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Discrimination of the transition order extremely close to a tricritical point

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Abstract

The cubic to tetragonal phase transition of the ferroelastic $KMn_{0.997}Ca_{0.003}F_3$ has been studied by a conduction calorimetry technique. The comparison of the specific heat data, the sensitivity of the calorimeter and the DTA trace obtained with the same apparatus and under similar thermal conditions shows that the transition is extremely close to the tricritical point and its latent heat is evaluated to be 0.010 ± 0.005 J g^{-1}. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Latent heat; Specific heat; Tricritical point; $KMnF_3$; Conduction calorimetry

1. Introduction

The latent heat (L) is the thermodynamic magnitude that determines the first-order character of a phase transition. Its measurement becomes even more important when the transition is very near to the tricritical point, as it is in the case of systems crossing the borderline between first-order and second-order phase transitions by the effect of external fields or compositional changes.

The methods used for determining latent heat, differential scanning calorimetry (DSC), differential thermal analysis (DTA), really measure changes of enthalpy (ΔH). In the case of a first-order phase transition, ΔH has two contributions: one due to the specific heat variation with the temperature and another due to the latent heat.

The determination of the baseline, respect to which the DTA trace must be integrated in order to obtain the latent heat, presents a great difficulty when the specific heat changes significantly with the temperature below and above the transition temperature. That is the case of a transition near a tricritical point, where the difficulty increases because the latent heat is very small. To solve this problem, it is necessary to compare the DTA trace and the specific heat data; both obtained under the same thermal conditions. Nevertheless, it is not easy to fulfill this comparison because, generally, both sets of data are obtained with different devices and under very different temperature scanning rates. DTA and DSC instruments work at scanning temperature rates in the range of 1–100 K min^{-1} while the techniques that measure specific heat such as adiabatic calorimetry, AC calorimetry or conduction calorimetry work at rates of 1 K h^{-1} or lower.

It is necessary to use methods where the measurement of heat flux and specific heat are comparable. Recently, a new technique, the dynamic differential

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scanning calorimetry (dynamic DSC) [1,2], has been developed where the same apparatus works simultaneously as a differential scanning calorimeter and an AC calorimeter, working at scanning temperature rates of about $1\ \mathrm{K\,h^{-1}}$. This technique allows the discrimination of the order of the transition and the evaluation of the latent heat, although the temperature resolution is lower than in high precision AC calorimetry.

We have recently developed a new method [3], based on conduction calorimetry, which discriminates the change of enthalpy due to the latent heat from that due to the temperature dependence of the thermal capacity. The sensor of the calorimeter is formed by two identical fluxmeters, each one having 50 chromel–constantan thermocouples.

The specific heat and the heat flux exchanged by the sample (DTA trace, V_D) are measured in two different runs at the same constant scanning temperature rate as low as $0.1\ \mathrm{K\,h^{-1}}$. As both sets of data are obtained with the same device, on the same sample and under similar thermal conditions, it is possible to compare them. From the specific heat data $c(T)$ we calculate the DTA trace, $V_C(T)$, which would correspond exclusively to the thermal capacity contribution. The effect of the latent heat is only present in the temperature range (T_0, T_1) where $V_C(T)$ and $V_D(T)$ do not coincide. The latent heat is calculated integrating the DTA trace $V_D(T)$ respect to the straight line $V_D(T_0) - V_D(T_1)$.

This method has been applied to the study of the crystal $KMnF_3$ [3], which undergoes [4] a ferroelastic phase transition from the cubic perovskite structure to a tetragonal structure at 186 K. The order parameter is related to the angle ϕ of the MnF_6 octahedral rotation around the $\langle 0\ 0\ 1 \rangle$ axis [5]. The transition is first-order but it has been shown that it is near a tricritical point [6,7]. Using the previous method, the latent heat was evaluated to be $0.129 \pm 0.002\ \mathrm{J\,g^{-1}}$ [3].

