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SPIN-PEIERLS INSTABILITY IN THE QUASI d=1 MAGNETOSTRICTIVE XY MODEL*

by

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ABSTRACT

We discuss, within a framework where the magnetic (structural) degrees of freedom are exactly (adiabatically) taken into account, the spin-Peierls instability occuring in the magnetically one-dimensional and structurally three-dimensional magnetostrictive spin-$\frac{1}{2}$ XY model. Emphasis is given to the influence of an external magnetic field (along the Z-axis) on the thermodynamical (phase diagram, structural order parameter, specific heat, magnetization, susceptibility) and dynamical (acoustic and optic phonons spectrum) quantities. We recover and extend several already known results; furthermore a certain amount of facts is established and possible new effects are exhibited. In the T-H phase diagram, a *structural* Lifshitz point (LP) exists where the uniform (U), *pure* dimerized (D) and modulated (M) phases converge (the relative arrivals, on the LP, of the three critical and two metastability lines are determined); another special point is detected on the U-M line at large magnetic fields; the slope of the D-M first-order frontier is discussed; for high elastic constants, fixed temperatures and increasing magnetic field, the unusual sequence (non uniform) - uniform - (non uniform) - uniform is possible. The thermal dependence of the sound velocity presents a gap. The present theory is hopefully applicable (at least qualitatively) to substances like TTF-BDT, MEM(TCNQ)$_2$ and eventually alkali-TCNQ.

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I - INTRODUCTION

An interesting type of structural phase transition driven by magnetic interactions occurs in insulating substances like TTF-Cu BDT, TTF-Au BDT, TTF-Cu BDSe, MEM(TCNQ)$_2$ (eventually some alkali-TCNQ). These systems are structurally *three-dimensional* (a fact which makes possible the spontaneous break-down of symmetry) although quasi *one-dimensional* in what magnetic interactions are concerned. It is by now well established (see Bray et al [1] for an excellent review of the present experimental and theoretical state of the art) that the underlying phenomenon is the so called spin-Peierls instability (SPI). This type of phenomenon (basically a structural *dimerization*, or even a more complex *modulation*, of an *uniform* linear chain, i.e. presenting chemical units which are equidistant along the chain) can in principle occur in any quasi-one-dimensional crystalline system in which free (or almost free) *fermionic* particles (electrons for the standard Peierls instability, associated with a conductor-insulator phase transition) or quasi-particles (spinless magnetic excitations for the spin-Peierls instability). The typical modification, under dimerization, of the fermionic spectrum is depicted in Fig. 1a; the T=0 associated free energy variation ΔF_m is presented, together with a typical elastic contribution ΔF_e, in Fig. 1b. By increasing the temperature T, ΔF_m becomes a smoother and smoother function of the dimerization η in the neighborhood of $\eta=0$, up to the point where ΔF_e "wins the game" and the phase transition from the dimerized (D) phase to the uniform (U) one occurs.

Magnetic interactions in real substances (exhibiting the SPI) known up to now are Heisenberg-like, however nothing but a moderate weakening of the phenomenon happens if we assume instead XY-like interactions (which share with the Heisenberg ones the fact of being associated with a *continuous* group of symmetry, contrarily to the Ising model for which the T=0 SPI does not exist [2-4]), and we benefit from the advantage of being theoretically tractable on *exact* grounds. The work of the Rio de Janeiro group follows along this line.

Pincus [5] showed in 1971 that an XY antiferromagnetic chain is, at T=0, unstable with respect to dimerization. Beni and Pincus [6] exhibited next that this instability in-

duces a second order phase transition between the U and D phases, under the assumption that *no other phases* have to be considered. Dubois and Carton [2] proved next that the structural order which appears at the critical temperature T_c is indeed a *dimerization*. Finally we have recently exhibited [7] that below T_c down to T=0, *no other contributions* to the structural order appear that the *pure dimerization* one (as a matter of fact this seems to be still true [4] in the presence of an XY coupling anisotropy [2,3]). If we apply now a magnetic field H (along the Z-axis) on the system, the wavevector q_c characterizing the structural mode which will become unstable might no longer be that corresponding to a dimerization (i.e. $q_c = \pi/a$ in the extended first Brillouin zone; a ≡ crystalline parameter), and consequently phase transitions towards a new phase, namely the modulated (M) one, might occur. The influence of H on q_c has been detected both theoretically [8,9] and experimentally [10]. The detail of this influence has been recently exhibited [11] (for selected values of the elastic constant) along the complete U-(non U) second order critical line in the T-H space. Two special points have been shown on this line: the first of them (associated with $q_c=\pi/a$) clearly plays the role of a *structural Lifshitz point* (its existence had previously been detected for the Heisenberg model [12-14]); the second one (associated with $q_c=0$) presents a peculiar nature (later on we come back onto this point) and, to the best of our knowledge, had never been exhibited before. We respectively dedicate Sections II and III to the analysis of the T-H phase diagram and to the presentation of the results concerning the main thermodynamical quantities.

