87Rb nuclear magnetic resonance evidence for solitons and phasons in Rb2ZnBr4

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The temperature and angular dependences of the 87Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR spectra and spin-lattice relaxation times have been studied in the paraelectric (P), the incommensurate (I), and the ferroelectric commensurate (C) phases of Rb2ZnBr4, and the distributions of the electric-field-gradient (EFG) tensors at the Rb sites have been determined in the P and I phases. The NMR line shapes can be described by "broad solitons" over most of the I phase whereas the soliton width becomes small as compared to the intersoliton distance close to the transition into the C phase. The temperature dependence of the soliton density has been determined. The spin-lattice relaxation rate in the I phase is dominated by phasons if the nuclear displacement is small, whereas it is dominated by amplitudons if the nuclear displacement from the paraelectric site is large. Soliton pinning by defects has been confirmed.

I. INTRODUCTION

Incommensurate (I) systems have attracted a great deal of attention in the last few years.1,2 They are characterized by the appearance of a superlattice with a periodicity which is an irrational fraction of the periodicity of the basic lattice.

Rb2ZnBr4 represents one of the first known examples of one-dimensionally modulated incommensurate systems.3–5 It undergoes successive phase transitions at $T_I = 346$ K and $T_e = 187$ K.5 The high-temperature space group is $D_{2h}^{18}$-Pemn and the low-temperature space group is $C_{2h}^{19}$-Pe2$_1$1n. When it is cooled through $T_I$ the crystal exhibits an instability against a soft mode which condenses out at a general point in the Brillouin zone. The order parameter of such a transition

$$u = A \cos \phi(z)$$

is characterized by its amplitude $A$ and its phase $\phi(z)$. Mc Millan7 has proposed that the I phase actually consists of commensurate regions $[\phi(z) = \text{const}]$ separated by solitonlike "discommensurations" where the phase changes rapidly. Many attempts have been made to use this concept in explaining various experimental results.5–17 Advanced NMR (Ref. 15) and nuclear quadrupole resonance16 (NQR) studies have shown that in the isomorphic Rb2ZnCl4 solitons are narrow only close to the lock-in transition ($T_e < T < T_e + \sim 10$ K), while in the bulk of the I phase they are broad compared with the intersoliton distance and can be suitable described by the "plane-wave" limit. The same picture was proposed for K2SeO4 on the basis of ultrasonic measurements of the shear stiffness $c_{55}$.17

The 87Rb NMR measurements of Rb2ZnCl4 (Refs. 11 and 18) and Rb2ZnBr4 (Ref. 12) demonstrated that the Rb nucleus is very suitable for the study of the local structure and the dynamics of the I phase. In the present paper we present a detailed study of the incommensurate modulation in Rb2ZnBr4. Experimental details are described in Sec. II. 87Rb electric field gradient (EFG) tensors in the paraelectric (P) and the incommensurate (I) phase are reported in Sec. III, while the temperature dependence of the spectra is analyzed in Sec. IV. The temperature dependence of the soliton density is reported in Sec. V together with a discussion of the large thermal hysteresis at the lock-in transition. Section VI describes the "incommensurate" line shape and spin-lattice relaxation around $T_I$. The phason and the amplitudon contributions to the relaxation rate are reported in Sec. VII.
II. EXPERIMENTAL

A single crystal of Rb$_2$ZnBr$_4$ was grown at 303 K from an aqueous solution of RbBr and ZnBr$_2$ in a 2:1 molar ratio. The crystal was colorless though not completely transparent. The orientation of the crystallographic axes has been determined from its morphology and was further checked by x-ray diffraction.

