

COMPARISON OF DSC AND OPTICAL TRANSMISSION
MEASUREMENTS OF POLYMORPHIC TRANSITIONS

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Using optical measurements on single crystals, the speed of first order transitions ($K_2Cr_2O_7$, KNO_3 , $AgNO_3$) was determined and compared with the strongly smeared DSC signals. Such optical measurements are proposed to select materials which are suitable for the determination of the DSC apparatus function.

Introduction

Thermal analysis methods measuring optical constants are called thermoptometry [1]. Because of the nearly infinite velocity of light, thermoptometry allows real time measurements of thermal events, contrary to DTA and DSC, where the signals measured are influenced by the finite conductivity of heat. Thermoptometric measurements are applied rather rarely, so far and only a few thermophotometric [1] results are reported e.g. [2], [3], [4], [5], [6], [7], [8], [9], [10], [11].

In the present paper polymorphic transitions of single crystals are investigated by optical transmission measurements and the results are compared with corresponding DSC investigations. A possibility to determine the apparatus function of DSC instruments is proposed.

Experimental

The measuring equipment (Fig.1) was put together from individual parts: A Leitz polarizing microscope, a Knott photomultiplier, a Leitz hot stage up to 1350°C for transmitted light, a temperature controller for heating rates from 0.05 to 10 K/min, a light source with a filter for monochromatic light (usually 589 nm) and two recorders for individual, but

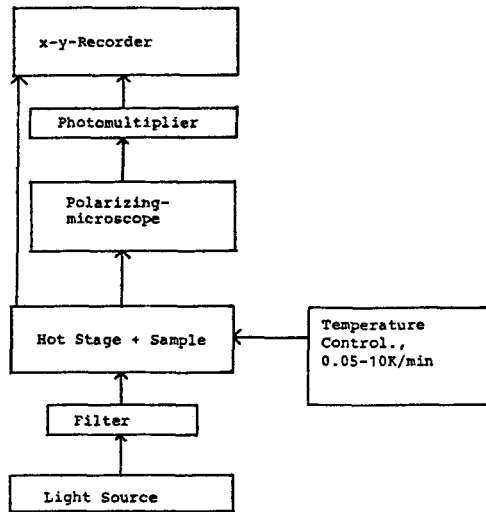


Fig.1 Schematic presentation of the thermophotometric measuring equipment

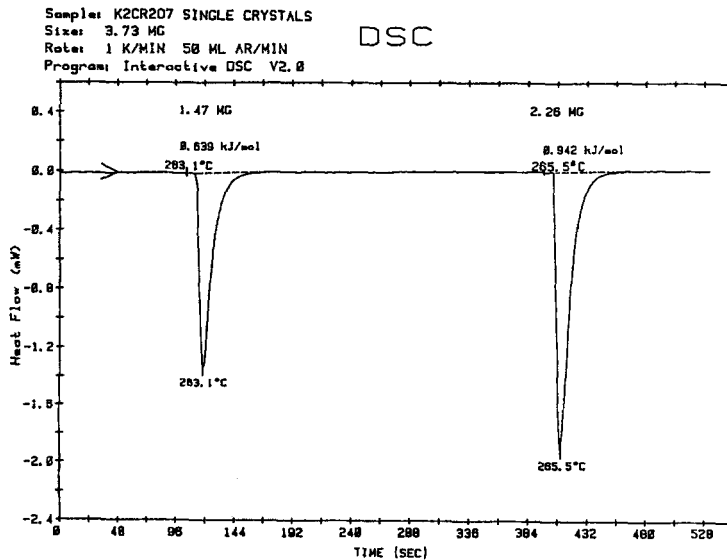


Fig.2 DSC heating run for two K₂Cr₂O₇ crystals (1.47 and 2.26 mg) in Argon atmosphere [14]

simultaneous registration of the light intensity as function of time (t) and temperature (T), respectively. For a sensitive resolution, recorders with very small time constants were used ($\tau = 25$ msec).