II - MODEL, FORMALISM AND PHASE DIAGRAM

Let us consider a fixed length cyclic linear chain (a being the unitary crystalline parameter in the U phase) of spins 1/2 whose Hamiltonian is given by

$$\mathcal{H} = -\sum_{j=1}^{2N} J_j (S_j^x S_{j+1}^x + S_j^y S_{j+1}^y) - \mu H \sum_{j=1}^{2N} S_j^z + \sum_{j=1}^{2N} \frac{C}{2}(X_{j+1}-X_j)^2 \qquad (1)$$

where J_j ≡ local exchange integral = $J(0)+J'(0)(X_{j+1}-X_j)$ (typically $J(0) < 0$ and $J'(0) > 0$), μ ≡ elementary magneton, $H \geq 0$ (convention), C ≡

nearest-neighbors harmonic elastic constant, $X_j \equiv$ *mean* position of the j-th spin with respect to its position in the U phase (adiabatic approach) and where, for future convenience, we have considered an even number of spins; it can be shown [15] that the introduction of higher-order terms in the expansion of J_j as well as in the elastic contribution to Hamiltonian (1) provides relatively irrelevant consequences. By Jordan-Wigner transforming the spin operators into fermionic creation and annihilation ones, then introducing Fourier transformed quantities and finally diagonalizing s x s matrices, it is possible to decompose Hamiltonian (1) in the form $\mathcal{H} = \mathcal{H}_o^{(s)} + V^{(s)}$, where the superscript (s) indicates s spins per unitary crystalline cell ($\mathcal{H}_o^{(1)}$ and $\mathcal{H}_o^{(2)}$ respectively refer to the U and D chains; $s \geq 3$ refer to structural configurations of the M phase which, as the D phase, are comensurable with the U chain); $\mathcal{H}_o^{(s)}$ essentially represents an ideal gaz of pseudo-fermions whose spectrum contains s bands (Fig. 1a represents the $s = 1$ spectrum). Through quite complex and tedious calculations within the temperature-dependent Green functions framework, it is possible to treat $V^{(s)}$ as a perturbation to $\mathcal{H}_o^{(s)}$ and obtain, as a function of $t \equiv k_B T/|J(0)|$, $h \equiv \mu H/|J(0)|$, $K \equiv C|J(0)|/|J'(0)|^2$ and the s-merization long range order parameter η_s, the reduced free energy of the system

$$f(t,h,K;\eta_s) \equiv \frac{F}{N|J(0)|} = f_o^{(s)}(t,h,K;\eta_s) + \frac{1}{2}\sum_{\alpha=1}^{s} \sum_{-\frac{\pi}{as} \leq q < \frac{\pi}{as}} \left[\omega_q^{(\alpha)}(t,h,K;\eta_s)\right]^2 \left|\eta_q^{(\alpha)}\right|^2 \qquad (2)$$

where $f_o^{(s)}$ is the *(exact)* reduced free energy associated with the s-merized chain, $\eta_q^{(\alpha)}$ is proportional to the Fourier transformed position $X_q^{(\alpha)}$ ($\eta_q^{(\alpha)}$ vanishes for $\alpha = 1,2,\ldots,s$ and all q if the structure is *precisely* s-merized) and $\{\omega_q^{(\alpha)}\}$ are the corresponding structural (or phonon) spectra. We have performed ([15] and references therein) the full calculations of $f_o^{(s)}$ for s=1,2,3,4, and those of the spectra $\{\omega_q^{(\alpha)}\}$ for s=1,2. The thermoequilibrium condition $\partial f_o^{(s)}/\partial \eta_s = 0$ provides two solutions, namely $\eta_s \equiv 0$ (the U phase occurs if $\eta_s \equiv 0$, $\forall s$) and $\partial f_o^{(s)}/\partial(\eta_s^2) = 0$, which yields the order parameter equation of states in the s-merized phase.

Furthermore the soft-mode criterion $\omega_q^{(1)}(t,h,K;0) = 0$ for $q=q_c$ indicates that the uniform chain is unstable with respect to a structural mode whose wavevector is q_c, where q_c is by definition the *first* (coming from the U phase) wavevector for which this condition is fulfilled. To be more precise this criterion determines the metastability limit of the U phase; this limit coincides with the phase boundary if and only if the phase transition is a second order one (this seems to be indeed the case all over the U - (non U) frontier, as strongly suggested by the analysis of various selected particular cases; this fact justifies a posteriori the perturbative approach we have mentioned before). As an illustration of the structural spectra we present, for selected values of (t,h,K), $\omega_q^{(1)}(t,h,K;0)$ vs. q in Fig.2. The (t,h,K)-evolution of such spectra together with the analysis of $f_o^{(s)}$ for s=1,2,3,4 led to several important conclusions depicted in Fig.3. Let us stress in particular the following facts: (a) as mentioned before, two special points appear on the critical line in the (t,h)-space for fixed K, namely a *Lifshitz point* (associated with $q_c=\pi/a$) and a point of a new kind, hereafter referred as *starting point* (associated with $q_c=0$); between these two points, modes with commensurate (with the U chain case) as well as incommensurate wavevectors "freeze"; (b) in the interior of a large region (at sufficiently low values of h) the structural order is a *pure* dimerization (D phase); in the rest of the non-U region the structure presents complex modulations (M phase); (c) the slope of the first-order D-M critical line is positive (negative) for sufficiently small (large) harmonic elastic constants; (d) for fixed h, it is possible to observe the sequence U-(non U)-U by varying t; (e) for fixed t and sufficiently high K, it is possible to observe the unusual sequence (non U)-U-(non U)-U by increasing t.

Let us finally stress attention on two interesting facts present in the thermal evolution of the phonon spectrum in the U and D phases. The first of them concerns the frequency of the q=0 optical mode (see Fig.4a): a *soft behavior* of the usual type is recovered (on both sides of the critical temperature) within the present approach (some experimental evidence of this effect is already available for MEM$(TCNq)_2$ [16]). The second one concerns the sound velocity (see Fig.4b): it presents a *gap* across the critical

temperature, and this gap increases with the external magnetic field (the experimental confirmation of this effect should be very interesting).