The NMR measurements of the $^{87}$Rb ($I = \frac{3}{2}$) line shapes and relaxation times have been done on the Bruker SXP spectrometer. The $^{87}$Rb satellites ($\frac{3}{2} \rightarrow \frac{1}{2}$ and $-\frac{3}{2} \rightarrow -\frac{1}{2}$) are too broad to be observed in the $I$ phase, therefore only the central lines ($\frac{1}{2} \rightarrow -\frac{1}{2}$) were studied. Since second-order quadrupolar shifts are inversely proportional to the quadrupole shift frequencies, the EFG tensor components in the interval $\pm 1$ are continuous in the $I$ phase, we expect a quasicontinuous distribution to the EFG tensor comes from, we find $^{21}$

$$ V_{\mu l}^l(l) = V_{0l}^l(l) + A \cos(2\theta) V_{0l}^l(l) + \cdots, $$

where $V_{0l}^l(l)$ and $V_{0l}^l(l)$ are constants. Since $\cos(2\theta)$ is continuous in the $I$ phase, we expect a quasicontinuous distribution of the EFG tensor components in the interval

$$ V_{\mu l}^l(l) = V_{0l}^l(l) \pm A V_{0l}^l(l) + A^2 V_{0l}^l(l) \pm \cdots. $$

The limiting values $V_{\mu l}^l(l)$ correspond to nuclei which are near the maximum positive or negative displacements. These values were determined by measuring the angular dependence of those central $\frac{1}{2} \rightarrow -\frac{1}{2}$ transitions which correspond to the edge singularities in the frequency distribution $f(v)$.

The results have been analyzed by the method of Volkoff. $^{20}$

The paraelectric unit cell contains eight Rb ions which can be divided into two chemically inequivalent sets, Rb(1) and Rb(2). All Rb sites have site symmetry $m$. $^{21}$ Because of the presence of the center of symmetry at most two Rb sites can be distinguished for each chemically inequivalent set. We thus expect to see at most four Rb lines for $T > T_c$. For a general direction of the magnetic field in the $(a-c)$ plane all four lines should be seen whereas only two lines should be seen in the $(a-b)$ and $(b-c)$ planes. In view of the Rb site symmetry, the EFG tensor components $V_{a}^l$ and $V_{bc}$ should vanish for $T > T_c$ and one of the principal axes should be parallel to the crystal $b$ axis which becomes the axis of spontaneous polarization below $T_c$. $^{19,22}$

The experimental data (Fig. 1 and Table I) agree very well with the predictions based on the crystal structure. We find two chemically inequivalent Rb sites. Each of them occurs in two different orientations generated by the $c$ mirror. The quadrupole coupling constants equal $e^2qQ/h = 4.5$ MHz for Rb(1) and $e^2qQ/h = 3.0$ MHz for Rb(2). The corresponding asymmetry parameters are $\eta = 0.87$ and $\eta = 0.57$ (Table II). The principal axes of the Rb(2) EFG tensor coincide with the crystallographic axes within the limits of experimental error ($\pm 3^\circ$) and the smallest principal axis points along the $b$ direction. The principal axes of the Rb(1) EFG tensor are, however, rotated with respect to the crystallographic axes for $\pm 2.5^\circ$ around the $b$ axis. The largest principal axis is here parallel to the $b$ direction (Table II).

The orientation of the EFG tensors in good agreement with the results of de Pater $^{23}$ whereas our values for the quadrupole coupling constants are significantly lower than his values [Rb(1)$\leftrightarrow$6.28 MHz and Rb(2)$\leftrightarrow$4.32 MHz]. The reason for this discrepancy is not known.

In view of the $a$-$c$ mirror plane above $T_c$ the EFG tensor is in the crystal fixed $x |a, y| b, z| c$ frame of the following

$$ V^l = \begin{pmatrix} V_{xx} & 0 & V_{xz} \\ 0 & V_{yy} & 0 \\ V_{xz} & 0 & V_{zz} \end{pmatrix}, \quad T > T_c. $$

The frozen-in soft-mode displacements destroy the $a$-$c$ mirror plane in the $I$ phase resulting in nonzero values of $V_{xy}$ and $V_{yx}$. We thus expect for a given Rb site the EFG tensor in the $I$ phase to be of the following form:
FIG. 1. Angular dependence of second-order quadrupolar shifts in the paraelectric (P) and the upper part of the incommensurate (I) phase. Hatched regions denote quasicontinuous frequency distributions, limited by edge singularities.

\[ V' = V^p + \begin{vmatrix} 0 & \alpha & 0 \\ \alpha & 0 & \gamma \\ 0 & \gamma & 0 \end{vmatrix} A \cos \phi, \ T < T_I \]  

(5)

If only the leading nonzero terms in the expansion of \( V' \) in powers of the incommensurate modulation are considered. Here \( \alpha \) and \( \gamma \) are constants and \( A \) is the amplitude of the incommensurate order parameter.

