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## Thermal properties of $K_2Ba(NO_2)_4$

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**Résumé.** — Nous avons mesuré la chaleur spécifique de monocristaux de nitrite de baryum et potassium  $K_2Ba(NO_2)_4$  entre 130 K et 435 K. Il apparaît deux transitions, respectivement à 208,6 K et 428 K. La transition basse-température présente les caractéristiques d'une transition du second ordre et l'excès de chaleur spécifique est caractérisé par les exposants critiques  $\alpha = \alpha' = 0,60 \pm 0,03$ . La transition haute-température apparaît à quelques degrés de la décomposition de  $K_2Ba(NO_2)_4$  et ne peut être complètement étudiée.

**Abstract.** — The specific heat of single crystals of potassium baryum nitrite  $K_2Ba(NO_2)_4$  has been measured between 130 K and 435 K. There are two transitions at 208.6 K and 428 K, respectively. The low temperature transition exhibits second order features and the excess specific heat is characterized by critical exponents

$$\alpha = \alpha' = 0.60 \pm 0.03.$$

The high temperature transition occurs a few degrees below the decomposition temperature and so cannot be studied in detail.

1. **Introduction.** — Little [1-6] has been published on the properties of potassium baryum nitrite  $K_2Ba(NO_2)_4$ . Their crystallographic properties at room temperature were first described a long time ago by Fock [1]. More recently, Ivanov [4] reported optical, dielectric and ferroelastic properties of  $K_2Ba(NO_2)_4$  and pointed out that this crystal undergoes a phase transition in the vicinity of 146 °C between a high temperature hexagonal phase 6/mmm ( $\alpha$  phase) and an orthorhombic mmm phase ( $\beta$  phase) stable below 146 °C. Moreover, from birefringence measurements, he suggests that a second phase transition takes place in the vicinity of - 70 °C between the orthorhombic  $\beta$  phase and a third phase ( $\gamma$  phase). It is suggested that the high temperature transition ( $T \simeq 146$  °C) is second order [4] whereas there is no information relating to the character of the low temperature phase. We have investigated the thermal properties of  $K_2Ba(NO_2)_4$  over a large range of temperature, in order to clarify the existence and type of the low temperature phase transition suggested by Ivanov [4].

2. **Results.** — We have investigated the specific heat  $C$  of single crystals of  $K_2Ba(NO_2)_4$  with a differential scanning calorimeter (Perkin Elmer DSC<sub>2</sub>)

fitted with a liquid nitrogen subambient accessory. The values of  $C$  are determined during successive thermal cycles scanned at rates of 1.25 K/min., 0.62 K/min. or 0.31 K/min. between 130 K and 435 K.

In addition to the high temperature transition (428 K), another transition clearly appears at 208.6 K in agreement with Ivanov's results on birefringence. For neither transition, we have observed any latent heat of transition within the limit of accuracy of our experiments (1 J/mole). Both transitions can be assumed to be second order. Figure 1 shows the variations of  $C$ , measured with an accuracy of 1 %, in the temperature range explored.

In the vicinity of the high temperature transition  $C$  exhibits a peak at 428 K, but an anomalous, non reproducible variation of  $C$  arises for temperatures above 429 K (Fig. 1). We can explain this anomaly by the decomposition of the sample, according to Protzenko [2]. Note that the maximum of  $C$  is at a higher temperature than that of 419 K and 422 K respectively given by Ivanov [4] or Sorge [6].

The low temperature transition is well defined, (Figs. 1 and 2). The maximum of  $C$  is obtained at  $T = 208.6 \text{ K} \pm 0.2 \text{ K}$  on heating but on cooling this maximum is about 1 K lower. This slight difference depends on the cooling rate; we cannot then decide if  $K_2Ba(NO_2)_4$  exhibits thermal hysteresis. The increase  $\Delta C$  in the specific heat associated with

(\*) E.R.A. n° 13.

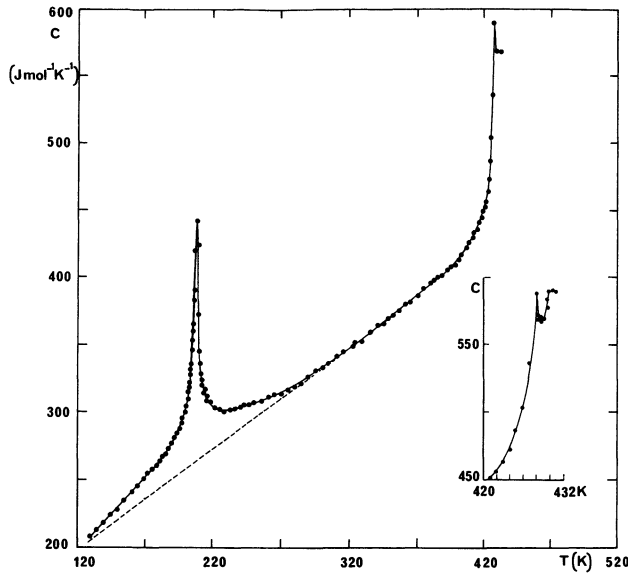


Fig. 1. — Specific heat  $C$  of  $K_2Ba(NO_2)_4$  versus temperature. Dashed line : estimated background specific heat (see text).

