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1996 J. Phys.: Condens. Matter 8 517

(http://iopscience.iop.org/0953-8984/8/5/002)

J. Phys.: Condens. Matter **8** (1996) 517–526. Printed in the UK

The incommensurate phase of Cs_2ZnI_4

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Received 18 September 1995, in final form 14 November 1995

Abstract. The incommensurate state and the incommensurate–commensurate (IC–C) transition in a minimal Landau model for Cs_2ZnI_4 are investigated using rigorous analytical and numerical techniques. The Euler—Lagrange equations are solved numerically using parameters for Cs_2ZnI_4; the results differ significantly from those obtained using the constant-amplitude approximation. The minimal model predicts that the IC–C transition is first order, in agreement with experiment; the predicted discontinuity of the wavenumber q at the transition is 42% of the maximum q, rather than the measured 50%. The predicted temperature dependence of the IC wavenumber is too strong, and the predicted entropy change at the transition is too small, suggesting that the transition in Cs_2ZnI_4 is more strongly first order than predicted by the minimal model. Some general results for the asymptotic interaction of discommensurations are also obtained.

1. Introduction

The compound Cs_2ZnI_4 belongs to the K_2SeO_4 family of incommensurate systems [1], but is distinguished from the majority by a commensurate modulation $\boldsymbol{k}_C = \boldsymbol{a}^*/2$ (rather than $\boldsymbol{k}_C = \boldsymbol{a}^*/3$). Various physical properties of Cs_2ZnI_4 have been investigated by a variety of experimental techniques [2–12]: nuclear quadrupole resonance [2, 5, 6], x-ray [2, 5, 6, 10], dielectric constant [3, 5, 6], Raman scattering [4, 9], nuclear magnetic resonance [5], optical birefringence [7, 8, 9], and heat capacity methods [11, 12]. Cs_2ZnI_4 has five phases [8, 9, 12]: $Pnma$ ($Z = 4$) $\leftrightarrow$ incommensurate $\leftrightarrow$ ferroelastic $P2_1n$ ($Z = 8$) $\leftrightarrow$ ferroelastic $P1$ $\leftrightarrow$ ferroelastic $P1$; the respective transitions occur at $T_I = 117$ K (second order), $T_L = 108$ K (first order), 104 K (second order) and 94 K (first order).

The three high-temperature phases (abbreviated as N, IC and C) of interest here are described by a complex (two-component) order parameter $Q = |Q|\exp(\mathrm{i}\theta)$ which, unfortunately, has no simple physical interpretation; in almost the words of Cummins [1], Q is neither a local variable (like the magnetization or the polarization) nor a pure normal-mode coordinate, but rather a hybrid of both. For unit area normal to the x-direction and length L in this direction, the average free-energy density is

$$F/L = L^{-1}\int_{-L/2}^{L/2}\mathcal{F}[p_1(x),\, p_2(x)]\,\mathrm{d}x \tag{1a}$$

where $p_1 = |Q|\cos\theta$ and $p_2 = |Q|\sin\theta$; these are formal definitions (p_j is not the jth component of a physical vector $\boldsymbol{p}$). The minimal free-energy density for Cs_2ZnI_4 (relative to

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the disordered (N) state in which $Q = 0$) is the fourth-order Landau functional [13–18, 11]

$$\mathcal{F}[p_1(x), p_2(x)] = \tfrac{1}{2}\alpha(p_1^2 + p_2^2) + \tfrac{1}{4}\beta_1(p_1^2 + p_2^2)^2 - \tfrac{1}{4}\beta_2(p_1^4 - 6p_1^2p_2^2 + p_2^4) - \Delta(p_1\, \mathrm{d}p_2/\mathrm{d}x - p_2\, \mathrm{d}p_1/\mathrm{d}x) + \tfrac{1}{2}\kappa[(\mathrm{d}p_1/\mathrm{d}x)^2 + (\mathrm{d}p_2/\mathrm{d}x)^2] \qquad (1b)$$

where only terms essential for describing the IC and C states are included. All of the parameters but α (which has the dependence $\alpha = \alpha_0(T - T_0)$ where T_0 is the superheating limit of the C state) are assumed independent of the temperature T. For stability, $\beta_1 > 0$, $|\beta_2| < \beta_1$, and $\kappa > 0$; the phase θ can be defined so that $\Delta \geqslant 0$ and $\beta_2 \geqslant 0$. The third (anisotropy) term is $-\frac{1}{4}\beta_2|Q|^4 \cos 4\theta$ expressed in terms of p_1 and p_2.

