Phase transitions in lawsonite: a calorimetric study

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The specific heat of lawsonite, $CaAl_2Si_2O_7(OH)_2 \cdot H_2O$, has been measured in the temperature range $[125\,K, 325\,K]$. An anomaly is seen at $273\,K$, which is related to the Cmcm–Pmcn phase transition. The magnitude of the total excess entropy associated with this transition is not reproducible, varying in the range $[5.93\,J\,K^{-1}\,mol^{-1}, 6.24\,J\,K^{-1}\,mol^{-1}]$. On heating, the specific heat anomaly is consistent with a tricritical phase transition. However, on cooling, significant hysteresis is observed, and the form of the C_p anomaly is quite different. In all measurements extensive pre-transitional effects are observed above T_c. Analysis of existing specific heat data in the temperature range $[75\,K, 175\,K]$ shows an anomaly associated with the Pmcn–P2$_1$cn phase transition. The excess entropy associated with this transition is $6(1)\,J\,K^{-1}\,mol^{-1}$. These data are interpreted as showing that both transitions are caused by the interaction of proton ordering and displacive changes in the aluminosilicate framework. The standard entropy of lawsonite at 298 K is recalculated, incorporating the effects of the two transitions. Two methods are used for this recalculation, giving values of $S_{298}^0 = 233.27\,J\,K^{-1}\,mol^{-1}$ and and $S_{298}^0 = 234.96\,J\,K^{-1}\,mol^{-1}$ respectively.

I. INTRODUCTION

Introduction Lawsonite, $CaAl_2Si_2O_7(OH)_2 \cdot H_2O$, is a common constituent of high-p, low-T metamorphic rocks, such as blueschists. As a relatively dense hydrous mineral, lawsonite has frequently been investigated as providing a potential mechanism to carry water deep into the Earth's interior. These studies (Chatterjee and Leistner, 1984; Pawley, 1994; Schmidt and Poli 1994) have indicated that lawsonite remains stable down to the pressure and temperature conditions of the mantle. Water in the lawsonite structure is significant for another reason. X-ray diffraction and infraredspectroscopy experiments (Libowitzky and Armbruster, 1995; Libowitzky and Rossman, 1996) have shown that lawsonite undergoes phase transitions at low temperatures, associated with the orientation of the H_2O molecules and hydroxyl groups within the lawsonite structure. These transitions are interesting since they allow the interaction between hydrogen atoms and an aluminosilicate framework to be studied.

The room-temperature structure of lawsonite has space group Cmcm. At $273\,K$, the H_2O molecules rotate around [100], reducing the symmetry to Pmcn. The second phase transition, at $120\,K$, reduces the symmetry of the structure to P2$_1$cn. This transition is associated

with a further rotation of the H_2O molecules around a different axis.

Two distinct mechanisms may be envisaged for this transition. In a displacive model of the transition, these rotations occur as a function of temperature below the transition. In an order-disorder transition, the orientation of the water molecules hops between a number of almost fixed positions; the crystal structure observed experimentally is then a dynamic average of the various orientations. For a purely order-disorder transition, the excess entropy of the transition may be calculated directly using configurational mixing models. In a displacive transition, the excess entropy comes from changes in phonon frequencies associated with the structural changes, which are rather less simple to calculate.

In order to investigate these effects further, a single sample of lawsonite has been characterised by a number of different methods. The experimental quantities measured have been elastic constants, dielectric constants, birefringence, macroscopic dilatation (Sondergeld et al., 2000), lattice parameters and infrared spectra (Meyer et al., 2000). In this article, we report the results of calorimetric measurements across the $273\,K$ transition, and relate them to some of these other data. A number of other calorimetric studies of lawsonite have been performed (King and Weller, 1961; Perkins et al., 1980) but the purpose of these studies was to understand the stability of lawsonite in metamorphic reactions. As a result, the data close to the transitions are rather scanty.

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II. EXPERIMENTAL METHODS

A. Sample description

The lawsonite sample used in this study came from Valley Ford, Sonoma County, California, and is no. 120943 of the Harvard University mineral collection. This sample was generously provided by Dr. C. Francis (Harvard University, USA). In handspecimen, the sample contained a vein several cm wide consisting predominantly of interlocking lawsonite grains, along with a small proportion of calcite. A small disc approximately 10 mm in diameter and 3.9 mm thick was cut from this vein for the calorimetric measurements. The mass of this sample was 0.9 g.

