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The critical temperature dependence of birefringence near the normal–incommensurate phase transition in Rb_2ZnBr_4

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Abstract. Anomalous (non-classical) temperature behaviour of birefringence at the second-order normal–incommensurate phase transition in Rb_2ZnBr_4 crystals is studied experimentally. An attempt is undertaken to discuss it using the existing theoretical approach. A critical review of some theoretical results concerning the temperature dependence of the local mean square of an order parameter is given both for the region of small corrections to the results of the Landau theory and for the scaling region. It is shown that, in the region of 'small corrections' (at $|\tau| \simeq 10^{-1}$), qualitative agreement of the experiment with the results of fluctuation theory can be recognised. Near the critical point, at $|\tau| < 10^{-3}$, the deviation from the critical behaviour of the XY model is found; the nature of this deviation is not clear.

1. Introduction

Deviations from classical (mean-field) behaviour near structural phase transitions, in particular, near transitions from normal (N) to incommensurate (I) phase have been repeatedly observed in experiments (see, e.g., Flerov and Iskornev 1980, Hamano *et al* 1980, Havlicek *et al* 1986, Iskornev and Flerov 1983, Mashiyama 1981, Sawada *et al* 1981, Unruh *et al* 1979). The interpretation of such deviations consists usually in comparing the observed critical indices with the theoretical values for the XY model, but it is not evident *ab initio* that one deals with the scaling region, i.e. that a true asymptotic critical behaviour is observed. To clarify the possible nature of these deviations we have performed a careful experimental study and analysis of the temperature dependence of birefringence for Rb_2ZnBr_4 crystals in both the N and the I phases (for preliminary information see Ivanov *et al* (1989)). Some results for Rb_2ZnCl_4 are discussed too.

Investigation of the temperature dependence of birefringence is a conventional method of studying the critical phenomena. The method is both convenient and precise; therefore many experimental results obtained by this method have been reported (Bruce and Cowley 1981, Fousek and Petzelt 1979, Gehring 1977, Melnikova and Anistratov

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1983, Schafer and Kleemann 1985). Surprisingly, one observes many inconsistencies and errors in the interpretation of experimental data. Taking this into account, we begin with a review of the theoretical results concerning the temperature dependence of birefringence near phase transitions (section 2). Then in section 3 we present the experimental data and discuss them.

2. Theory

We shall deal with the birefringence non-zero in the symmetrical phase; its change at the phase transition depends on invariant combinations of order parameter components, η_i, the lowest order invariant being $\Sigma_i \eta_i^2$ (Fousek and Petzelt 1979).

For simplicity, we consider the case of a single-component order parameter (Ising-type system) but present also the results for XY-type systems including I phases.

In the experiment, in fact, one measures the total phase shift for the plane wave in an inhomogeneous medium:

$$\psi = \left\langle \frac{1}{s} \int_s \mathrm{d}z\, \mathrm{d}y \int_0^l \Delta n(x, y, z)\, \mathrm{d}x \right\rangle \tag{1}$$

where s is the cross section of the light beam and l is a distance along the light path. As by symmetry we have $\Delta n(r) = \Delta n_0 + a\eta^2(r)$,

$$\psi = l\,\Delta n_0 + \frac{a}{s} \sum_K \langle \eta_{K_1} \eta_{K_2} \rangle \int_V \exp[\mathrm{i}(K_1 + K_2)r]\, \mathrm{d}r \simeq l\,\Delta n_0 + la \sum_{K=0}^{K_{\mathrm{at}}} \langle \eta_K \eta_{-K} \rangle \tag{2}$$

where K and r are three-dimensional vectors, $V = sl$, η_K is the Fourier transform of $\eta(r)$, $\eta_K = (1/V)\int \eta(r) \exp(-\mathrm{i}Kr)\, \mathrm{d}r$ and K_{at} is a cut-off wavevector arising as usual in the continuous-media approximation. The problem of the temperature dependence of the refractive index or birefringence Δn reduces to that for $\Sigma_0^{K_{\mathrm{at}}} \langle \eta_K \eta_{-K} \rangle \equiv \langle \eta^2 \rangle_{\mathrm{loc}}$. Indeed, the anomalous temperature dependence of $l \sim V^{1/3}$ coincides with that of $\langle \eta^2 \rangle_{\mathrm{loc}}$ (see below) and the temperature dependence of the coefficient a can be neglected.

