effects being important was tested by performing experiments with pure natural lawsonite and a deuterium-exchanged sample; the heat treatment associated with the exchange experiments

would be expected to anneal out many of the crystalline defects in the natural sample. The other advantage of studying both natural and deuterated lawsonite is the possibility to study what effect (if any) deuteration has on the transitions.

Experimental methods

Samples

The base material for these experiments was a natural lawsonite from Valley Ford, Sonoma County, California (sample no. 120943, Harvard University mineral collection), kindly supplied by C. Francis (Harvard University, USA). The hand-specimen form of the sample is a vein, several cm wide, consisting of interlocking lawsonite grains (98 % by volume), together with a small quantity of calcite. From a microprobe analysis (Meyer *et al.*, 2001), the composition of the lawsonite phase is $\text{Ca}_{1.00}\text{Al}_{1.95}\text{Fe}_{0.05}\text{Si}_{2.00}\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$.

For the conduction calorimetry experiments (Martín-Olalla *et al.*, 2001), a small disc was cut from this vein, and placed in the calorimeter. It was not possible to purify the sample while in the form of a solid block, and so corrections for the impurity were applied when converting the experimental data from mass to molar units.

The ac calorimetry and dsc experiments were performed on powdered, purified material taken from this sample. Marion *et al.* (2001) ground the natural lawsonite to an average grain size of 77 μm . The calcite was then removed from the sample using heavy-liquid separation methods.

Some of this pure hydrogen lawsonite was then deuterated by exchange between the sample and D_2O in a thermobalance furnace. Details of this process are given in Marion *et al.* (2001). The annealing time required for $\text{H} \leftrightarrow \text{D}$ exchange was 120 h, heating at 700 K. Proton NMR spectroscopy on the resulting material indicated that the sample had become approximately 90 % deuterated.

Calorimetric experiments

Calorimetric measurements were made on heating and cooling with a Perkin Elmer DSC-7 differential scanning calorimeter between 230 K and 320 K, with a custom-built ac calorimeter between 77 K and 310 K, and a custom-built conduction calorimeter between 125 K and 325 K. The conduction calorimetry experiments have been described fully elsewhere (Martín-Olalla *et al.*, 2001).

The samples used for the ac measurements were pressed pellets of 3 mm diameter and 0.2 mm thickness made of polycrystalline powder. In the ac calorimeter the sample is excited with a square wave heating produced by a chopped light. The beam is obtained from a halogen lamp and is driven through an optical fibre onto the sample, producing a temperature oscillation of a few mK. The temperature oscillation is detected with a Chromel-Alumel thermocouple of 0.025 mm diameter wires, glued to the sample with GE7031 varnish. A small pressure (10 mbar)

of He gas provides a heat leak from the sample to a surrounding Cu block. Platinum and Cernox thermometers give the absolute temperature value of the block. The temperature of the sample is slightly above the temperature of the Cu block. The average difference, ΔT (dc), is obtained from measurements of the thermocouple signal with the heating beam on and off. The value ΔT (dc) is inversely proportional to the thermal conductivity of the exchange He gas. The correction to the sample temperature, ΔT (dc), can be extrapolated at every temperature with the conductivity of He.

The thermal relaxation of the apparatus is characterised by two important timescales: the internal relaxation of the sample (which is short), and the relaxation between the sample and the Cu block (which is substantially longer). Provided the oscillation period of the excitation lies between these two values, the amplitude of the thermal oscillation is inversely proportional to the specific heat.

Frequencies between 1 and 4 Hz and heating and cooling scanning rates between 10 and 30 K h^{-1} were used. The sample temperatures were corrected for the dc overheating of the sample and the corresponding sensitivity of the thermocouple was recalculated. The ac measurements provide relative specific-heat values that were subsequently scaled with an absolute value taken from the dsc data.

For the dsc measurements low temperatures were obtained with an aluminium block attached to the sample holder, refrigerated with a flow of liquid nitrogen and controlled at a fixed temperature. The sample holder was kept in a dry box with a flow of helium gas to avoid water condensation. The measurements were carried out using around 20 mg of each powdered sample sealed in aluminium pans with a mechanical crimp. Temperature and enthalpy calibrations were made with standard samples of indium and cyclohexane. An empty pan and a synthetic sapphire sample were also measured to assure the accuracy of the heat capacity results. The temperature ramp rate was 10 K min^{-1} . An overall accuracy of 0.2 K in temperature and 2 % in heat capacity is estimated over the whole temperature range.