As can be seen from Table I this is exactly what happens below \( T_I \). The main effect of the incommensurate phase transition is a rotation of the principal axes of the EFG tensors (Table II) whereas there is only a slight change in the quadrupole coupling constants and asymmetry parameters. For nuclei which are at sites of extreme nuclear displacement of the modulation wave the Rb(2) EFG tensors are at 10 K below \( T_I \) rotated for \( \pm 19.5^\circ \) around the \( a \) and for \( \pm 8.7^\circ \) around the \( c \) axis whereas the rotation of the Rb(1) EFG tensors amounts to \( \pm 8.5^\circ \) around the \( c \) and to \( \pm 4.5^\circ \) around the \( b \) axis. There is a quasicontinuous dis-

<p>| Table I. ( ^{87}\text{Rb} ) quadrupole coupling tensors (in MHz) in the crystal fixed a,b,c frame in Rb(_2)ZnBr(_4): (i) ( T = 353 &gt; T_I ), (ii) ( T = 336 &lt; T_I ), (iii) ( T = 316 &lt; T_I ). For ( T &lt; T_I ) only those tensors are listed which correspond to the extreme displacements of the incommensurate displacement wave. |</p>
<table>
<thead>
<tr>
<th>Rb(1)</th>
<th>Rb(2)</th>
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</thead>
<tbody>
<tr>
<td><strong>T = 353 K &gt; T(_I)</strong>:</td>
<td><strong>T = 353 K &gt; T(_I)</strong>:</td>
</tr>
<tr>
<td>( 0.30 )</td>
<td>( 0.30 )</td>
</tr>
<tr>
<td>( -4.50 )</td>
<td>( -4.50 )</td>
</tr>
<tr>
<td><strong>T = 336 K &lt; T(_I) = 346 K</strong>:</td>
<td><strong>T = 336 K &lt; T(_I) = 346 K</strong>:</td>
</tr>
<tr>
<td>( 0.30 )</td>
<td>( 0.30 )</td>
</tr>
<tr>
<td>( -4.50 )</td>
<td>( -4.50 )</td>
</tr>
<tr>
<td><strong>T = 316 K &lt; T(_I) = 346 K</strong>:</td>
<td><strong>T = 316 K &lt; T(_I) = 346 K</strong>:</td>
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<tr>
<td>( 0.30 )</td>
<td>( 0.30 )</td>
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<td>( -4.50 )</td>
<td>( -4.50 )</td>
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</table>
distribution of EFG tensors between these extremes. The fact that the Rb(2) EFG tensor is more affected than the Rb(1) agrees with the structural data of de Pater. 21

The rotation angles significantly increase on further cooling into the I phase. At 316 K and the Rb(2) rotation angles increase to $\pm 23^\circ$ around the $a$ and to $\pm 13^\circ$ around the $c$ axis whereas the Rb(1) rotation angles now amount to $\pm 11^\circ$ around the $c$ and to $\pm 6^\circ$ around the $b$ axis. It is as well interesting to note (Fig. 2) that with decreasing temperature the asymmetry parameter $\eta$ decreases for Rb(1) whereas it increases for Rb(2).

IV. TEMPERATURE DEPENDENCE OF SPECTRA

It has been shown previously that the second-order quadrupolar shift of the frequency of the central $^{87}$Rb line can be expanded in a Taylor series in powers of the order parameter

$$v = v_0(T) + a_1 u + \frac{1}{2} a_2 u^2 + \cdots$$

(6)

Here $v_0(T)$ denotes the noncritical part of the second-order shift while the parameters $a_1, a_2, a_3, \ldots$ depend on the EFG tensor elements and the orientation of the external magnetic field with respect to the crystal axes. Taking into account that $u = A \cos \phi$, we find

$$v = v_0(T) + a_1 A \cos \phi + \frac{1}{2} a_2 A^2 \cos^2 \phi + \cdots$$

(7)

The frequency distribution $f(v)$ in the I phase is obtained from

$$f(v) dv = N(z) dz$$

(8)

As the number of nuclei per unit length in the direction of the modulation $N(z)$ is constant, we find

$$f(v) = \frac{\text{const}}{|dv/dz|}$$

(9)

The derivative

$$\frac{dv}{dz} = -(a_1 A + a_2 A^2 \cos \phi + \cdots) \sin \phi \frac{d\phi}{dz}$$

(10)

therefore describes the shape of the quasicontinuous spectrum in the I phase. The frequency distribution is peaked whenever $dv/dz = 0$.