2.1. Scaling region

The temperature dependence of $\langle \eta^2 \rangle_{\mathrm{loc}}$ has been discussed, in fact, repeatedly (see, e.g., Bruce and Cowley 1981, Gehring 1977, Ma 1976, Meissner and Binder 1975). One has for the immediate vicinity of the critical point T_{c} (the scaling region)

$$\langle \eta^2 \rangle_{\mathrm{loc}} \simeq \begin{cases} C_0 - C^+ \tau^{1-\alpha} + C'\tau + \ldots & \text{at } T > T_{\mathrm{c}} \quad (3a) \\ C_0 + C^- |\tau|^{1-\alpha} + C'\tau + \ldots & \text{at } T < T_{\mathrm{c}} \quad (3b) \end{cases}$$

where α is the specific heat critical index, and C_0, C^+, C^- and C' are non-universal constants depending in particular on K_{at}; $\tau = (T - T_{\mathrm{c}})/T_{\mathrm{c}}$.

It is instructive to obtain equations (3) in the following way. (We shall use a specific choice of the effective Landau Hamiltonian. The results to be obtained are valid in the general case as far as the universality assumption is correct.) Let us consider the effective Hamiltonian

$$\mathcal{H} = \int_V \left(\frac{A_T}{2}(T - T_0)\eta^2 + \frac{D}{2}(\nabla\eta)^2 + \frac{B}{4}\eta^4 \right) \mathrm{d}V \tag{4}$$

where $A_T = \tilde{A}_T T$, $D = \tilde{D}T$, $B = \tilde{B}T$ and $\tilde{A}_T$, $\tilde{B}$, $\tilde{D}$ are temperature-independent quantities; V is the volume of the system.

Then the free energy F and the entropy S are given by

$$F(T) = -T\ln\left\{\int\prod_r \mathrm{d}\eta(r)\exp\left[-\int\left(\frac{\tilde{A}_T}{2}(T-T_0)\eta^2+\frac{\tilde{D}}{2}(\nabla\eta)^2+\frac{\tilde{B}}{4}\eta^4\right)\mathrm{d}r\right]\right\} \qquad (5)$$

$$S = -\frac{\partial F}{\partial T} = -\frac{F}{T} - \frac{T\tilde{A}_T}{2}\left\langle\int \eta^2(r)\,\mathrm{d}r\right\rangle = -\frac{F}{T} - \frac{T\tilde{A}_T V}{2}\langle\eta^2\rangle_{\mathrm{loc}}. \qquad (6)$$

The singular part of S (as well as that of V, l) is known to be proportional to $|\tau|^{1-\alpha}$. At the same time the leading singularity of the first term in equation (6) is $|\tau|^{2-\alpha}$. Thus the leading singularity of $\langle\eta^2\rangle_{\mathrm{loc}}$ is just the same as that in S (i.e. $|\tau|^{1-\alpha}$). Note that equation (6) and consequently the latter conclusion is valid at both $T > T_c$ and $T < T_c$. In the case $T < T_c$, $\langle\eta\rangle^2$ is non-zero at $V \to \infty$ (in contrast with the case $T > T_c$) and is proportional to $|\tau|^{2\beta}$. However, the sum $\Sigma_{K=0}^{K_{\mathrm{at}}}\langle\eta_K\eta_{-K}\rangle$ is given by equation (3b), i.e. has a much weaker singularity than $|\tau|^{2\beta}$ does.

One might think that equations (3) are in disagreement with the direct calculation of the sum $\Sigma_{K=0}^{K_{\mathrm{at}}}\langle\eta_K\eta_{-K}\rangle$ (see, e.g., Shafer and Kleemann 1985). Indeed, we have (Landau and Lifshitz 1958)

$$\sum_{K=0}^{K_{\mathrm{at}}}\langle\eta_K\eta_{-K}\rangle = \frac{T}{V}\sum_{K=0}^{K_{\mathrm{at}}}\chi(K) = \frac{1}{2\pi^2}\chi(0)r_c^{-3}\int_0^{K_{\mathrm{at}}r_c} x^2 f(x)\,\mathrm{d}x \qquad (7)$$

where $\chi(K)$ is the susceptibility corresponding to η_K presented in the scaling form $\chi(0)f(Kr_c)$, r_c is the correlation radius and $\chi(0) \sim \tau^{-\gamma}$, $r_c \sim \tau^{-\nu}$. Let us take $f(x)$ in the form that provides correct asymptotic behaviour at $x \to \infty$ and $x \to 0$, e.g. $f(x) = 1/(1+x^{2-\hat{\eta}})$ or $f(x) = 1/(1+x^2)^{(2-\hat{\eta})/2}$. Then we obtain from equation (7)

$$\langle\eta^2\rangle_{\mathrm{loc}} \sim (\text{constant} - |\tau|^{2\beta}). \qquad (8)$$

It is just this result that many researchers use (for references see Meissner and Binder (1975)). We see that it is in contradiction to equations (3) that were obtained with the use of the universality assumption only. In other words, equation (8) must be wrong. One can find a criticism of equation (8) in the work of Bruce and Cowley (1981) and Meissner and Binder (1975). We shall present here a more simple but not less strict argument.