The above density and extensions of it have been studied previously [13–18, 11]. The N–IC transition is second order, occurring at $\alpha = \Delta^2/\kappa$. In the IC state, p_1 and p_2 are periodic functions of x, with wavenumber q; the physical structure is modulated at $\boldsymbol{k}_I = (1/2 + q/a^*)\boldsymbol{a}^*$. When the domain structure is well developed, wide regions where the phase θ is close to the commensurate values 0, $\pm\pi/2$ and π (and the amplitude $|Q|$ is close to the C value $Q_c = p_c = [-\alpha/(\beta_1 - \beta_2)]^{1/2}$, with $\alpha < 0$) alternate with narrow regions (discommensurations) where θ passes through the unfavourable values $\pm\pi/4$ and $\pm 3\pi/4$ (and $|Q|$ is typically depressed below p_c). The wavenumber q, which is Δ/κ just below the N–IC transition, decreases with decreasing temperature; the IC–C transition occurs at a value α_L which must be found numerically. The C state, which exists for $\alpha < 0$ and is stable for $\alpha < \alpha_L$, is fourfold degenerate, with $(p_1, p_2) = (\pm p_c, 0)$, $(0, \pm p_c)$; the C-state density is $\mathcal{F}_c = -\alpha^2/[4(\beta_1 - \beta_2)]$ (with $\alpha < 0$).

Recent experiments [11] make attractive a further Landau theory study of Cs_2ZnI_4. First, the heat capacity in the IC phase just below the N–IC transition is constant (as predicted by mean-field theory), rather than increasing sharply with temperature as observed in many other compounds; that is, fluctuation effects appear to be small. Second, the data are sufficient for estimation of enough of the parameters that quantitative comparison with experiment is possible for quantities (also available) not used in estimating the parameters.

In [11] such a comparison for the minimal model of equation (1) was presented, but the value of the parameter α at the IC–C transition was estimated using the constant-amplitude approximation [19] which, unfortunately, can be quantitatively inaccurate, and even qualitatively incorrect. The following presents rigorous analytical and numerical treatments of the modulation of both the amplitude and the phase. Emphasis is on parameter values appropriate for Cs_2ZnI_4, but more general results are also presented. Section 2 describes the results of numerical solution of the Euler–Lagrange equations. Section 3 investigates analytically the order of the IC–C transition. Section 4 compares predictions of the minimal model with experiment. The appendix gives a general analytical treatment of the IC–C transition, valid for many models in the Lifshitz-invariant class.

The constant-amplitude approximation (whose inadequacy was already shown by Shiba and Ishibashi [15]) gives results significantly different from those of numerical solution of the Euler–Lagrange equations; it should not be used in a serious effort to confront theory with experiment. The minimal Landau model predicts successfully that the IC–C transition is first order, and the predicted discontinuity in the wavenumber q at the transition agrees reasonably well with experiment. On the other hand, the predicted temperature dependence of q just above the transition is too strong, and the predicted change in the entropy at the transition is too small; that is, the IC–C transition is apparently more strongly first order than predicted. Since Cs_2ZnI_4 appears to be well described by mean-field theory [11], it would be reasonable to extend the minimal model; the additional terms necessary to improve agreement with experiment involve, however, parameters difficult to estimate.

2. Numerical results

Numerical solutions of the Euler–Lagrange equations

$$-\kappa \frac{d^2 p_1}{dx^2} - 2\Delta \frac{dp_2}{dx} + \alpha p_1 + (\beta_1 - \beta_2) p_1^3 + (\beta_1 + 3\beta_2) p_1 p_2^2 = 0 \qquad (2a)$$

$$-\kappa \frac{d^2 p_2}{dx^2} + 2\Delta \frac{dp_1}{dx} + \alpha p_2 + (\beta_1 - \beta_2) p_2^3 + (\beta_1 + 3\beta_2) p_2 p_1^2 = 0 \qquad (2b)$$

for the density of equation (1*b*) were obtained (for given wavenumber q) as in [20]; the free energy was then minimized with respect to q. The equations were solved from $x = 0$ (the centre of a discommensuration) to $x = X$ (a point mid-way between two discommensurations). Boundary conditions compatible with the differential equations are the following. At $x = 0$: $|Q(x)|$ is even and $\theta(x) + \pi/4$ is odd; equivalently, $p_1(-x) = -p_2(x)$ and $p_2(-x) = -p_1(x)$. At $x = X$: $|Q(x)|$ is even and $\theta(x)$ is odd; equivalently, $p_1(x)$ is even and $p_2(x)$ is odd. The free energy, the order parameter and the spatial coordinate can be scaled as $F = \beta_1 \gamma^4 \bar{F}$, $p_j = \gamma \bar{p}_j$ $(j = 1, 2)$, and $x = \kappa \bar{x}/\Delta$, with $\gamma = \Delta/\sqrt{\beta_1 \kappa}$. The scaled density $\bar{\mathcal{F}}$ depends on only two parameters, $r = \beta_2/\beta_1$ and $\tilde{\alpha} = \kappa\alpha/\Delta^2$.