Results

Using ac calorimetry and differential scanning calorimetry, specific-heat data were collected for H-lawsonite and D-lawsonite at two different heating / cooling rates, both of them faster than that for the conduction calorimetry experiments. In Fig. 2 to 5 below, we compare the results of these experiments with each other, and with the conduction calorimetry data of Martín-Olalla *et al.* (2001), in order to study the effect of heating / cooling rate and deuteration on the $Cmcm$ – $Pm\bar{c}n$ transition. The $Pm\bar{c}n$ – $P2_1cn$ phase transition was harder to access in the conduction calorimeter, and so a complete comparison of the data for different cooling rates was not possible. The ac calorimetry data, and the data that exist from conduction calorimetry for natural and deuterated lawsonite are shown in Fig. 6 and 7.

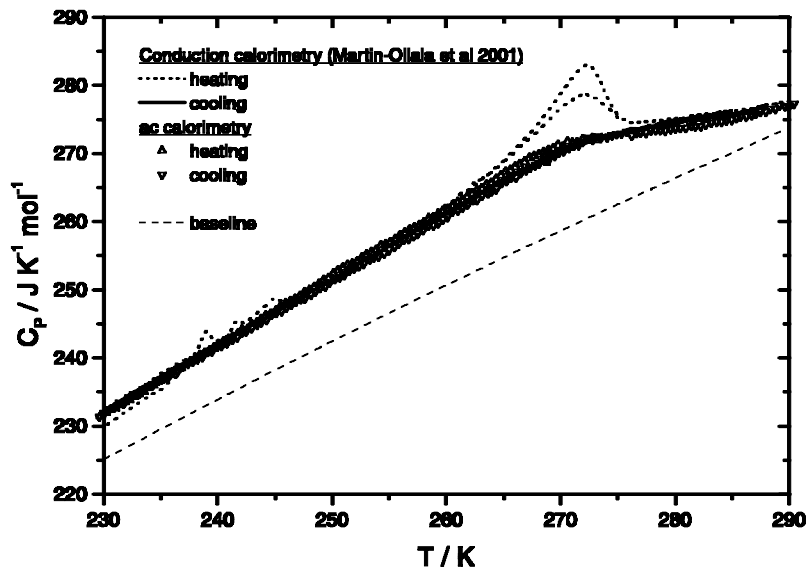


Fig. 2. Comparison of specific-heat data for lawsonite, measured by conduction calorimetry and ac calorimetry.

Effect of temperature ramp rate on the $Cmcm$ – $Pmcn$ phase transition

Figure 2 shows the results of the ac and conduction calorimetry experiments for heating and cooling runs. The ac data for both heating and cooling the material show a rounded C_p anomaly, which is essentially the same as the anomaly seen when cooling the sample more slowly. These curves all differ significantly from the form of the C_p anomaly resulting from slow heating of an ordered sample.

The temperature ramp rate in differential scanning calorimetry is even more rapid than in ac calorimetry. This leads to a rounded C_p anomaly, whether the sample is heated or cooled, as shown in Fig. 3.

To summarise, two qualitatively distinct types of specific-heat anomaly are seen in lawsonite, depending

on the heating conditions. If the sample is heated slowly, a lambda anomaly is seen, which is consistent with a near-tricritical model of the transition. This conclusion coincides with the results of other types of experiment performed on this material (Meyer *et al.*, 2000, 2001; Sondergeld *et al.*, 2000), and with an adiabatic calorimetry study of lawsonite (Perkins *et al.*, 1980), as re-analysed by Martín-Olalla *et al.* (2001). If specific-heat measurements are taken while cooling lawsonite, or if the temperature ramp rate is large, qualitatively different specific-heat behaviour results. The rounded C_p anomaly is more characteristic of a limiting second-order phase transition. Thus, the correlation between the specific heat and other anomalies associated with the phase transition expected in a Landau-like phase transition is lost.