After the calorimetric measurements were completed the disc was cut into circular slices and mounted as thin sections. Point counting of these sections in a petrographic microscope gave the volume fractions of lawsonite and calcite as 97.95 % and 2.05 % respectively. Electron-microprobe analysis (EDS) showed the major cation elements in lawsonite to be Ca, Al, Fe, and Si only. Analyses of Ti, Cr, Mn, Ni, Mg, Na, K, Cl, P and S were also carried out, but these elements were only present at levels less than 1σ on counting statistics. Water content for this material was determined using thermogravimetry (S. Marion, pers. comm.); within experimental error the sample is fully hydrated.

Previous analyses (Deer et al. 1992, and references therein) indicate that the water content does not vary substantially between natural lawsonites; the quoted water contents are in the range 10.61 to 11.70 (wt %). Using the average of four probe analyses, the composition of the lawsonite phase in this sample is $Ca_{1.00}Al_{1.95}Fe_{0.05}Si_{2.00}O_7(OH)_2 \cdot H_2O$.

B. Calorimetric experiments

The sample was placed in a conduction calorimeter of a type described previously (del Cerro, 1987; del Cerro et al., 1987). The calorimeter consists of a large block of aluminium, which acts as a thermal reservoir. Two fluxmeters, each consisting of 48 thermocouples, are placed electrically in series and thermally in parallel. The outer junction of each fluxmeter is fixed to the calorimetric block, and the sample is pressed between the inner junctions. The contacts between the fluxmeters and the sample are silver plates, to ensure good thermal contact and homogenisation. The entire assembly is evacuated to 10^{-5} mbar, and placed in an alcohol bath. This bath may be cooled from room temperature to liquid-nitrogen temperature. The sample temperature may be adjusted by heating or cooling the alcohol bath. By cooling the system slowly, equilibrium may be maintained between the sample and the heat bath.
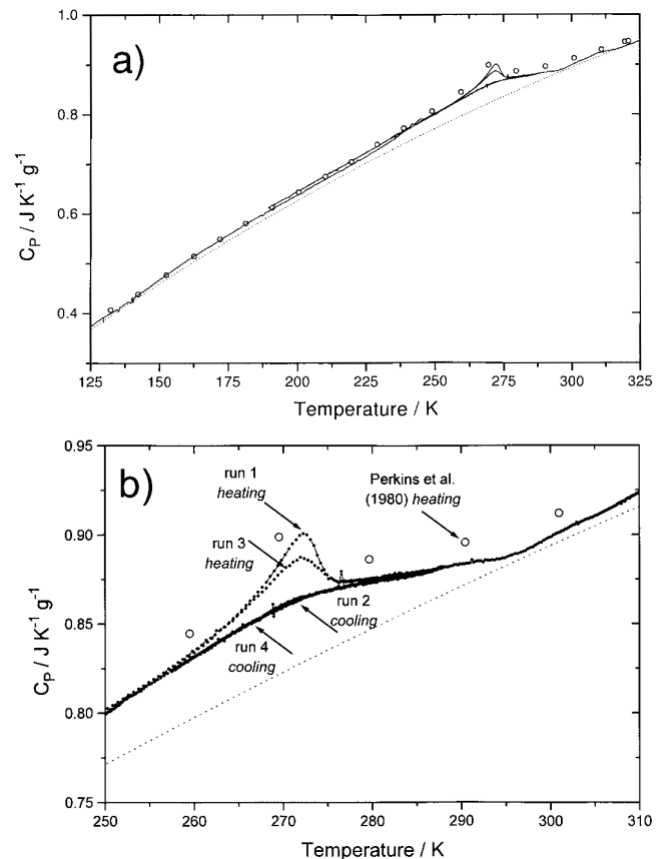

FIG. 1 Experimental measurements of specific heat as a function of temperature in lawsonite. Part a) shows the data over the whole temperature range of the experiments, and part b) is a magnifcation of the data in the vicinity of the Cmcm–Pmcn transition. The four solid lines show the data for the two heating and two cooling runs performed in this study, and the circles show the data obtained by Perkins et al. (1980) for heating a different lawsonite sample.