III - SPECIFIC HEAT, MAGNETIZATION AND SUSCEPTIBILITY

The reduced isochore specific heat is given by $-t\ \partial^2 f/\partial t^2|_h$ and the results we obtain [15] for the U and D phases are presented in Fig.5. It is interesting to remark that, according to the value of K, the specific heat peak (which exists even at vanishing magnetic field) can occur on *both* sides of the maximum of the universal (K-independent) curve corresponding to the U phase.

The reduced magnetization is given by $m = -\ \partial f/\partial h|_t$; the t- and h-dependences obtained within the present theory [15] are illustrated in Fig.6. Finally the isothermal magnetic susceptibility $\chi \equiv \partial m/\partial h|_t$ results [15] are depicted in Fig.7; remark that the typical SPI "knees" at vanishing magnetic field become peaks if $h \neq 0$ (as in the case of the specific heat, these peaks can occur, according to the value of K, on *both* sides of the maximum of the universal U phase).

IV - CONCLUSION

Let us herein present a few numerical results in order to compare with other available theoretical and experimental ones. $T_L/T_c(H=0)$ ($T_L \equiv$ Lifshitz point temperature) range, for TTF-Au BDT, TTF-Cu BDT and MEM$(TCNQ)_2$, between about 0.65 and 0.8 (see [1] and particularly its Fig.24); theories from Bulaevskii et al [12] and Bray [13] yield 0.54, that of Cross [14] yields 0.77 and the present theory provides values ranging from 0.59 to 0.68 while the reduced elastic constant K decreases from 0.6 to 0.06. $H_L/T_c(H=0)$ ($H_L \equiv$ Lifshitz point magnetic field) equals 10.5 ± 0.6 ($[H] = KO_e$ and $[T] = {}^oK$) for the same three substances; available theories yield 11.2 [12,13] and 10.3 [14]; the present results vary from 7.4 to 8.0 while K increases from 0.3 to 0.6. In the limit $H \to 0$ it is found, both experimentally and theoretically, that $[T_c(H=0) - T_c(H)]/T_c(H=0) \sim \lambda [\mu_B H/k_B T_c(H=0)]^2$; λ calculations provide 0.44 [12,13], 0.36 [14] and 0.9 (present); a first analysis [1] of the experimental data was compatible with our value, while further analysis [1] was more compatible with the other two values. The TTF-CuBDT

result (Fig.10 of [1]) for $d[\chi(T)/\chi(T_c)]/d[T/T_c]\Big|^{D}_{T=T_c}$ is 2.7; ours is 2.5 for K=0.4. The same experiment provides $T_{max}/T_c \simeq 4$ ($T_{max} \equiv$ temperature corresponding to the maximum χ_{max} of χ in the U phase); the present theory provides 4 for $K > 0.6$. The T=0 extrapolation of χ in the U phase yields, still for the same experiment, $\chi_{max}/\chi(T=0;\ extrap) \simeq 1.4$; the present theory yields 1.1 for $K \simeq 0.4$.

Similarly to the other theoretical approaches, the present one does not recover, *with a single set of parameters*, a large variety of experimental results; this is clearly due to its intrinsic simplicity (in particular no soliton effects are taken into account). However we have exhibited that, with values of K ranging in the interval 0.4-0.6, an overall description is possible which qualitatively is no doubt quite satisfactory. Further experimental work should be very wellcome; in particular it should be very interesting to actually exhibit the existence of the "starting point" (see Fig. 3; because of their low critical temperatures, and presumably low critical magnetic fields, TTF-Au BDT and TTF-Cu BDSe could be good candidates) as well as that of the sound velocity effect (see Fig.4b).

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CAPTION FOR FIGURES

Fig. 1 - Role played by the dimerization order parameter η (η=0: U chain; $\eta \neq 0$: D chain). (a) Fermionic spectrum as a function of the wavevector k (a ≡ crystalline parameter; ε_F ≡ Fermi level). (b) T=0 variation of the free energy $\Delta F = \Delta F_m + \Delta F_e$ with η (ΔF_m ≡ fermionic or magnetic contribution; ΔF_e ≡ elastic contribution).

Fig. 2 - U chain phonon spectra (t,h and K are the reduced temperature, magnetic field and elastic constant respectively). Cases I and III: trigger of structural instabilities.

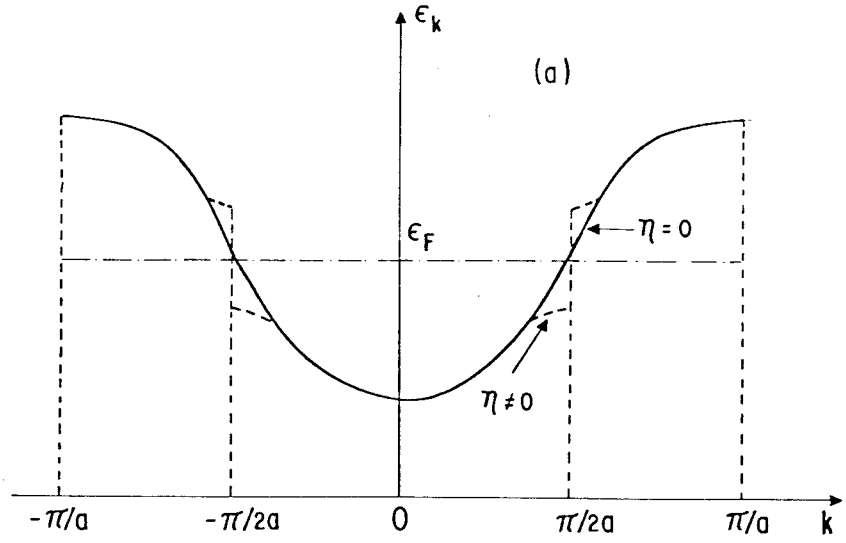
Fig. 3 - Critical lines (continuous); $q_c=\pi$ and $q_c=0$ respectively correspond to Lifshitz and starting points (a=1). (a) and (b) dashed: iso-q_c lines; (c) dotted: iso-q_c line for $q_c=\pi/2$; dashed: η=0 metastability line associated with the fictitious U-tetramerized transition; (d) first-order (dot-dashed) and metastability (dashed) lines; (e) possible iso-q_M lines (dashed) corresponding to the main structural modulation.

