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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 apparait 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 (z phase) and an orthorhombic mmm phase (β 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 β phase and a third phase (γ phase). It is suggested that the high temperature transition ($T \approx 146 ^\circ C$) 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 DSC2) fitted with a liquid nitrogen subambiant 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 Protseiko [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 $T = 208.6 K \pm 0.2 K$ 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
Fig. 1. — Specific heat $C$ of K$_2$Ba(NO$_2$)$_4$ versus temperature. Dashed line : estimated background specific heat (see text).

Fig. 2. — Specific heat of K$_2$Ba(NO$_2$)$_4$ near the low temperature transition. Black dots : experimental values; full line : values plotted according to $\Delta C \propto \left| \frac{T - T_c}{T_c} \right|^{-\alpha'}$ above (a) and below (b) the low temperature transition. $T_c = 208.6$ K.

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$_2$Ba(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 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]:

$$\Delta C \propto \left( \frac{T_c - T}{T_c} \right)^{-\alpha} \quad \text{for } T < T_c . \quad (1)$$

$$\Delta C \propto \left( \frac{T_c - T}{T_c} \right)^{-\alpha'} \quad \text{for } T > T_c . \quad (2)$$

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 ($\alpha' \approx 0.50$) 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$_2$Ba(NO$_2$)$_4$ especially the space groups of the three phases which are presently not known.

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References