If the measurement is carried out with crossed polars the intensity I is given by [12]

$$I = I_0 \sin^2 \phi \sin^2 \left(\frac{\pi t}{\lambda} \right) \Delta n$$

where I_0 = incident intensity, ϕ = optical extinction angle, t = sample thickness and Δn = birefringence. During a phase transition (except isotropic \longleftrightarrow isotropic*) the birefringence and correspondingly the measured intensity change.

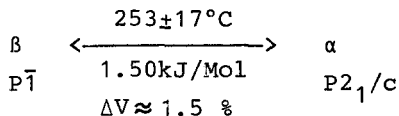
The DSC measurements were carried out with a Du Pont 1090 Thermal Analyzer equipped with a 910 DSC cell (heat flux type). The program INTERACTIVE DSC V 2.0 was used.

For comparison of the DSC and transmission measurements the same crystals (size 0.5 to 1 mm) were used if this was not excluded by disintegration during the transition; otherwise crystals of the same origin and comparable size were selected.

Using single crystals, various phase transitions were investigated with numerous runs. Experimental parameters as heating rate, crystal size, crystal sector selected for optical measurements, λ etc. were varied. Here only some typical examples are discussed. A more detailed presentation is given elsewhere [13].

Results

$K_2Cr_2O_7$ exhibits a polymorphic transition



*Opaque crystals and isotropic \longleftrightarrow isotropic transitions can be investigated by reflection measurements.

which is of 1. order, reconstructive and strongly dependent on nucleation. Extended superheating and undercooling appear resulting in the large uncertainty ($\pm 17^\circ\text{C}$) of the transition temperature T_p as determined by dynamic methods [14]. Single crystals usually disintegrate during one transition cycle. DSC runs of a few large crystals (Fig.2) instead of a fine powder show individual transition signals, depending on the time and temperature of nucleation. On heating the low temperature form is strongly overheated and the transition proceeds very fast once a nucleus is formed. If the time axis is expanded (Fig.3), it is evident that the DSC run pretends a transition time (from the first baseline deviation to peak maximum*) of about 3.3 seconds. The optical measurement, however, proves clearly that the transition itself does not last longer than 0.2 seconds, which can also be confirmed by just watching the transition by eye. The DSC retardation occurs, because the temperature change has to be conducted to the thermocouple before being recorded.

Fig.4 compares thermophotometric tracings of the polymorphic first order transitions of $\text{K}_2\text{Cr}_2\text{O}_7$, AgNO_3 and KNO_3 . Fig.5 shows the corresponding DSC runs against time and temperature, respectively. Obviously the AgNO_3 and KNO_3 transitions need much more time (53 and 80 seconds in Fig.4) than the $\text{K}_2\text{Cr}_2\text{O}_7$ transition. These differences in time can easily be explained: The superheated $\text{K}_2\text{Cr}_2\text{O}_7$ crystal has stored so much excess energy, that, in the moment of the α nucleation, this energy is sufficient for the transformation. Actually, the necessary heat of transition is available everywhere along the moving transition front and no or nearly no additional heat is needed from outside. The consumption of internally stored heat is visible from the retrograde temperature change of the $\text{K}_2\text{Cr}_2\text{O}_7$ signal in Fig.5b.

*Only this first part of the DSC signal is considered in this paper. The second part represents the normal temperature relaxation (exponential function) and is not observable by optical means.

