PHASE TRANSITIONS IN FERROIC CRYSTALS OF KMPO$_4$ (M=Fe^{2+}, Co^{2+}, Ni^{2+}) STUDIED BY ODSC

M. Lujan, H. Schmid and P. Tissot

Department of Inorganic, Analytical and Applied Chemistry, Faculty of Sciences,
University of Geneva, 30, quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland

Abstract

The influence of the temperature program parameters of an ODSC experiment on the calculated "reversing" and "kinetic" signals has been studied. Mixed orthophosphate salts of KMPO$_4$ (where M=Ni^{2+}, Co^{2+} and Fe^{2+}) which present at least one structural phase transition have been used for this purpose. On these crystalline compounds we have shown that the non reversing heat flow is partly associated with the formation and disappearance of ferroelastic and ferroelectric domain walls. However a proper choice of the temperature program parameters is important so that the calculated "reversing" and "kinetic" curves have the supposed physical meaning according to the assumptions made for the calculations.

Keywords: crystalline compounds, mixed orthophosphate salts, oscillating DSC, phase transitions

Introduction

The modulated or oscillating DSC (ODSC) has become recently available as a new technique of thermal analysis [1]. Recent papers on the applications of ODSC have shown the general interest of this technique applied to material science, in particular the characterization of polymers. The main advantage of ODSC is the possibility of decomposing the "total" signal of a classic DSC experiment into two components. One of them corresponds to all kinds of reversible thermal phenomena which give rise to a reversing heat flow. The other component is calculated from the difference between the "total" (D) and the "reversing" (C_p) thermal effects and is called the "non reversing" or "kinetic" component (K). The "kinetic" component is any thermal event which is non reversible like evaporation, chemical reactions, relaxation events accompanying structural transitions, etc. Therefore this technique can be advantageously used to characterize weak glass transitions, to increase the resolution, to separate complex overlapping transitions, etc. [2].

The calculation of these two components is based on the assumption that the total heat flow has two contributions; one which is heating rate dependent and another one which is dependent only on the absolute temperature. Hence the heat flow is expressed by the following equation:

$$\frac{dQ}{dt} = C_p \frac{dT}{dt} + f(t,T) \qquad (1)$$

where Q is the amount of heat evolved, C_p is the heat capacity, T is the absolute temperature and $f(t, T)$ is some function of time and temperature that governs the "kinetic" response of the transformation taking place in the sample. The first term on the right corresponds to the "reversing" part of the heat flow and is proportional to the heat capacity of the sample [3]. In the case of oscillating or modulated DSC, the temperature program as a function of time applied to the sample is given by:

$$T = bt + B\sin(\omega t) \tag{2}$$

where b is the heating rate, B is the amplitude of the superimposed temperature modulation and ω is the angular frequency of the modulation. As a consequence, the heat flow measured is also an oscillating signal. In order to give a mathematical expression for this signal, it is assumed that the temperature modulation is small enough so that the response of the kinetic process to the temperature can be considered linear. Then Eq. (1) can be expressed as a function of the variable determining the temperature program as follows:

$$\frac{dQ}{dt} = C_{p,t}[b + B\omega\cos(\omega t)] + f'(t, T) + C\sin(\omega t) \tag{3}$$

A mathematical treatment of the modulated heat flow signal provides the total heat flow as in a normal DSC experiment. In addition the heat flow corresponding to the "reversing" part can also be calculated by a Fourier transform approach [4]. The relative amount of each of these contributions will depend on the transition being evaluated. As this technique has been applied essentially to polymers, the interpretation of the measured curves was rather straightforward, assigning the "reversing" part of the signal to the heat capacity of the sample studied, and the "kinetic" part to some kind of relaxation phenomena. However, not much work has been done on other kind of samples with a different type of phase transitions where the interpretation of the "reversing" and "kinetic" components of the heat flow may not be so straightforward.