The point is that one cannot choose the form of $f(x)$ taking into account asymptotic behaviour only. We shall show that non-asymptotic singular terms in $f(x)$ are of importance (Fisher and Langer 1968). It turns out also that the validity of equations (3) means that there exists some 'sum rule' for $f(x)$. Without pretending to derive the exact 'sum rule' let us illustrate its origin.

In accordance with the scaling theory, $f(x) \to 1$ at $x \to 0$ and $f(x) \to gx^{-2+\hat{\eta}}$ at $x \to \infty$ (g is a constant). From equation (7) we have

$$\langle\eta^2\rangle_{\mathrm{loc}} \sim \tau^{2\beta}\int_0^{K_{\mathrm{at}}r_c} f(x)x^2\,\mathrm{d}x = \tau^{2\beta}\int_0^{K_{\mathrm{at}}r_c} gx^{\hat{\eta}}\mathrm{d}x + \tau^{2\beta}\int_0^{K_{\mathrm{at}}r_c}[f(x)x^2 - gx^{\hat{\eta}}]\,\mathrm{d}x \qquad (9a)$$

and

$$\langle\eta^2\rangle_{\mathrm{loc}} \sim \text{constant} + \tau^{2\beta}\int_0^{\infty}[f(x)x^2 - gx^{\hat{\eta}}]\,\mathrm{d}x - \tau^{2\beta}\int_{K_{\mathrm{at}}r_c}^{\infty}[f(x)x^2 - gx^{\hat{\eta}}]\,\mathrm{d}x. \qquad (9b)$$

The factor $\tau^{2\beta}$ in the last term in equation (9b) is temperature dependent. To reveal the temperature dependence one has to take into account the non-asymptotic terms in $f(x)$. From the paper of Fisher and Langer (1968) it follows that

$$[f(x)x^2 - gx^{\hat{\eta}}]_{x\to\infty} \to C_1 x^{-(1-\alpha)/\nu+\hat{\eta}} - C_2 x^{-1/\nu+\hat{\eta}}. \qquad (10)$$

One finds now that the leading singularity in the third term of equation (9b) is $|\tau|^{1-\alpha}$.

Therefore equation (7) gives the same result as correct equations (3), provided that the second term in equation (9*b*) disappears. This is possible under the condition ('sum rule')

$$\int_0^\infty [f(x)x^2 - gx^{\tilde\eta}]\,dx = 0. \tag{11}$$

(Note that for illustration we have omitted non-asymptotic terms in r_c and $\chi(0)$ in equation (8); therefore the condition for $f(x)$ should be more complicated than equation (11). Moreover, taking into account these terms, one obtains a condition additional to equation (10).)

By similar arguments one can obtain the same equations (3) for the *XY* system. In this case $\alpha < 0$; therefore the singular part of $\langle\eta^2\rangle_{loc}$ includes $|\tau|^{1+|\alpha|}$ and higher-order powers of $|\tau|$. Let us emphasise that in this case both $\langle\eta^2\rangle_{loc}$ and $d\langle\eta^2\rangle_{loc}/dT$ are continuous at $\tau = 0$.

Note that unlike the mean-field situation the temperature dependence of Δn in the scaling region provides no direct information on the temperature dependence of the order parameter (if $\Delta n \not\equiv 0$ in the symmetrical phase). That is why the results of some papers on determination of the non-classical index β from the $\Delta n(T)$ dependence are incorrect.

2.2. *Corrections to the Landau theory*

For structural phase transitions the anomalies are often proved to be described by the Landau theory and by small corrections to it. We shall discuss the 'first fluctuation corrections' to $\Delta n(T)$ in both phases. When interpreting experimental data it is natural to represent $\Delta n(T)$ as a sum of the 'Landau (mean-field) part' and the fluctuation contribution. We calculate $\langle\eta^2\rangle_{loc}$ taking into account the first fluctuation correction. Using the effective Hamiltonian (equation (4)) for the symmetrical phase we obtain the well known result

$$\langle\eta^2\rangle_{loc} = \frac{T}{V}\sum_{K=0}^{K_{at}}\frac{1}{A + DK^2} = \frac{T}{2\pi^2 D}\left(K_{at} - \frac{\tan^{-1}(K_{at}r_c^+)}{r_c^+}\right) \simeq \frac{T_0}{2\pi^2 D}K_{at} - \frac{T_0^{3/2}A_T^{1/2}\tau^{1/2}}{4\pi D^{3/2}} \tag{12}$$

where $r_c^+ = \sqrt{D/A}$, $A = A_T(T - T_0)$, $\tau = (T - T_0)/T_0$. The last approximation is valid close enough to the transition, where $K_{at}r_c \gg 1$.