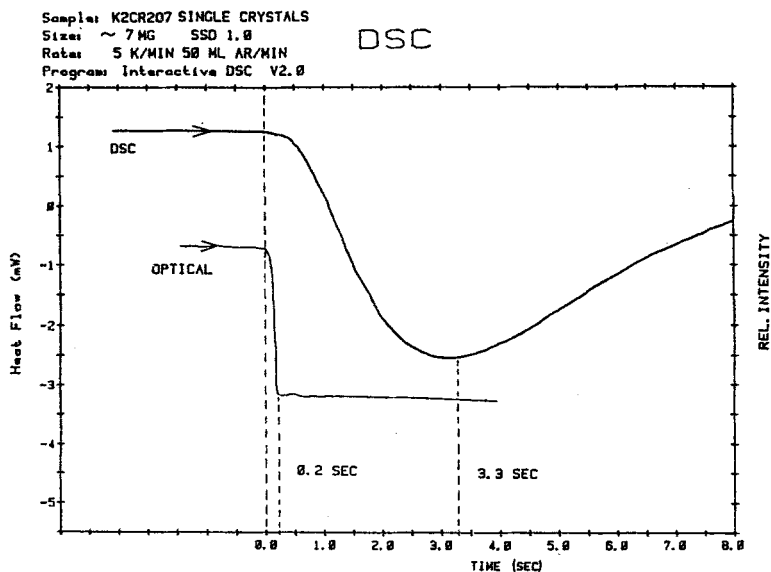


Fig.3 DSC and optical heating runs of equivalent single crystals (~7 mg) of $K_2Cr_2O_7$. The first baseline deviation was taken as time zero ($t = 0$)

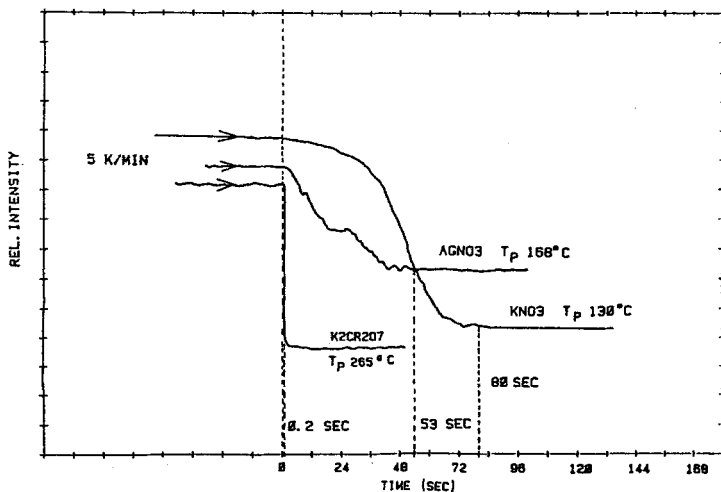


Fig.4 Photometric curves of the transitions of single crystals (~2 mm diameter) of $K_2Cr_2O_7$, $AgNO_3$ and KNO_3 . Note different time scale in Fig.3. T_p = equilibrium temperature. 5 K/min

