



TEMPERATURE DEPENDENCE OF THE STATIC DIELECTRIC CONSTANT OF  $\text{Rb}_2\text{ZnBr}_4$ :  
SOLITONS IN A MODULATED STRUCTURE?

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The static dielectric constant of  $\text{Rb}_2\text{ZnBr}_4$  was measured as a function of temperature for a number of different single crystals. In a part of the samples a Curie-Weiss behaviour was observed at the lock-in transition from the incommensurate to the commensurate phase. Besides, in a few samples, a deviation of this behaviour was observed which can be ascribed to the appearance of solitons yielding a soliton density  $n_s$  proportional to  $(T-T_c)^2$ . At temperatures below  $T_c$  two new peaks are observed in the direction of the  $\vec{a}$ -axis.

In the last few years there is a strongly growing interest in systems which show an incommensurate modulated structure. This new incommensurate phase is characterized by the fact that below a certain transition temperature  $T_i$  a new periodic lattice distortion appears, characterized by a wave vector  $\vec{q}_i = \vec{q}_c(1-\delta)$  which does not fit into the original underlying lattice periodicity.  $\delta \ll 1$  denotes the relative deviation from the nearby commensurate wave vector  $\vec{q}_c = \vec{\tau}/p$ , where  $\vec{\tau}$  is a reciprocal lattice vector and  $p$  an integer. This incommensurability implies the loss of the usual translational symmetry of the crystal which, however, is usually recovered by cooling down below a new critical temperature  $T_c$ , where a so-called "lock-in transition" takes place and the modulation becomes commensurate ( $\delta \rightarrow 0$ ) again.

For temperatures just below  $T_i$ , it is usually assumed that the modulation can be described simply by a sinusoidal distortion<sup>1</sup>; however, for temperatures well below  $T_i$  several authors have predicted that this simple description should break down and that the incommensurate phase will consist of almost commensurate regions, separated by narrow domain walls or "phase solitons", where the phase of the modulation changes rapidly<sup>2,3</sup>. According to this picture, the transition to the commensurate phase at  $T_c$  takes place by a continuous growth of these different commensurate regions at the expense of the domain walls. Thus, unlike earlier suggestions, the lock-in transition should not be described by a discontinuous change of an order parameter, but rather by a continuous vanishing of the soliton density on approaching  $T_c$  from above. Unfortunately, it is difficult to distinguish unambiguously between these two theoretical models on the basis of existing experiments. Therefore, we decided to extend our work on  $\text{Rb}_2\text{ZnBr}_4$ <sup>1,4,5</sup> reported previously by measurements of the static dielectric constant. Here, we present experimental results obtained from a number of different single crystals. For some of the samples we have observed a straight forward Curie-Weiss behaviour, whereas in other

cases the experimental results can be interpreted as being due to the presence of solitons. Therefore, it looks as if the proposed soliton picture is sample dependent. In addition, below  $T_c$  we have observed two new peaks in the dielectric constant for a field direction along the  $\vec{a}$ -axis, confirming the recently reported new phase transitions found by Raman<sup>6</sup> and far-infrared work<sup>5</sup>.

In  $\text{Rb}_2\text{ZnBr}_4$  the incommensurate phase lies between  $T_i = 355$  and  $T_c = 200$  K with  $\vec{q}_i = (1-\delta)\vec{c}^*/3$  and a modulation amplitude along the  $\vec{b}$ -axis (here  $a \approx \sqrt{3}b$ ). Below  $T_c$ ,  $\text{Rb}_2\text{ZnBr}_4$  is ferroelectric with a polarization in the direction of the modulation amplitude<sup>7-10</sup>. Several single crystals were grown by slow evaporation from an aqueous solution; from these bulk crystals, different thin plates were cut with the planes either perpendicular to the ferroelectric  $\vec{b}$ -axis or to the  $\vec{a}$ -axis. These samples were placed in a guard-ring type capacitor and the dielectric constant was measured in a conventional way using a bridge circuit and an alternating electric field, with an amplitude of about 15 V/cm and a measuring frequency of 1 kHz. In order to vary the temperature, the capacitor was placed in the chamber of a gas-flow cryostat filled with He gas.