For the non-symmetrical phase, account must be taken also of the first correction $\langle\Delta\eta_{K=0}\rangle \equiv \langle\eta_{K=0} - \eta_0\rangle$ to the mean order parameter η_0 calculated in the framework of the Landau theory ($\eta_0 = (|A|/B)^{1/2}$); here we can write

$$\langle\eta^2\rangle_{loc} = \eta_0^2 + 2\langle\Delta\eta_{K=0}\rangle\eta_0 + \sum_{K\neq 0}^{K_{at}}\langle\Delta\eta_K\Delta\eta_{-K}\rangle \tag{13}$$

where

$$\langle\Delta\eta_{K=0}\rangle = -\frac{3B\eta_0}{2|A|}\sum_{K\neq 0}^{K_{at}}\langle\Delta\eta_K\,\Delta\eta_{-K}\rangle.$$

As a result we have

$$\begin{aligned}\langle\eta^2\rangle_{loc} &= \eta_0^2 - 2\sum_{K\neq 0}^{K_{at}}\langle\Delta\eta_K\,\Delta\eta_{-K}\rangle = \eta_0^2 - \frac{T}{lp^2 D}K_{at} + \frac{T}{\pi^2 D}\frac{\tan^{-1}(K_{at}r_c^-)}{r_c^-}\\ &\simeq \left(\eta_0^2 - \frac{3T_0}{2\pi^2 D}K_{at}\right) + \frac{T_0}{2\pi^2 D}K_{at} + \frac{T_0^{3/2}A_T^{1/2}|\tau|^{1/2}}{\pi\sqrt{2}D^{3/2}}\end{aligned} \tag{14}$$

where $r_c^- = (D/2|A|)^{1/2}$.

The first term in the right-hand part of equation (14) equals zero at the renormalised transition temperature (Vaks *et al* 1966, Strukov and Levanyuk 1983) $T_0^* = T_0 - (3BT_0/2A_T\pi^2 D)K_{at}$, which should be identified with the experimentally observed transition temperature T_c, if one deals with the first correction to the Landau theory. Within the 'improved' perturbation theory (Vaks *et al* 1966) one has to substitute T_0^* for T_0 also in the last term in equations (12) and (14). Note that $\langle\eta^2\rangle_{loc}$ approximated by equations (12) and (14) is continuous at $\tau = 0$ (although these approximations themselves are valid at $\tau \neq 0$). We see that the temperature dependence of $\langle\eta^2\rangle_{loc}$ and consequently of the anomalous part of Δn coincides with that of the anomalous part of entropy.

When interpreting the experiment it is more convenient to analyse not Δn but its temperature derivative $\zeta = \mathrm{d}(\Delta n)/\mathrm{d}T$. Using equations (12) and (14) one obtains

$$\zeta^+ = \zeta_B + + \lambda^+\tau^{-1/2} \qquad \text{at } \tau > 0 \qquad (15a)$$

$$\zeta^- = \zeta_B + \zeta_L + \lambda^-|\tau|^{-1/2} \qquad \text{at } \tau < 0 \qquad (15b)$$

where $\zeta_L = (A_T/B)a$, ζ_B is the 'background' (i.e. the normal or regular part of the 'thermo-optic coefficient'), $\lambda^-/\lambda^+ = 2\sqrt{2}$, and $\tau = 0$ corresponds to experimentally observed critical point T_c. In the case of XY systems (N-I phase transitions), $\lambda^-/\lambda^+ = \sqrt{2}$.