The C_p measurements are performed using a small heater attached to the fluxmeters. The sample is heated until a steady state is attained, at which point the heater power is cut off. The relaxation of the sample back to equilibrium with the heat sink depends on the heat capacity of the sample, and so CP may be measured as a function of temperature. In this experiment, four measurement runs were carried out. The sample was quenched from room temperature to 125 K. Measurements of the specific heat were carried out as the sample was heated slowly (ca. $0.6\,K\,h^{-1}$) to 320 K (run 1). For the second run, the sample was cooled at the same rate to 200 K. The sample was then heated back to room temperature, again at the same rate (run 3). Finally, the sample was cooled to 260 K, again at the same temperature rate (run 4). In each case, there was a minimal time interval between the various measurement runs.

III. EXPERIMENTAL RESULTS FOR THE $Cmcm - Pmcn$ TRANSITION

A. Specific heat as a funciton of temperature

Fig. 1 shows the specific heat as a function of temperature for each of the four experimental runs. These data are not corrected for the sample purity. The data of Perkins et al. (1980), which were measured using a different 95 % pure lawsonite sample from Valley Ford, California, are also shown for comparison.

Examination of the data close to T_c (Fig. 1b) indicates that the specific heat anomaly in lawsonite has two parts. There is a distinct change in the $C_p(T)$ slope at ca. 295 K, which is evidence for a pronounced tail in the heat capacity anomaly above T_c. Similar effects have been seen in other types of experiments; Sondergeld et al. (2000) note pre-transitional effects in birefringence measurements up to ~ 200 K above the transition temperature. The tail is quite reproducible between the different experimental runs, for both heating and cooling the sample.

At the transition temperature, a distinct peak is expected, but the magnitude of this peak varies greatly between the experimental runs. In particular, the peak is far more pronounced when the sample is being heated than when it is cooled.

B. Excess entropy calculations

Analyses of birefringence, dielectric constant, elastic constant and co-elastic spontaneous strain data (Sondergeld et al., 2000), as well as infrared spectroscopic data (Meyer et al., 2000) are consistent with a Landau model for the Cmcm–Pmcn transition, where the transition is close to the tricritical point. Additional account must be taken of the tails seen above T_c. Calculation of the excess entropy as a function of temperature provides a further test of this model. In addition, we may compare the total excess entropy with the entropy predicted for a dipole order-disorder process. In order to reliably calculate excess quantities associated with the phase transition, it is necessary to know accurately the "baseline" behaviour of the experimental data (that is, in the absence of the phase transition). This issue is particularly problematic for calculations of excess entropy from C_p data. Well below T_c, the specific heat anomaly is small, and so even small errors in the baseline specific heat may have a large systematic effect on the final entropy calculation.

For this study, we have therefore used a twostage process to determine the excess entropy associated with the transition. First, we have used a simple interpolation method to generate a "preliminary" baseline. Because this preliminary baseline is well-anchored by experimental data from just above the transition temperature, it
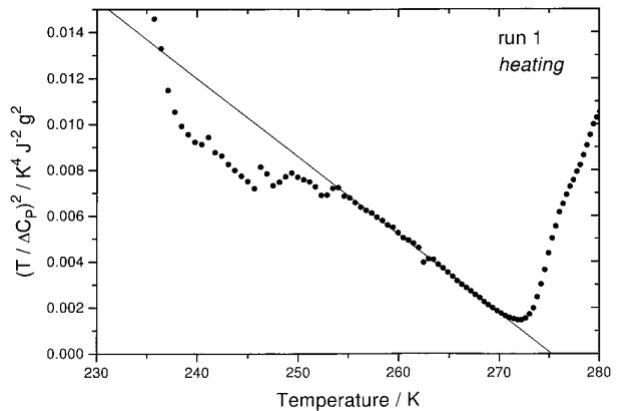

FIG. 2 Temperature dependence of $(T/\Delta C_p)^2$ for lawsonite. For a transition obeying Landau theory, this function is expected to be linear. The deviations from linearity at low temperature are likely to be due to small errors in the prediction of the baseline C_{p_0}.

is expected to be reasonably accurate immediately below the transition temperatature. In any case, the largeness of ΔC_p near T_c means that the uncertainties in the baseline are proportionally less significant there than at low temperatures. We then use a theoretical model of the transition (parameterised by these initial results), to determine the behaviour of ΔC_p at lower temperatures. From this, we determine a "back-calculated" C_p baseline, whose form may be informally checked for its plausibility. The excess entropy is then calculated with respect to this back-calculated baseline.