If the solitons are so broad that the commensurate regions can be neglected, the plane-wave approximation $d\phi/dz = \text{const}$ is suitable and the derivative (10) becomes

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**TABLE II.** Eigenvalues $\lambda_i$ (in MHz) and direction cosines of the $^{87}$Rb quadrupole coupling tensors in Rb$_2$ZnBr$_4$: (i) $T = 353$ K $> T_1$, (ii) $T = 336$ K $< T_1$. Here again only those tensors are listed for $T < T_1$ which corresponds to the extreme displacements of the incommensurate displacement wave, and the crystallographic axes are chosen according to $Pcmn$: $a = 13.343$ Å, $b = 7.656$ Å, $c = 9.708$ Å.

<table>
<thead>
<tr>
<th>$T &gt; T_1$</th>
<th>$T &lt; T_1$</th>
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</thead>
<tbody>
<tr>
<td>Rb(1)</td>
<td>Rb(2)</td>
</tr>
<tr>
<td>$\gamma_1$</td>
<td>$-0.030$</td>
</tr>
<tr>
<td>$\gamma_2$</td>
<td>$4.2$</td>
</tr>
<tr>
<td>$\gamma_3$</td>
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</tr>
<tr>
<td>$\mu_a$</td>
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</tr>
<tr>
<td>$\mu_b$</td>
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<tr>
<td>$\mu_c$</td>
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</tr>
<tr>
<td>$\gamma_3$</td>
<td>$-4.656$</td>
</tr>
<tr>
<td>$\mu_a$</td>
<td>$0.9860$</td>
</tr>
<tr>
<td>$\mu_b$</td>
<td>$0.9866$</td>
</tr>
<tr>
<td>$\mu_c$</td>
<td>$0.9846$</td>
</tr>
</tbody>
</table>

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**FIG. 2.** Temperature dependence of the asymmetry parameters $\eta$. 

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21. de Pater, private communication.
The first possibility

$$\sin \phi = 0$$

(12)

gives rise to singularities

$$v_{\pm} = v_0 \pm a_1 A + \frac{1}{2} a_2 A^2 \pm \cdots$$

(13)

which represent signals of nuclei close to the extreme displacements in the incommensurate wave. Their difference

$$v_+ - v_- = 2a_1 A \propto (T_1 - T)^\beta$$

(14)

is proportional to the amplitude of the order parameter. If we orient the crystal in such a way that higher-order odd terms can be neglected ($a_3 = a_5 = \cdots = 0$), the critical exponent $\beta = 0.35 \pm 0.03$ is obtained by plotting $v_+ - v_-$ versus $T_1 - T$ in a log-log scale (Fig. 3). The obtained value is significantly smaller than the classical mean-field result (0.50), but agrees fairly well with the predictions of the $d = 3$, $n = 2$ Heisenberg model as well as with neutron scattering experiments on $\text{Rb}_2\text{ZnBr}_4$, $\text{Rb}_2\text{ZnCl}_4$, and $\text{K}_2\text{SeO}_4$. It also agrees with NMR, NQR, EPR, and ultrasonic measurements on these and related compounds.

Additional singularities ($v_3, v_4, \ldots$) might appear in the spectrum if

$$a_1 A + a_2 A^2 \cos \phi + \cdots = 0.$$  

(15)

They arise from the nonlinearity in the relation between the frequency and displacements and are shifted for a constant value with respect to $v_0(T)$. Since these signals do not depend on $A$ their presence might be used to study the properties of the basic lattice in the $I$ phase.