Let us emphasise that there are, strictly speaking, many reasons for equations (15) to be invalid or useless far enough from the critical point. The first reason is evident from equation (14). The next reason follows from the temperature dependences of A_T, B, D, which were neglected, as well as the higher-order terms, in the Landau thermodynamic potential. When interpreting experimental data, one should take into account also the temperature dependences of ζ_B and ζ_L. The temperature dependence of ζ_B is quite similar to that of the thermal expansion or heat capacity. For the temperature region around T_D (T_D is the Debye temperature), one can estimate $\zeta_B(T)$ as $\zeta_B(T_D)[1 + m(T - T_D)/T_D]$ where $m \simeq 10^{-1}$ for the Debye model. If $T_c \simeq T_D$ (it is so in our case) and the phase transition is far from the tricritical point the temperature dependence of ζ_L can be estimated as $\zeta_L(T_c)[1 + (T - T_c)/T_c]$ for both order–disorder and displacive phase transitions. Taking into account that usually $\zeta_L \ll \zeta_B$ ($\zeta_L \simeq 10^{-1}\zeta_B$) and the uncertainty of the above estimations one can assume that the temperature-dependent parts of both ζ_B and ζ_L can be estimated as $\zeta_L\,|T - T_c|/T_c$. Using equations (15) one can see that the temperature dependences of ζ_B and ζ_L can be neglected (one should demand it to be much smaller than the fluctuation contribution), when $|\tau| \ll G^{1/3}$, where $G = T_cB^2/8\pi^2 A_T D^3$. (It is evident from the argument presented above that the upper limit of applicability of equations (15) can be estimated by an order of magnitude only.) On the other hand, $G \ll |\tau|$ is, in fact, the condition of applicability of both the Landau theory and the first fluctuation correction to it. Let us mention that, as for the applicability range of the Landau theory, the given expression for G is valid for an order of magnitude too. As a result the region of applicability of equations (15) is given by the condition

$$G \ll |\tau| \ll G^{1/3}. \qquad (16)$$

Therefore a well defined temperature interval of validity of equations (15) can exist if G is very small.

2.3. *The role of defects*

The deviations from classical behaviour may also be due to defects. Let us briefly discuss the influence of point defects on the temperature dependence of $\langle\eta^2\rangle_{loc}$ in the critical region at the N–I phase transition. As is known from the work of Harris (1974) the presence of 'random local temperature' (or 'symmetry-conserving') defects does not change the critical behaviour of systems with $\alpha < 0$. One could expect that 'random local field' (or 'symmetry-breaking') defects influence the phase transition significantly. According to Larkin (1970) and Imry and Ma (1975) these defects break down the long-range order in I phase; therefore one could expect smooth anomalies at T_i.

For the non-critical region where defects provide only small deviations from the results given by the Landau theory (Levanyuk *et al* 1979, Levanyuk and Sigov 1990) one obtains for the system with 'random local field' defects

$$\langle \eta^2 \rangle_{\mathrm{loc}} = \lambda_{\mathrm{d}}^{+} \tau^{-1/2} \qquad \text{at } \tau > 0 \qquad (17a)$$

$$\langle \eta^2 \rangle_{\mathrm{loc}} = T_{\mathrm{c}} A_T |\tau| / B - \lambda_{\mathrm{d}}^{-} |\tau|^{-1/2} \qquad \text{at } \tau < 0 \qquad (17b)$$

where λ_{d}^{+} and λ_{d}^{-} are constants proportional to the concentration of the defects, and $\lambda_{\mathrm{d}}^{-}/\lambda_{\mathrm{d}}^{+} = \sqrt{2}$. Equations (17) are valid if $|\tau| \gg (T_{\mathrm{c}} A_T / B\lambda_{\mathrm{d}})^2$. Having this in mind we can conclude from equations (17) that there is no indication of a maximum of the 'defect contribution' to $\langle \eta^2 \rangle_{\mathrm{loc}}$ at $T = T_{\mathrm{c}}$. This is contrary to the statement by Levanyuk *et al* (1983).

The contribution of more symmetrical 'random local field' defects (P defects in the notation of Levanyuk *et al* (1979)) is given by equations (15), where λ^{+} and λ^{-} depend on the concentration of the defects and $\lambda^{-}/\lambda^{+} \neq 2\sqrt{2}$. At present there are no corresponding theoretical results for I phases. For the N phase the correction to $\langle \eta^2 \rangle_{\mathrm{loc}}$ which is linearly dependent on concentration of such defects, takes the form of equation (17*a*).