It can be shown (see, for example, Salje, 1990) that, for any phase transition described by a standard 2:4.6 Landau potential, whether first order or second order, the specific heat anomaly may be linearised as

$$\left(\frac{T}{\Delta C_p}\right)^2 \propto (T{-}T_2), \qquad (1)$$

where the difference between T_c and T_2 is a measure of the closeness of the transition to the tricritical point; for a transition which is strictly Landau tricritical (i.e. $\Delta S \propto Q^2; Q \propto |T_c - T|^{1/4}$), T_c and T_2 are equal. In any case, we may test the validity of Equation (1) close to T_c using the preliminary baseline. If this proves to be reasonable, Equation (1) then defines the behaviour of ΔC_p at lower temperatures, where the determination of the baseline is more problematic. A preliminary empirical baseline C_{p_0} was easily determined by fitting a parabola though the data of the first experimental run for $T > 315$ K and $T < 150$ K. Since ΔC_p is expected to be non-zero at low temperatures, this preliminary baseline is not totally correct. The error will be most significant at lower temperatures, where the true value of ΔC_p will be systematically larger than we obtain with the preliminary baseline. The main consequence will be
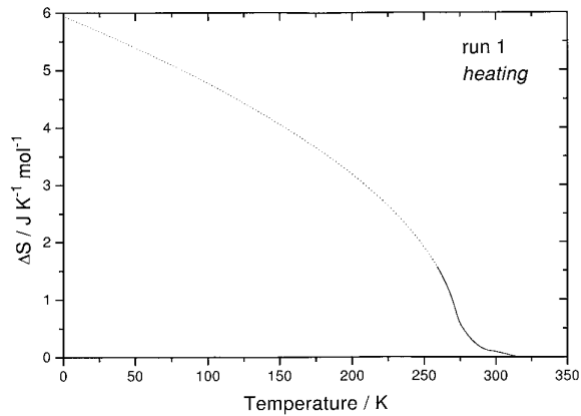
FIG. 3 Temperature dependence of excess entropy in lawsonite. Above $260\,\mathrm{K}$ (solid line), this curve is calculated by simple integration of $(\Delta C_p/T)$. Below $260\,\mathrm{K}$ (broken line), it is assumed that the linearity of $(T/\Delta C_p)^2$ seen in Fig. 2 may be extrapolated.

FIG. 4 Temperature dependence of excess entropy for two heating and two cooling runs in lawsonite.

that the total excess entropy of the transition will be underestimated. However, the error close to T_c will be smaller and we can use the preliminary baseline to study the behaviour of ΔC_p in the vicintiy of T_c. Fig. 2 shows the dependence of $(T/\Delta C_p)^2$ on temperature for the first heating cycle (this being the experiment where the peak in ΔC_p was most pronounced). The figure clearly shows the linear behaviour close to the transition point and the interception of the straight line with temperature axis give us $T_2 = 275.3(1)\,\mathrm{K}$. The largest value of ΔC_p is observed at $T = 272.8(4)\,\mathrm{K}$. The position of the ΔC_p peak provides one definition of T_c, albeit a somewhat problematic one in a transition with a significant ΔC_p tail above the transition temperature. It is clear, however, that the transition is very close to the Landau tricritical point.

This preliminary baseline may then be improved by taking account of Fig. 2. If we assume that the observed linearity should continue to lower temperatures, we may calculate the expected value of ΔC_p at any temperature. This, in conjunction with the experimental data $C_p(T)$ allows the baseline to be calculated from $C_{p_0} = C_p - \Delta C_p$. The broken line in Fig. 1 shows the resulting baseline, after the back-calculated $C_{p_0}(T)$ has been smoothed. Close to the transition temperature, the preliminary and back-calculated baselines agree well. At lower temperatures, the back-calculated baseline is lower than the preliminary baseline, but it is more realistic as it takes account of the small (but non-zero) ΔC_p expected for any theory of the transition.