It is important to keep in mind that these calculations have a physical meaning only if the following conditions are fulfilled:

− The measuring instrument behaves ideally,
− No temperature gradients are present within the sample
− The function describing the "kinetic" heat flow has a linear dependency on temperature

These are rather tough conditions which will greatly limit the values of heat rate, amplitude and frequency modulation that can be applied in an ODSC experiment. However none of the publications available gives a clear information about the range of heating rate, amplitude and frequency modulation where the assumptions made for deriving Eq. (3) are valid. Most of the recommendations given are based on experience and are limited to a certain kind of materials and phenomena such as glass transitions in polymers and polymer melting. Therefore we decided to carry out a series of studies of the phase transitions of crystalline compounds pre-

senting several phase transitions which were also characterized by diffraction and optical methods. In particular, the influence of the different parameters determining the temperature program on the measured transition enthalpy has been studied. For this purpose we choose double orthophosphate salts of $KMPO_4$ where M stands for Ni^{2+}, Co^{2+} and Fe^{2+}. These compounds present at least one phase transition in the temperature range of 20 to 1000°C. Because of these transitions, they also have ferroelastic and ferroelectric properties. The structure of these crystals is close to a stuffed tridymite type. In the structure we have rings of alternating six MO_4 and PO_4 groups which form a very flexible network. This is the reason for the presence of at least one structural phase transition [5].

Former studies of the phase transitions in $KMPO_4$ crystals

KNiPO$_4$ undergoes two structural phase transitions (PT): one at 491°C and one at 585°C. The crystal symmetry changes on cooling are:

$$Pnma \xrightarrow{\text{585°C}} Pna2_1 \xrightarrow{\text{491°C}} Pna2_1.$$
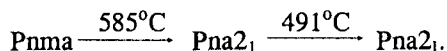
The structural changes are mainly due to small rotations of the PO_4 groups [5]. Birefringence *vs.* temperature measurements indicate that both phase transitions are of the first order [6]. Optically, a coexistence of two phases is seen at the temperature of the PT occurring at 491°C which confirms the alleged first order. However, this was not observed for the PT at 585°C hence this transition must be of the first order close to second order. On the other hand, "heating" and "cooling" DSC experiments show no hysteresis for this second phase transition; this supports the possibility that it might have a second order character. Whereas, for the PT at 491°C, a clear hysteresis of about 10°C is present which is consistent with the first order character of this transition.

During the transition at 585°C ferroelectric domains are formed which can be seen by etching a crystal cut perpendicular to the polar axis. The presence of these ferroelectric walls may produce some relaxation phenomena associated with the structural changes occurring during the phase transitions [5].

The structure of $KCoPO_4$ depends on the method of crystal growth. From aqueous solutions, a hexagonal form is obtained which has space group P6$_3$ [7]. When the crystals are grown from a KCl flux, a monoclinic modulated structure is obtained [8]. This second form presents ferroelastic domains at room temperature which are clearly visible with the help of a polarized light microscope on a (010) cut. An interesting characteristic of this form is that three kinds of ferroelastic wall are present instead of the two which are expected for a mmm → 2/m phase transition. Two of these ferroelastic wall types are symmetry forbidden walls and must bring about some mechanical stress in the crystal. When a (010) plate was heated under optical examination, the ferroelastic walls disappear at about 619°C and the crystal adopts an orthorhombic structure. On cooling, the ferroelastic domains begin to form at about 560°C. The final pattern is adopted at about 450°C, marked by a sud-

den formation of a large number of ferroelastic walls. Hence the transition seem to be completed only after a cooling of more than 110°C after the onset of the PT.

KFePO$_4$ has a more unusual behaviour; the structure at room temperature depends on the rate of cooling of the crystal from the high temperature phase, which has an orthorhombic symmetry with a probable space group Pnma. The structure of the different phases was studied by single crystal X-ray diffraction [5]. If the crystal is cooled rapidly ($>100°C$ min^{-1}), the symmetry changes are:

$$\text{Pnma} \xrightarrow{\ 320°C\ } \text{Pna2}_1 \xrightarrow{\ 130°C\ } \text{P2}_1/c.$$
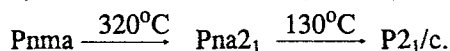
Ferroelastic domains appear during the transition at 130°C which were easily seen on a crystal cut perpendicular to the monoclinic axis. If the crystal is cooled slowly, the symmetry changes are

$$\text{Pnma} \xrightarrow{\ 320°C\ } \text{Pna2}_1 \xrightarrow{\ 160°C\ } \text{Pna2}_1.$$
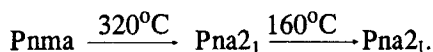
In this case no ferroelastic domains are seen at room temperature. The structure of this compound shows disorder of the positions of the oxygen atoms, and a form of dynamic disorder in the prototype phase may be the origin of this peculiar behaviour [5].

