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Latent heat in uniaxially stressed KMnF_3 ferroelastic crystal

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Abstract. The influence of weak uniaxial stress on both the latent heat and the coexistence interval of the ferroelastic phase transition of KMnF_3 has been measured using a sensitive conduction calorimeter. The latent heat of the sample without stress is 0.129 J g^{-1} and, in the range of 0–12 bar, it increases weakly with the stress. The width of the interval where the latent heat appears increases with stress, with an apparently larger coexistence interval. Heating and cooling processes show different kinetic behaviours. On cooling, the maximum of the differential thermal analysis traces splits into two peaks when a uniaxial stress is applied, which is related to the formation of ferroelastic domain patterns.

1. Introduction

Potassium manganese fluorite, KMnF_3 , undergoes a ferroelastic phase transition from a cubic perovskite structure to a tetragonal phase at 186 K [1]. This phase transition is first order and close to a tricritical point [2–4]. Stokka *et al* [5, 6] measured the influence of the uniaxial stress σ on the thermal hysteresis, ΔT , of the transition temperature. ΔT increases for small values of σ , while for $\sigma > 100$ bar, ΔT decreases in such a way that they estimated that the tricritical point ($\Delta T = 0$) is obtained when a uniaxial stress of about 0.25 kbar is applied along the [100] direction.

The transition is driven by the softening of the Γ_{25} phonons at the R points of the cubic Brillouin zone involving the staggered rotation of the MnF_6 octahedra around the cubic c -axis. Any of the three crystallographic axes with fourfold symmetry in the cubic phase may become the unique tetragonal axis during the transition. Consequently the crystal may develop three orthogonal structural domains; the order parameter has three components each of which corresponds to one specific domain orientation. When a uniaxial stress is applied along an appropriate direction, the orientational degeneracy of the domain structure is broken. As a consequence of the broken degeneracy different domain structures are expected for transitions with and without applied uniaxial stress. The temperature dependence of the domain population has been investigated by x-ray methods by Tietze *et al* [7], Hirakawa *et al* [8] and Okazaki *et al* [9]. The results were not conclusive: Tietze *et al* [7] obtained that near the transition the three domain volumes are equally distributed while Hirakawa *et al* [8] and Okazaki *et al* [9] give an unequal domain population from the beginning of the appearance of the tetragonal phase. The latter two groups of authors agree that at low temperatures the domain population is not equally distributed over the three possible orientations.

Similar studies have been performed on SrTiO₃ which undergoes a structurally similar phase transition of second order, also near to a tricritical point [10]. In this case the domain populations are equally [11] distributed near T_c and weak uniaxial stress (<1 kPa) along the cubic [100] and [110] directions of SrTiO₃ modifies significantly the domain structure near the crystal surface on cooling to the tetragonal phase, and changes of the transition behaviour were found [11, 12].

Structural changes are directly correlated with changes of enthalpy as measured by calorimetric methods. The uniqueness of calorimetric measurements is that they allow one to calibrate the excess Gibbs free energies of a phase transition. In the case of the phase transition in SrTiO₃, both the excess specific heat and the excess entropy were determined and the energetic properties of this transition were correlated with its order parameter behaviour [12]. It is the purpose of this paper to show that even more aspects of a phase transition, namely the changes of the twin structure, can be inferred using high-resolution calorimetry.

Here we make use of the fact that the transition in KMnF₃ is first order but close to a tricritical point where the latent heat is rather small, while the specific heat contribution is important. When the twin structure of the sample is changed by external uniaxial stress, the latent heat contribution and the entropy excess are also expected to change. We show in this paper that these changes are large enough to be observed calorimetrically.

2. Experimental procedure

The sample was prepared at University du Maine (Le Mans, France) using the Bridgman–Stockbarger method. The sample was approximately cylindrical, with a thickness of 5 mm and circular (001) faces with area 0.8 cm². The faces were polished and plane parallel with a difference lower than 3 μm. Diffuse x-ray scattering experiments performed on this sample show extremely large mosaic spread of the diffraction peaks, which indicates the existence of inhomogeneities in it.

The measurements of the heat flux and specific heat were performed by means of high-resolution conduction calorimetry, which has been described in detail in [13]. The sample is pressed between two identical heat fluxmeters, which are made from 50 chromel–constantan thermocouples [14] connected in series with the wires placed in parallel lines. One of the fluxmeters is fixed to a calorimeter block while the other is pressed by a bellows, which is also in thermal contact with the block. The fluxmeters, which have cross-section 1 cm², are rigid enough to apply a controlled uniaxial stress on the sample. In this study we have applied a stress in the range between 0 and 12 bar on the face (100) of the sample. The assembly has a degree of freedom which allows coupling between the sample, the fluxmeter and the bellows. This ensures a homogeneous stress on the sample. Between the sample and the fluxmeters there are two electrical resistances which can act as uniform heaters.

