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TEMPERATURE DEPENDENCE OF THE STATIC DIELECTRIC CONSTANT OF Rb_2ZnBr_4: SOLITONS IN A MODULATED STRUCTURE?

R.P.A.R. van Kleef, Th. Rasing, J.H.M. Stoelinga and P. Wyder

Research Institute for Materials, University of Nijmegen,
Toernooiveld, 6525 ED Nijmegen, The Netherlands

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The static dielectric constant of Rb_2ZnBr_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 $(T-T_c)^{\frac{1}{2}}$. 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[1]; 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[2,3]. 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 Rb_2ZnBr_4 [1,4,5] 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[6] and far-infrared work[5].

In Rb_2ZnBr_4 the incommensurate phase lies between $T_i = 355$ and $T_c \simeq 200$ K with $\vec{q}_i = (1-\delta)\vec{c}^{*}/3$ and a modulation amplitude along the $\vec{b}$-axis (here $a \simeq \sqrt{3}\, b$). Below T_c, Rb_2ZnBr_4 is ferroelectric with a polarization in the direction of the modulation amplitude[7-10]. 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 ε_b with the field along the $\vec{b}$-axis appeared to be strongly sample dependent. Fig. 1 shows two typical examples of ε_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 (~ 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 ε_b, also showing a much bigger hysteresis in temperature (~ 14 K). In both cases, a second anomaly in ε_b can be seen below

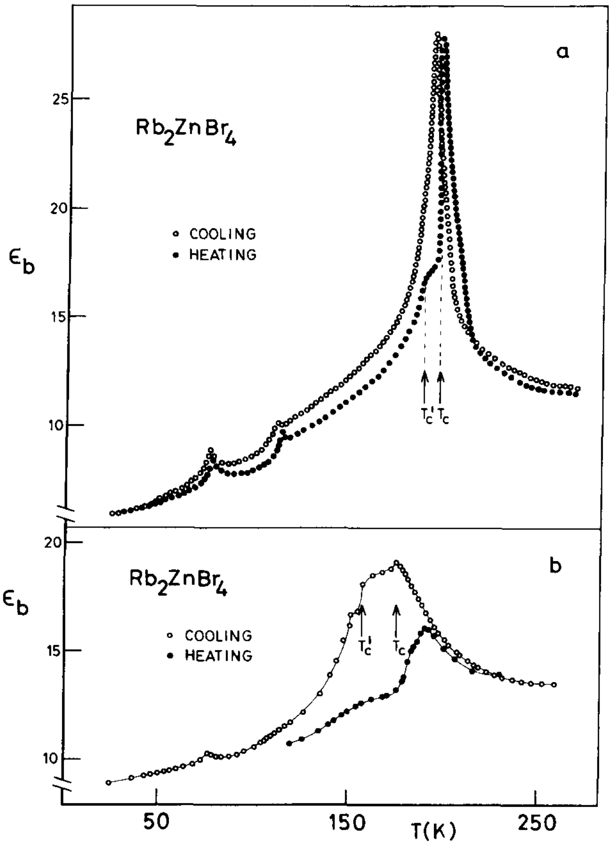

Fig. 1 : The dielectric constant ε_b measured along the $\vec{b}$-axis of Rb_2ZnBr_4 for two samples, originating from two different single crystals. T_c denotes the position of the peak in ε_b, and T'_c indicates the place of an additional anomaly in ε_b. In Fig. 1a, the temperatures T_c and T'_c are 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 ε_a as measured with the field along the $\vec{a}$-axis is plotted as a function of temperature. Though the change in ε_a is only a few percent of the change in ε_b, one sees two maxima at T_c and T'_c particularly clear in the heating run. Below T'_c, two new peaks in ε_a are observed at 113 and 78 K respectively.