Experimental and results

Determination of the temperature program parameters

The instrument used for all measurements was a DSC 220C from Seiko Instruments. As mentioned above, the temperature program parameters are important in order to satisfy the conditions required for the assumptions made in the calculation of the "reversing" and "kinetic" components of the heat flow. The conditions recommended by some authors working with this type of instrument are shown in Table 1 [3–4], together with the conditions we have chosen for the ODSC experiments. These recommendations are based essentially on experimental results. Most of them are determined already by practical reasons. The heating rate has to be slow enough so that at least four cycles are accomplished between the onset and the end of the phase transition. This also depends on the frequency which is also restricted by the fact that at least 100 data acquisitions have to be made within a single cycle. Hence a high frequency would imply a very large number of points which may produce a huge file. Another limit to the frequency is the rate of temperature transfer to the sample and that one has to keep the instrument within a frequency range where it can be considered to behave almost ideally. Therefore we decided to set periods of 50 s. The thermal events to be studied occur in a temperature interval of about 5°C. Therefore, heating rates no higher than 2°C min^{-1} are required in order to have at least 4 cycles between the onset and the end of the thermal event. We can see that the only parameter that can be varied more or less freely is the amplitude of the modulation, and to a fewer extent the frequency and the heating rate.

Normally all three parameters: b (heating rate), B (amplitude) and ω (frequency) should be given for defining the conditions of an ODSC experiment. How-

Table 1 Recommemded and selected parameters of the temperature program used in the ODSC experiments

Parameter	Recommended	Selected value
Amplitude	1 to 3°C	0 to 4°C
Period	40–50 s	50 s
Sample weight	10–30 mg	13 mg
Heating rate	selected to obtain at least 4 cycles between the onset and end of the PT	1–2°C

ever, in order to compare the results obtained with different experimental conditions, we decided to define a single value parameter which represents somehow the experimental conditions used. For this purpose we have defined the following dimensionless parameter (Par)

$$Par = \frac{T_c \omega}{b} \, 60 \quad \text{where,} \quad T_c = B - b \, \frac{P}{2\pi 60} \tag{4}$$

in this equation P is the modulation period in seconds. By definition, if $Par \le 0$ we have "heat only" conditions for the ODSC experiment.

ODSC measurements on KNiPO₄

A series of ODSC measurements were done on a 13 mg sample of $KNiPO_4$ single crystals, applying the temperature programs shown in Table 1. An interesting dependence of the relative value of the "reversing" and "kinetic" part of the heat flow was observed on the value of the oscillation amplitude applied to the temperature heating ramp. As an illustration of these dependency, we present on Fig. 1 three heating ODSC experiments with a different amplitude of the temperature modulation. In all three measurements a heating rate of $1°C$ min^{-1} and a period or 50 s were used.

On Fig. 1a we have set the modulation amplitude to $B=\pm0.133°C$, so that $Par=0$. Hence we have in this case "heat only" conditions. On the total heat flow signal (D) we can see a curve similar to that of a normal DSC, both transitions appear as very well defined peaks with a transition enthalpy of 4.5 and 5.0 J g^{-1} respectively. However, the corresponding peaks of the "reversing" part (C_p) of the signal present a higher thermal effect, resulting in a "kinetic" part (K) which shows two exothermic peaks with a particular "M" shape. Such exothermic peaks do not have any physical meaning and one must conclude that this is due to some strong deviation from the ideal conditions required for an ODSC experiment.