3. Experiment and discussion

Rb_2ZnBr_4 crystals have an N–I phase transition at $T_i = 347$ K. The spontaneous distortions correspond to the wavevector $(\frac{1}{3} - \delta)a^*$ (Iizumi and Gesi 1983). In Rb_2ZnBr_4, contrary to other crystals of the K_2SeO_4 family, the value of $\delta = \delta_{\mathrm{I}} = 0.04$ does not depend on temperature in the wide region from T_i down to about 210 K, which corresponds to nearly commensurate modulation, $\frac{1}{3} - \delta_{\mathrm{I}} \simeq \frac{5}{17}$. Near the lock-in transition temperature T_{L} the picture of structural distortions becomes more complicated, and the situation can be described as, in addition to δ_{I}-modulation, two incommensurate modulations with $\delta_{\mathrm{II}}(T)$ and $\delta_{\mathrm{III}}(T)$ (Iizumi and Gesi 1983). The transition to the commensurate (C) ferroelectric phase $Pna2_1$, which is weakly polar along the c axis, takes place at $T_{\mathrm{L}} = 193$ K; two additional phase transitions (out of scope of this discussion) were observed at lower temperatures (Nomoto *et al* 1983). It should be noted that the existence region of the I phase is very extended.

Here we shall concentrate our attention on the discussion of birefringence anomaly Δn near T_i. Irregular and hysteresis behaviour of $\Delta n(T)$ near T_{L} is of separate interest; here we mention it very briefly having in mind that the microscopic and macroscopic structure of these (defect) crystals in the I phase near T_{L} has not yet been made clear.

Temperature dependences of Δn were recorded at constant speeds of temperature scans (1 K min^{-1} far from and 0.2 K min^{-1} near to T_{L} and T_i) using an automatic Babinet–Soleil compensator (with optical retardation resolution of about 0.002λ at $\lambda = 633$ nm). The temperature coefficient $\zeta = \mathrm{d}(\Delta n)/\mathrm{d}T$ of birefringence ('thermo-optic coefficient') was calculated as the graphic derivative. The Rb_2ZnBr_4 crystals were grown from the melt; solution-grown Rb_2ZnCl_4 crystals were investigated too. Samples in the form of parallelepipeds 2 mm × 2.5 mm × 3 mm were selected to have good optical homogeneity and the sharpest anomalies at the transitions. The samples were mounted on a copper stage in a temperature-controlled chamber filled with helium or nitrogen.

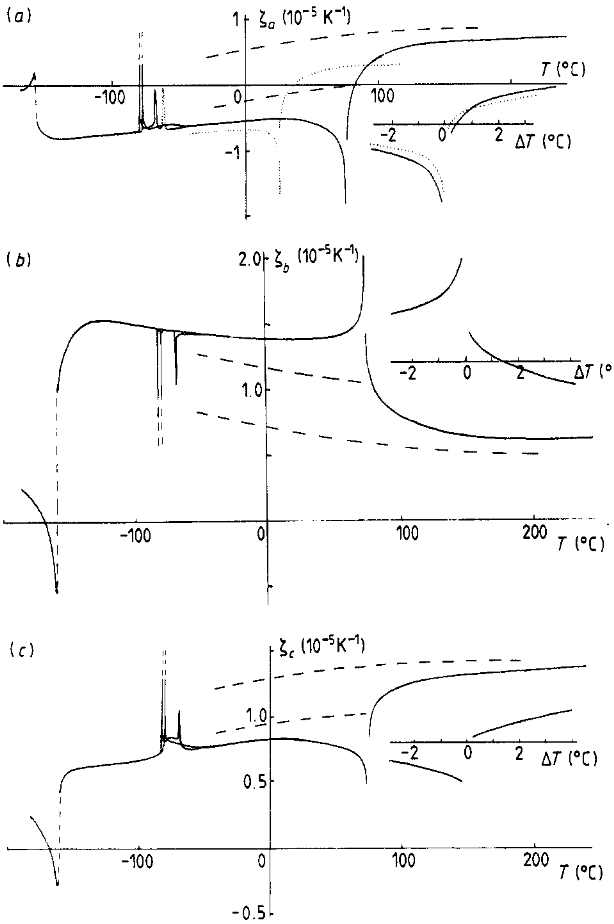

Figure 1. Temperature dependences of the temperature coefficient of birefringence for Rb_2ZnBr_4 for three different crystallographic directions: (*a*) a axis; (*b*) b axis; (*c*) c axis. The results for Rb_2ZnCl_4 are given in (*a*) by the dotted curves. The broken lines correspond to the background ζ_B and to the sum $\zeta_B + \zeta_L$, where ζ_L = constant, satisfying equations (15) at $|\tau| > 4 \times 10^{-2}$. The behaviour near T_i is given in the insets.

