## Specific Heat of the Ferroelectric $AgNa(NO_2)_2$

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The specific heat of a $AgNa(NO_2)_2$ single crystal was measured between −90 and +55 °C. The entropy of the ferroelectric transition was found to be 9.9 J/mol·K and the critical exponent of the specific heat in the ferroelectric region is $\alpha' = 0.50 \pm 0.02$.

It has been shown in several investigations [1, 2] that $AgNa(NO_2)_2$ is a ferroelectric crystal which undergoes a phase transition of the first order, close to a second order one, at about 38 °C. The transition may be assumed to be of the order-disorder type with the $NO_2^-$-groups forming the permanent electrical dipoles. The ordering process of the dipoles should lead to a characteristic contribution to the specific heat of the material. First measurements of the heat capacity of $AgNa(NO_2)_2$ powder were performed by Gesi [3]. As it is expected there is a rather strong influence of the dielectric instability on the thermal behaviour. However, no detailed data on the temperature dependence of the specific heat are presented. Furthermore, no latent heat could be detected although the dielectric measurements indicate a phase transition of the first order.

We therefore started specific heat measurements on $AgNa(NO_2)_2$ in order to obtain more precise informations on the temperature behaviour of the specific heat anomaly and, in particular, on the existence of a latent heat. Since in a powdered sample the critical effects generally are smeared out we used a single crystal with a mass of 4.74 g. It was grown from an aqueous solution between 25 and 23.5 °C by a method described elsewhere [2]. The heat capacity of the short circuited sample was measured with a precise conventional calorimeter with double adiabatic shielding [4]. The absolute error of the calorimetric measurements amounted to about 0.8% and the scatter of the measuring points to 0.4%. The sample was located within a nitrogen atmosphere at atmospheric pressure. Simultaneously the dielectric constant was recorded by an ac-bridge at a frequency of 1 kHz.

In Fig. 1 our results are presented. The absolute values of the specific heat of the paraelectric phase agree with those given by Gesi [3] within an error of less than 1%. As expected the general temperature behaviour of the specific heat anomaly is quite similar to that reported by Gesi [3]. However, very close to $T_c$ we found much larger values. At $T_c$ our anomaleous part of the specific heat exceeds that of Gesi [3] by a factor of more than 2. This is probably due to the fact that we used a single crystal. In these measurements no latent heat could be detected. This

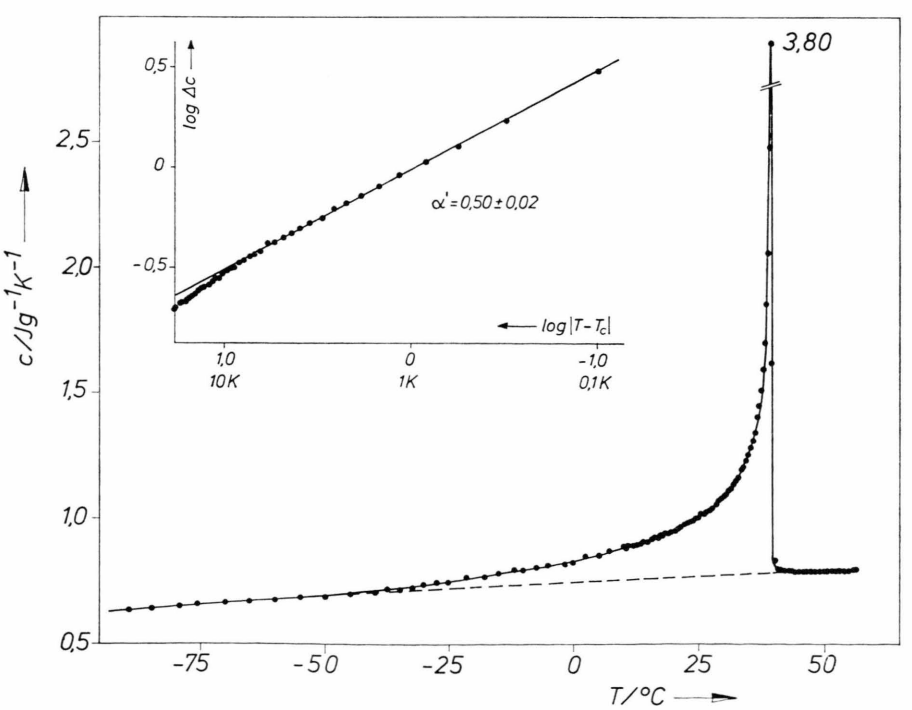


Fig. 1. Temperature dependence of the specific heat of $AgNa(NO_2)_2$ measured with a temperature increment of 0.5 K. Insert: Anomaleous part $\Delta c$ of the specific heat in the ferroelectric region plotted according to the power law $\Delta c \propto (T_c - T)^{-\alpha'}$.

result does not exclude the existence of a small latent heat since we used a rather large temperature increment of about 0.5 K. The maximum values of the specific heat and of the dielectric constant appeared at 39.3 °C. This phase transition temperature is about 1.3 K above that often reported in the literature [1, 2]. This is probably caused by a slight deviation of the composition of the sample from that used by the other authors [5]. The dotted line in Fig. 1 represents the lattice specific heat. It was quadratically fitted to the measured points above 45 °C and below −70 °C. Then the transition entropy amounts to $\Delta S = 9.9$ J/mol·K. This value is about 15% smaller than 2Rln2 which corresponds to a perfect order-disorder mechanism. This difference may be accounted for by taking into consideration the fact that the estimated value of the transition entropy depends sensitively on the fit of the lattice specific heat to the measured points at low temperatures. This leads to a value of $\Delta S$ which is about 10 – 15% larger than that given above. Thus in accordance with the previous work of Gesi [3] and with the results of the dielectric measurements [1, 2] it can be stated that the presented entropy value favours a perfect order-disorder phase transition mechanism.

Because of the large temperature increment from the observed data the precise temperature dependence of the specific heat in the paraelectric phase cannot be resolved. On the other hand, according to Fig. 1 in the ferroelectric phase our values are consistent with a critical exponent of $\alpha' = 0.50 \pm 0.02$. This law holds in a temperature range up to about 10 K below $T_c$. It corresponds to a Landau type behaviour of the $AgNa(NO_2)_2$ crystal near $T_c$. Calculating now the spontaneous polarization $P_0$ at $T = 0$ K from the Landau relation for the transition entropy density $S = (2\,\varepsilon_0 C)^{-1} P_0^2$, where $C = 4.5 \cdot 10^3$ K is the Curie constant [2] we obtain $P_0 = 10.7\ \mu C/cm^2$. This value agrees fairly well with that of $P_0 = 9.85\ \mu C/cm^2$ determined from pyroelectric measurements of the spontaneous polarization [6].

More reliable data concerning the temperature law of the specific heat in both phases and the latent heat can be obtained only by measuring with higher temperature resolution. Measurements of this type are in progress. The dielectric data [1, 2] suggest that the thermal behaviour of $AgNa(NO_2)_2$ follows a Landau theory. Since, on the other hand, this material is an uniaxial dipolar ferroelectric crystal according to the Larkin Khmel'nitskii theory [7] there should be logarithmic corrections to the Landau type behaviour which possibly may become observable in more precise measurements of the heat capacity.

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