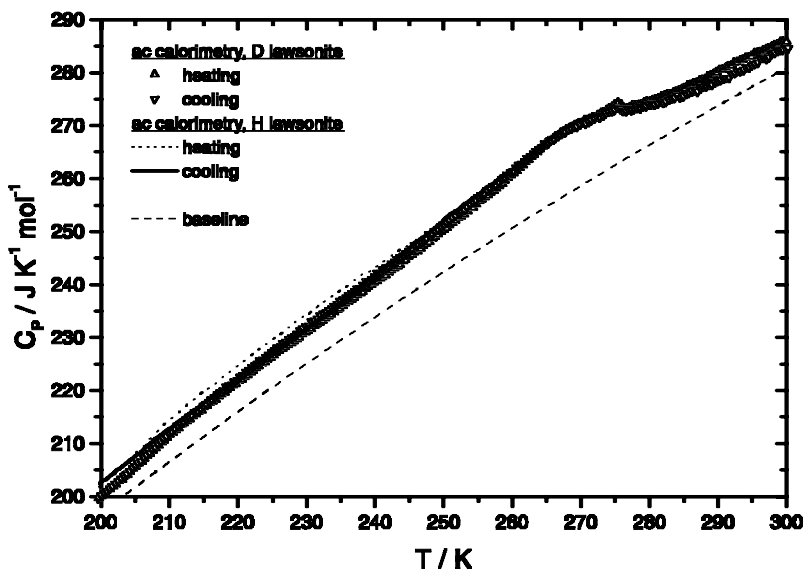


Fig. 3. Comparison of specific-heat data for lawsonite, measured by conduction calorimetry and dsc calorimetry. The apparent hysteresis of *ca.* 2 K between heating and cooling cycles is an artefact of the calorimetric technique. The data series “conduction calorimetry-cooling” (solid line) and “dsc-heating” (up-pointing triangles) virtually coincide.

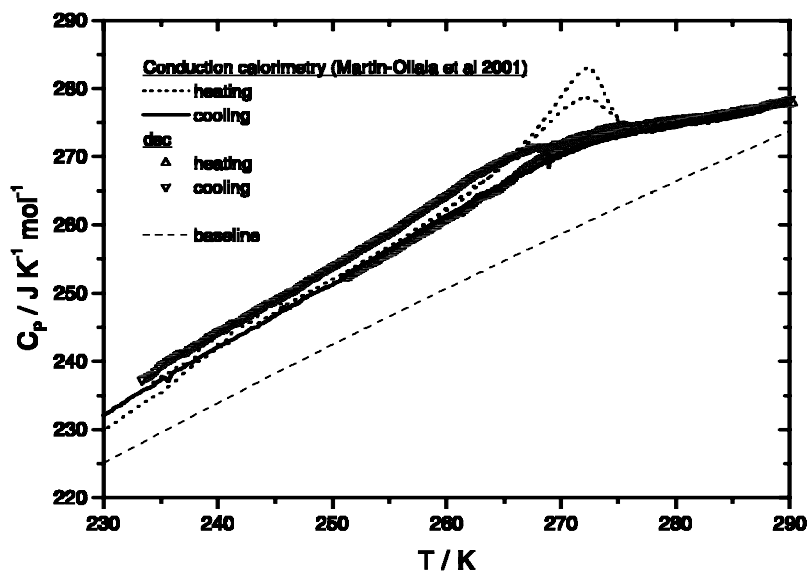


Fig. 4. Specific heat in natural hydrogen lawsonite and deuterated lawsonite, measured by ac calorimetry.

Effect of deuteration on the $Cmcm$ – $Pmcn$ phase transition

The specific heat of deuterated lawsonite was measured by ac calorimetry and differential scanning calorimetry. The powdered material resulting from the deuterium exchange experiment was not suitable for use in the conduction calorimeter. Figures 4 and 5 compare the results of these two types of calorimetry with the equivalent experiments carried out on the natural samples. The resulting differences are mostly insignificant. One difference that may be important is the peak that appears around 275 K when the sample is heated in a dsc experiment. The absence of a similar peak in the ac data may be due to kinetic effects. An alternative

possibility is that the peak in the dsc data represents a latent heat associated with the transition, which would not be recorded in the ac calorimetry experiment. This would imply that the transition is slightly first order.

Effect of temperature ramp rate on the $Pmcn$ – $P2_1cn$ phase transition

For experimental reasons, the data for the lower-temperature transition are less extensive than for the 273 K transition. In particular, the conduction calorimetry data stop at approximately 125 K, and so show little beyond the pre-transition effects. Comparison of these (rather limited) data with the results of ac calorimetry do not display any differences