Fig. 4 - t- and h-dependences of the q=0 optical square reduced frequency (a) and the reduced sound velocity (b) (in the limit $t \to \infty$, ω_0 and v respectively saturate at $\sqrt{2K}$ and $\sqrt{K/2}$).

Fig. 5 - Reduced specific heat; the dot-dashed line is the locus of the maxima of C_v.

Fig. 6 - Reduced magnetization; the dot-dashed (dotted) line corresponds to the locus where the "knees" occur (to the first-order DM-line).

Fig. 7 - Reduced isothermal magnetic susceptibility; the dot-dashed line is the locus of the peaks.


ϵ_k
(a)
ϵ_F
$\eta = 0$
$\eta \neq 0$
$-\pi/a$
$-\pi/2a$
0
$\pi/2a$
π/a
k

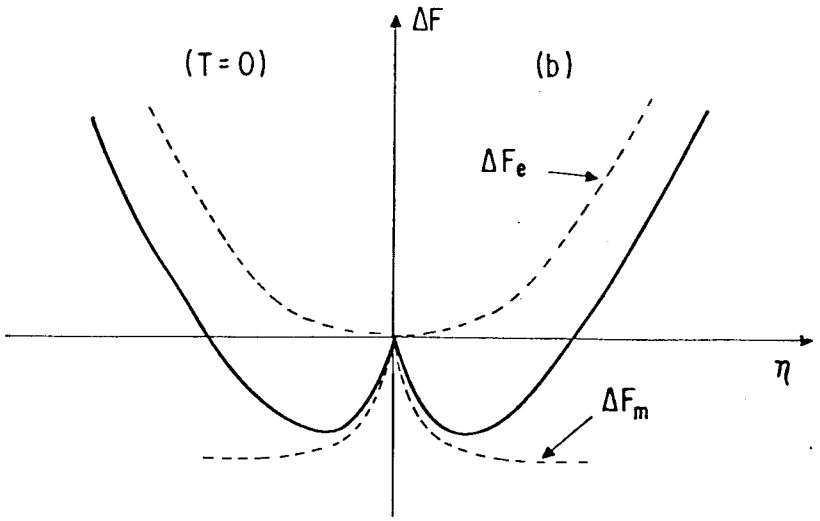

ΔF
(T = 0)
(b)
ΔF_e
η
ΔF_m

FIG.1

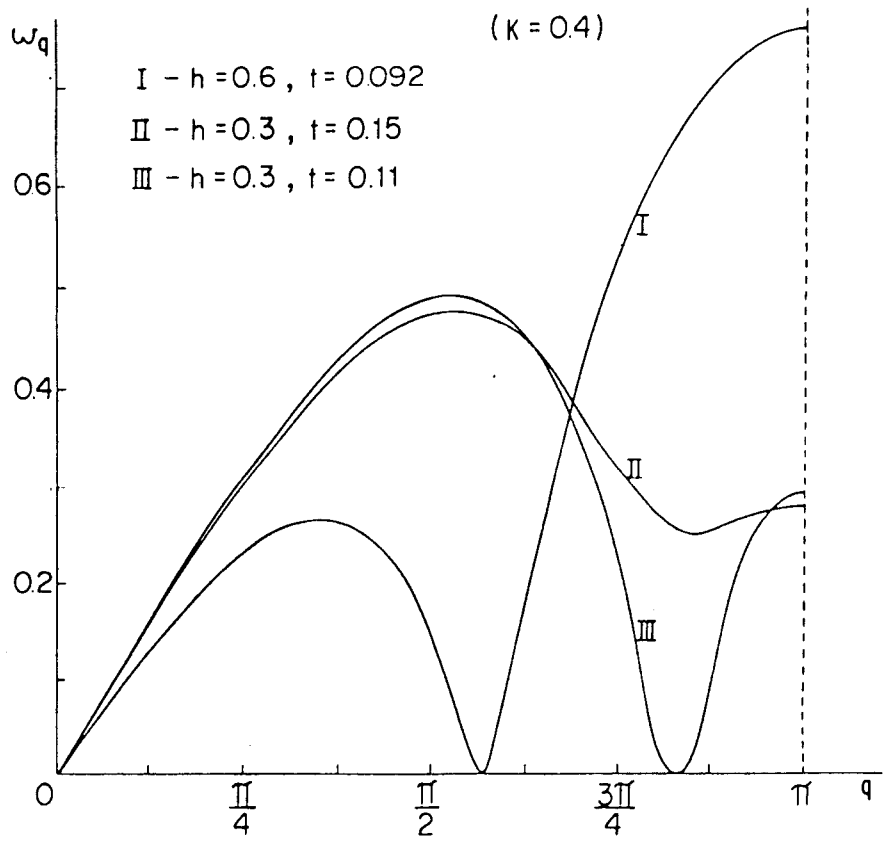
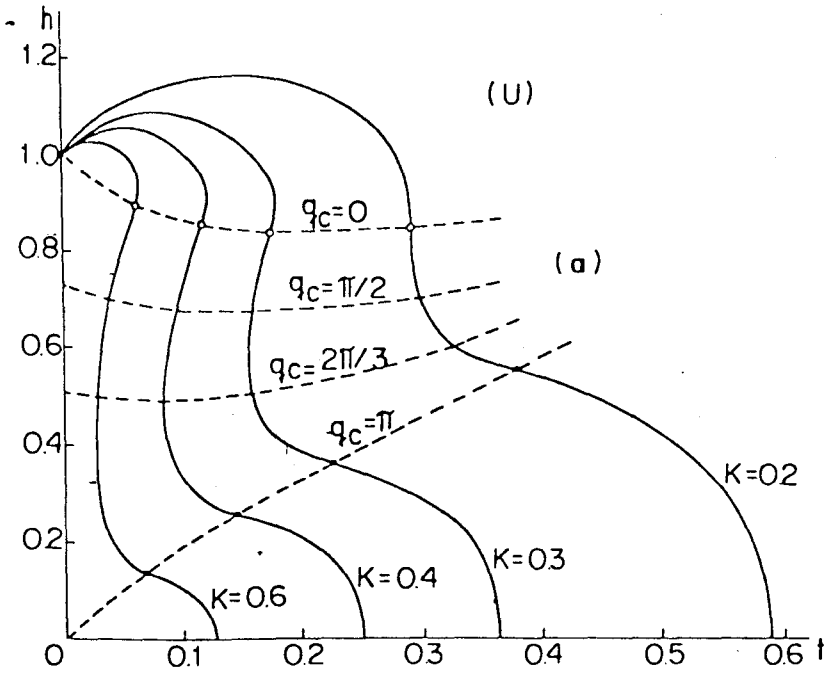
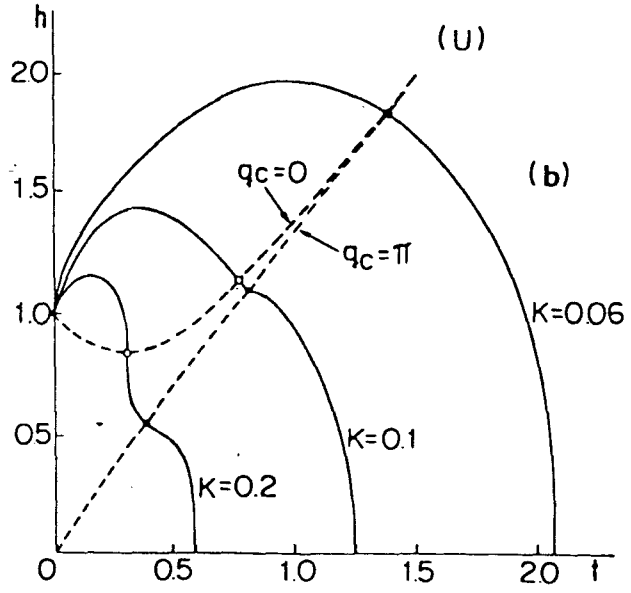

ω_q
(K = 0.4)
I - h = 0.6 , t = 0.092
II - h = 0.3 , t = 0.15
III - h = 0.3 , t = 0.11
0.6
0.4
0.2
0
$\frac{\pi}{4}$
$\frac{\pi}{2}$
$\frac{3\pi}{4}$
π
q
I
II
III

FIG. 2


h
1.2
1.0
0.8
0.6
0.4
0.2
0
0.1
0.2
0.3
0.4
0.5
0.6
t
(U)
(a)
$q_c=0$
$q_c=\pi/2$
$q_c=2\pi/3$
$q_c=\pi$
K=0.2
K=0.3
K=0.4
K=0.6