It has been also shown that the order of this transition can be changed by substituting Ca for Mn [3,8–10]. Thus, the $KMn_{1-x}Ca_xF_3$ crystals are very suitable to study a system very close to the tricritical point. In a previous paper [3], we have shown, using the previously described technique, that the addition of 2.3% Ca ($KMn_{0.977}Ca_{0.023}F_3$) shifts the transition to be second-order. It was obtained that the anomaly, which appears in the DTA trace at the transition temperature, is entirely due to the specific heat contribution because $V_C(T) = V_D(T)$ over all the temperature range and, thus, there is no latent heat.

On the other hand, if the transition is first-order but extremely close to the tricritical point, the difference between $V_C(T)$ and $V_D(T)$ must be very small and it would be difficult to discriminate if this difference is due to the existence of a extremely small latent heat or to experimental errors. The situation gets complicated if we realize that, due to the effect of the latent heat during the measuring process of the specific heat, the data of c obtained in the coexistence interval (T_0, T_1) are wrong and higher than the right values corresponding to the monophasic states. Consequently, the calculated $V_C(T)$ trace in this interval would be higher than the corresponding contribution due to the thermal capacity. In this case, the comparison between the experimental $V_D(T)$ and the calculated $V_C(T)$ traces may not be enough to discriminate the order of the transition.

In this paper, we have performed, using the same technique, a study of the cubic to tetragonal phase transition of the crystal $KMn_{0.997}Ca_{0.003}F_3$, whose composition is supposed to make the transition be extremely close to the tricritical point. In this case, the experimental trace V_D and that calculated from the specific heat V_C practically coincide. Nevertheless, it is shown in this paper that the additional analysis of the sensitivity α of the fluxmeters allows us to establish the discontinuous character of this transition. The latent heat is estimated to be $L = 0.010 \pm 0.005\ \mathrm{J\,g^{-1}}$.

2. Experimental

The conduction calorimeter used in this work was described previously in detail by Gallardo et al. [11]. The sample is pressed between two identical heat fluxmeters, which are made from 50 chromel–constantan thermocouples [12], 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. The fluxmeters, which have a cross-section of $1\ \mathrm{cm^2}$, are rigid enough to apply a controlled uniaxial stress of between 0 and 12 bar on the sample. Two electrical resistances (heaters) are placed between each face of the sample and fluxmeters. These resistances can dissipate a uniform heat power on the sample faces or measure the temperature of the fluxmeters junctions near the sample.

The sample was a single crystal of $KMn_{0.997}Ca_{0.003}F_3$, 5 mm thick, with a cross-section of 0.6 cm^2 and a mass of $m = 0.97$ g. It was grown using the Bridgman–Stockbarger technique.

The specific heat of the sample was measured using the method previously described in detail [13]. The same constant power W is dissipated in both heaters for 10 min to reach a steady-state characterized by a constant temperature difference between the sample and the calorimeter block, ΔT. Let be V_1, the constant electromotive force (emf) of the fluxmeters in this steady-state. Then the power is cut off and the emf $V(t)$ of the fluxmeters is integrated for another period of 10 min. Let be V_0, the constant emf given by the fluxmeters at the final state. The integration of $(V(t) - V_0)/(V_1 - V_0)$ respect to time allows us to determine the thermal capacity of the sample. Then, the power is switched on again and the sequence is repeated while the temperature of the sample is changed at a constant rate as low as 0.1 $K\,h^{-1}$.

The sensitivity α of the fluxmeters is defined as the relationship between the emf V given by the fluxmeters and the heat flux W crossing them at a steady-state. It is evaluated in each cycle of specific heat measurement as

$$\alpha = \frac{V_1 - V_0}{W} = \frac{(V_1 - V_0)R}{\Delta T} = \varepsilon r \qquad (1)$$

where R is the thermal resistance of the fluxmeters and ε and r are, respectively the thermoelectric power and the thermal resistance of each thermocouple of the fluxmeters. It does not depend on the sample properties and presents a smooth dependence with the temperature. As we will show below, the measurement of α helps us to discriminate the character of the transition.

On the other hand, the latent heat of the sample is measured using this equipment as a very sensitive DTA device: the temperature of the calorimeter block is changed at the same constant rate used for the measurement of the specific heat to make comparable both sets of data.

The emf V_D given by the fluxmeters is continuously measured without dissipation in any heater. V_D is proportional to the variation with the temperature of the total enthalpy of the sample, which includes the latent heat, if it exists, and the variation of the specific heat with the temperature.