In another measurement, the amplitude was increased to $B=2°C$ giving a value of $Par=2.24$. Under these conditions the curve shown on Fig. 1b was obtained. The total signal (D) is very similar to the one obtained with $Par=0$. In contrast, the signal corresponding to the "reversing" part (C_p) shows two peaks with a much smaller area compared to the area of the peaks on the total heat flow signal. Consequently, the "kinetic" signal (K) shows two endothermic peaks as one would ex-
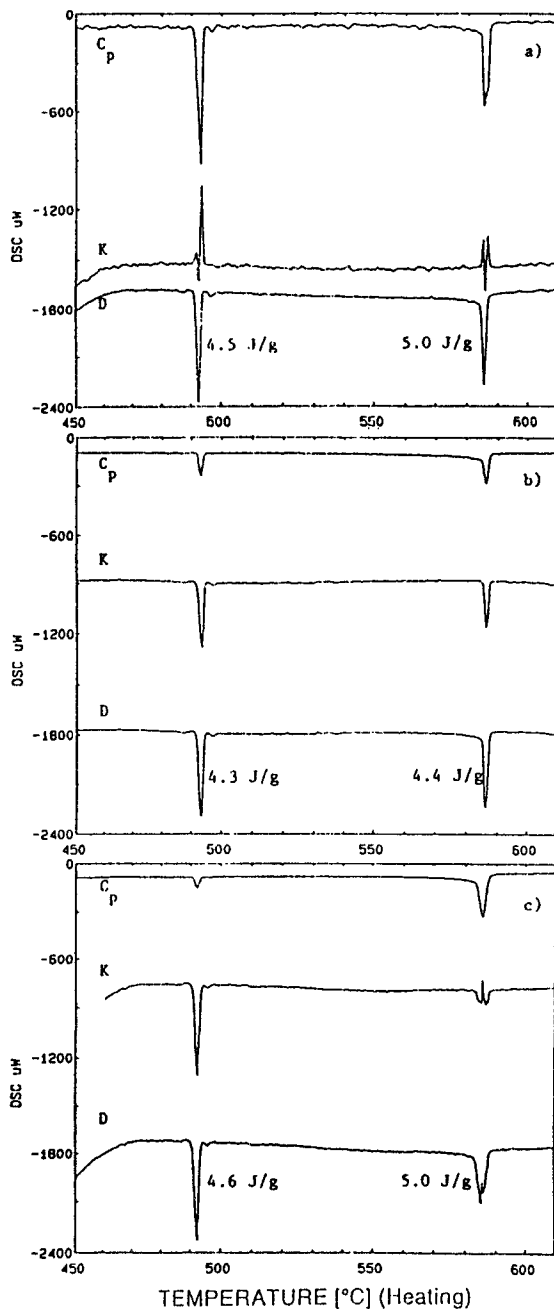
Fig. 1 Heating ODSC measurements on a sample (13 mg) of single crystals of KNiPO$_4$. A heating rate of 1°C min^{-1} and a period of 50 s were used for all three measurements. The only changing parameter is the amplitude of the modulation (B) which was a) $B=0.133$°C, $Par=0$, b) $B=\pm2.0$°C, $Par=2.24$ and c) $B=\pm4.0$°C, $Par=4.64$

pect. For the PT at 585°C, the fraction of heat evolved due to irreversible thermal events is quite important relative to the total heat evolved. In principle in the case of a second order phase transition, the "kinetic" component should be nil, hence its presence supports the conclusion that this PT is of the first order close to the second order. It is interesting to note that the "reversing" part of this PT shows a λ shape peak, typical of second order phase transitions and a change of the base line is also observed, whereas on the "kinetic" part a symmetric peak without change of the base line is seen. When the amplitude of the modulation is increased up to $B = 4$°C (cf. Fig. 1c), the peak due to the PT at 491°C do not change significantly, only a decrease on the "reversing" thermal effect is observed. In contrast, the peaks corresponding to the PT at 585°C show an increase in the amount of the "reversing" thermal effect (C_p) but the peak still has very well defined λ shape. The shape of the peak corresponding to the total signal (D) is split and this results in a "kinetic" peak (K) with an up side down "M" or "W" shape. In order to have a better idea of the influence of the temperature program conditions on the "total" and the "reversing" signals, a series of experiments were done with different values of *Par*. Essentially the amplitude of the modulation was modified; in some cases the frequency and the heating rate were changed, but most of the measurements were made with $b = 1$°C min^{-1} and $P = 50$ s. On Fig. 2 we have plotted the enthalpy change of the transitions measured on the "total" and on the "reversing" heat flow signals for heating and cooling ODSC experiments as a function of the parameter *Par*. For both PT the transition enthalpy does not depend significantly on the temperature program conditions; a mean value of 4.7 J g^{-1} is measured for the PT at 491°C and a value of 4.9 J g^{-1} for the PT at 585°C. However a strong dependency of the "reversing" signal on the temperature program parameters is observed in both cases. For a value of *Par* = 0 the transition enthalpy measured on the "reversing" part of the signal is higher than on the total signal for both PT. This may be because under these conditions, the instrument does not behave ideally or the presence of small temperature gradients inside the crystal become significant. As the value of *Par* increases, a different behaviour results. For the PT which is clearly of the first order (at 491°C), the thermal effect on the "reversing" signal decreases with increasing value of *Par*. Whereas for the PT at 585°C, which is close to the second order, a decrease of the thermal effect is observed first, but a minimum is reached at about *Par* = 2.0 from where the transition enthalpy begins to increase until it reaches a value of about 90% the value measured on the total signal. This seems to indicate that some thermal events, which are non reversing at a low modulation amplitude, become reversible at a larger amplitude modulation. The small hysteresis of this PT may allow such behaviour. This does not happen with the PT at 491°C, which is clearly of the first order and has a hysteresis of about 10°C.