V. SOLITON DENSITY

Close to the lock-in transition the distance between the solitons becomes large as compared to the soliton width. The plane-wave approximation no longer accounts for the observed spectrum and the nonlinear spatial variation of $\phi(z)$ must be taken into account. The quantitative theory of the NMR line shape in a multisoliton lattice has been described elsewhere.$^{27}$ Since $d\phi(z)/dz \approx 0$ in the commensurate regions, additional “commensurate” peaks start to grow at the position of ferroelectric lines when approaching $T_0$ (Fig. 4), whereas at the same time the intensity of the “incommensurate” edge singularities decreases. The normalized intensity of the $C$ lines measures the relative volume fraction $n_c$ of commensurate domains. The soliton density ($n_s$) is equal to

$$n_s = 1 - n_c.$$  

(16)

Our estimate of $n_s$ is not very accurate, since it is affected by several difficulties.
(i) The peaks in \( \text{Rb}_2\text{ZnRb}_4 \) are so broad that it is possible to separate commensurate signals from the other singularities only at favorable orientations.

(ii) The spectra were obtained by Fourier transforming spin-echo signals and might be thus distorted by pulse imperfections.

(iii) The spatial variation of the amplitude of the order parameter has been ignored.\(^{28}\) The results have been found, however, to be reproducible, when measurements were repeated several times under the same experimental conditions.

In Fig. 5 we plotted \( n_s^2 \) as a function of temperature. In the temperature interval of \( \sim 5 \) K the temperature variation of the soliton density is—as in \( \text{Rb}_2\text{ZnCl}_4 \) (Ref. 15)—consistent with\(^{29,15}\)

\[
n_s \propto (T - T_c)^{1/2}
\] (17)

though a logarithmic law\(^7\) cannot be definitely excluded. At higher temperatures saturation sets in and the soliton density is in the middle of the \( I \) phase greater than 95%.

The soliton density versus \( T - T_c \) curve shows a temperature hysteresis (\( \sim 10 \) K), which is considerably larger than in \( \text{Rb}_2\text{ZnCl}_4 \).\(^{15}\) This is probably due to soliton pinning on defects, as discussed and experimentally demonstrated by Hamano et al.\(^30\) It was also noticed that both the transition temperatures \( T_I \) and \( T_c \) (Refs. 6 and 31) and the undercooling of the \( I \) phase\(^32\) are sample dependent.

The \( \text{Rb}_2\text{ZnBr}_4 \) crystals used in this study were grown in the \( I \) phase, therefore a high concentration of defects is expected. It is possible that the behavior of a sample prepared above \( T_I \) will be closer to that of \( \text{Rb}_2\text{ZnCl}_4 \).

VI. SPECTRA IN THE VICINITY OF \( T_I \)

We have found that in \( \text{Rb}_2\text{ZnBr}_4 \) additional lines are observed close to \( T_I \) (Fig. 6). They are found at any orientation at exactly the same position as the corresponding paraelectric lines, so that existence of “domains” of the high-temperature phase is indicated.

Since these “paralectric” lines disappear when the sample is cooled more than \( \sim 10 \) K below \( T_I \) and since they are not observed in \( \text{Rb}_2\text{ZnCl}_4 \), we conclude that their origin is due to defects which stabilize partial paraelectric arrangements. When the temperature is decreasing away from \( T_I \) the stabilizing forces are not strong enough and the incommensurate displacements become dominant.

These lines do not represent signals of macroscopic domains of the undercooled paraelectric phase, because (i) the \( P-I \) transition is of the second order, (ii) no thermal hysteresis was observed at \( T_I \), (iii) the spin-lattice relaxation time \( T_1 \) (see Fig. 7) of these lines does not follow the paraelectric behavior below \( T_I \), and (iv) the plane-wave model suitably predicts the position of the edge singularities.

Our results demonstrate that the incommensu-
rate structure is very subtle and that "defects" must be considered in any complete theoretical description of this phase in "real" crystals.