h
20
1.5
1.0
05
0
0.5
1.0
1.5
2.0
t
(U)
(b)
$q_c=0$
$q_c=\pi$
K=0.06
K=0.1
K=0.2

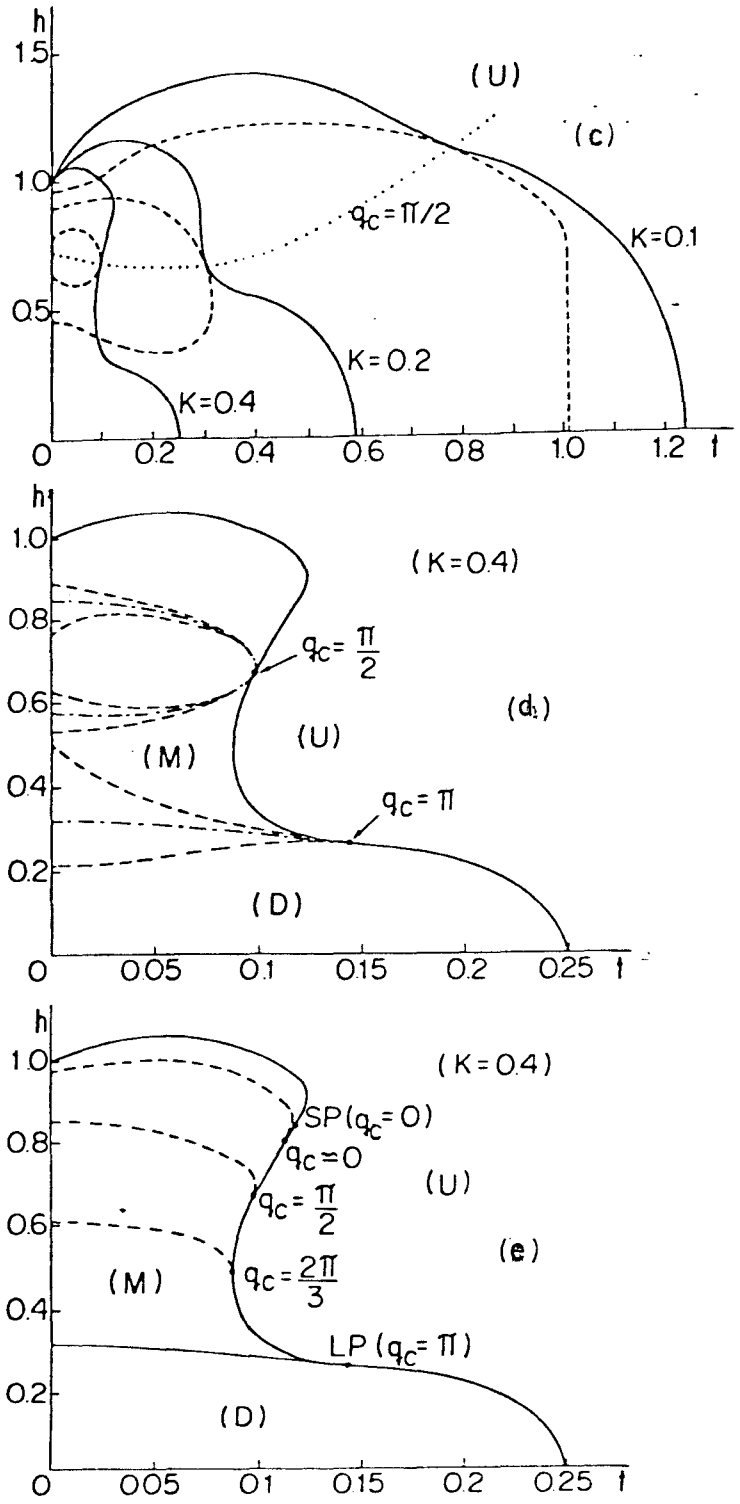

h
1.5
1.0
0.5
0
0.2
0.4
0.6
0.8
1.0
1.2
t
(U)
(c)
$q_c=\pi/2$
K=0.1
K=0.2
K=0.4
h
1.0
0.8
0.6
0.4
0.2
0
0.05
0.1
0.15
0.2
0.25
t
(K=0.4)
$q_c=\frac{\pi}{2}$
(U)
(M)
$q_c=\pi$
(D)
(d1)
h
1.0
0.8
0.6
0.4
0.2
0
0.05
0.1
0.15
0.2
0.25
t
(K=0.4)
SP($q_c=0$)
$q_c=0$
$q_c=\frac{\pi}{2}$
(U)
(M)
$q_c=\frac{2\pi}{3}$
LP($q_c=\pi$)
(D)
(e)

FIG.3

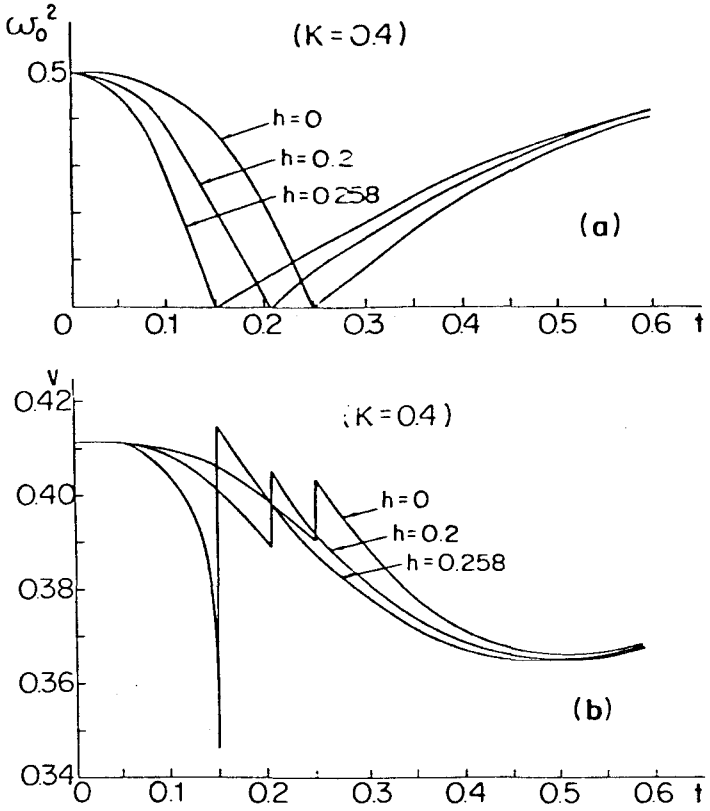

ω_0^2
(K=0.4)
0.5
h=0
h=0.2
h=0.258
(a)
0
0.1
0.2
0.3
0.4
0.5
0.6
t
V
0.42
(K=0.4)
0.40
h=0
h=0.2
h=0.258
0.38
0.36
(b)
0.34
0
0.1
0.2
0.3
0.4
0.5
0.6
t