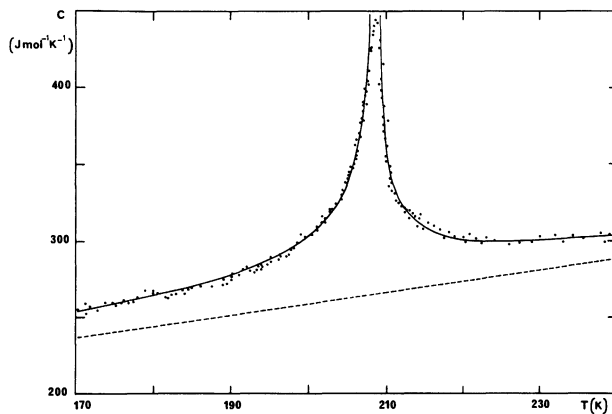


Fig. 2. — Specific heat of  $K_2Ba(NO_2)_4$  near the low temperature transition. Black dots : experimental values; full line : values plotted according to  $\Delta C \propto \left| \frac{T - T_c}{T_c} \right|^{-x' \text{ or } -x}$ .

the transition is usually determined by subtracting from the experimental  $C$  the background specific heat obtained by extrapolation of its value far above the transition. Unfortunately,  $K_2Ba(NO_2)_4$  cannot be investigated above the 428 K transition. We have assumed that, far from both transitions, in the  $\beta$  phase, as well as at very low temperatures,  $\Delta C$  is negligible. The background specific heat is then given by the dashed line in figures 1 and 2.

We have analysed the variation of  $\Delta C$  as a function of the reduced temperature  $t = \frac{T - T_c}{T_c}$ , for the low temperature transition ( $T_c = 208.6$  K). A Log-Log plot of  $\Delta C$  versus  $|t|$ , figure 3, shows that  $\ln \Delta C$  is a

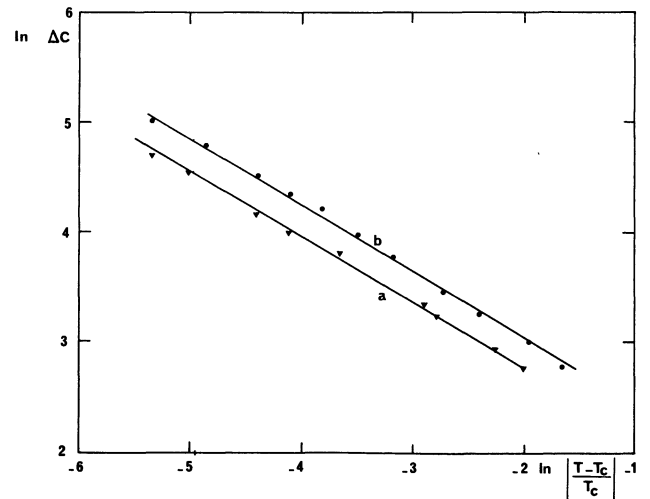


Fig. 3. —  $\ln \Delta C$  versus  $\ln \left| \frac{T - T_c}{T_c} \right|$  above (a) and below (b) the low temperature transition.  $T_c = 208.6$  K.

linear function of  $\ln |t|$  over a large range of temperature in the  $\gamma$  phase ( $T < 208.6$  K) as well as in the  $\beta$  phase, leading to [7] :

$$\Delta C \propto \left( \frac{T_c - T}{T_c} \right)^{-x'} \quad \text{for } T < T_c. \quad (1)$$

$$\Delta C \propto \left( \frac{T - T_c}{T_c} \right)^{-x} \quad \text{for } T > T_c. \quad (2)$$

The critical exponents  $\alpha$  and  $\alpha'$  have the values

$$\alpha' = \alpha = 0.60 \pm 0.03.$$

The values of  $\Delta C$  computed with these experimental  $\alpha$  and  $\alpha'$  are reported in figure 2 as a full line in order to show the good agreement of the relations (1) and (2) with the experimental data over a very large temperature range.

**3. Conclusion.** — The low temperature phase transition ( $T = 208.6$  K) has been clearly observed and exhibits second order characteristics. The variations of  $\Delta C$  in the vicinity of  $T = 208.6$  K are accounted for by a power law characterized by the critical exponents  $\alpha$  and  $\alpha'$ . The values of these exponents are high compared to the values usually predicted by the various theories [7]. Nevertheless analogous values ( $\alpha' \simeq 0.50$ ) have already been found in  $AgNa(NO_2)_2$  [8]. A theoretical understanding of the behaviour of this heat capacity needs more information on  $K_2Ba(NO_2)_4$  especially the space groups of the three phases which are presently not known.

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