In figure 1 the temperature dependences of ζ for three principal cuts are presented (the index indicates the coincidence of the crystallographic axis for the P*na*m space group of the N phase with light propagation direction). Here one can see the anomalies at both T_i and T_L and one or two, depending on the sample, additional anomalies above T_L. The latter are observable only on cooling. In the same temperature region, splitting of superstructural satellite reflections were observed by Iizumi and Gesi (1983) on both heating and cooling. Hysteresis of $\zeta(T)$ and $\Delta n(T)$ between T_L and $T_L + 40$ K is observable too. The sharp peaks of ζ at T_L correspond to jumps of $\Delta n \simeq 10^{-5}$ at the first-order phase transition; the temperature hysteresis of this transition is 4 K. The transition at 114 K is continuous. It should be noted that additional anomalies (on cooling) for the same crystal were not observed in thermal expansion (Havlicek *et al* 1986, Ivanov and Fousek 1990); however, in the dielectric constant at least one anomaly was definitely recorded as a small ($\Delta\varepsilon \simeq 1$), faintly smoothed ($\Delta T \simeq 1$ K) jump of ε upwards.

Let us discuss now in detail the anomalies of Δn near the second-order phase N–I transition, trying to answer the question of whether it is possible to describe them in the

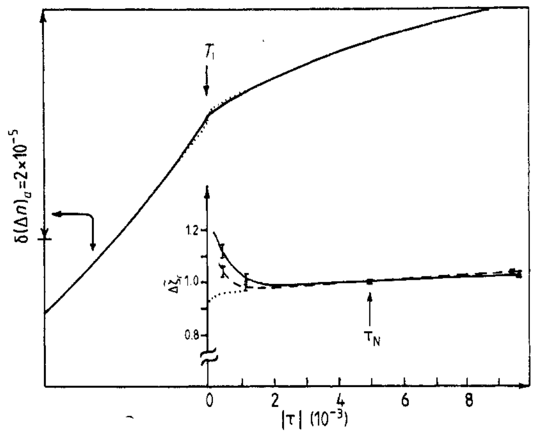

Figure 2. Temperature dependences of the normalised critical differences $\Delta\tilde{\zeta}_c$ (see equation (19) and text below it) of the temperature coefficients of birefringence for the a axis in the region of small $|\tau|$ for Rb_2ZnBr_4 (broken curve) and Rb_2ZnCl_4 (full curve). The temperature behaviour of the change in the birefringence for the a axis for Rb_2ZnCl_4 (full curve) in the vicinity of $T_i =$ 304 K, recorded under high-resolution conditions (birefringence, $\pm 1.5 \times 10^{-7}$; temperature $\tau = \pm 5 \times 10^{-5}$); the τ-scale coincides with that for $\Delta\tilde{\zeta}_c$. The dotted curves qualitatively show the expected although unobserved 'true critical behaviour' at $|\tau| < 10^{-3}$.

framework of the theory reviewed above. The $\Delta n(T)$ curves are continuous at T_i and strongly non-linear below and above T_i. The $\zeta(T)$ curves have the shape of a broad peak which is relatively large in comparison with the total change in ζ; however, in an interval near T_i of the order of magnitude of the temperature resolution of the experiment, $(T - T_i)/T_i = \tau \simeq 10^{-4}$, they look discontinuous; because of this an interval with unreliable values of ζ is excluded, and T_i is inside this interval in the middle (see figure 1). Note that qualitatively the same shapes of anomalies (deviations from the results of the Landau theory) are observable in thermal expansion, heat capacity, etc.

Let us suppose that these deviations are due to fluctuations. Then one can expect that far from the transition point the deviations, being small in this region, can be described using equation (15). Surely, what one calls 'deviations' depends on the choice of background, which is one of the most obscure problems in an experimental study of the phase transitions. In figure 1 the background ζ_B and $\zeta_B + \zeta_L$ are shown which satisfy equation (15) and the condition $\lambda^-/\lambda^+ = \sqrt{2}$ in the regions of 'small, but not too small' deviations in both phases; here ζ_L was assumed to be constant, and ζ_B to be temperature dependent. Obviously the procedure for choosing $\zeta_B(T)$ is ill defined. Indeed, let us take, for a start, some constant ζ_B, using equation (15*a*). Then, taking ζ_L approximately as the difference between the ζ-values in the I and N phases somewhere in the regions of small deviations, we can estimate G as the value of τ for which a deviation, or $\lambda|\tau|^{-1/2}$-term, equals ζ_L. Immediately one can see that this G is not small enough (10^{-2} in order of magnitude; see inequality (15)); therefore it is not surprising that in the I phase the behaviour of the deviation from any constant level $\zeta_B + \zeta_L$ does not follow equation (15*b*) (Ivanov *et al* 1989). The situation improves if we take $\zeta_B(T)$ in the form of a τ expansion (G almost does not change and is about 2×10^{-2}). However, in this case some additional terms should be added to equation (15). Therefore the total situation for the analysis with the use of equation (15) in the region of small deviations for the case of not very small G cannot be defined strictly. Nevertheless we would like to emphasise that qualitatively the experimental data do not contradict the fluctuation theory.