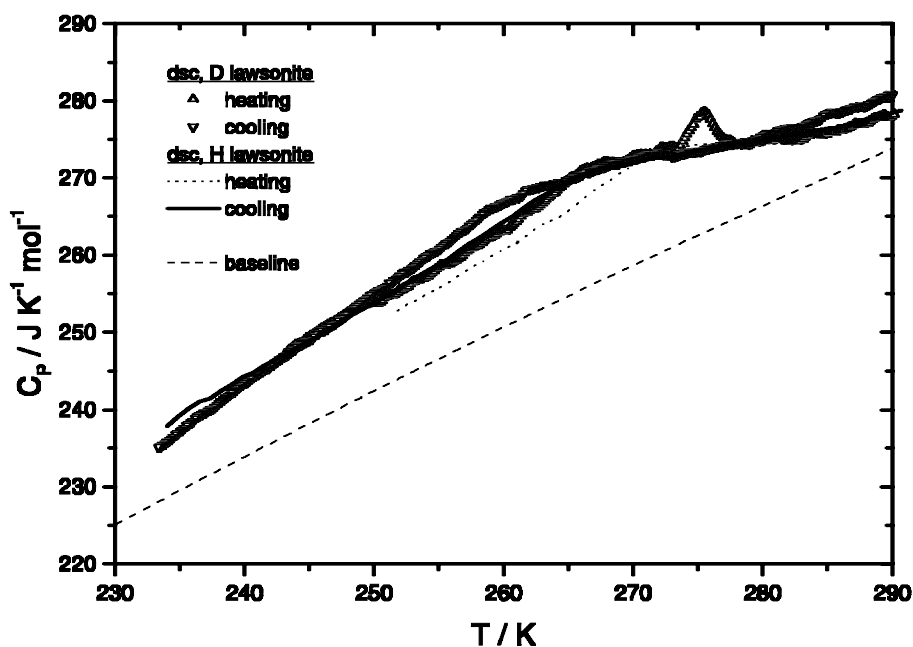


Fig. 5. Specific heat in natural hydrogen lawsonite and deuterated lawsonite, measured by differential scanning calorimetry. The apparent hysteresis of *ca.* 2 K between heating and cooling cycles is an artefact of the calorimetric technique.

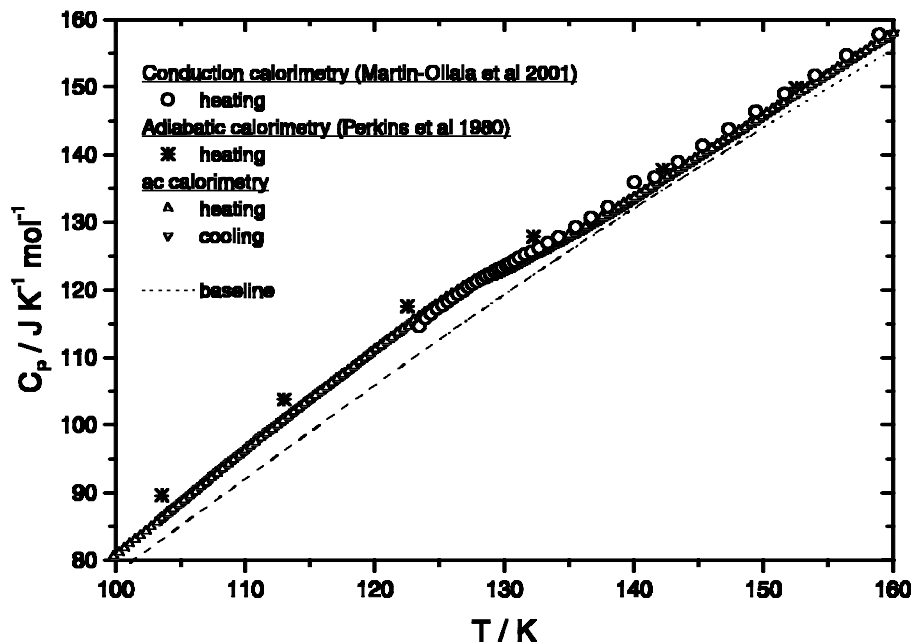


Fig. 6. Comparison of specific-heat data in natural lawsonite near the $Pmcn-P2_1cn$ phase transition, measured by conduction calorimetry, adiabatic calorimetry, and ac calorimetry. The two ac calorimetry data sets (heating and cooling) virtually coincide.

due to changes in heating rate; these data are shown in Fig. 6. The anomaly measured using adiabatic calorimetry by Perkins *et al.* (1980) has a similar form, though its magnitude is somewhat larger. The same effect is seen at the 273 K transition (Fig. 1); its origin is unclear. It should be noted that the lawsonite studied by Perkins *et al.* (1980) was from a different locality, and that even small differences in composition or microstructure may mean that the data are not strictly comparable with the data reported here.

Effect of deuteration on the $Pmcn-P2_1cn$ transition

Comparison of the data for pure and deuterated lawsonite indicates that the $Pmcn-P2_1cn$ transition does

have an important isotope effect (Fig. 7). This result is consistent with the neutron-diffraction study of Meyer *et al.* (2001), who found transition temperatures $T_2 = 130$ K for natural lawsonite and $T_2 = 143$ K for D-lawsonite. However, there is no significant hysteresis in the transition.

Excess entropy calculations

Comparison of the various $C_p(T)$ curves in Fig. 1 to 7 shows that the evolution of the specific heat varies with the rate and direction of the temperature ramp. However, the total entropy difference between the fully ordered low-temperature state, and the disordered $Cmcm$ state should be independent of the kinetic pathway taken between these two states.