It has been shown previously [3] that, when there is no latent heat, this emf is given by

$$V = \alpha v\left(\frac{C_0}{2} + C_1 + C_s\right) = \alpha v(C_F + C_s) \qquad (2)$$

where v is the scanning temperature rate and C_0, C_1 and C_s are, respectively the thermal capacity of the fluxmeter, the heater and half of the sample. To determine, if an anomaly in the emf V_D is due to a latent heat or if it is due to a specific heat anomaly, we proceed as it follows: from thermal capacity data C_s and emf data V_D, we consider the values of $C_s(T)$ and $V_D(T)$ at two different temperatures, where we assume that there is no effect from the latent heat, above and below the temperature T_m of the maximum value of V_D (in this case we have considered 3 K above and below T_m). Using these data in Eq. (2), we evaluate the term C_F at those temperatures. As in this temperature range, there is no anomaly in the thermal capacity of both fluxmeters and heaters, we can assume a linear temperature dependence of C_F in this small temperature range.

Now, using this linear relation together with specific heat data of the sample in that temperature range, the expression (2) allows us to calculate the emf V_C, which is the DTA trace due exclusively to the thermal capacity behavior. Comparing the measured V_D and the calculated V_C, we deduce that only in the temperature range (T_0, T_1) where they do not coincide there is effect from the latent heat. The latent heat is determined by integrating the emf V_D between T_0 and T_1 and using the straight line $V_D(T_0) - V_D(T_1)$ as baseline.

3. Results

3.1. DTA traces

In Fig. 1, we represent the specific heat data of $KMn_{0.997}Ca_{0.003}F_3$ versus temperature in a range of 3 K around the transition temperature. A complete analysis of these data is in progress and it will be shown in a forthcoming paper.

In Fig. 2, the experimental DTA trace V_D and the calculated trace V_C of $KMn_{0.997}Ca_{0.003}F_3$ are

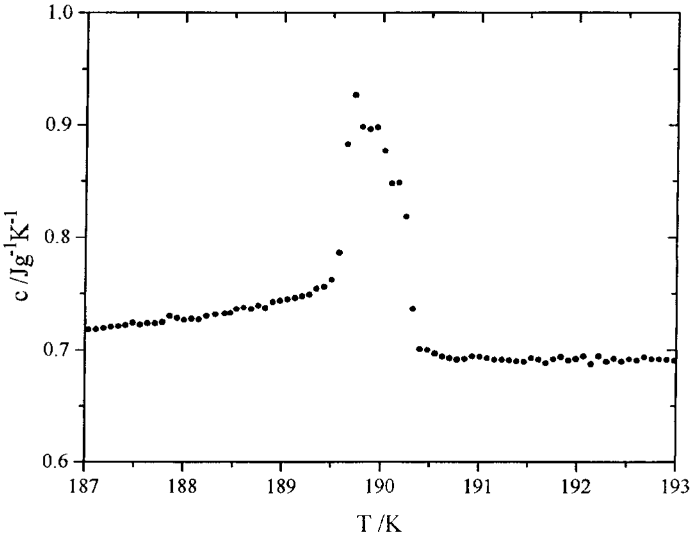

Fig. 1. Specific heat of $KMn_{0.997}Ca_{0.003}F_3$ vs. temperature near the transition point.

represented versus temperature in a range of 2 K around the transition point. Although, V_D seems to be higher than V_C in a narrow range of temperature, the difference between both sets of data is so small that it is difficult to distinguish if it is due to the existence of a latent heat or to experimental errors.

It is useful to compare this curve with the corresponding ones to pure $KMnF_3$ (Fig. 3a) and $KMn_{0.977}Ca_{0.023}F_3$ (Fig. 3b), which we have studied previously [3]. In the case of the 2.3% Ca doped crystal, V_D and V_C were found to coincide over all the temperature range, confirming that the transition is second-order.