The block is suspended within a cylindrical shield and the entire assembly is placed in a hermetically sealed outer case where a high vacuum (10^{-7} Torr) is obtained. This high vacuum together with the small temperature difference between the sample and the calorimeter block (lower than 10^{-2} K) avoids lateral heat losses in the sample and it ensures unidimensional heat conduction in the sensor. The calorimeter is placed in an automatically controlled thermostat. The large thermal inertia of the calorimeter allows the block to have a very good thermal stability. These features, together with the high number of thermocouples, make the device highly sensitive. As a result, it is possible to measure the heat flux changing the temperature of the sample at a rate as low as 0.1 K h⁻¹ without observing significant temperature fluctuations (always less than 10^{-4} K) in the block temperature, which is measured by a platinum resistance thermometer connected to an automatic resistance bridge.

It is important to note that the system produces two sets of results: the heat flux and the specific heat; they are measured independently under the same thermal conditions and using the same sample.

The specific heat is measured by starting from the steady state obtained when the same power is dissipated by both heaters during 10 min. At the time t_0 the power is cut off and the electromotive force (e.m.f.) $V(t)$ is integrated up to the time t_1 ($t_1 - t_0 = 10$ min) when equilibrium is reached again. The thermal capacity of the sample is proportional to the integral of $V(t)$ with respect to t between t_0 and t_1 . This sequence is repeated every 20 min while the temperature of the calorimeter is changed at a constant rate of 0.18 K h^{-1} . The specific heat data have been given in [15].

The latent heat (L) of the transition is measured by heating or cooling the calorimeter at the same constant rate of 0.18 K h^{-1} but without dissipation in the heaters and recording the e.m.f. $V(t)$ trace. This e.m.f. is proportional to the heat flux ϕ crossing the fluxmeters: $\phi(t) = \alpha V(t)$, where α is the sensitivity of the fluxmeter determined by calibration.

This heat flux has two contributions: one due to the latent heat and another due to the variation of the thermal capacity with temperature. In the case of a transition near a tricritical point (like in KMnF_3) the latent heat is small and the specific heat shows a strong anomaly at the transition, in such a way that the second contribution is very significant. Under these circumstances it is necessary to evaluate the latent heat L very carefully.

For this evaluation we follow the procedure described by del Cerro *et al* [16]. As the DTA trace $\phi(T)$ and the thermal capacity of the sample $C(T)$ have been obtained at similar thermal conditions, the two sets of data are comparable. From the thermal capacity data we can calculate the ϕ_c -trace due exclusively to the thermal capacity contribution and compare it with the measured ϕ -trace. Only in the temperature range ($T_F - T_P$) where the calculated $\phi_c(T)$ is different from the measured $\phi(T)$ is the latent heat present. T_P and T_F are respectively the maximum and minimum temperatures where ferroelastic and paraelastic phases coexist in each experiment. The measured trace $\phi(T)$ and the calculated $\phi_c(T)$ on cooling the stress-free sample are shown versus temperature in figure 1. The two sets of data coincide over the whole

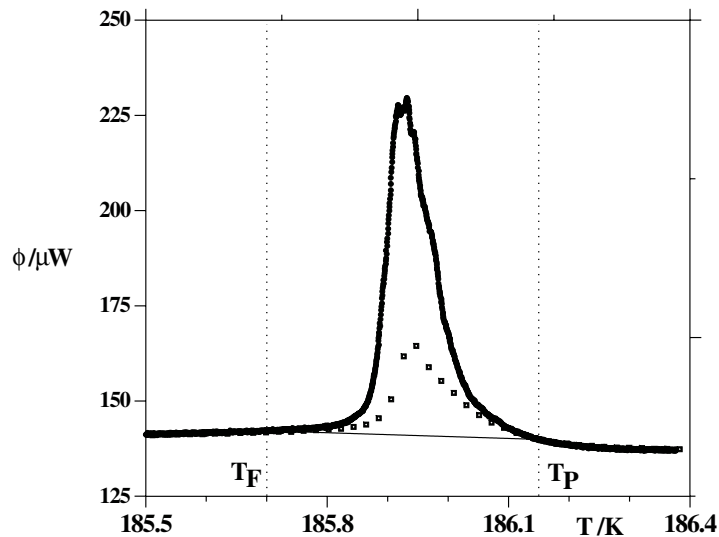


Figure 1. The differential thermal analysis (DTA) trace (full circles) and heat flux calculated from specific heat data (open squares) versus temperature on cooling for stress-free KMnF_3 .

temperature range except in the interval $(T_P, T_F) = (186.15 \text{ K}, 185.70 \text{ K})$ where the effect of the latent heat is present. The integration of the ϕ -trace with respect to time, using as base-line the straight line $\phi(T_F) - \phi(T_P)$, determines the latent heat.