DSC and ODSC measurements on KCoPO₄

The phase transitions in this compound were found by normal DSC and DTA experiments as reported by Engel [9]. He also mentioned the presence of two peaks
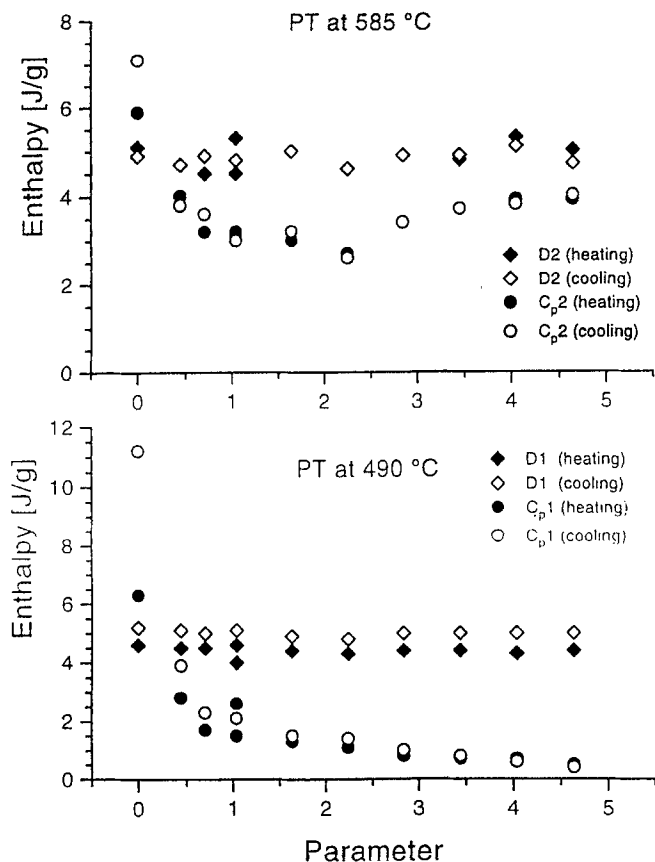
Fig. 2 Dependence of the transition enthalpy change of both transitions of KNiPO$_4$ measured on the total and the reversing signal as a function of the temperature program conditions *Par*

on the cooling measurements instead of one as is expected from the presence of only one phase transition on the heating experiment. Former studies have shown that there is some dependency on the size of the crystal grains on the spontaneous strain produced by cooling the crystals through the phase transition. The unusual behaviour of this compound might be due to the presence of the symmetry forbidden ferroelastic walls and the presence of a modulation in the structure.

On Fig. 3 we have two heating and cooling DSC measurements made on a sample of powder grains of less than 7 μm size (plot *a*) and on a sample consisting of small crystals of about 200 μm (plot *b*). A heating rate of 4°C min^{-1} was applied in both cases. Similar results are observed in the heating run; a single well defined peak is observed which begins at 592°C. On the cooling run the onset of the PT occurs at 561°C in both cases, but the rest of the curve at lower temperatures is quite different, showing a different heat flow as the temperature is lowered. However in
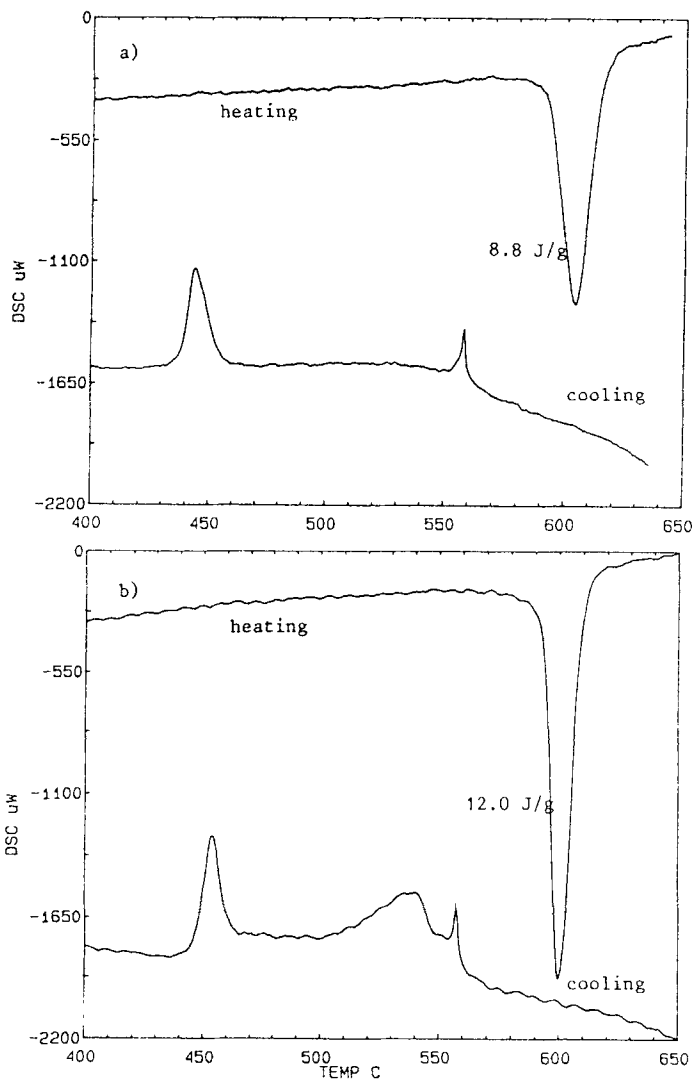
Fig. 3 Heating and cooling DSC measurements on $KCoPO_4$ at a heating rate of $4°C$ min^{-1}
a) powder sample (18 mg) with a grain size of less than 7 μm, b) sample (14 mg) of single crystal of about 200 μm size