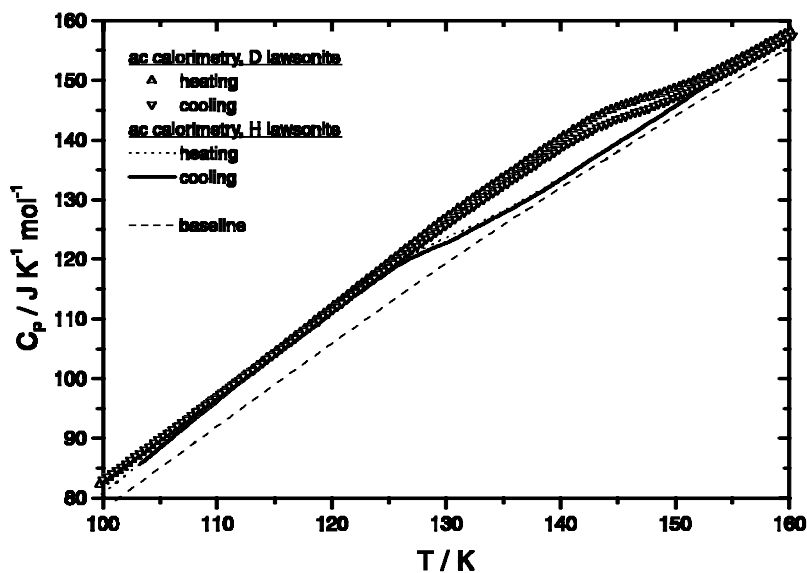


Fig. 7. Specific heat in natural hydrogen lawsonite and deuterated lawsonite near the $Pmcn-P2_1cn$ phase transition, measured by ac calorimetry. The two data sets for natural lawsonite (heating and cooling) virtually coincide.

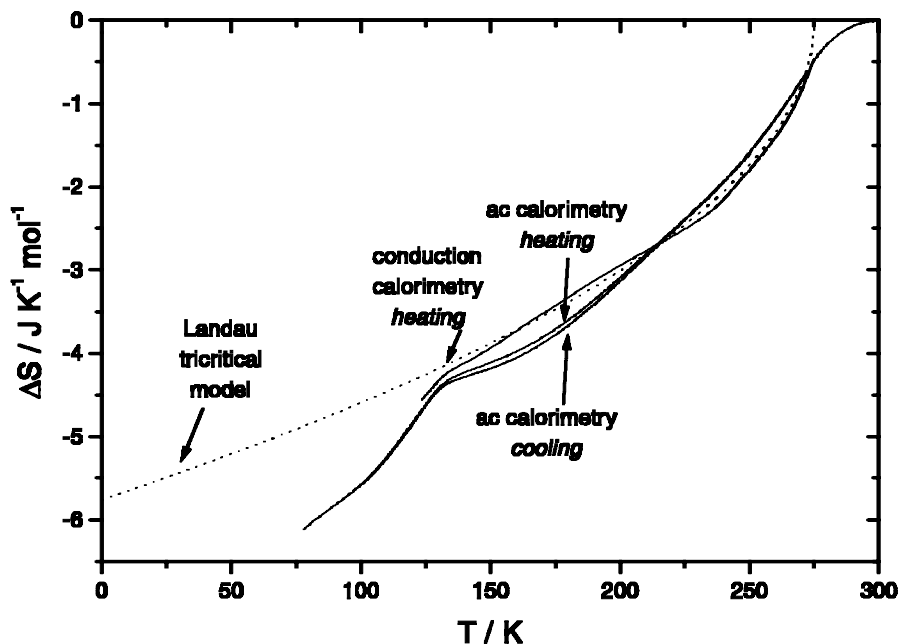


Fig. 8. Temperature dependence of excess entropy due to the phase transitions in lawsonite, measured using conduction calorimetry and ac calorimetry. The “Landau tricritical model” curve shows the $\Delta S(T)$ behaviour expected for a single tricritical transition, with $T_C = 275$ K and $\Delta S_{\max} = 5.76$ J K⁻¹ mol⁻¹.

Figure 8 shows the excess entropy against temperature for those experiments where a sufficiently long series of $C_p(T)$ data was collected. The excess specific heat in each experiment was calculated with respect to a common baseline, shown as a dotted line in Fig. 1 to 7. At 125 K (*i.e.* just above the transition temperature for the $Pm\bar{c}n-P2_1cn$ transition), the total entropies measured by the three experiments do agree reasonably well.