As the temperature variation rate is very small, the transition takes between three and four hours to complete, depending on the applied stress. From the values of the heat flux and the thermal resistance of the fluxmeter, the temperature difference between the faces of the sample in contact with the fluxmeters and the calorimetric block is evaluated to be practically constant and lower than 0.01 K, even during the phase transition.

On the other hand, from thermal conductivity data, the thermal gradient in the sample during the measurement, defined as the difference between the middle and the end planes of the sample, is estimated to be lower than 0.01 K.

As both temperature differences are much lower than the temperature interval $T_P - T_F$ where the latent heat is present, we deduce that the temperature of the sample is not constant during the phase transition. So, the temperature range $T_P - T_F$ corresponds well with the temperature interval of phase coexistence with an error estimated to be lower than 0.03 K.

Our experiments have been carried out cooling the sample under stress from 200 K to 160 K at the rate of 0.18 K h^{-1} and then heating the sample, always maintaining the applied stress. Then the sample was kept under uniaxial stress for about a week in the tetragonal phase.

3. Results

We have carried out six experiments, each involving cooling and heating the sample at a rate of $v = 0.18 \text{ K h}^{-1}$ and with a uniaxial stress σ applied on the face (100) whose values were 0, 9 and 12 bar. The DTA traces, related exclusively to the latent heat, are shown in figures 2 and 3. The results are summarized in table 1.

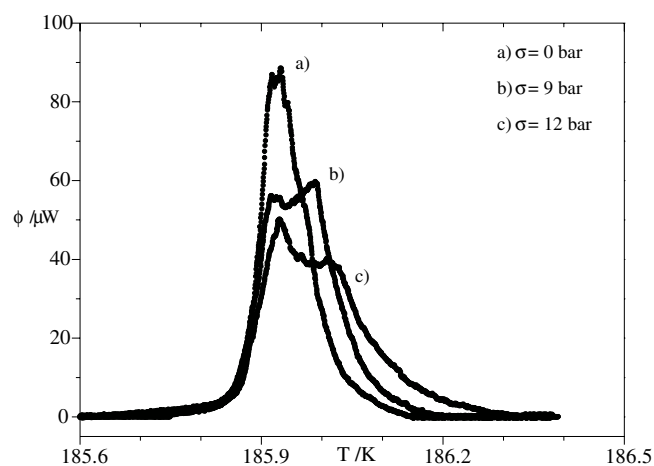


Figure 2. The heat flux (ϕ) due to the latent heat versus temperature when cooling KMnF_3 crystal under different stresses applied on the face [100].

The latent heat value in the absence of stress is 0.129 J g^{-1} . This value increases with stress at an average rate of $9 \times 10^{-4} \text{ J g}^{-1} \text{ bar}^{-1}$ (table 1). This result is in qualitative agreement with observations of Stokka *et al* [5, 6] who showed that the thermal hysteresis of the maximum value of the specific heat increases with the stress up to 100 bar, indicating that the transition becomes more first order for weak uniaxial stresses, although for values of stress higher than

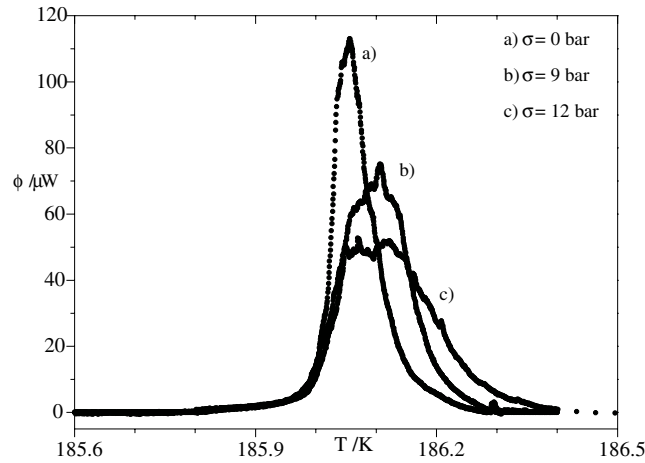


Figure 3. The heat flux (ϕ) due to the latent heat versus temperature when heating KMnF_3 under different stresses applied on the face [100].