Table 1. Values of the anisotropy parameter $r = \beta_2/\beta_1$ used in the solution of equation (2). Column 2 gives numerical values for α_L (the value of α at the IC–C transition), column 3 the difference $\tilde{\alpha}_L - \alpha_L$ ($\tilde{\alpha}_L$ is the value of α for which the single-discommensuration state and the commensurate state have the same free energy), column 4 the discriminant at $\alpha = \tilde{\alpha}_L$, and column 5 the wavenumber q just above the IC–C transition.

r	$\kappa\alpha_L/\Delta^2$	$\kappa(\tilde{\alpha}_L - \alpha_L)/\Delta^2$	$\mathcal{D}$	$\kappa q/\Delta$
0.9	−0.5496	2.4×10^{-2}	44.0	0.765
0.8	−1.019	1.8×10^{-3}	18.0	0.568
0.7	−1.589	1×10^{-8}	1.9	0.201
0.685	−1.685	2×10^{-8}	−0.2	0.241
0.6	−2.305	9×10^{-6}	−11.6	0.343
0.5	−3.259	3×10^{-5}	−24.5	0.398
0.44	−4.017	1×10^{-4}	−32.0	0.416
0.4	−4.637	1×10^{-4}	−36.9	0.422
0.3	−6.856	6×10^{-5}	−46.0	0.413
0.2	−11.17	1×10^{-7}	−31.8	0.304
0.16	−14.35	0	3.6	0
0.1	−23.77	0	229.5	0

Column 1 of table 1 gives the values of the anisotropy parameter r at which the IC state and the IC–C transition were examined; $r = 0.44$ is believed appropriate for Cs_2ZnI_4 [11]. Some of the numerical results differ slightly from those of [18]. At the values $r \geqslant 0.2$ in the table, the transition is clearly first order numerically (and also analytically, as shown in [18] and in section 3). At the values $r \leqslant 0.16$, there is no evidence for a first-order transition, but a very weak one cannot be ruled out numerically or analytically. Of course there is no IC–C transition at $r = 0$; p_1 and p_2 are sinusoidal for all $\alpha < \Delta^2/\kappa$, with wavenumber $q = \Delta/\kappa$ and amplitude $[(\Delta^2/\kappa - \alpha)/\beta_1]^{1/2}$. Columns 2 to 5 give (2) the value α_L at the transition, (3) the difference between α_L and $\tilde{\alpha}_L$ (the latter is the value of α at which the single-discommensuration state and the C state have the same free energy), (4) the discriminant $\mathcal{D}$ (defined in the appendix) at $\alpha = \tilde{\alpha}_L$, and (5) the wavenumber q just above the transition. The nonmonotonic dependence of q on r (note the minimum

near $r = 0.69$) is clearly connected with the change discussed below in the asymptotic behaviour of the order parameter and the vanishing of the second-order interaction energy when $\mathcal{D} = 0$. Consequently the discontinuity in q cannot be used in general to estimate the anisotropy parameter.

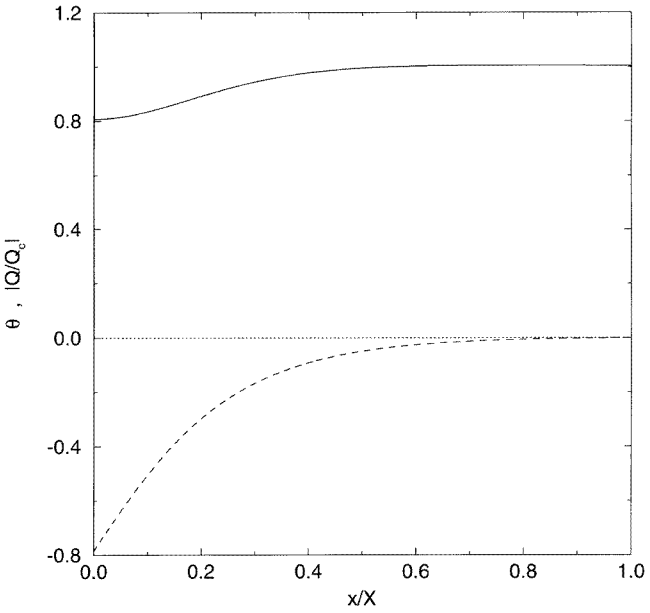

Figure 1. The reduced amplitude $|Q/Q_c|$ (solid line) and phase θ (dashed line) of the IC order parameter as functions of x/X for $r = 0.44$ (the value for Cs_2ZnI_4) at a temperature just above the IC–C transition. The point $x = 0$ is at the centre of a discommensuration and the point $x = X$ is mid-way between two discommensurations.