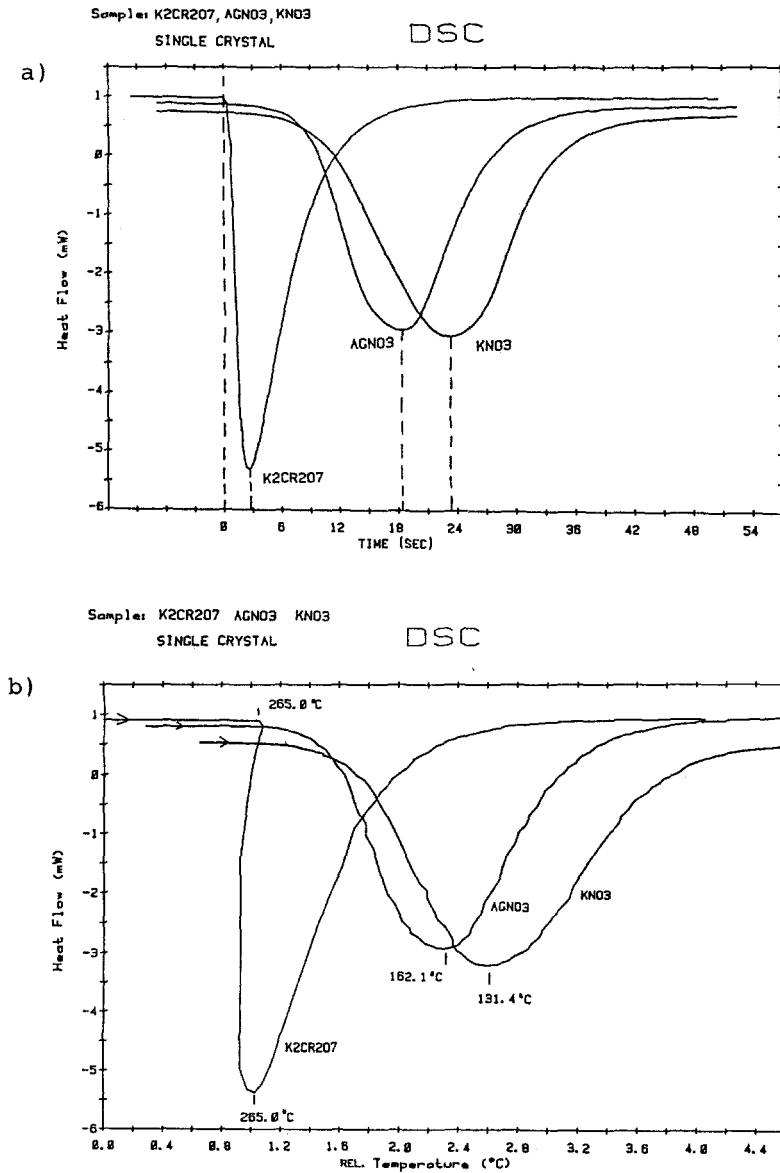


Fig.5 DSC runs of single crystals ($\sqrt{2}$ mm diameter) of $K_2Cr_2O_7$, $AgNO_3$ and KNO_3 , plotted against time (a) and temperature (b). 5 K/min

The AgNO_3 and KNO_3 transitions show quite different characteristics: Obviously they have stored not enough excess energy. The progress of these transitions, therefore, is controlled by the conductivity from the heater to the moving transition front in the crystal. As a consequence, they proceed much slower than the $\text{K}_2\text{Cr}_2\text{O}_7$ transition.

The fact, that the transition times for one and the same compound in Figs.4 and 5b disagree, is due to the significant differences of the optical cell (hot stage) and the DSC cell and consequently of their conductivities. In addition, the sample carriers are SiO_2 glass and aluminium pans, respectively, and different purge gases were used (air and Argon).

It should be mentioned, that the "zig-zag-curve" of AgNO_3 in Fig.4 is caused by an irregular progress of the transition front through the crystal so that different volume elements are transformed per time unit. In the sluggish DSC this effect is not visible.

Whereas the spontaneous $\text{K}_2\text{Cr}_2\text{O}_7$ transition exhibits no measurable dependence on the heating rate, such dependences are shown for KNO_3 in Fig.6. As to be expected, with increasing heating rate the transition requires larger temperature and smaller time intervalls.

Discussion

The following discussion concerning the apparatus function of DSC instruments is based on the presentation of the problem in chapters 5 and 6 of Ref. [15]. The observations on $\text{K}_2\text{Cr}_2\text{O}_7$ may be taken as a particularly suitable example, confirming the more general and partly schematic presentation in this book.

The DSC apparatus function is usually determined by shooting a heat pulse with an electric micro resistance heater into the sample. The resulting DSC signal and the corresponding instrument function consist of an initial part with increasing and a second (relaxation) part with decreasing heat flux. The strongly smeared thermal event discussed here is represented only by the intervall from the first baseline deviation to about the signal maximum.