The measurements for the dielectric constant  $\epsilon_b$  with the field along the  $\vec{b}$ -axis appeared to be strongly sample dependent. Fig. 1 shows two typical examples of  $\epsilon_b$  as measured on two samples cut from two different single crystals. For a transition to a ferroelectric state, one normally expects a sharp peak in the dielectric constant along the ferroelectric axis near the transition point, as illustrated on the measurements shown in Fig. 1a. The small hysteresis in temperature ( $\sim 4$  K between cooling and heating run) seems to be intrinsic and is not due to an experimental error in temperature stabilization. In the measurements illustrated in Fig. 1b, the transition manifests itself as a broad maximum in  $\epsilon_b$ , also showing a much bigger hysteresis in temperature ( $\sim 14$  K). In both cases, a second anomaly in  $\epsilon_b$  can be seen below

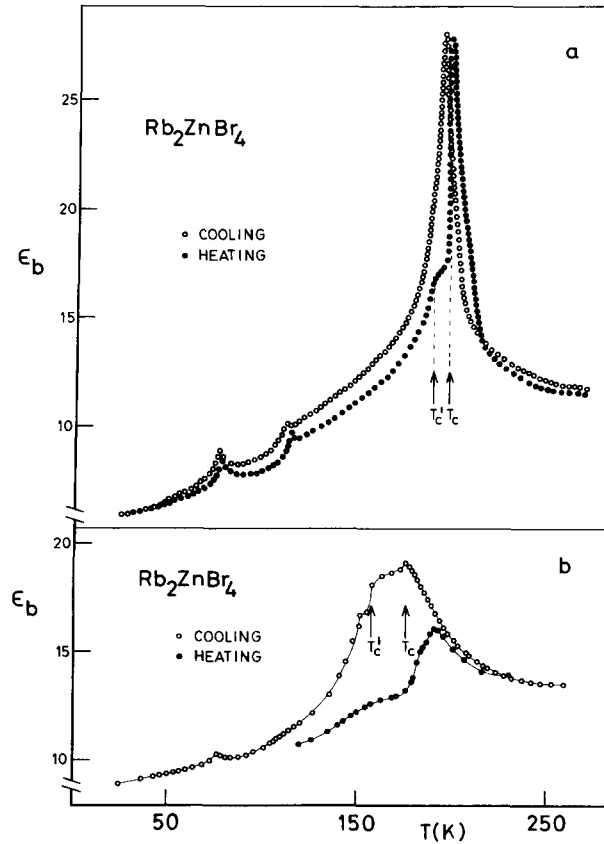


Fig. 1 : The dielectric constant  $\epsilon_b$  measured along the  $\vec{b}$ -axis of  $\text{Rb}_2\text{ZnBr}_4$  for two samples, originating from two different single crystals.  $T_c$  denotes the position of the peak in  $\epsilon_b$ , and  $T'_c$  indicates the place of an additional anomaly in  $\epsilon_b$ . In Fig. 1a, the temperatures  $T_c$  and  $T'_c$  are connected to the heating run. In 1b, these temperatures belong to the cooling run.

the maximum, as indicated by the arrows in the figure and denoted by  $T_c$  and  $T'_c$  respectively. This effect can be seen even more clearly in Fig. 2 where the dielectric constant  $\epsilon_a$  as measured with the field along the  $\vec{a}$ -axis is plotted as a function of temperature. Though the change in  $\epsilon_a$  is only a few percent of the change in  $\epsilon_b$ , one sees two maxima at  $T_c$  and  $T'_c$  particularly clear in the heating run. Below  $T'_c$ , two new peaks in  $\epsilon_a$  are observed at 113 and 78 K respectively.

The data of Fig. 1a can be fitted very well by a Curie-Weiss law

$$\epsilon_b = \epsilon_b^\infty + \frac{\alpha}{T - T'_c} \quad (1)$$

with  $\epsilon_b^\infty = 6.83$ ,  $\alpha = 202.6$  K and a Curie-Weiss temperature of  $T'_c = 189.5$  K for the heating run (see Fig. 3a) which has its maximum at  $T_c = 199$  K. Note that this Curie temperature  $T'_c$ , which is smaller than  $T_c$ , shows up as the second anomaly in Fig. 1a. Remarkably, a similar

attempt to fit the data of Fig. 1b to a Curie-Weiss law was not successful.

