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COMMENSURATE-INCOMMENSURATE PHASE TRANSITIONS.

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1. Soliton interaction

Phase transitions from commensurate to incommensurate state(CIT) were observed in numerous physical systems (see Table 1; for a recent review see

	The physical systems displaying the incommensurability	Incommensurate subsystems	Examples
1	Helimagnets	Spins and ions	Ce,ErPb3,HoPb3,ErTl3 HoTl3
2	Helical ferroelectrics	The polarization and a fundamental lattice	K ₂ SeO ₄ , Rb ₂ ZnCL ₄
3	Chiral smectics C	Director orientation and density	DOBAMBC (in the magn. field)
4	charge density waves	The Peierls charge modu- lation and a fundamental lattice	$\begin{array}{cccc} TTFTCNQ \\ Hg_{3-x}AsF_{6} \\ K_{0.30} & MOO_{3} \\ TaSe_{2} \\ \end{array} \begin{array}{c} 1d \\ 2d \end{array}$
5	Spin density waves	The Peierls spin modula- tion and a fundamental lattice	Ni _{0.92} Zn _{0.08} Br ₂
6	Submonolayers of adsorbed atoms on crystal faces	A lattice of an overlayer and a lattice of subs- trate	Ar,Kr,Xe,H ₂ ,N ₂ etc on graphite : Na,K,Ba,Sr,O ₂ ,Xe on W,Mo,Cu,Ni
7	Atoms and molecules interca- lated into graphite	A lattice of intercalated atoms and a matrix lattice	Br ₂
8	Reconstructed faces of crystal, interfaces	Surface and bulk lattices	?
9	Superconducting films with the modulated thickness in the transverse magn. field	The vortex lattice and the modulation	AL films
10	Electrons on the liquid He sur- face over a periodic electrode	The Wigner electron lat- tice and modulation	2

T A B L E 1

[1-2]). The incommensurate structures arise as a result of competition of two different periods fixed by different forces, e.g. a substrate and an overlayer periodicity in a system of adsorbed atoms on a crystal surface, or a lattice and exchange forces periodicity in helimagnets etc.

A misfit is localized in a set of topological defects : domain walls or solitons. The dimensionality of these defects is less by unity than the dimensionality of a system. At zero temperature solitons form a periodic superstructure as it was predicted by Frank and Van der Merwe [2]. According to continuum theory, soliton interaction decreases at large distances exponentially. Continuum theory is invalid at large distances due to contribution of nonlocal powerlike interactions [3],[4].

As a result, the mechanical interaction between solitons decreases always powerlike at large distances. Assuming solitons provide compression or rarification of particles, the powerlike interaction is

$$\mathcal{E}_{int} = const \cdot l^{d-\alpha - 1}, \qquad (1)$$

where α is the exponent corresponding to the interaction between particles, d is the real space dimensionality and ℓ is the distance between solitons. For d=3 and for direct Coulomb and multipole interaction the constant turns to zero, and effective interaction is exponentially decreasing. However, at least Van der Waals forces always give a nonzero contribution to the powerlike interaction in 3 dimensions resulting in the law const $\cdot \ell^{-4}$ with a negative constant. Dipole and multipole forces are effective in 2-dimensional systems.

If a soliton lattice has crossing points they contribute extra energy approximately indendently if they are sufficiently far distanced [5]. Heat fluctuations strongly affect the soliton interaction in one and two dimensions. They totally destroy any long-range order in one dimension. In two dimensions they give rise to the soliton bending and collisions implying an additional effective repulsion between solitons which can be evacuated as

$$\varepsilon_{int}^{h} = \frac{\pi^2 T^2}{6 K \ell^2} . \qquad (2)$$

Here T is the temperature, K is the effective elastic constant of an individual soliton lines, connected with an effective elastic constant of particles $\bar{\lambda}$ and a renormalized amplitude of periodic potential \bar{V} and the lattice constant a by the relationship :

$$K = \sqrt{\bar{\lambda} \, \bar{V}} \, \alpha \,. \tag{3}$$

The result (2) was first obtained in the works [6,7] and then it was redireved by many authors [8]. Normally the fluctuation-induced interaction plays the main role at large distances.