both cases the thermal event spreads over about 110°C and ends up with a pronounced peak at about 450°C.

An ODSC experiment was made with the sample of single crystals of $KCoPO_4$. The temperature program conditions were: $b = 1°C$ min^{-1}, $B = 2°C$ and $P = 50$ s giving $Par = 2.24$. The heating and cooling experiments are shown on Fig. 4. Note that the "total" and "reversing" signals are plotted on a different scale. On the heating

run a single peak is seen in the total signal which is essentially due to non reversing thermal events. The "reversing" signal which in principle is proportional to the heat capacity of the sample has a λ shape and presents a change in the base line be-
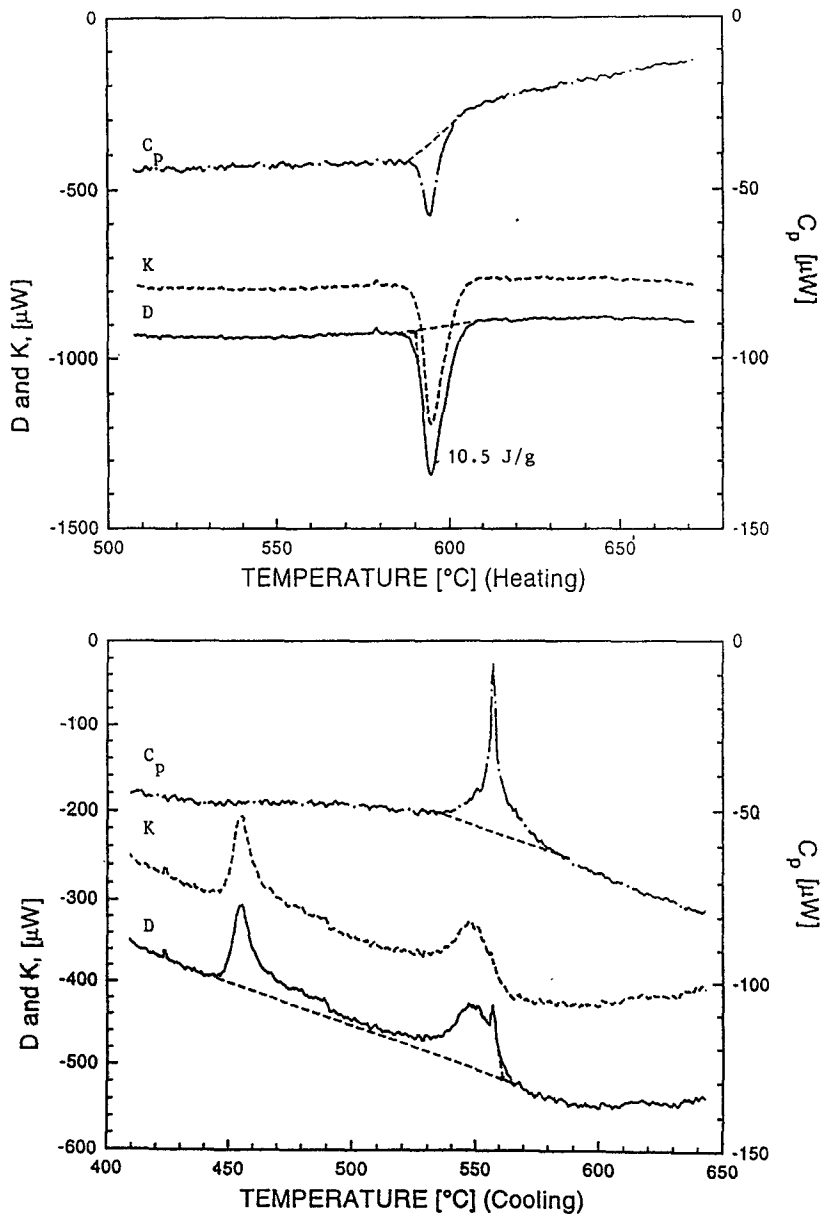