From a theoretical point of view, Dvôřák and Petzelt<sup>11</sup> have described the dielectric anomaly by

$$\epsilon_b = \epsilon_b^\infty + S \left( \frac{1}{\Omega_K^2} + \frac{1}{\omega_K^2} \right) \quad (2)$$

where  $S$  denotes the oscillator strength, and  $\Omega_K$  and  $\omega_K$  the frequencies of the infrared active amplitudon and phason modes respectively, with wave vector  $\vec{K} = \vec{c}^* - 3\vec{q}_1$ . The amplitudon mode softens near  $T_i$ , but will only vary smoothly at  $T_c$ . Therefore the effect on  $\epsilon_b$  is mainly determined by the softening of the phason branch. Comparing Eq. (2) with Eq. (1), the temperature dependence of this softening is then given by

$$\frac{2}{\omega_K^2} = \alpha(T - T'_c), \quad (3)$$

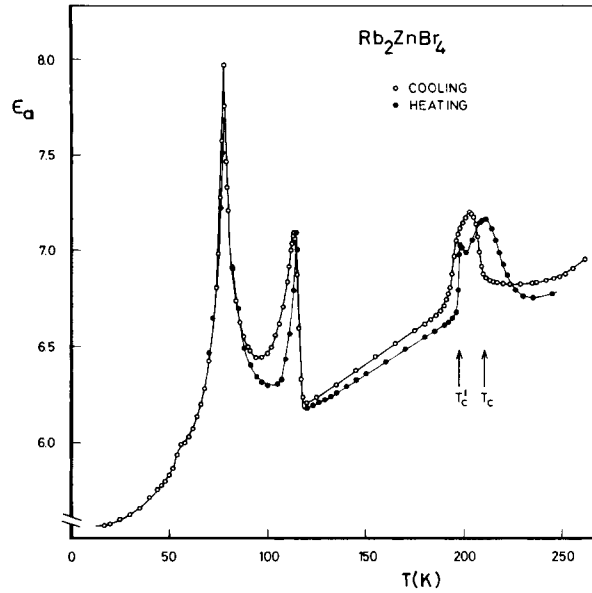


Fig. 2 : The dielectric constant  $\epsilon_a$  measured along the  $\vec{a}$ -axis of  $\text{Rb}_2\text{ZnBr}_4$  indicating phase transitions at 78 and 113 K. Note the two anomalies around the lock-in transition.

and below  $T_c$  the phason contribution should disappear, resulting in a quick drop in  $\epsilon_b$  in accordance with the results as plotted in Fig. 1a.

The different behaviour of  $\epsilon_b$ , as shown in Fig. 1b, can be interpreted by adapting the soliton picture to the dielectric constant measurements by constructing the following simplified model. Consider the crystal as being build up of commensurate and incommensurate domains with a dielectric constant  $\epsilon^c$  and  $\epsilon^i$  respectively. This should be a reasonable approximation for temperatures not too close to  $T_c$ , as the domain walls are not yet very sharp.  $\epsilon^c$  is expected to vary only slowly with temperature because the commensurate domains are already in the ferroelectric state, whereas for  $\epsilon^i$  we take the observed Curie-Weiss behaviour  $\epsilon^i \propto (T - T_c)^{-1}$ . The total dielectric response will be the weighted sum of the two contributions  $\epsilon^c$  and  $\epsilon^i$ . When  $n_c$  denotes the density of commensurate regions and  $n_s$  that of the incommensurate ones, the dielectric constant will be

$$\epsilon_b = \epsilon_b^\infty + n_c \epsilon^c + n_s \epsilon^i. \quad (4)$$

For temperatures  $T$  above  $T_c$   $n_c = 0$  and  $n_s = 1$ , whereas below  $T_c$  we have  $n_c = 1$  and  $n_s = 0$ . On approaching  $T_c$  from above,  $n_c$  will grow at the expense of  $n_s$  but because  $\epsilon^i \propto (T - T_c)^{-1}$ , the main temperature effect will come from the incommensurate regions. Thus

$$\epsilon_b - \epsilon_b^\infty \approx n_s \left( \frac{\alpha}{T - T_c} \right). \quad (5)$$