Table 1. The latent heat of KMnF_3 and temperatures which limit the coexistence interval for different applied stresses.

	σ (bar)	L (J g^{-1})	T_F (K) (± 0.05 K)	T_P (K) (± 0.05 K)
Cooling	0	0.129	185.70	186.15
	9	0.138	185.70	186.25
	12	0.141	185.70	186.30
Heating	0	0.130	185.80	186.30
	9	0.134	185.80	186.35
	12	0.139	185.80	186.40

100 bar, the thermal hysteresis decreases and disappears at about 240 bar at a tricritical point.

Previously a 2–4–6 Landau potential was used to describe the specific heat and latent heat data of this stress-free sample over a wide temperature range [15]:

$$\Delta G = \frac{1}{2}A(T - T_c)Q^2 + \frac{1}{4}BQ^4 + \frac{1}{6}CQ^6$$

with $A = 2.781 \text{ J mol}^{-1}$, $B = -57.63 \text{ J K}^{-1} \text{ mol}^{-1}$, $C = 574.2 \text{ J mol}^{-1}$, $T_c = 185.76 \text{ K}$. The theoretical behaviour of the order parameter deduced from the above potential agrees very well with the experimental behaviour of the order parameter obtained from x-ray diffraction studies. Furthermore, the theoretical value of the coexistence interval predicted by the Landau potential is 0.52 K which is in good agreement with the value $T_P - T_F = 0.45 \text{ K}$ obtained in this work for the stress-free sample. This value is lower than the value of 1.2 K, estimated from x-ray diffraction measurements [8].

The effect of the uniaxial stress (figures 2 and 3) is to broaden the peak with the appearance of several, closely spaced maxima. The uniaxial stress expands the coexistence interval by increasing the temperature T_P in both heating and cooling runs, while the temperature T_F and the shape of the DTA trace at temperatures close to T_F are not affected by the stress. This can be interpreted by considering that this weak uniaxial stress only affects the part of the coexistence interval where the cubic phase predominates. Here, the uniaxial stress stabilizes the tetragonal phase.

4. Discussion

In figure 4, we represent the increase of entropy ΔS versus temperature for all the experiments summarized in table 1. ΔS has been calculated by integrating the heat flux represented in figures 2 and 3 and considering as reference the para-phase at 186.5 K.

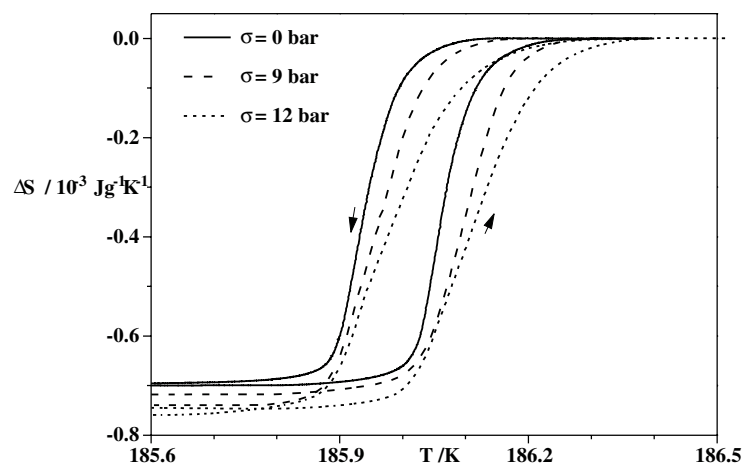


Figure 4. The increase of entropy (ΔS) due to the latent heat versus temperature when cooling and heating the sample under different uniaxial stresses.

As ΔS is proportional to the molar fraction of ferroelastic and paraelastic phases and the temperature variation rate was practically the same in all of the experiments, the slope of the ΔS curves is proportional to the transformation rate of both phases.

For each stress, the heating and cooling curves are almost parallel, indicating that the transformation from paraelastic to ferroelastic phase (growing of domains) is not very different to the transformation from the ferroelastic to the paraelastic phase (destruction of domains). It seems that the small difference of each pair of curves increases with the stress.

On the other hand, if we had only one phase front, the magnitude ΔS would behave like a step function. Its slope would be practically vertical and the transition would be produced in a narrow temperature interval. Otherwise, if we had a crystal with strong inhomogeneities we would obtain a lower slope and a broader temperature interval. In our results (figure 4) we see that, for $\sigma = 0$, ΔS is not vertical. The inhomogeneities lead to heterogeneous nucleation of phase fronts in the stress-free sample and the transition takes place over a larger temperature range. The existence of these inhomogeneities in our sample has been confirmed by diffuse x-ray scattering which shows extremely large mosaic spread of diffraction peaks as was indicated above.