FIG.4

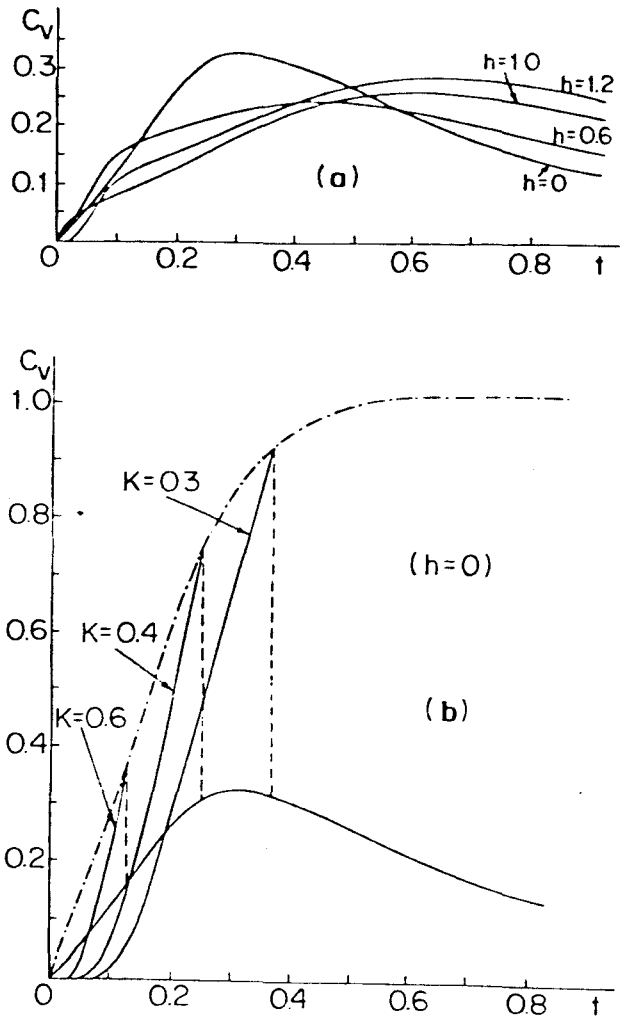
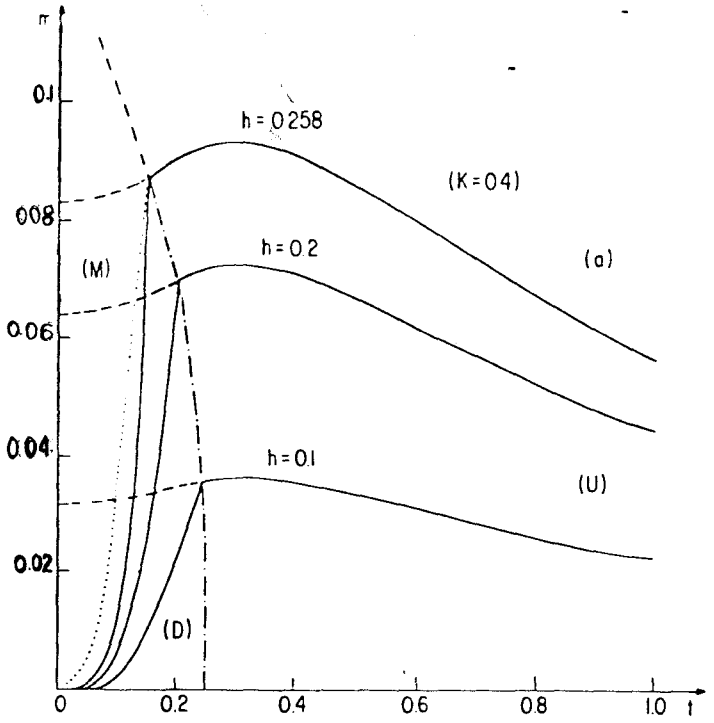
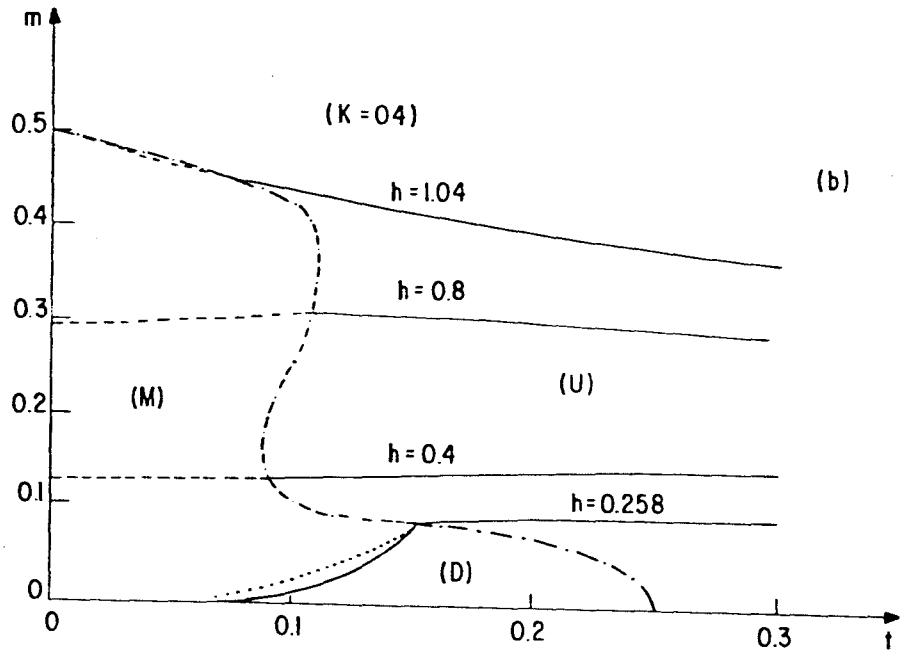

C_V
0.3
0.2
h=1.0
h=1.2
h=0.6
0.1
(a)
h=0
0
0.2
0.4
0.6
0.8
t
C_V
1.0
K=0.3
0.8
(h=0)
0.6
K=0.4
(b)
K=0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
t