Fig. 4 ODSC measurement on single crystals of KCoPO$_4$ (14 mg). Total (D), reversing (C$_p$) and kinetic (K) signals are shown. B=2.0°C; b=1°C min^{-1}; P=50 s; Par=2.24. Note that the reversing signal is drawn on a different scale

fore and after the phase transition. The total transition enthalpy is 10.5 J g^{-1}, with about 95% due to non reversing thermal events. On the cooling run, the total signal is again spread over 110°C as in the DSC experiments; however the "reversing" signal is limited to a single very narrow λ shaped peak which appears at the onset of the transition. Hence the heat flow measured at temperatures below this point is due to non reversing thermal events. The coincidence of the temperatures observed for the "kinetic" heat flow with the temperatures at which the formation of the ferroelastic walls occurs, indicates that this non reversing component of the heat flow is due to the formation of the stressed domain walls. Hence the broad peak in the cooling experiment is due to a single phase transition, which reaches its completion 110°C after the onset of the transformation, and not to two phase transitions as would suggest the two well defined peaks seen in the DSC of a powder sample. To our knowledge this is the first example of such a transition, but in fact this kind of transition might be a rather common one among modulated ferroelastic crystals, and may explain the disagreement in the number of phases transitions present in this type of compounds that is often found in the literature.

DSC measurements on single crystals of KFePO$_4$

As explained above the structure of KFePO$_4$ crystals depends on the cooling rate applied to the crystals starting from the prototype phase above 360°C. DSC experiments were made with a 10.33 sample of single crystals of KFePO$_4$ which were rapidly cooled. Two consecutive cycles of heating and cooling were done with the same sample at 2°C min^{-1} in order to study the dependence of thermal signal on the thermal history of the sample.

As expected, two-phase transitions were observed (cf. Fig. 5). In the first heating cycle, the first PT begins at 102°C and the second at 312°C. On the cooling run, the first PT occurs at a higher temperature which is rather unexpected. In the second heating cycle, after a slow cooling at 2°C min^{-1}, the first PT begins at 139°C, about 37°C above the temperature observed on the first cycle. On the cooling run of the second cycle a "normal" hysteresis is observed for both PT. The peaks are rather large with a half width of about 20°C. The value of the transition enthalpy is similar for both transitions, about 5–7 J g^{-1}. However, in the first heating run the enthalpy of the first transition is about half this value, 3.5 J g^{-1}. On the heating run of the second cycle, the enthalpy of the first transition increases to about 6 J g^{-1}, which is closer to the value of the cooling run of the second cycle. These results are summarized in Table 2.