The order parameter is sinusoidal at the N–IC transition. At the IC–C transition it is solitonic at small r, but neither solitonic nor sinusoidal at $r = 0.9$. Figure 1 plots the amplitude and phase for $r = 0.44$ at T just above the IC–C transition. The phase increases monotonically. The amplitude at the centre of the discommensuration ($x = 0$) is reduced to 81% of the C value Q_c; it overshoots the C value (by a maximum of 0.5% at $x/X \approx 0.76$) over a broad region between the discommensurations (at $x = 0$ and $x = 2X$). Overshooting at the IC–C transition in a one-dimensionally IC system appears to have been noticed first in [21], for a charge-density-wave (CDW) model. The oscillations discussed in the appendix occur at larger discommensuration spacing.

3. Analysis of the IC–C transition

An analysis similar to the following (with minor differences) was given in [18]. The second-order interaction energy of discommensurations is obtained using $g_1 = -2\bar{\alpha}$ and $g_2 = -4r\bar{\alpha}/(1-r)$, with $\bar{\alpha} = \kappa\alpha/\Delta^2$, in the results of the appendix; the discriminant is

$$\mathcal{D} = 4 + 4(1+r)\bar{\alpha}/(1-r) + [(3r-1)\bar{\alpha}/(1-r)]^2. \tag{3}$$

For the purpose of examining the order of the transition, $\bar{\alpha}$, $\mathcal{D}$ and other quantities are to be evaluated at the temperature $\tilde{T}_L$ ($\tilde{\alpha}_L$ can be found from table 1). Figure 1 of [18]

($\hat{\alpha}$ and $\hat{\gamma}_2$ there are $\kappa\alpha/\Delta^2$ and r here) shows that $\mathcal{D}$ is negative in the central region of the α–r plane and positive elsewhere. The lines $\mathcal{D} = 0$ cross the IC–C transition line at $(\kappa\alpha/\Delta^2, r) \approx (-14, 0.16)$ and $(-1.7, 0.69)$, from table 1.

If the discriminant is positive, a simple analysis shows that equation (A9) gives four real decay constants. In agreement with equation (19) of [18], the square bracket in equation (A10) for the second-order interaction energy is

$$B = \mathcal{D}^{1/2} + 2 - (1 - 3r)\bar{\alpha}/(1 - r) = -(2\kappa a/\Delta)(d_2/d_1). \tag{4}$$

For strong anisotropy ($r \gtrsim 0.69$), B is negative and the transition is first order [18]. For weak anisotropy ($r \lesssim 0.16$), B is positive (suggesting a second-order transition) but no conclusion can be drawn about the order without further analysis, for equation (A10) gives only the asymptotic interaction; a numerical investigation of the dependence of $F - F_c$ on X is required. An extensive search for an interior minimum was conducted at $r = 0.1$ and 0.16, but none was found. For intermediate anisotropy ($0.16 \lesssim r \lesssim 0.69$), the discriminant is negative and the transition is first order (as shown in the appendix).

4. Comparison with experiment

The experimental results, plus the theoretical value of α_L, give only five relations for the six parameters of the minimal Landau theory. Explicitly, the experimental results for (a) the wavenumber at T just below T_I, (b) the heat capacity C_p at T just below T_I (relative to the value at high T), (c) the heat capacity at T just below T_L, (d) the value of T_I (116.9 K), (e) the value of T_L (107.6 K), plus some straightforward analysis, give [11]

$$q(T_I^-) = 0.135\, a^* = \Delta/\kappa \tag{5a}$$

$$C_p(T_I^-) = 0.54\, R = T_I\alpha_0^2/(2\beta_1) \tag{5b}$$

$$C_p(T_L^-) = 0.88\, R = T_L\alpha_0^2/[2(\beta_1 - \beta_2)] \tag{5c}$$

$$\alpha_0(T_I - T_0) = \Delta^2/\kappa \tag{5d}$$

$$\alpha_0(T_L - T_0) = \alpha_L \tag{5e}$$

where R is the gas constant. Despite the incomplete determination of the parameters, checks of the theory are provided by measurements of two separate quantities, the IC-phase wavenumber as a function of T (particularly the discontinuity at the IC–C transition) and the entropy change at this transition. Equations (5*b*) and (5*c*) give immediately $\beta_1/\alpha_0^2 = 108._2$ K/R and $r = \beta_2/\beta_1 = 0.43_5$, both as in [11].