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

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

with $\varepsilon_b^\infty = 6.83$, $\alpha = 202.6$ 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, Dvôrak and Petzelt[11] have described the dielectric anomaly by

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

where S denotes the oscillator strength, and Ω_K and ω_K the frequencies of the infrared active amplitudon and phason modes respectively, with wave vector $\vec{K} = \vec{c}^* - 3\vec{q}_i$. The amplitudon mode softens near T_i, but will only vary smoothly at T_c. Therefore the effect on ε_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

$$\omega_K^2 = \alpha(T - T'_c) , \qquad (3)$$

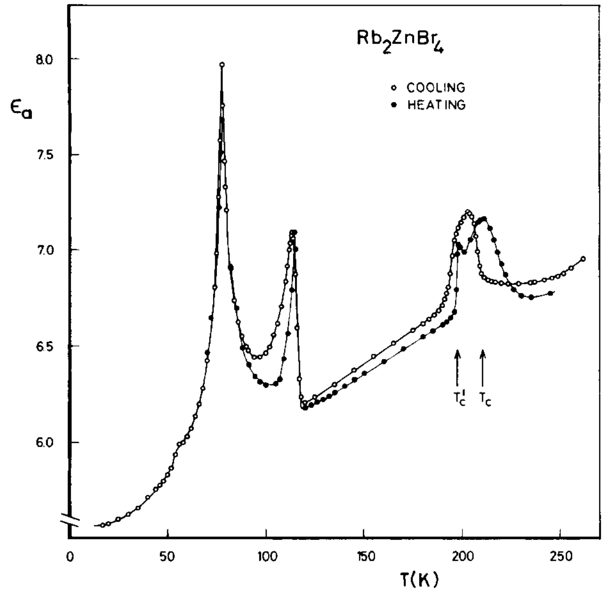

Fig. 2 : The dielectric constant ε_a measured along the $\vec{a}$-axis of Rb_2ZnBr_4 indicating phase transitions at 78 and 113 K. Note the two anomalies around the lock-in transition.

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

The different behaviour of ε_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 ε^c and ε^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. ε^c is expected to vary only slowly with temperature because the commensurate domains are already in the ferroelectric state, whereas for ε^i we take the observed Curie-Weiss behaviour $\varepsilon^i \propto (T-T_c)^{-1}$. The total dielectric response will be the weighted sum of the two contributions ε^c and ε^i. When n_c denotes the density of commensurate regions and n_s that of the incommensurate ones, the dielectric constant will be

$$\varepsilon_b = \varepsilon_b^\infty + n_c\varepsilon^c + n_s\varepsilon^i \ . \qquad (4)$$

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 $\varepsilon^i \propto (T-T_c)^{-1}$, the main temperature effect will come from the incommensurate regions. Thus

$$\varepsilon_b - \varepsilon_b^\infty \simeq n_s \left(\frac{\alpha}{T - T_c}\right) \ . \qquad (5)$$

According to recent theoretical calculations by Natterman[12] the temperature dependence of the soliton density is expected to vary as

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

With a Curie temperature $T_c' < T_c$, we get from Eq. (5) and Eq. (6)

$$\varepsilon_b - \varepsilon_b^\infty \simeq \frac{\alpha}{(T - T_c')^{\frac{1}{2}}} \ . \qquad (7)$$

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 $\varepsilon_b^\infty = 6.72$ and $\alpha = 60.1\ K^{\frac{1}{2}}$, except for the temperature region close to T_c. Note that again the Curie temperature T_c' shows up as an anomaly in the $\varepsilon_b(T)$ curve and that $T_c' < T_c = 176$ K. This means that the different temperature dependence of ε_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 Rb_2ZnCl_4 [13] and Rb_2ZnBr_4 [14], but differs significantly from McMillan's[2] theoretical result of $n_s \propto \ell n^{-1}[(T-T_c)/T_c]$. It should be emphasized that our experiments indicate that the proposed soliton picture depends strongly on the specific single crystal understudy. The origin of this pronounced sample dependence probably lies in the presence of dislocations which can favour the building up of commensurate regions[15]. This may also effect the actual temperature where the transition takes place, and