Let us now discuss the region of small τ ($\tau < G$) where the theory of small corrections to the Landau theory is invalid. From equations (3), for negative and small α, ζ should have a very sharp but finite peak at $T = T_i$, and at $|\tau| \to 0$

$$\zeta^{\pm} = \zeta_B + \zeta_{\text{peak}} - \lambda_c^{\pm}|\tau|^{|\alpha|}. \tag{18}$$

In the experiment, nearest to T_i (see insets in figure 1 or $\Delta n(\tau)$ curve in figure 2), we do not observe such behaviour down to $\tau \simeq 10^{-4}$. There are, strictly speaking, possibilities that either the presence of infinitely sharp peak will become evident at smaller τ or the peak is cut off by the defects. Still we may hope that we can observe the wings of the peak. From equation (18) ζ_{peak} and the main background contribution are eliminated if we consider the critical difference

$$\Delta\zeta_c = \zeta^- - \zeta^+ \simeq \Delta\lambda_c|\tau|^{|\alpha|}. \tag{19}$$

Figure 2 shows the dependence of the difference $\Delta\tilde{\zeta}_c$ on $|\tau|$ for an a-cut of the crystal section, for example. Here $\Delta\tilde{\zeta}_c = \Delta\zeta_c/\Delta\zeta_N$ where $\Delta\zeta_N$ is the value of $\Delta\zeta_c$ at some temperature of normalisation $\tau_N < G$ (we take $\tau_N = 5 \times 10^{-3}$; note that $\Delta\zeta_N \simeq \zeta_L$ and the deviation from the 'square root law' starts at $\tau < 4 \times 10^{-2}$), taken on a falling (at $|\tau| \to 0$) part of the curve. The decrease in $\Delta\tilde{\zeta}_c$ is observed down to $|\tau| \simeq 10^{-3}$ and can be described here by equation (19) with $\alpha = -0.03$ for Rb_2ZnCl_4 and -0.05 for Rb_2ZnBr_4 ($\Delta\alpha = \pm 0.02$). These values are fairly close to that obtained in numerical calculations ($\alpha = -0.02 \pm 0.03$) cited by Ma (1976). However, at $|\tau| < 10^{-3}$, deviations from this probably critical behaviour of a 'pure' crystal are observed (figure 2) which can be ascribed to the role of some defects (not of the 'random local field' type). To draw more definite conclusions one should consider the curves $\zeta^{\pm}(\tau)$ separately; unfortunately there are no theoretical results on the critical amplitudes as well as no experimental evidence on the value of the critical peak.

There is also the possibility that the deviations from the Landau behaviour over the total wide temperature interval ($|\tau| \simeq 10^{-1}$) are caused by defects. Unfortunately even within the theory of small deviations from the results of the Landau theory the ratio λ_d^-/λ_d^+ of the 'critical' amplitudes is not known for the XY systems. However, at T_i the experimentally observed sharp jump of ζ seems to be inconsistent with the expectation of the smooth anomaly coming from the conclusion (Larkin 1970, Imry and Ma 1975) that 'random local field' defects should suppress long-range order in the I phase.

In addition, recently we measured the birefringence for a Rb_2ZnCl_4 crystal that had been specially purified by multiple recrystallisation and was kindly supplied by Dr Hamano. Hamano *et al* (1988) had shown that the purification of the crystal significantly changes the dielectric behaviour in the region of the I–ferroelectric phase transition temperature T_L, making the temperature hysteresis of this transition very small. It follows from our optical measurements that hysteresis of T_L is less than 0.1 K; however, the anomaly around T_i is almost the same as in the case of the crystal grown by the usual technology. This is an argument in favour of the fluctuation but not defect nature of the anomaly discussed here.

4. Summary

The anomalous temperature behaviour of the temperature coefficient of birefringence in the vicinity of the N–I phase transition at $10^{-1} > |\tau| > 10^{-3}$ in both phases qualitatively corresponds to the theory, taking into account critical fluctuations of the order parameter. The nature of the deviations from the critical behaviour at $|\tau| < 10^{-3}$ is not clear (tentatively these deviations could be ascribed to some defects not of the 'random local field' type).

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