Given the temperature dependence of C_p and C_{p_0}, the total excess entropy as a function of temperature is calculated in Fig. 3. In Fig. 3, the conversion from mass units to molar units includes a correction for the calcite impurities in the experimental sample. For the purposes of this calculation, it has been assumed that the linear
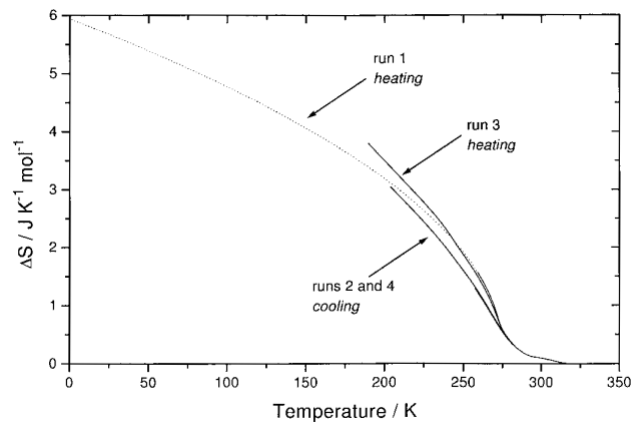
behaviour of $(T/\Delta C_p)^2$ may be extrapolated to $0\,\mathrm{K}$. Two arguments indicate that this is not wholly realistic.

Firstly, it takes no account of the tendency for the order parameter to approach a constant value at absolute zero (Salje et al., 1991). Secondly, it ignores the effect of the phase transition at $120\,\mathrm{K}$. The classical extrapolation is still useful, however, since it provides the best estimate of ΔS between the high-temperature phase and the structure at zero kelvin. As shown in Fig. 3, the extrapolated value of ΔS at absolute zero is $5.93(1)\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

The random error in this quantity is small (it depends only on the error in the gradient of the straight line fit in Fig. 2, which is of the order of $1\,\%$). The systematic errors, due to the two factors given above, are probably larger, but difficult to quantify.

C. Analysis of subsequent experimental runs

Fig. 4 shows the temperature dependence of the excess entropy for all four experimental runs performed in this study. The two heating experiments show very similar, almost tricritical behaviour; the effect of the difference in the height between the two ΔC_p peaks is rather small. If the excess entropy in the second heating experiment (run 3) is extrapolated to $0\,\mathrm{K}$, the resulting $\Delta S = 6.24(1)\,\mathrm{J\,K^{-1}\,mol^{-1}}$. This result may simply be an artefact of the fitting method used; the lowtemperature ΔC_p values are slightly higher for run 3 than for run 1. Fitting both data sets to a single baseline has a significant effect of the final calculation of entropy.

However, comparison between the two heating curves and the two cooling curves (which are very similar to each other) indicates a significant degree of hysteresis in the transition. The form of the cooling curves is not consistent with tricritical behaviour, and the magnitudes of ΔS are also inconsistent.
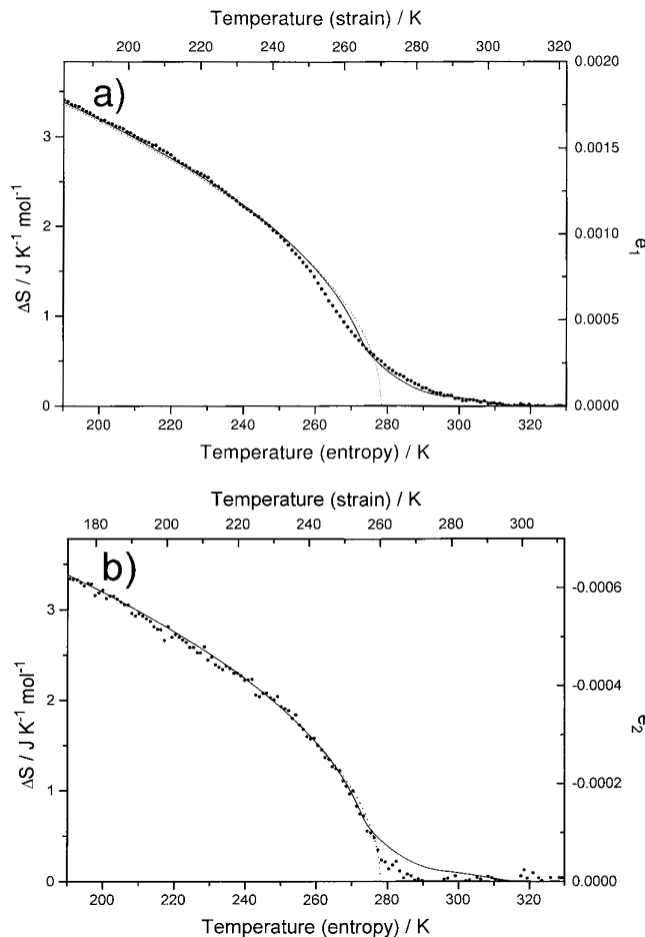
FIG. 5 Temperature dependence of entropy (solid line) and co-elastic spontaneous strains a) e1 and b) e2 (solid points) in lawsonite. The broken line shows the behaviour expected for both these quantities for strict tricritical behaviour ($Q^4 \propto |T_c - T|$). The temperature scales in the two experiments have been adjusted such that the transition temperature T_c is the same in each case.