VII. SPIN-LATTICE RELAXATION TIMES

Since the spin-lattice relaxation times provide additional information about the dynamics of the $I$ phase, 11,18 we decided to extend our previous $T_1$ measurements. 12 When approaching $T_I$ from above, $T_1$ rapidly decreases as in other related crystals. 33,34 The relaxation is governed by an overdamped soft mode, which condenses out producing a sharp $T_1$ minimum at $T_I$. 35 In the $I$ phase $T_1$ remains short and nearly temperature independent at the center of the incommensurate frequency distribution (Fig. 8). On the other hand, a normal soft-mode behavior has been observed at the edge singularity close to $T_I$ only, while on further cooling $T_1$ remains nearly constant till the lock-in transition.

The excitation spectrum of the $I$ phase consists of two modes: the amplitudon branch corresponding to oscillations of the amplitude of the displacement wave and a phason branch reflecting changes of the phase. 36 The last mode—acousticleike mode—has for the critical wave vector zero frequency over whole $I$ phase as it represents only another choice of the phase and therefore needs no excitation energy. In view of its low frequency and large nuclear displacements it represents a very efficient spin-lattice relaxation mechanism. Our measurements have indeed confirmed the presence of such a low-lying, nearly temperature-independent and strong relaxation mechanism. Phasons disappear at $T_c$ where $T_1$ starts to increase rapidly.

The above statement is further supported by the fact (Fig. 8) that the relaxation time $T_1$ varies over the spectrum as theoretically predicted. 18,37 At the edge singularities $T_1$ is significantly longer than in the middle of the broad background. These results fit very well to the theoretical model 37 which predicts that the strong phason contribution dominates the relaxation of the nuclei, which are only slightly displaced ($u \sim 0$), while amplitudons become important for extreme displacements ($u = \pm A$). The phason contribution is temperature independent whereas the amplitudon contributions varies as the amplitude of the order parameter.

The above model is only qualitatively correct as it neglects coupling between phasons and amplitudons as well as the finite width of the resonance signals. Both of these effects result in a mixing of phason and amplitudon contributions. 37 At a special orientation of the crystal in the magnetic field, an additional minimum was found at $\sim 280$ K (Fig. 9). Since it is not observed in

![FIG. 7. Temperature dependence of the spin-lattice relaxation time $T_1$ as measured on the "paraelectric" line near $T_I$.](image)

![FIG. 8. Temperature dependence of the spin-lattice relaxation time. Circles denote $T_1$ at the distinct edge singularity, while crosses represent values, obtained in the middle of the frequency distribution in the $I$ phase.](image)

![FIG. 9. Temperature dependence of $T_1$ at a special orientation, where an additional minimum has been observed at $\sim 280$ K. It is tentatively attributed to the cross relaxation with bromine nuclei.](image)
Rb$_2$ZnCl$_4$, the best explanation is cross relaxation with bromine nuclei. Unperturbed $^{81}$Br NQR frequencies lie between 55 and 70 MHz, and together with Zeeman interaction the level crossing with $\nu_L(^{87}$Rb) = 88.3 MHz can be fulfilled at special orientations.

VIII. CONCLUSIONS

The above results show the following.

(i) The incommensurate modulation in Rb$_2$ZnBr$_4$ can be over most of the $I$ phase described by the "broad soliton," or what amounts to the same, the "plane-wave" limit as the soliton width is large compared to the intersoliton distance.

(ii) Close to $T_c$, the intersoliton distance becomes large as compared to the soliton width and the soliton density vanishes as $T \rightarrow T_c^+$. 

(iii) The critical exponent for the amplitude of the order parameter is $\beta = 0.35 \pm 0.03$.

(iv) The spin-lattice relaxation rate has been found to be dominated by phasons at the center of the incommensurate frequency distribution and by amplitude at the points of extreme nuclear displacements.

(v) Whereas the above results are analogous to what has been found in Rb$_2$ZnCl$_4$ the appearance of paraelectric lines is the $I$ phase and the soliton pinning effects together with the sample dependence of $T_I$ and $T_c$ are tentatively attributed to the influence of defects on the properties of the Rb$_2$ZnBr$_4$ samples grown in the $I$ phase. These effects have not been observed in Rb$_2$ZnCl$_4$ where the sample was grown in the $P$ phase.

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1For a review see R. Pynn, Nature (London) 281, 433 (1979), and references therein.


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