In the constant-amplitude approximation, the solution of the Euler–Lagrange equation for the phase is $\cos(2\theta) = \mathrm{cd}(\lambda x|m)$ where $\lambda = 2|Q|\sqrt{\beta_2/(m\kappa)}$ and cd is the Jacobian elliptic function [22]; the average density is given by equation (2) of [11], but the following replacements must be made to conform with the conventions of [22]: $K(u) \to K(m)$, $E(u) \to E(m)$ and (except in the arguments of the elliptic integrals) $u \to \sqrt{m}$. For $r = \beta_2/\beta_1 = 0.44$, one finds the following results at the IC–C transition: $\alpha_L = -3.438\,\Delta^2/\kappa$, the discontinuity in the wavenumber is $\Delta q = 0.750\,\Delta/\kappa$ (as in [11]), and the change in the entropy is $\Delta S = 0.550\,\alpha_0\Delta^2/(\beta_1\kappa)$. Melero *et al* [11] obtained the first and third of these but did not quote the values. Equations (5) then give $\Delta/\alpha_0 = 15.5$ K$(a^*)^{-1}$, $\kappa/\alpha_0 = 115$ K$(a^*)^{-2}$ and $T_0 = 114.8$ K; these differ slightly from the values quoted in [11], for unknown reasons. The entropy change is then $\Delta S = 0.0106\,R$ (versus $0.010\,R$ [11]).

Full numerical solution of the Euler–Lagrange equations (for $r = 0.44$) gives significantly different values, namely $\alpha_L = -4.017\,\Delta^2/\kappa$, $\Delta q = 0.416\,\Delta/\kappa$, and $\Delta S =$

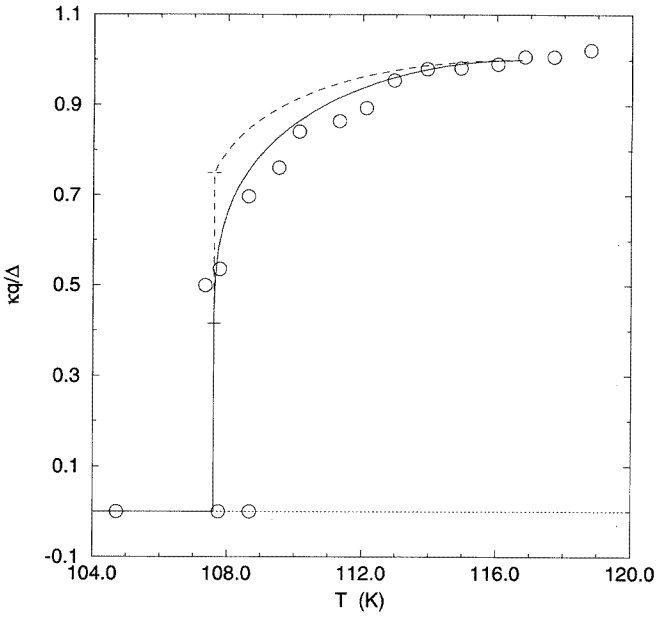

Figure 2. The reduced wavenumber $\kappa q/\Delta$ in the IC phase of Cs_2ZnI_4. The points are the experimental values (from [11]); the solid line gives the rigorous numerical result and the dashed line the constant-amplitude approximation, both for $r = 0.44$. The N–IC and IC–C transitions occur at 116.9 K and 107.6 K; the short horizontal lines mark the discontinuity at the latter.

$0.289\,\alpha_0\Delta^2/(\beta_1\kappa)$. The revised parameters are $\Delta/\alpha_0 = 13.7\ \mathrm{K}(a^*)^{-1}$, $\kappa/\alpha_0 = 102\ \mathrm{K}(a^*)^{-2}$ and $T_0 = 115.0$ K, giving $\Delta S = 0.0049\,R$.

Figure 2 compares the measured wavenumber $\kappa q/\Delta$ in the IC phase with the two numerical results (for $r = 0.44$); the horizontal and vertical axes have been scaled, but the comparison does not otherwise involve the Landau parameters. The measured discontinuity in q at T_L is 50% of the value at the N–IC transition (this may be an overestimate, because of sample inhomogeneities), in good agreement with the rigorous numerical result (42%) and poor agreement with the result of the constant-amplitude approximation (75% [11]). The rigorous numerical result for the temperature dependence of q also agrees better with experiment, but the predicted dependence is too strong.

The entropy change at the IC–C transition is given as $\Delta S = 0.035\,R$ in [11] and $0.02\,R$ in [12], but both are overestimates because of the difficulty in removing background. The rigorous numerical result, $\Delta S = 0.0049\,R$, is considerably smaller. There seems then no justification for presenting the predictions of the minimal model for the heat capacity.