According to recent theoretical calculations by Natterman<sup>12</sup> the temperature dependence of the soliton density is expected to vary as

$$n_s \propto (T - T_c)^{\frac{1}{2}}. \quad (6)$$

With a Curie temperature  $T'_c < T_c$ , we get from Eq. (5) and Eq. (6)

$$\epsilon_b - \epsilon_b^\infty \approx \frac{\alpha}{(T - T'_c)^{\frac{1}{2}}}. \quad (7)$$

In Fig. 3b we have plotted the data of Fig. 1b as a function of  $(T - T'_c)^{-\frac{1}{2}}$ , with  $T'_c = 156$  K. As can be seen from the figure, the data agree very well with Eq. (7) with  $\epsilon_b^\infty = 6.72$  and  $\alpha = 60.1 \text{ K}^2$ , except for the temperature region close to  $T_c$ . Note that again the Curie temperature  $T'_c$  shows up as an anomaly in the  $\epsilon_b(T)$  curve and that  $T'_c < T_c = 176$  K. This means that the different temperature dependence of  $\epsilon_b$  near  $T_c$  can be ascribed by the creation of commensurate domains on approaching  $T_c$  from above, yielding a soliton density with a temperature dependence as given in Eq. (6). This latter is also in agreement with recent NMR work on  $\text{Rb}_2\text{ZnCl}_4$ <sup>13</sup> and  $\text{Rb}_2\text{ZnBr}_4$ <sup>14</sup>, but differs significantly from McMillan's<sup>2</sup> theoretical result of  $n_s \propto \ln^{-1}[(T - T_c)/T_c]$ . It should be emphasized that our experiments indicate that the proposed soliton picture depends strongly on the specific single crystal under study. The origin of this pronounced sample dependence probably lies in the presence of dislocations which can favour the building up of commensurate regions<sup>15</sup>. This may also effect the actual temperature where the transition takes place, and

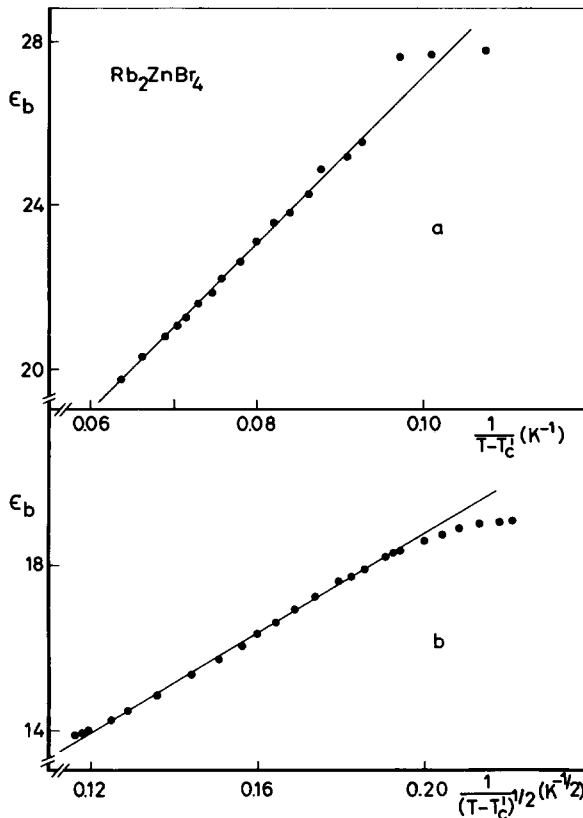


Fig. 3a: The dielectric constant  $\epsilon_b$  of the sample of Fig. 1a plotted as a function of  $(T-T'_c)^{-1}$ , showing a Curie-Weiss behaviour with  $T'_c = 189.5$  K.

3b: The dielectric constant  $\epsilon_b$  of the sample of Fig. 1b plotted as a function of  $(T-T'_c)^{-1/2}$ , yielding  $\epsilon_b = \epsilon_b^\infty + \alpha(T-T'_c)^{-1/2}$  as predicted from a soliton model.

explains the variety of observed  $T_c$ 's as reported in the literature.