The thermal hysteresis is often evaluated from the temperature difference between the maximum of the specific heat curve in heating and cooling runs. We cannot follow this procedure because the DTA curves under stress do not present a clear maximum. One procedure for evaluating this thermal hysteresis is to analyse the temperature shift between the heating and cooling curves in figure 4.

For $\sigma = 0$, the thermal hysteresis is evaluated to be 0.13 K. Due to the low rate of temperature change used in these experiments, the process can be considered as quasistatic, so it is reasonable for this value to be lower than the theoretical coexistence interval 0.52 K calculated from the 2–4–6 Landau potential. Within our experimental error, this thermal

hysteresis slightly increases with the stress, in agreement with the results of Stokka *et al* [5, 6] and with the increase that we have observed in the latent heat. Nevertheless, this increase rate is much lower than the value obtained by Stokka *et al* applying higher stresses.

Let us analyse the DTA traces to investigate the influence of the uniaxial stress on the twin structure of this crystal. We must keep in mind that this analysis will be only qualitative because the details of the DTA traces are not completely reproducible as they can depend on defects in the crystal, on the previous history, on the experimental procedure etc.

For cooling and heating runs for the stress-free sample (figures 2 and 3), we observe that the DTA traces present a single peak. Theoretically, the three variants of domains are equivalent and we may expect them to grow or disappear in the same temperature intervals. The total latent heat contribution is the superposition of the three equivalent domains, thus resulting in a single peak.

From figure 2, the cooling DTA trace for an applied stress of 9 bar shows a double peak, one of the peaks being at the same temperature as for the stress-free sample.

This can be explained by considering that the stress applied along the direction [100] favours the formation of the domains (called a and b) whose respective tetragonal axes are perpendicular to the stress direction. The formation of these two domains must begin at a higher temperature, thus producing a maximum whose temperature increases with the stress.

On the other hand, the applied stress is so weak that it is reasonable to assume that it cannot completely prevent the formation of the third type of domain (named c) whose tetragonal axes are parallel to the stress direction.

Consequently, when cooling, the DTA trace has clearly two contributions: one due to the formation of domain c which produces a maximum at the same temperature as for the stress-free sample and another contribution due to the formation of domains a and b, which produces a second maximum whose temperature increases with the stress.

For $\sigma = 9$ bar, the peak due to domains a and b is the highest because it corresponds to the domains in favourable orientations and it is reasonable to assume that the volume of these domains is greater than that corresponding to domains c.

The decrease of the peak due to domains a and b for $\sigma = 12$ bar can be attributed to the fact that the temperature interval where a and b domains are formed increases with the stress, thus producing a broadness of its DTA trace contribution and, consequently, a decrease of its height.

As the temperature range of a and b domains increases with the stress, T_P also increases with σ . Nevertheless, as the weak uniaxial stress does not affect the temperature range where c domains are formed, T_F stays constant. For these reasons, the DTA traces under stress are clearly non-symmetrical. Although there could be other reasons, the small asymmetry of the DTA trace for the stress-free sample could be related to the existence of an internal stress in the sample.

When heating under stress, the DTA traces (figure 3) show a similar behaviour to when cooling (figure 2): the stress also produces an increase of the temperature limit T_P , where the phase transition ends. The stress is sufficient to stabilize the tetragonal phase at higher temperatures. Nevertheless, the clear double peak observed when cooling does not appear and the transformation occurs in a more heterogeneous fashion.

Previous authors [7, 8] propose a different domain population for the different domains at low temperature even without stress. For example, Tietze *et al* [7] propose that the population of one orientation decreased to $\approx 5\%$ when the temperature of the sample was decreased to well inside the stability regime of the tetragonal phase.

Similarly, it appears reasonable to assume that in our heating experiments at $T \ll T_c$, the proportion of c domains is small with respect to that of the a and b domains (the sample has

been kept under stress for more than a week in the tetragonal phase before carrying out the phase transition). The contribution of c domains to the DTA trace is masked by the contribution of the dominant a and b domains, so we observe only a single peak, with an irregular plateau due to the different contributions of individual a and b domains.

In conclusion, we have shown for the first time that the influence of a uniaxial stress on the latent heat of a phase transition can be measured. We have developed a technique able to discriminate between the heat flux contribution and the excess specific heat. A careful distinction is needed for the analysis of microstructural features. We have also demonstrated that this experimental technique is suitable for assessing the influence of the uniaxial stress on twinning during phase transitions.

It would be very interesting to correlate the DTA traces with optical observations of the evolution of domain patterns and phase fronts but our system does not allow it. We are planning to carry out this kind of study in the future.

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