Of course the minimal model must fail quantitatively unless the order parameter (which, unfortunately, cannot be measured directly) remains small throughout the IC phase. One justification for the use of the minimal model, as a first approximation, is that T_L is close to T_I: $T_L \approx 0.92T_I$. A second is that the thermodynamic data are consistent with the integrated intensity of the x-ray satellite peak in the sense that the value of $|Q|^2$ obtained from the Landau theory scales with the latter [11]. But without estimates of the coefficients of the higher-order terms, neither can one rule out the possibility that the agreement found above is fortuitous; in fact, the evidence is that the higher-order terms have significant effects.

Acknowledgment

This research was supported by the Natural Sciences and Engineering Research Council of Canada.

Appendix. Asymptotic interaction of discommensurations

This appendix determines the interaction energy of discommensurations, following [20]; the approach, which grew out of the theory of superconductivity, has been applied to other IC systems [23, 24, 18, 25, 26, 27, 28], but all these previous results are model specific. The following provides a general method for finding the interaction energy, and obtains results valid for a wide class of models, including the density of equation (1*b*); the following restrictions apply: (a) the primary order parameter has two components, (b) any secondary order parameters can be eliminated explicitly in favour of the primary order parameter, (c) the incommensurate state is driven by a Lifshitz invariant and is spatially dependent in only one direction, (d) the discommensurations are equally spaced and contribute equally to the free energy, (e) systems with continuously degenerate commensurate states (such as the frustrated antiferromagnet $CsCuCl_3$ [29] and some liquid crystals [30]) are excluded, plus a few other mild restrictions noted below.

The free-energy density is assumed to have the form

$$\mathcal{F}[p_1, p_2] = G(p_1, p_2) - D(p_1, p_2)\,(p_1 p_2' - p_2 p_1') + \tfrac{1}{2}K(p_1, p_2)\,[(p_1')^2 + (p_2')^2] \qquad \text{(A1)}$$

where the primes denote differentiation with respect to x; all derivatives are written explicitly. G, D and K are analytic functions of p_1 and p_2 with no explicit dependence on x; they can include external fields provided that these do not favour any commensurate state over any other (violating restriction (d) above). The commensurate states are given by $\theta = m\,2\pi/n$, $m = 0, \ldots, n-1$, through an anisotropy term like $-|Q|^n \cos(n\theta)$ in G. The functions D and K may include higher-order terms in the Landau expansion in the strict sense; for example, the forms $D = \Delta_1 + \Delta_2(p_1^2 + p_2^2)$ and $K = K_a + K_b(p_1^2 + p_2^2)$ are important in the theory of liquid crystals (the Δ_2 term is responsible [27] for the re-entrance of the smectic-C* phase under transverse magnetic field [31]). Or D and K may include terms generated on eliminating secondary order parameters.

The discommensuration spacing is $2X$, so the sample contains $N_{dc} = L/(2X)$ discommensurations; their interaction energy (which vanishes as $X \to \infty$) is defined by

$$[F(X) - F_c]/L = (F_s - F_c)/(2X) + F_{inter}(X)/L \qquad \text{(A2)}$$

where F, F_c and F_s are the free energies of the IC, C and S states; the last is the state with a single discommensuration, with order parameter p_{sj} and density $\mathcal{F}_s = \mathcal{F}[p_{s1}, p_{s2}]$. By assumption, attention can be focused on one discommensuration, taken to be centred at $x = 0$ where $\theta = -\pi/n$; boundary conditions are given below equation (2). A rearrangement of equation (A2) gives

$$\frac{F_{inter}(X)}{L} = \frac{1}{2X}\int_{-X}^{X} (\mathcal{F} - \mathcal{F}_s)\,\mathrm{d}x - \frac{1}{2X}\left(\int_{X}^{\infty} + \int_{-\infty}^{-X}\right)(\mathcal{F}_s - \mathcal{F}_c)\,\mathrm{d}x. \qquad \text{(A3)}$$

Analytical determination of $F_{inter}(X)$ is possible only for large X. In the first integral ($|x| \leqslant |X|$), the IC order parameter is written as $p_j(x) = p_{sj}(x) + \tilde{p}_j(x)$ where $\tilde{p}_j(x)$ is the perturbation due to the other discommensurations. In the other two integrals ($|x| \geqslant X$), the S order parameter is written as $p_{sj}(x) = p_{cj} + \delta_j(x)$; the commensurate values p_{cj} are different in the two regions (for $x \geqslant X$, $p_{c1} = p_c$ and $p_{c2} = 0$). With this choice of signs,

the deviations δ_j (which go to zero as $|x| \to \infty$) are negative if the approach to the C values is monotonic. The perturbations and the deviations are of the same size.