D. Comparisons with other experimental data

Fig. 5a and 5b compare the temperature dependence of the entropy observed in run 1 with measurements of the co-elastic spontaneous strain (Meyer et al., 2000). In order to compare the various data, it was necessary to add a constant offset to all the temperatures for the spontaneous strain data. This may be due to different temperature calibrations in separate apparatus. This constant was fixed by determining the temperature at which linear extrapolations of both $(\Delta S)^2$ and e_i^2 (both of which are proportional to Q^4) went to zero.

Far from T_c, the expected Landau relationship ($\Delta S \propto e_i \propto Q_2$) is obeyed for all three components of the strain tensor. However, e1 deviates from this relationship over a range of ca. 20 K below T_c. The most probable reason for this is that the simple relationship between short-range order and long-range order is not applicable for small
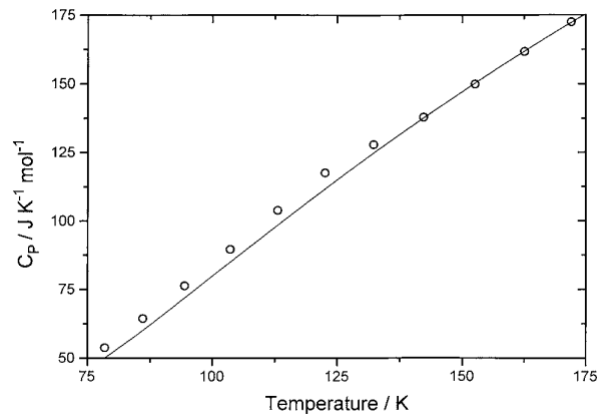

FIG. 6 Specific heat data for lawsonite in the vicinity of the Pmcn − P2$_1$cn transition, taken from Perkins et al. (1980). The data shows a step anomaly, consistent with a second order phase transition.

degrees of long-range order. From Fig. 5, it is apparent that e1 is rather more sensitive to shortrange order than e^2. The tail in e1 above T_c is significantly more pronounced, and correlates well with the entropy in this temperature range (which, since the long-range order parameter is zero, must be from short-range order).

E. Reanalysis of the Perkins et al. (1980) data for the Pmcn–$P2_1cn$ transition

Previous calorimetric studies of lawsonite (King and Weller 1961; Perkins et al., 1980) noted two anomalies in the $C_p(T)$ curve. As we have shown above, there is a good correlation between the lambda peak at 273 K and other data for a phase transition at this temperature. The temperature of the second anomaly noted by Perkins et al. (1980) is approximately 130 K. This is close to the temperature of the Pmcn–P2$_1$cn transition, determined as 120 K by Sondergeld et al. (2000).

Fig. 6 shows the data of Perkins et al. (1980) in the vicinity of this transition. The transition shows limiting second-order behaviour (based on X-ray diffraction measurements, Sondergeld pers. comm.); the expected form of the C_p anomaly in this case is a step, rather than a lambda peak. From Fig. 6, the magnitude of this step at the transition temperature is $6(1) \, \mathrm{J \, K^{-1} \, mol^{-1}}$. Thus the estimated ΔS for the Pmcn–$P2_1cn$ transition at completion is $6(1) \, \mathrm{J \, K^{-1} \, mol^{-1}}$.