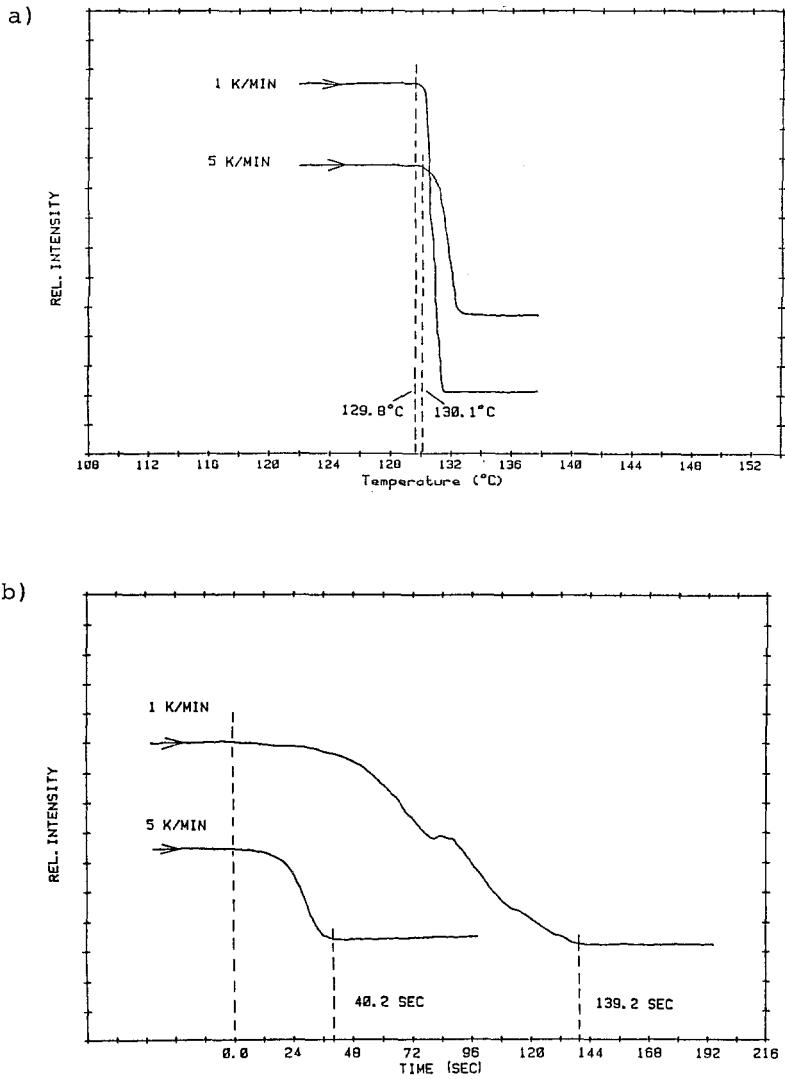


Fig.6 Photometric transmission curves of KNO_3 as function of temperature (6a) and time (6b). Single crystals of about 0.5 mg

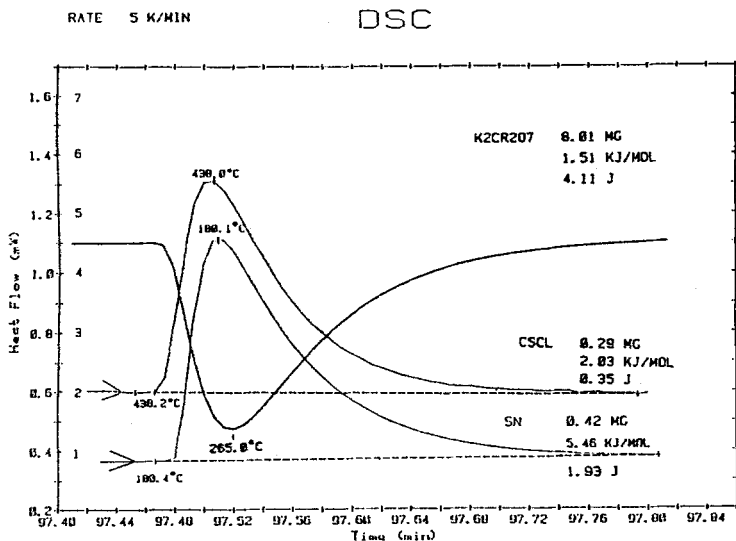


Fig.7 DSC signals of strongly undercooled transitions of a single crystal of CsCl (a), a single drop of molten tin (b) and of a strongly overheated crystal of $K_2Cr_2O_7$ (c)