A comparison can also be made with a theoretical value of the excess entropy. Assuming that the $Cm\bar{c}m-Pm\bar{c}n$ transition is strictly Landau tricritical, and that the maximum value of $\Delta S = -5.76$ J K⁻¹ mol⁻¹ (*i.e.*, the expected value for one H species ordering from two sites to one), we obtain the dotted line in Fig. 8. The experimental $\Delta S(T)$ curve for the conduction calorimetry experiment agrees quite well with this at all temperatures, except for a slight break in curvature around 200 K. The more rapidly measured ac calorimetry data do not agree with theory so well, particularly for T slightly below 275 K. At lower temperatures, around 150 K, these experimental curves appear to be coming into better agreement with theory. At very low temperatures, there is a kink in the entropy *vs.* temperature curve, as the $Pm\bar{c}n-P2_1cn$ begins to contribute to the total entropy.

Below the transition temperature for the $Pm\bar{c}n-P2_1cn$ transition, the excess entropy contains contributions from both the transitions. Separation of these two effects will be problematic, in part because the two order parameters should couple, which will affect their temperature dependencies.

Although the exact evolution of the two parameters is not known at low temperatures, we may make an estimate of the entropy associated with the $Pm\bar{c}n-P2_1cn$ transition on the basis of Fig. 8. If we assume that the dotted line, representing a Landau tricritical transition with $T_C = 275$ K and $\Delta S_{\max} = 5.76$ J K⁻¹ mol⁻¹, is an accurate description of the $Cm\bar{c}m-Pm\bar{c}n$ transition, then the excess is the contribution of the $Pm\bar{c}n-P2_1cn$ transition. This excess is plotted in Fig. 9.

There are a number of problematic aspects to this analysis. As well as the uncertainty in the exact temperature evolution of the order parameters, the assumption that the ac calorimetry data are accurately described by a Landau tricritical model is not borne out by the experimental data in the range $T > 125$ K. It is true that the total entropy around 125 K is approximately correct, but it is not necessarily the case that this agreement continues at lower temperatures. Nevertheless, the excess in the excess entropy (Fig. 9) is linear in the temperature range 105 K $< T < 130$ K, which is consistent with the X-ray diffraction observations of Sondergeld (*pers. comm.*), that the behaviour of the $Pm\bar{c}n-P2_1cn$ transition is limiting second order. Extrapolating this line to 0 K gives a maximum value of the excess entropy $\Delta S_{\max} = 3.75$ J K⁻¹ mol⁻¹. This is rather lower than the value $\Delta S_{\max} \approx 6$ J K⁻¹ mol⁻¹, which Martín-Olalla *et al.* (2001) obtained by measuring the size of the C_p step in the data of Perkins *et al.* (1980). However, these results are all very sensitive to the exact form of the C_p baseline used; depressing the baseline shown in Fig. 7 by approximately 2 J K⁻¹ mol⁻¹ would be sufficient to bring the experimental value of ΔS into agreement with the theoretical predictions. Such a change would not affect the qualitative form of the baseline, neither would it alter the linearity of the entropy *vs.* temperature graph. The deviation from linearity seen in Fig. 9 may also be the result of a small baseline error.

Discussion

In this study, we have measured the specific heat of natural and deuterated lawsonite across two phase transitions, using three different calorimetric methods. The most obvious difference between conduction calorimetry, ac calorimetry and dsc calorimetry is the temperature ramp rate – approximately 1000 times faster in dsc than in

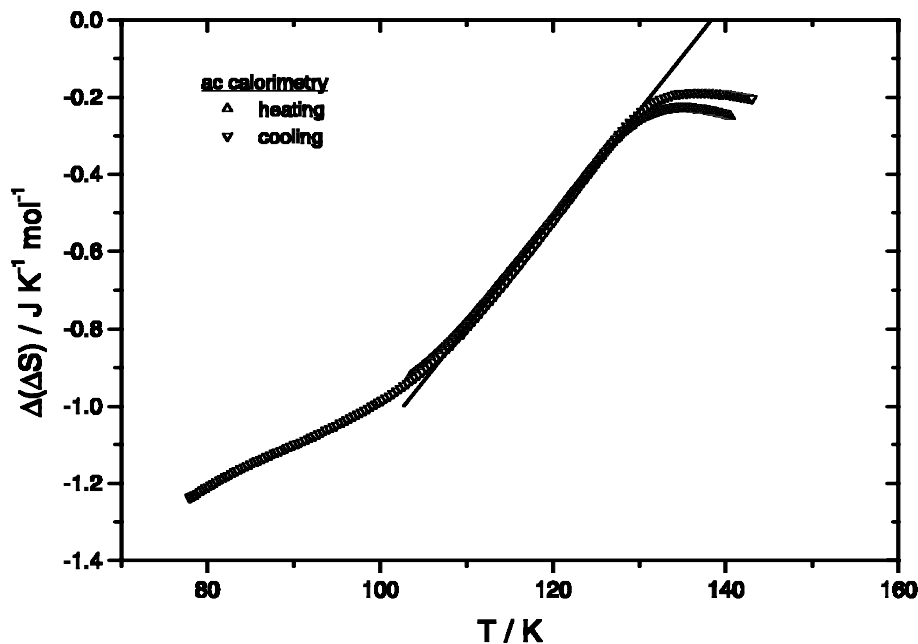


Fig. 9. Temperature dependence of the excess entropy associated with the $Pm\bar{c}n-P2_1cn$ phase transition in lawsonite, measured by ac calorimetry.