In the case of pure $KMnF_3$, whose transition is first-order, V_C was found to be clearly lower than V_D between $T_0 = 186.15$ K and $T_1 = 185.80$ K. In this

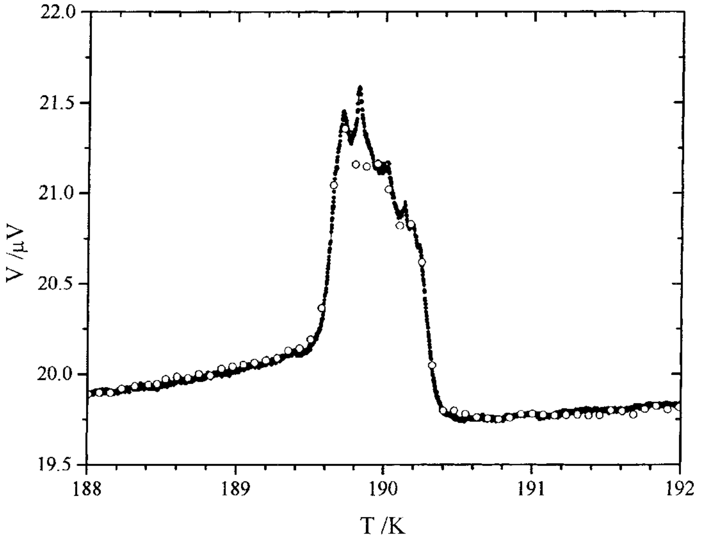

Fig. 2. Measured V_D (full circles) and calculated V_C (open circles) vs. temperature of the block when cooling the $KMn_{0.997}Ca_{0.003}F_3$.

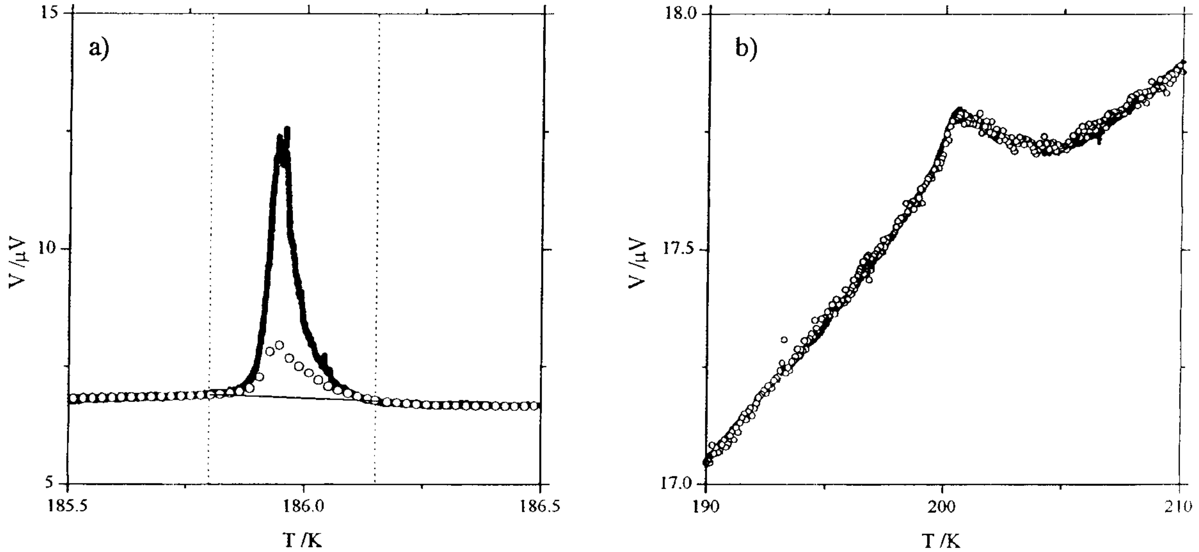

Fig. 3. Measured V_D (full circles) and calculated V_C (open circles) vs. temperature of the block for: (a) pure $KMnF_3$ and (b) $KMn_{0.977}Ca_{0.023}F_3$.

interval, both phases coexist and the specific heat data obtained are affected by the latent heat, resulting in c values higher than those corresponding to each single phase, $c(T_0)$ and $c(T_1)$. To determine the latent heat, we used the straight line between $V_D(T_0)$ and $V_D(T_1)$ as the baseline, which is also shown in Fig. 3a. The latent heat was evaluated to be $L = 0.129 \pm 0.002$ J g^{-1}.