IV. DISCUSSION

A. Implications for standard entropy calculations

In this study, we have shown that the anomalies in the specific heat curve of lawsonite are associated with two phase transitions undergone by this mineral. They are thus an intrinsic part of the behaviour of lawsonite, and their effect should be included in calculations of the standard entropy at 298 K, S_{298}^0. It was not possible to simply integrate either of the existing data sets to determine S_{298}^0; the data of Perkins et al. (1980) do not contain sufficient points close to the 275 K transition to properly characterise the peak, whereas our experiment did not measure C_p below 125 K. We used two methods to deal with this difficulty; first, combining the data from the two experiments, and second, using our knowledge of the character of the transition to produce an interpolation through the C_p data measured by Perkins et al. (1980).

Our C_p data agree well with those of Perkins et al. (1980) in the temperature range [140 K, 180 K] (e.g. Fig. 1(a)), and so we used our data in the temperature range [160 K, 298 K], and the data of Perkins et al. (1980) in the range [0 K, 160 K]. Numerical integration of these data gave a value of $S_{298}^0 = 233.27(1)\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The disadvantage of this method is that it is not clear that the two data series may be combined in this way; different samples were used for the two experiments, and the C_p peak is apparently higher in the Perkins et al. (1980) sample than in the one used in this study (Fig. 1(b)).

We therefore also fitted the C_p data of Perkins et al. (1980) to a lambda peak characteristic of a Landau tricritical phase transition. This was done by the same method used above, and the resulting interpolation is shown in Fig. 7.

Integration of the curve in Fig. 7 leads to a value of the standard entropy, S0298 = 234.96(1) JK-1mol-1. Both methods of calculation lead to a higher value of S0298 than previously published (S0298 = 230.19 JK-1mol-1, Perkins et al., 1980).

B. Significance of the magnitude of the excess entropy

Both observed phase transitions in lawsonite are associated with apparent rotation of the H_2O molecules breaking a symmetry plane; the (001) plane at ca. 275 K, and (100) at 120 K. As a result, each H site in the Cmcm structure becomes two sites in the Pmcn structure, each of which undergoes a further twofold splitting in the $P2_1cn$ structure. There is evidence from neutron diffraction studies (Lager et al., 1998) for further H-site splitting at low temperatures, but this is not directly implicated in the phase transitions.

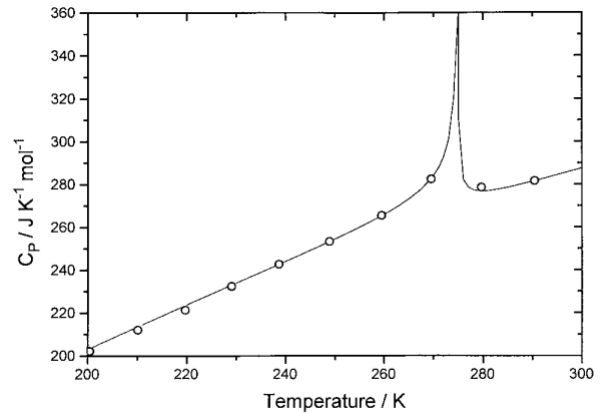The excess entropy associated with both of the phase

FIG. 7 Specific heat data for lawsonite, determined by Perkins et al. (1980), with an interpolation (solid line) consistent with a Landau tricritical phase transition.

transitions has two main possible sources. The first is the configurational entropy associated with mixing the two possible structural configurations as two distinct sites in the high-temperature phase become indistinguishable in the lowtemperature phase. In a simple Bragg-Williams model of these two phase transitions, we would expect the excess entropy associated with each transition to be solely the configurational entropy, which would imply $\Delta S = 5.76\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for each transition.

A contribution to the entropy may also come from the effect of the spontaneous strain on the phonon frequencies. This excess vibrational entropy is expected to scale as the square of the order parameter, but it is not trivial to calculate its magnitude. It is also unclear how much vibrational entropy is required to drive a transition from configurational behaviour (e.g., Bragg-Williams) to the Landau limit. In the case of albite, the excess of the experimentally estimated entropy over the calculated configurational entropy is only about 10 % (Carpenter, 1988), and this appears to be sufficient.