conduction calorimetry. By considering the effect of this change in ramp rate, and the effect of deuterium substitution, on the specific heat data for each transition, we may be able to gain insights into the mechanisms of each transition.

Cmcm–*Pmcn* transition

Other experimental methods (Meyer *et al.*, 2000, 2001; Sondergeld *et al.*, 2000) essentially measure the macroscopic order parameter of the phase transition, and show that its behaviour is near to the Landau tricritical point. The calorimetric data are only consistent with this for a sample heated very slowly (*i.e.*, conduction calorimetry or adiabatic calorimetry). If the sample is cooled instead of being heated, or heated too rapidly, the appropriate correlation is lost. The heating regime used in ac calorimetry (a linear ramp of 30 K h⁻¹, with oscillations of, on average, ±200 K h⁻¹ superimposed), is “too fast” in this context, though further experiments would be required to determine the critical heating rate. Another open question is whether there is some cooling rate (which would need to be below 0.6 K h⁻¹) below which the measured specific-heat anomaly correlates with the changes in the order parameter in the way expected by a simple theory.

The failure of the specific-heat data to correlate with the changes in the order parameter is not improved by powdering and purifying the sample, or by the annealing associated with H–D exchange. Both of these processes would be more likely to reduce the effects of defect microstructures on the transition than to increase them. The calorimetric data therefore seem to imply that this behaviour is an intrinsic result of the transition mechanism, rather than being the consequence of a defect-rich sample.

A further point is the absence of any isotope effect; the same result was found by Meyer *et al.* (2001). The importance of this result is that most transitions involving proton

ordering have different transition temperatures for hydrogen and deuterium phases; examples include KH₂PO₄–KD₂PO₄ (Samara, 1973) and TIH₂PO₄–TID₂PO₄ (Ríos *et al.*, 1998). In general, the isotope effect is related to the different quantum mechanical tunnelling probabilities for a proton or deuteron hopping between two crystallographic sites. This change in tunnelling probability may arise from changes in the geometry of the tunnelling sites, or it may come from the difference in mass between a proton and a deuteron. Both these mechanisms imply a phase transition driven by the ordering of the protons or deuterons. Conversely, the fact that the *Cmcm*–*Pmcn* transition in lawsonite does not display an isotope effect indicates that the proton ordering is not the instability driving the transition.

Combining these observations, we may envisage that the transition involves two processes: a displacive collapse of the aluminosilicate framework, and the ordering of protons. Cooling from the *Cmcm* phase, the framework instability causes a collapse at 273 K, irrespective of whether the structure is filled with protons or deuterons. The hydrogen species then order within the collapsed framework. This ordering happens heterogeneously, by the nucleation and growth of ordered domains.

This model explains the various effects seen in the *Cmcm*–*Pmcn* transition. The spontaneous strain, and quantities closely related to it, such as birefringence and hard phonon frequencies, will be dominated by the changes to the framework. These changes happen as a simple reversible displacive transition. The free energy, on the other hand, will include a contribution from the proton ordering, which appears to be kinetically constrained from coupling perfectly to the framework collapse.

The peak in C_p seen near 275 K for heating deuterated lawsonite in a dsc experiment (Fig. 5) could be an example of this imperfect coupling. Since the heating rate is very rapid (some 10 K min⁻¹), the disordering may not proceed

rapidly enough to maintain equilibrium with the rest of the structure. A peak in the heat flow would then be expected if a first-order increase in the degree of proton disorder took place.

Consequently, the excess entropy is, in general, not a simple function of the displacive order parameter only. The exception is that, if the sample is heated very slowly, the disordering of the protons does seem to be proportional to the changes in the framework. However, even in this case, there are anomalies just below and above T_C (Sondergeld *et al.*, 2000; Martín-Olalla *et al.*, 2001), which may be due to the persistence of some short-range order above the transition temperature.