Therefore, the thermal effect of the crystal when it transforms from the monoclinic disordered state to the high temperature phases is smaller than when it transforms from the orthorhombic disordered state. This indicates that the monoclinic-disordered structure is closer to the high temperature state because less energy is needed to reach it, despite the fact that from the symmetry point of view it has a lower symmetry. On cooling, the transition at 320°C may be a transition from a dynamic to a static disorder. This may explain the particular dependency of the structure of this compound on the cooling rate.
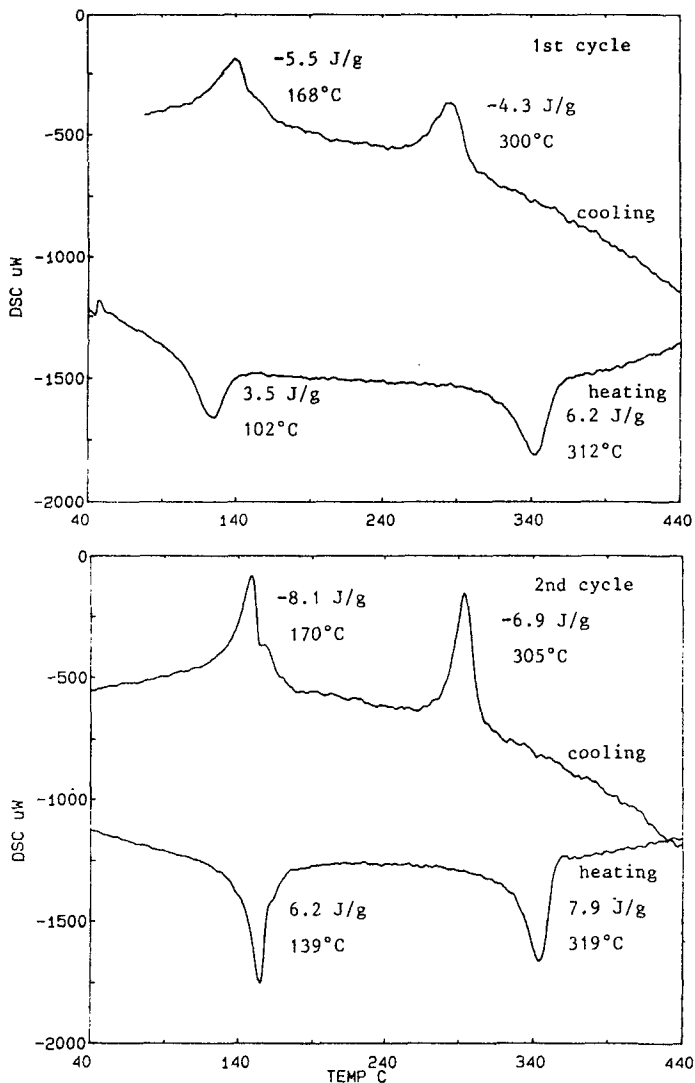
Fig. 5 Consecutive DSC heating and cooling cycles at 2°C min⁻¹ on a rapidly cooled sample
       of KFePO₄ (10.33 mg)

Conclusions

The present results show that the choice of the experimental conditions have a
great influence on the calculated "reversing" and "kinetic" signals of an ODSC ex-
periment. This dependency comes from the fact that in order to make the calcula-
tions of the "reversing" heat flow, special conditions have to be fulfilled, and this
is true only for a certain range of temperature program parameters. Therefore, spe-

Table 2 Enthalphy change of the phase transitions of $KFePO_4$ measured in two consecutive cycles of DSC heating and cooling. Before the first cycle the crystals were in the monoclinic disordered state

	Run	First PT	Second PT
First cycle	heating	3.5 J g^{-1}	6.2 J g^{-1}
	cooling	5.5 J g^{-1}	$4.3 \text{ J g}{-1}$
Second cycle	heating	6.2 J g^{-1}	$7.9 \text{ J g}{-1}$
	cooling	8.1 J g^{-1}	$6.9 \text{ J g}{-1}$

cial care has to be taken when choosing the temperature program parameters which will depend on the type of transformation studied.

In order to simplify the description of the experimental conditions, we have defined a single value parameter (Par) which is given by Eq. (4). In the case of a first order phase transition like in $KNiPO_4$, coherent results are obtained for a value of $Par \geq 2.0$. Hence $Par = 2.0$ would be taken as a first choice for a new ODSC experiment. This value has been used for the ODSC measurement on single crystals of $KCoPO_4$ and it has given quite consistent and easy interpretable results. Further questions arise as a consequence of the results presented above. First of all, we can mention the phase transition of $KCoPO_4$. This transition has a first order character if we consider the rather large hysteresis that is observed, but in addition the heat flow measured in the cooling experiment has a very unusual behaviour. The transition occurs over a temperature range of more than 110°C. For this reason we can wonder if the phase existing within this interval should be considered as a new phase or not. In our opinion this is not a new phase because the reason why this transformation is difficult to complete is the presence of the stressed ferroelastic walls. The usefulness of the ODSC technique is apparent in this case. It clearly makes the difference between relaxation phenomena which are associated with the formation and disappearance of the ferroelastic walls, and reversing thermal events.

However most of the results obtained still need an explanation on a theoretical basis. This is a more complicated task and needs the contribution of other authors working with this technique. Nevertheless these results are useful as a first guide for choosing the temperature program parameters and gives some idea of the unusual behaviour that can be found in ferroic materials. They will also contribute to a better understanding of the possibilities that offers the ODSC technique, in particular for the study of crystalline materials.

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