Fig. 1 Bragg reflections of Xe on (110)Cu face. ∇-peaks of diffraction by diffraction by copper, *-peaks of diffraction by Xe, a and b coalesce in the commensurate phase. Experiment was made by LEED method [9].



- Fig. 2a Arrangement of the commensurate structure molecules N₂ adsorbed on graphite [10].
- Fig. 2b The LEED diffraction pattern for the incommensurate phase. It corresponds to striped phase. The hexagonal symmetry would result in six-fold splitted sattelite lines. A seeming hexagonal symmetry is due to polycrystal [10].

2. Soliton structures in anisotropic systems

When one or both of twocompeting periodic structures is highly anisotropic, theory predicts a striped soliton structure [7]. This prediction was experimentally confirmed for Xe atoms adsorbed by the anisotropic surface (110) of Cu [9], for N₂ molecules adsorbed on graphite [10] and for Br₂ molecules intercalated in graphite [11] (see Figs 1 and 2).

Minimizing the energy per unit area of a soliton system the density of solitons near CIT, proportional to the shift of Bragg reflexes can be shown to be proportional to $(\delta - \delta_c)^{\frac{1}{2}}$, where δ is a parameter governing the incommensuracy [6,7]. For the case of adsorbed atoms δ can be identified with the chemical potential of the gas in equilibrium with the overlayer, while for the intercalated system δ is the temperature, and for superconducting film and helical magnets δ is the external magnetic field. This theoretical prediction was convincingly confirmed by the experiments [10] and [11] (see Figs 3 and 4).



Fig. 3 The dependence of the inter-satellite distance (soliton density) on chemical potential for Xe on Cu(110). Chemical potential is fixed with the temperature and pressure of the gaseous Xe in equilibrium with the overlayer [9].



- Fig. 4a Schematic picture of Bragg reflexes for Br₂ intercalated into graphite (X-ray diffraction pattern). Arrows show the direction of motion of reflexes in the incommensurate phase. Here the governing parameter is the temperature. [11]
- Fig. 4b The dependence of the satellites splitting (shift) on the temperature for different commensurate Bragg reflexes. Solid curves correspond to the square-root dependence [11].

The value $\delta_{\mathbf{C}}$ is associated with the amplitude $\overline{\mathbf{V}}$ of an effective periodic potential and an effective elastic constant $\overline{\lambda}$ by the equation

$$\delta_c = \left(\overline{V}_{\overline{\lambda}} \right)^{\frac{1}{2}} . \tag{4}$$

Theory [6,7] predicts a strong decrease of effective periodic potential with the temperature and turning it into zero at critical temperature,

$$T_{c} = \frac{4}{\pi} \overline{\lambda} \alpha^{2} . \qquad (5)$$

The dependence $\overline{V}(T)$ is defined by equation

$$\overline{V}(T) = \overline{V}(o) \left[\overline{V}(o)/\overline{\lambda} \right]^{1-\frac{1}{2}} .$$
(6)

So the phase diagram in a vicinity of some definite commensurate phase has a form depicted in Fig. 5. The existence of the critical temperature was confirmed in the experiments by Martinoli et al.[12]. Martinoli et al. [13] established the form of CIT curve which fits very well the Eq. (6). Details can be found in the report by Martinoli at this conference. It should be noted that the superconducting films with modulated thickness represent a unique realization of ^a two-dimensional Sine-Gordon field.