According to previous results on pure crystal, the facts that V_D (Fig. 2) is slightly higher than V_C and that the DTA trace presents several irregular peaks suggest that the transition in $KMn_{0.997}Ca_{0.003}F_3$ is still first-order but extremely close to the tricritical point. In the next section, we will discuss the experimental behavior of the sensitivity α, which supports this statement.

3.2. Analysis of the sensitivity α

As it has been indicated above, the sensitivity α is determined in each cycle of specific heat measurement by expression (1). The steady-state is obtained after the dissipation in both heaters of a constant power W during a time $\tau = 10$ min. The time τ is chosen as the minimum time necessary for the assembly sample-fluxmeter to reach the steady-state under these conditions, so that the measurement time is minimized and the number of experimental points is increased. When the steady-state is reached, all the heat power W crosses the fluxmeters and a uniform temperature increase ΔT is produced in the sample. This temperature increase is evaluated to be 0.06 K.

In Fig. 4a–c, we represent α versus temperature for pure $KMnF_3$, $KMn_{0.997}Ca_{0.003}F_3$ and $KMn_{0.977}Ca_{0.023}F_3$, respectively. For pure and 0.3% Ca doped crystals, there is a decrease of α around the transition temperature while for the 2.3% Ca doped crystal α presents a smooth temperature dependence around the transition temperature without any anomaly. It suggests that the anomaly in α is related to the existence of latent heat, that is, to the first-order character of the transition.

Let us analyze the behavior of α in the pure crystal. To explain the decrease in α, we have to take in account that the total heat dissipated to reach the steady-state during the specific heat measurement process is $W\tau = 0.55$ J while the change of enthalpy of pure $KMnF_3$ due to the latent heat is $\Delta H_0 = mL = 0.19$ J ($m = 1.47$ g).

When there is no effect from the latent heat, the heat $W\tau$ is used to increase uniformly the temperature of the sample and to reach the steady-state. When the temperature of the sample is close enough to the temperature interval where the effect of the latent heat is present or when the sample is in the coexistence interval, a part of the heat $W\tau$ is used to produce a

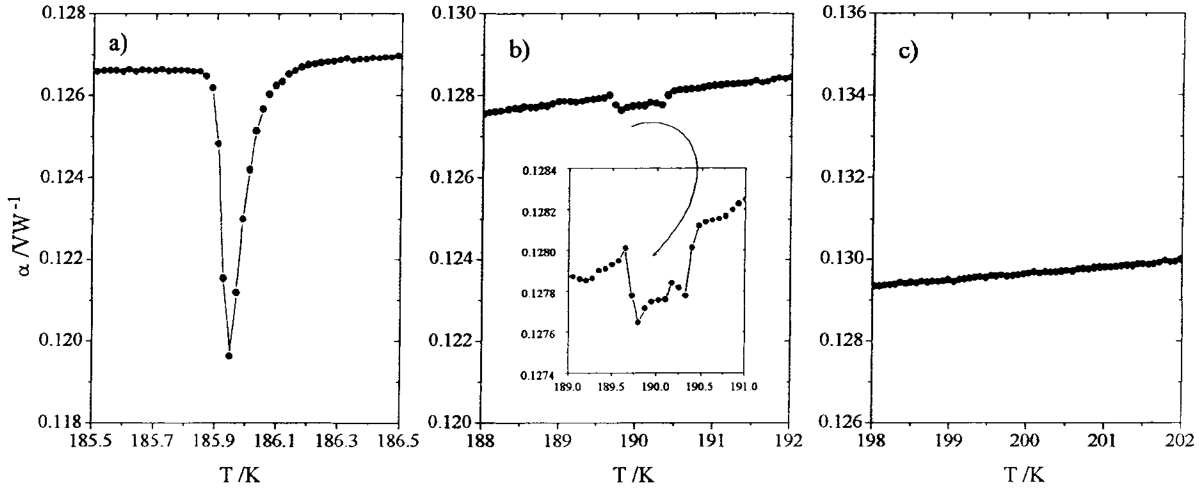

Fig. 4. Sensitivity of the fluxmeters (α) vs. temperature for: (a) pure $KMnF_3$; (b) $KMn_{0.997}Ca_{0.003}F_3$ and (c) $KMn_{0.977}Ca_{0.023}F_3$.

partial or total change of phase and the rest is used to increase the temperature of the sample ($W\tau > mL$). Due to the effect of the latent heat, there is not enough time for the sample to reach the steady-state necessary for the determination of α, since the time t has been chosen as the minimum necessary time for the system to reach the steady-state under the conditions in which the latent heat is not present.