The first variation of the density,

$$\delta\mathcal{F} = \delta p_1\,(\delta\mathcal{F}/\delta p_1) + \delta p_2\,(\delta\mathcal{F}/\delta p_2) + \left[D(p_2\,\delta p_1 - p_1\,\delta p_2) + K\left(p_1'\,\delta p_1 + p_2'\,\delta p_2\right)\right]' \tag{A4}$$

gives the Euler–Lagrange equations as

$$\delta\mathcal{F}/\delta p_1 = G_1 - 2Dp_2' - D'p_2 - D_1(p_1p_2' - p_2p_1') - (Kp_1')' + \tfrac{1}{2}K_1[(p_1')^2 + (p_2')^2] = 0 \tag{A5a}$$

$$\delta\mathcal{F}/\delta p_2 = G_2 + 2Dp_1' + D'p_1 - D_2(p_1p_2' - p_2p_1') - (Kp_2')' + \tfrac{1}{2}K_2[(p_1')^2 + (p_2')^2] = 0 \tag{A5b}$$

where $G_j = \partial G(p_1, p_2)/\partial p_j$, etc. The second variation is then

$$\delta^2\mathcal{F} = \left[(D_1\delta p_1 + D_2\delta p_2)(p_2\delta p_1 - p_1\delta p_2) + K\left(\delta p_1\delta p_1' + \delta p_2\delta p_2'\right) + (K_1\delta p_1 + K_2\delta p_2)\left(p_1'\delta p_1 + p_2'\delta p_2\right)\right]'. \tag{A6}$$

These give the density differences in equation (A3) as perfect derivatives to the second order required by a cancellation in first order.

By symmetry, the terms evaluated at $x = \pm X$ are identical; symmetry also relates the perturbations and the deviations by $\tilde{p}_1(X) = \delta_1(X)$, $\tilde{p}_2(X) = -\delta_2(X)$, $\tilde{p}_1'(X) = -\delta_1'(X)$, and $\tilde{p}_2'(X) = \delta_2'(X)$. To leading order, the interaction energy is then

$$F_{\text{inter}}^{(2)}(X)/L = X^{-1}\left[2\Delta\delta_1\delta_2 + \kappa\left(\delta_1\delta_1' - \delta_2\delta_2'\right)\right]_{x=X} \tag{A7}$$

where we have $2\Delta = 2D_c + p_c\ \mathrm{d}D_c/\mathrm{d}p_c$ and $\kappa = K_c$, with $D_c = D(p_c, 0)$, $\mathrm{d}D_c/p_c = \partial D(p_1, p_2)/\partial p_1$ at $(p_1, p_2) = (p_c, 0)$, etc; the superscript is a reminder that the energy is obtained to only second order. The derivative-free part G of the density appears only implicitly in equation (A7), through the deviations.

Linear differential equations for the deviations are obtained by expansion of the Euler–Lagrange equations (A5) about the C state to first order in δ_j:

$$-\kappa\delta_1'' - 2\Delta\delta_2' + G_{c11}\delta_1 = 0 \tag{A8a}$$

$$-\kappa\delta_2'' + 2\Delta\delta_1' + G_{c22}\delta_2 = 0 \tag{A8b}$$

where $G_{cij} = \partial^2 G(p_1, p_2)/\partial p_i\partial p_j$ at $(p_1, p_2) = (p_c, 0)$; the quantity G_{c12} vanishes if G has the form $G(p_1, p_2) = f_1(|Q|) - f_2(|Q|)\cos(n\theta)$ with $f_2 > 0$. Substitution of the solutions $\delta_j(x) = d_j\exp(-ax)$ gives the ratio of the amplitudes as $d_2/d_1 = (\kappa a^2 - G_{c11})/(2\Delta a)$; the allowed values of the decay constant a are given by

$$(\kappa a/\Delta)^2 = \left[\tfrac{1}{2}(g_1 + g_2) - 2\right] \pm \mathcal{D}^{1/2} \tag{A9}$$

where $g_j = \kappa G_{cjj}/\Delta^2$, and the discriminant is $\mathcal{D} = \left[\tfrac{1}{2}(g_1 + g_2) - 2\right]^2 - g_1g_2$.