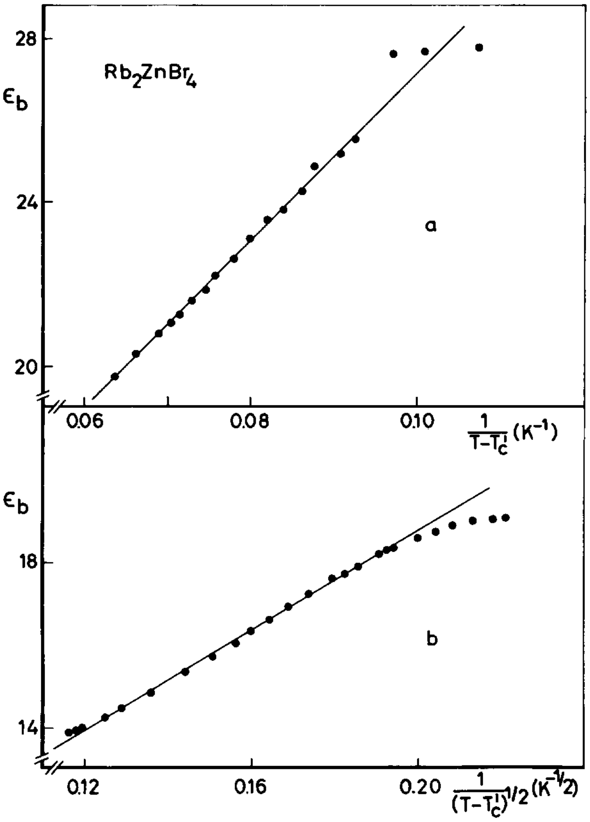

Fig. 3a: The dielectric constant ε_b of the sample of Fig. 1a plotted as a function of $(T-T_c')^{-1}$, showing a Curie-Weiss behaviour with $T_c' = 189.5$ K.

3b: The dielectric constant ε_b of the sample of Fig. 1b plotted as a function of $(T-T_c')^{-\frac{1}{2}}$, yielding $\varepsilon_b = \varepsilon_b^\infty + \alpha(T-T_c')^{-\frac{1}{2}}$ 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.[16] showed a mode softening in the a(c c)b geometry from which a transition temperature of 140 ± 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 ε_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[5]. However, from Figs. 1 and 2 one sees that no such indication can be found neither in ε_b nor in ε_a. But if the low temperature data of Fig. 2 are plotted as a function of $(T_o-T)^{-1}$ (see Fig. 4), again they can be fitted by a Curie-Weiss relation

$$\varepsilon_a = \varepsilon_a^\infty + \frac{\alpha}{T_o - T}\,, \tag{8}$$

with $\varepsilon_a^\infty = 5.43$, $\alpha = 13.71$ K for $5 < T < 56$ K, and with $\varepsilon_a^\infty = 5.73$, $\alpha = 5.49$ K for $56 < T < 70$ K, whereas for both cases $T_o = 77.8$ 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 $T_o = 78$ 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 ε_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 ε_b was observed, which tentatively can be ascribed to the appearance of solitons, in agree-

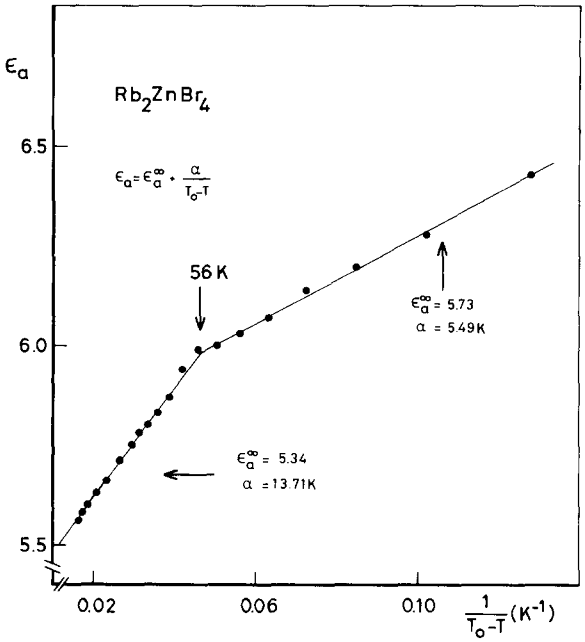

Fig. 4 : The dielectric constant ε_a of the sample of Fig. 2 plotted as a function of $(T_o-T)^{-1}$, with T_o = 77.8 K, showing a Curie-Weiss behaviour, with different Curie constants above and below a critical temperature T = 56 K.

ment with a temperature dependence of the soliton density of the type $n_s \propto (T-T_c)^{\frac{1}{2}}$. 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 ε_a, one which can be ascribed to the transition point of the soft mode as observed by Raman spectroscopy[6], whereas the other one indicates that the phase transition observed earlier[5] at roughly 50 K actually occurs at 56 K and is accompanied by the softening of a mode at a critical temperature T_o = 78 K.

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