Thus, at the end of the dissipation period during the measurement of c, a part of the heat power W is still increasing the temperature of the sample and we obtain an emf V_1' lower than the value V_1, which we would have obtained under the conditions in which the effect of the latent heat is not present. Thus, the obtained value of the sensitivity, α', is lower than the value α which we would have obtained if there is no effect from the latent heat. Consequently, the decrease of α indicates the first-order character of the transition.

It is observed that for $KMn_{0.977}Ca_{0.023}F_3$ (Fig. 4c) whose transition is continuous, there is no anomaly in α over all the temperature range.

In the case of $KMn_{0.997}Ca_{0.003}F_3$ crystal (Fig. 4b), a small decrease of α is also observed in the temperature range where the anomaly in the DTA trace is present. This confirms that the phase transition in this crystal is still first-order as we suggested above. The decrease of α in this crystal is lower than in pure crystal because the transition is closer to the tricritical point and the latent heat is smaller.

The last point is to evaluate the latent heat of the transition of $KMn_{0.997}Ca_{0.003}F_3$. As we noted above, V_D and V_C are so close that it is difficult to determine the temperature interval (T_0, T_1) where both sets of data are different, making the uncertainty in the determination of L increase. Nevertheless, we can estimate an upper and a lower limit of the value of L.

An upper value is obtained when we consider the continuous straight line labeled (a) in Fig. 5, between the temperatures $T_0 = 189.68$ and $T_1 = 190.24$ K, where V_D and V_C clearly coincide. The obtained value is $L_{max} = 0.015$ J g^{-1}.

A lower value of the latent heat is estimated with respect to the dotted straight line labeled (b) in Fig. 5. This straight line delimits the small peaks, which can be associated to the thermal effect due to partial changes of phase. The corresponding value is $L_{min} = 0.006$ J g^{-1}. We must point out that the deviation of the V_C data respect to this straight line is lower than our experimental error in the determination of V_C. Consequently, we evaluate the latent heat to be $L = 0.010 \pm 0.005$ J g^{-1}.

We can conclude that this method, where we combine the DTA trace, the specific heat data and the sensitivity data allows us to discriminate if a phase transition is first-order or second-order even when it is extremely close to the tricritical point and it allows us to evaluate latent heats as low as 0.01 J g^{-1}

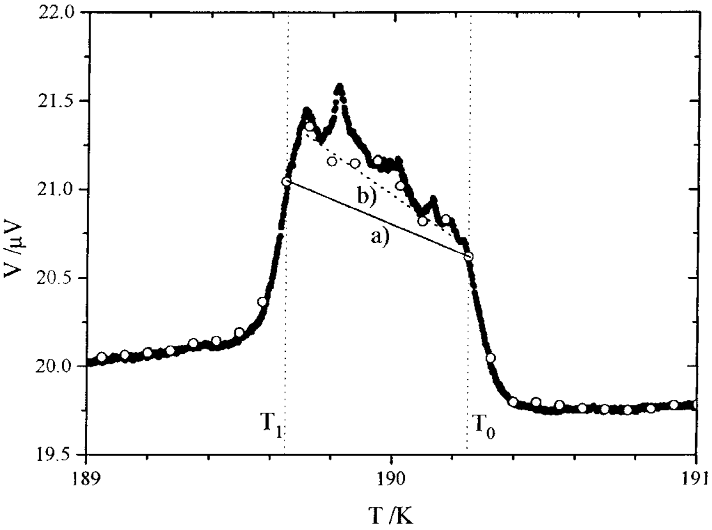

Fig. 5. Measured V_D (full circles) and calculated V_C (open circles) vs. temperature of the block when cooling the $KMn_{0.997}Ca_{0.003}F_3$ and the two baselines used to evaluate the latent heat.

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