These results for the second-order interaction energy are valid at all T (damped oscillations of the interaction potential have been observed [32] in Rb_2ZnCl_4), but they are useful for determining the order of the IC–C transition only at the temperature $T = \tilde{T}_L$ ($\alpha = \tilde{\alpha}_L$) where the S and C states have the same free energy (the energy does not change if a single discommensuration enters the C state). Some numerical effort may be necessary to estimate $\tilde{\alpha}_L$, but an accurate value is not needed in most cases. If $F_{\text{inter}}(X)$ (not $F_{\text{inter}}^{(2)}(X)$) is positive for all X at $\tilde{T}_L$ (it vanishes typically as $\exp(-2aX)/X$ in this case), energy is required to introduce more discommensurations; the IC–C transition is second order,

occurring at $T = \tilde{T}_L$. If, on the other hand, $F_{\text{inter}}(X)$ is negative for some X at $T = \tilde{T}_L$, energy can be gained if more discommensurations enter; a first-order transition occurs at some $T < \tilde{T}_L$.

If the discriminant is positive, one usually finds four real decay constants, two positive and two negative (the latter correspond to approach of the C-state values from $x > X$ and are of no interest); imaginary solutions are occasionally found. With a the smaller of the two positive decay constants, the second-order interaction energy is

$$\frac{F^{(2)}_{\text{inter}}(X)}{L} = d_1^2 \frac{\Delta^2}{2\kappa} \frac{\mathrm{e}^{-2aX}}{aX} \mathcal{D}^{1/2} \left[\mathcal{D}^{1/2} + 2 + \frac{1}{2}(g_1 - g_2) \right]. \tag{A10}$$

This vanishes when $\mathcal{D} = 0$, as found previously for specific models [18, 27]. No conclusion can be drawn without further analysis, which requires a specific model; the square bracket B in equation (A10) must be examined, as done in [20]. If $B < 0$, the transition is first order. If $B > 0$, the transition is not necessarily second order because of the possibility (raised and examined in [20]) that there exists an interior minimum where the interaction energy is negative; in this case the above analysis is inconclusive, and a full numerical treatment is necessary.

A consequence is that a point where the discriminant vanishes is not necessarily a multicritical point where the IC–C transition changes from first order ($\mathcal{D} < 0$) to second order. Some of the literature assumes that the transition is second order when $\mathcal{D} > 0$; this assumption, which is unjustified for any model without further analysis, is incorrect for several models [18], including the model of equation (1*b*) when $r \gtrsim 0.69$.

If the discriminant is negative, on the other hand, the transition is unambiguously first order. The second-order interaction energy is formally

$$\begin{aligned} \frac{F^{(2)}_{\text{inter}}(X)}{L} = |d_1|^2 \frac{\mathrm{e}^{-2a_R X}}{4X} \{ & \left[\left(2\Delta d_2/d_1 - \kappa a + \kappa a |d_2/d_1|^2 \right) + \text{CC} \right] \\ & + \left[\mathrm{e}^{-2\mathrm{i}a_I X} \mathrm{e}^{2\mathrm{i}\psi_1} \left(2\Delta d_2/d_1 - \kappa a + \kappa a (d_2/d_1)^2 \right) + \text{CC} \right] \} \end{aligned} \tag{A11}$$

where the real part a_R of the decay constant is positive; the deviations have been written as $\delta_j(x) = \frac{1}{2} d_j \exp(-a_R x - \mathrm{i}a_I x) + \text{CC}$ with complex amplitudes $d_j = |d_j| \exp(\mathrm{i}\psi_j)$. But the first square bracket vanishes identically because

$$2\Delta d_2/d_1 - \kappa a + \kappa a |d_2/d_1|^2 = G_{\text{c}11}(a - a^*)/|a|^2 \tag{A12}$$

and so equation (A11) simplifies to

$$\frac{F^{(2)}_{\text{inter}}(X)}{L} = |d_1|^2 \, \frac{\Delta^2}{2\kappa} \, \frac{\mathrm{e}^{-2a_R X}}{|a| X} \, (-g_1 \mathcal{D})^{1/2} \, \cos(2a_I X + \psi) \tag{A13}$$

where ψ is an unknown phase. The right-hand side can be made negative, and so the transition is always first order when the discriminant is negative at $T = \tilde{T}_L$. Of course the second-order interaction energy must vanish when $\mathcal{D} = 0$ is approached from $\mathcal{D} < 0$ as well as from $\mathcal{D} > 0$ (see equation (A10)), but this has not been demonstrated previously.

In some of the literature, the analysis for complex decay constants is stopped at equation (A11), leading to the incorrect conclusion that the second-order interaction energy has the form

$$F^{(2)}_{\text{inter}}/L = \exp(-2\alpha_R X)[C_1 + C_2 \cos(2\alpha_I X + \psi)]/X$$

with $C_1 \neq 0$; the possibility of a second-order transition (when $C_1 > |C_2|$) is firmly denied by equation (A13). The equivalent of equation (A12) was used for a CDW model in [20] (which did not simplify the second square bracket). Equation (8.21) of [20], which is easily obtained from the above results, is correct, contrary to the statement in [23].

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