The anomalies in the dielectric constant along the  $\vec{a}$ -axis at 78 K and 113 K indicate additional phase transitions. Raman experiments done by Francke et al.<sup>16</sup> showed a mode softening in the a(c c)b geometry from which a transition temperature of  $140 \pm 10$  K is extrapolated. A comparison of these results with the data from the measurements of the dielectric constants as shown in Fig. 1 and Fig. 2 indicate that the actual transition point should be connected with the anomaly in  $\epsilon_a$  at 113 K. In our previous far-infrared transmission experiments, we observed a phase transition of apparently first order around  $T = 50$  K, accompanied by a change in the optical activity in the a,b plane<sup>5</sup>. However, from Figs. 1 and 2 one sees that no such indication can be found neither in  $\epsilon_b$  nor in  $\epsilon_a$ . But if the low temperature data of Fig. 2 are plotted as a function of  $(T_0-T)^{-1}$  (see Fig. 4), again they can be fitted by a Curie-Weiss relation

$$\epsilon_a = \epsilon_a^\infty + \frac{\alpha}{T_0 - T}, \tag{8}$$

with  $\epsilon_a^\infty = 5.43$ ,  $\alpha = 13.71$  K for  $5 < T < 56$  K, and with  $\epsilon_a^\infty = 5.73$ ,  $\alpha = 5.49$  K for  $56 < T < 70$  K, whereas for both cases  $T_0 = 77.8$  K. The transition point between the two fits appears as a small shoulder at 56 K in Fig. 2. Therefore we are inclined to conclude that both temperatures,  $T = 56$  K and  $T = 78$  K, are connected to the same phase transition. This transition will then be accompanied by a soft mode, with critical temperature  $T_0 = 78$  K, whereas the actual transition takes place at 56 K, resulting in a change in the optical activity along the  $\vec{a}$ -direction.

Summarizing, we have observed a Curie-Weiss like behaviour of the dielectric constant  $\epsilon_b$  of  $Rb_2ZnBr_4$  at the lock-in transition from the incommensurate to the commensurate phase. Besides, in a few samples, a smearing of the anomaly in  $\epsilon_b$  was observed, which tentatively can be ascribed to the appearance of solitons, in agree-

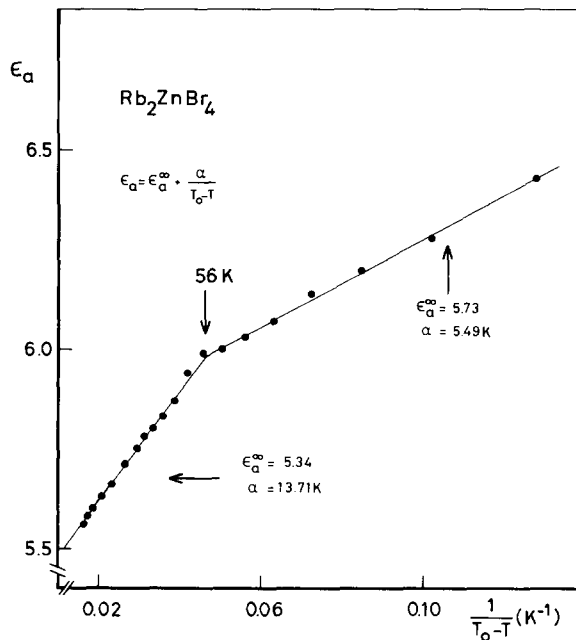


Fig. 4 : The dielectric constant  $\epsilon_a$  of the sample of Fig. 2 plotted as a function of  $(T_0 - T)^{-1}$ , with  $T_0 = 77.8$  K, showing a Curie-Weiss behaviour, with different Curie constants above and below a critical temperature  $T = 56$  K.

ment with a temperature dependence of the soliton density of the type  $n_s \propto (T - T_C)^{1/2}$ . The appearance of these solitons seems to be sample dependent and might be connected to the presence of dislocations. In addition, below  $T_C$ , two new peaks are observed in  $\epsilon_a$ , one which can be ascribed to the transition point of the soft mode as observed by Raman spectroscopy<sup>6</sup>, whereas the other one indicates that the phase transition observed earlier<sup>5</sup> at roughly 50 K actually occurs at 56 K and is accompanied by the soft-

ening of a mode at a critical temperature  $T_0 = 78$  K.

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