Pm $\bar{c}n$ –*P2* $_1$ *cn* transition

The experimental data for the second transition are less extensive, mainly because the transition temperature is less accessible. A particular difficulty is the lack of more extensive conduction calorimetry data for this transition. However, there is no evidence for the C_P anomaly showing any dependence on the temperature ramp rate, or any hysteresis between heating and cooling. What data there are indicate that this transition is close to the second-order limit, with the standard $\Delta S \propto Q^2$ proportionality of Landau theory. The extrapolated excess entropy for this transition is somewhat lower than the configurational entropy for two-site ordering (experimental $\Delta S = 3.75 \text{ J K}^{-1} \text{ mol}^{-1}$, compared with a theoretical value $5.76 \text{ J K}^{-1} \text{ mol}^{-1}$), but the error on the experimental figure is rather large, and so the discrepancy between the two figures may not be significant.

A further point is that there is an isotope effect on the transition temperature. This provides evidence that this transition is driven by an instability in the proton lattice, and that the framework distortion is a secondary effect.

Whereas the proton ordering in the *Cm* $\bar{c}m$ –*Pm* $\bar{c}n$ transition appears to develop by the growth of locally ordered domains, the ordering in the *Pm* $\bar{c}n$ –*P2* $_1$ *cn* transition is more homogeneous – hence the lack of hysteresis. One factor is that the *P2* $_1$ *cn* phase is a proper ferroelectric, unlike the higher-temperature structures. The resulting electrical coupling will probably be more effective at forcing uniform behaviour than the rather small elastic strain coupling. Another possible reason for the lack of hysteresis is the reversal of the “driving” and “secondary” processes, compared with the *Cm* $\bar{c}m$ –*Pm* $\bar{c}n$ transition. When proton ordering takes place as a response to the spontaneous strain of a displacive transition, it is possible for this ordering to build up gradually from short-range to long-range order. On the other hand, a displacive transition responding to proton ordering is more likely to change

uniformly, given the long-range nature of elastic interactions.

Acknowledgements: We would like to thank C. Francis (Harvard University, USA) for the natural lawsonite sample used in this study. This project is part of the EU TMR Network “Mineral Transformations” (ERB-FMRX-CT97-0108). Financial support from the Spanish CICYT, project MAT97-0987 is also acknowledged.

References

- Baur, W.H. (1978): Crystal structure refinement of lawsonite. *Am. Mineral.*, **63**, 311-315.
- Libowitzky, E. & Armbruster, T. (1995): Low-temperature phase transitions and the role of hydrogen bonds in lawsonite. *Am. Mineral.*, **80**, 1277-1285.
- Libowitzky, E. & Rossman, G.R. (1996): FTIR spectroscopy of lawsonite between 82 and 325 K. *Am. Mineral.*, **81**, 1080-1091.
- Marion, S., Meyer, H.-W., Carpenter, M.A., Norby, T. (2001): H₂O–D₂O exchange in lawsonite. *Am. Mineral.*, **86**, 1166-1169.
- Martín-Ollala, J.-M., Hayward, S.A., Meyer, H.-W., Ramos, S., del Cerro, J., Carpenter, M.A. (2001): Phase transitions in lawsonite: a calorimetric study. *Eur. J. Mineral.*, **13**, 5-14.
- Meyer, H.-W., Carpenter, M.A., Graeme-Barber, A., Sondergeld, P., Schranz, W. (2000): Local and macroscopic order parameter variations associated with low temperature phase transitions in lawsonite, CaAl₂Si₂O₇(OH)₂·H₂O. *Eur. J. Mineral.*, **12**, 1139-1150.
- Meyer, H.-W., Marion, S., Sondergeld, P., Carpenter, M.A., Knight, K.S., Redfern, S.A.T., Dove, M.T. (2001): Displacive components of the phase transitions in lawsonite. *Am. Mineral.*, **86**, 566-577.
- Perkins, D. III, Westrum, E.F. Jr., Essene, E.J. (1980): The thermodynamic properties and phase relations of some minerals in the system CaO–Al₂O₃–SiO₂–H₂O. *Geochim. Cosmochim. Acta*, **44**, 61-84.
- Ríos, S., Paulus, W., Cousson, A., Quilichini, M., Heger, M. (1998): Isotope effect in TiH₂PO₄ and TiD₂PO₄. *Acta Cryst. B*, **54**, 790-797.
- Samara, G.A. (1973): The effects of deuteration on the static ferroelectric properties of KH₂PO₄ (KDP). *Ferroelectrics*, **5**, 25-37.
- Sondergeld, P., Schranz, W., Tröster, A., Carpenter, M.A., Libowitzky, E., Kityk, A.V. (2000): Optical, elastic and dielectric studies of phase transitions in lawsonite. *Phys. Rev. B*, **62**, 6143-6147.

Received 10 December 2001

Modified version received 19 April 2002

Accepted 30 May 2002