Fig. 5 Phase diagram in the vicinity of a commensurate phase

3. Soliton structures in the isotropic case

These systems are much less investigated theoretically. For the case of zero temperature two alternative possibilities are predicted by the theory [5] first-order CIT into a hexagonally-symmetric soliton structure or second-order CIT into a striped soliton structure. This conclusion agrees with recent experiments (Kr adsorbed on graphite at $T \approx 50$ k [14]) and direct observations of a striped soliton structure in electronic microscope in Ta Se₂ [15,16,17]

The thermodynamics of these systems is not yet clear, though some preliminary semiqualitative arguments have been presented [18,19]. Experiments [20,21] with Kr on graphite at T \approx 90 k give the value 1/3 for the critical exponent β , the same as for 3-state Potts model. It gives rise to some theoretical speculations on the possible analogy between these systems [22].

4. <u>Points defects in commensurate and striped soliton structures</u> in two dimensions

Effects of dislocation on a striped incommensurate structure were studied theoretically in the works [19,23-25]. The stability of a soliton system with respect to the spontaneous creation of dislocations depends substantially on the number p of equivalent states (sublattices) accessible for an overlayer in the commensurate phase. In the works [24,19] the soliton system was shown to be unstable at low temperatures and sufficiently low distances for $p < \sqrt{8}$, i.e. for p = 1.2. For p = 2 the liquid phase separates commensurate and incommensurate crystals up to zero temperature. The commensurate-to-liquid phase transition is of the Ising type [26]. CIT is , as always, similar to that in XY-model. For p = 1 the long-range commensurate order can not be destroyed by heat fluctuations [27]. For p > 2 the commensurate phase transits only into incommensurate phase, and this last transits into liquid [27].

Experimentally there exist systems with p = 1 [12], p = 2 [9], p = 3 [10] and p = 7 [12]. However the detailed experimental phase diagram of these systems is not yet available.

5. Effects of discretness

The most important is effect of a soliton-pinning by the lattice [28,29]. It results in existence of pinned soliton structures in some region of governing parameter δ . In one dimension all the pinned structures are regular. The soliton concentration corresponding to a pinned structure is always a rational number $c = m/\ell$, where ℓ is the period of structure and m the number of solitons per elementary cell. Concentration represents a Cantor function of δ . The set of commensurate soliton phases at T = 0 can be also described as a branching sequence, in which between any two phases with elementary cells A and B a phase with elementary cell AB exists [30]. The

geometric construction of an elementary cell by the expansion of concentration C into a continuous fraction was indicated earlier [31,32]. The sequence of commensurate soliton phases has an explicitly pronounced scaling character as it is shown in Fig. 5 [30].

For two-dimensional anisotropic case each commensurate soliton structure persists up to a finite temperature $T_C(l) \sim [ln(V"(l))]^{-1}$ where V(l) is the effective potential interaction between solitons. Considering three phases only A,B and AB, it is possible to prove that the incommensurate phase is stable in the interval of temperature between the critical temperatures of phases A or B and that for the phase AB and in the interval of δ between critical curves for CIT at the fixed temperature. The heat fluctuation creates kinks on solitons interchanging neighbouring cells A and B. If z is the fugacity of a kink, then the critical point of existence of any commensurate soliton phase is defined by equation :

$$z = \mathcal{V}''(\ell) \tag{7}$$

where ℓ is the period of the phase under consideration. The property of the system near any critical point can be described by XYZ model [33]. The phase diagram in two dimensions represents also the scaling picture (Fig. 6).



Fig 6. Phase diagram for two-dimensional anisotropic case

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All the commensurate soliton phases are situated in the region of an incommensurate phase. The schematic phase diagram for p = 2 is shown in Fig.7.



Fig. 7 Schematic phase diagram for p = 2

Though there is no experimental evidence of existence of such a phase, something similar has been found recently for Ising-like layered magnets CeSb and CeBi [34,35]. I do not see any principal objection for the existance of commensurate soliton phases. Most probably, they can be found for not very small values V/λ in such a system as Br_2 intercalated into graphite [12] or Sodium and Potassium atoms on the surface of W,Mo,Cu,Zn [1].

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