FIG.5


m
0.1
0.08
0.06
0.04
0.02
h = 0.258
(K=04)
h = 0.2
(a)
(M)
h = 0.1
(U)
(D)
0
0.2
0.4
0.6
0.8
1.0
t


m
0.5
0.4
0.3
0.2
0.1
0
(K = 04)
h = 1.04
(b)
h = 0.8
(M)
(U)
h = 0.4
h = 0.258
(D)
0
0.1
0.2
0.3
t

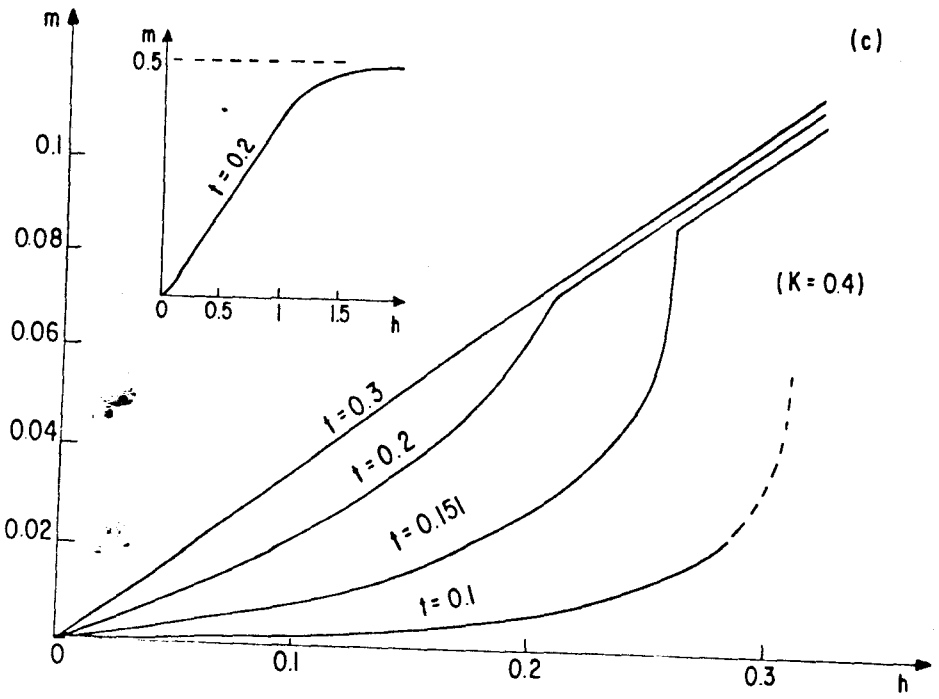

m
0.1
0.08
0.06
0.04
0.02
m
0.5
t = 0.2
0
0.5
1
1.5
h
(c)
(K = 0.4)
t = 0.3
t = 0.2
t = 0.151
t = 0.1
0
0.1
0.2
0.3
h

FIG.6

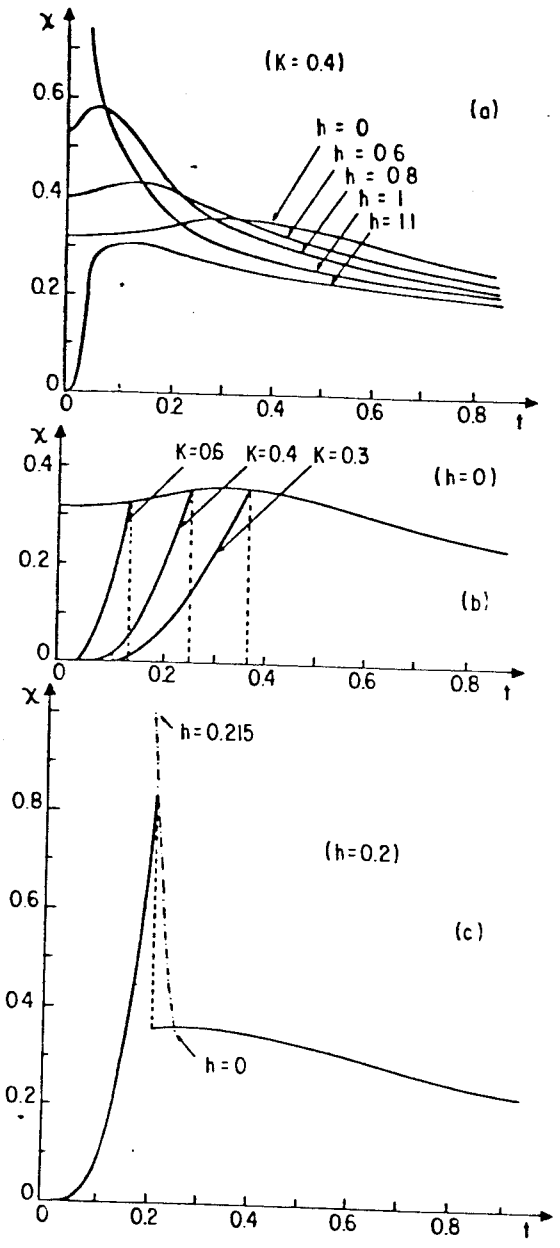

χ
(K = 0.4)
(a)
h = 0
h = 0.6
h = 0.8
h = 1
h = 1.1
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
t
χ
K=0.6
K=0.4
K=0.3
(h=0)
(b)
0.4
0.2
0
0.2
0.4
0.6
0.8
t
χ
h=0.215
(h=0.2)
(c)
h=0
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
t

FIG. 7