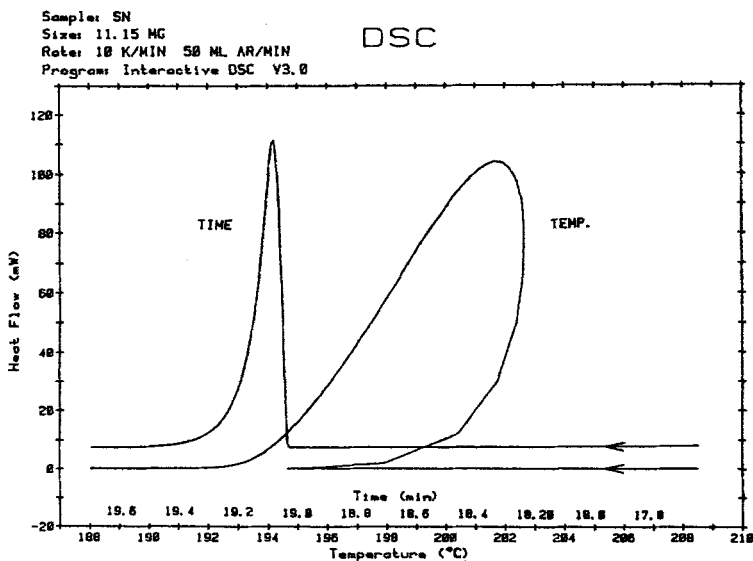


Fig.8 Crystallization of an undercooled drop of tin (equilibrium temperature = 232°C), as function of temperature and time

For instruments which do not enable electrical micro heaters (particularly heat flux instruments) phase transitions of single crystals of the $K_2Cr_2O_7$ type may be used. The transition is spontaneous resulting in a quick temperature change. Its energy is available directly at the transition front. This may be even superior to the electric heater, the heat of which has to migrate through the sample before it becomes effective.

Unfortunately the instrument function which is closely related to the calorimetric calibration function, depends on temperature, the operation mode (heating or cooling) and on the heating rate. Thus for different temperatures, suitable transitions have to be applied. So far, there was no systematic search for such materials, which exhibit strong overheating (like $K_2Cr_2O_7$) or undercooling accompanied by a spontaneous transformation after nucleation. The property of overheating seems rather rare but supercooling is often observed. Fig.7 shows as examples the cooling signals of the polymorphic transition of a single crystal of CsCl at $438^\circ C$ and the crystallization curve of molten tin at $180^\circ C$. The heating signal of $K_2Cr_2O_7$ is added. A comparison shows, that the heating signal of $K_2Cr_2O_7$ and the cooling signals of CsCl and Sn exhibit pronounced differences as to be expected: They are not mirror symmetric.

The nucleation in a single drop of melt corresponds to the nucleation in a single crystal. Therefore, the crystallization of many metal melts which are strongly undercoolable (c.f. Sn in Fig.8) may be used besides polymorphic transitions of single crystals. Thus the proposed determination of the instrument function seems easier for the cooling mode than for heating.

Acknowledgements

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Zusammenfassung

Mit Hilfe von optischen Messungen wird die Geschwindigkeit von polymorphen Phasenumwandlungen 1. Ordnung ($K_2Cr_2O_7$, KNO_3 , $AgNO_3$) bestimmt und mit entsprechenden stark verschmierten DSC-Signalen verglichen. Derartige optische Messungen erscheinen geeignet, um Substanzen zu suchen, welche für die Bestimmung der DSC-Apparatefunktion geeignet sind.

Резюме - Измерением оптического пропускания монокристаллов $K_2Cr_2O_7$, KNO_3 и $AgNO_3$ была определена скорость фазовых переходов первого порядка, которая затем была сопоставлена с сильно размытыми сигналами ДСК. Такие оптические измерения дают возможность выбирать вещества, которые пригодны для определения аппаратурной функции ДСК.