In both transitions, the observed excess entropy is approximately $6\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Thus the measured entropy in lawsonite is not inconsistent with a model of the transitions where dipole ordering is modified by strain effects.

C. Hyteresis in calorimetric measurements

There is a significant degree of hysteresis in the calorimetric measurements of this phase transition, which is not observed in other experiments. One significant factor is that the measurements of quantities such as the spontaneous strain depend on both the orientational ordering of H_2O molecules, and the response of the rest of the structure to this ordering. The absence of order on the length scale of the framework response may well mask significant short-range order. One of the best-
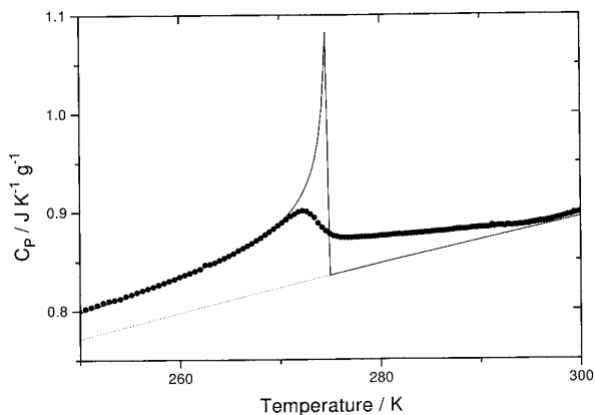
FIG. 8 Temperature dependence of specific heat in lawsonite, compared with a Landau model. Points show experimental data (first heating run), the solid line is a Landau fit, and the broken line shows the baseline function C_{p_0}.

documented examples of this is the study of cordierite by Putnis et al. (1987), in which NMR measurements of (Al, Si) ordering were compared with spontaneous strain data. In cordierite, the expected relationship between the strain and the degree of order ($Q \propto \varepsilon$) was only found for $Q > 0.9$; less wellordered samples showed no macroscopic strain. There are some parallels between this behaviour and the observation that the strain components e_1 and e_2 in lawsonite behave somewhat differently for small degrees of long-range order.

The application of this concept to the C_p hysteresis in lawsonite may be seen by starting with a fully ordered structure. On heating, the degree of orientational order decreases, and the remainder of the structure relaxes towards the high-temperature structure. The agreement between the calorimetric data and the spontaneous strains implies that this process is essentially homogeneous.

On cooling, however, the situation appears to be different. The relaxation of the structure is reversible, but the specific heat measurements indicate that the entropy does not scale with Q2 in the expected way. This implies that the local aspect of the transition (the H_2O orientational ordering) is not perfectly coupled with the longrange displacive changes in the lawsonite structure for small degrees of order. Further experiments to study this hysteresis are planned.

D. Anomalies close to T_c

As Fig. 2 shows, the heat capacity anomaly deviates from the predictions of Landau theory some 2 K to 3 K below the transition temperature. Fig. 8 shows the same effect for the actual anomaly, rather than the linearised function in Equation (1).

Fig. 8 emphasises that there are two deviations from the Landau model; immediately below T_c, the experimental C_p data are lower than Landau theory predicts, and above T_c, the C_p data are higher than the model. The contributions of these two terms to the excess entropy associated with the transition very nearly cancel each other out.

E. H ordering as a tricritical Landau process

Calorimetric data for the transition are consistent with other experimental data in indicating that the Cmcm–Pmcn transition in lawsonite follows a Landau model, close to the tricritical point. The excess entropy associated with the transition appears to be somewhat variable, which may indicate that the either or both the degree of dipole order at low temperatures, and disorder at high temperatures, are incomplete. In any case, the ΔS for the transition is slightly higher than we would predict for a simple order-disorder model.

Qualitatively similar results have been obtained for order-disorder transitions in a number of mineral systems, including omphacite ($C2/c - P2/n$, Carpenter et al., 1990), calcite ($R\bar{3}m$–$R\bar{3}c$, Redfern et al., 1989), and albite ($C2/m - C\bar{1}$, Salje et al., 1985). As noted above, the fact that the thermodynamics of these transitions appear to follow a Landau model of the entropy, rather than a configurational model, is related to the role of the vibrational entropy and its dependence on the spontaneous strain.

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