Influence of a frozen defect density wave on an incommensurate modulation

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We report a theoretical study of the influence of an ordered periodic pattern of defects on an incommensurate modulation. We consider a one-dimensional model valid when the defect potential is much smaller than the potential of the underlying lattice, in which the discommensurations of the modulation (solitons) are handled as material objects. This model belongs to the class of Frenkel-Kontorowa problems. Between the normal-incommensurate transition and the transition of lock-in on the lattice, the soliton system undergoes a succession of transitions between two types of incommensurate phases either locked or unlocked on the defect wave. The average spacing between neighboring solitons as a function of the temperature is represented by a devil's staircase. The structure, the stability, and the Fourier spectrum of the unlocked phases are analyzed. In these phases, the soliton distribution is not uniform but modulated. As a consequence, the Fourier spectrum of the modulation splits into several components. Computed spectra account for the splitting of the incommensurate satellites observed in the scattering spectra of $Ba_2NaNb_5O_{15}$ or of Rb_2ZnBr_4.

I. INTRODUCTION

A specific memory effect has been observed in several incommensurate systems,[1-3] SC $(NH_2)_2$, $Ba_2NaNb_5O_{15}$, Rb_2ZnCl_4, etc., after they have been kept for some time (a few minutes to several days) at a fixed temperature T_0 within the incommensurate phase. This effect is believed to be induced by mobile extrinsic defects (vacancies, impurities, etc.) interacting with the incommensurate modulation. During the annealing at T_0, the defects become ordered in the field of the modulation; their spatial distribution acquires a periodic component at the wave vector of the modulation, i.e., a "defect density wave" (DDW).[1,2] When the sample temperature is varied after the annealing for a time which is short with respect to the defect ordering time, the DDW remains frozen and its existence is expected to influence the subsequent properties of the material (transition temperatures, dielectric susceptibility, birefringence, satellite characteristics, etc.).

In this paper, we investigate theoretically the influence of such a frozen DDW on the incommensurate modulation itself by considering a one-dimensional model in which the modulation is submitted to two lock-in potentials with different periodicities. One is the usual underlying potential due to the crystal lattice and the other is assumed to represent the influence of the DDW.

The study of the thermodynamic behavior of a continuous system with two competing periodicities has already been investigated by E. Fradkin *et al.*[4] and also by S. Aubry.[5] These authors considered the free energy

$$\mathcal{F}=\int dx\left[\frac{1}{2}\left[\frac{d\varphi}{dx}\right]^2-V_l\cos[\varphi(x)-q_l x]-V_d\cos[\varphi(x)-q_d x]\right], \tag{1}$$

whose minimization with respect to the new variable

$$\phi(x)=\varphi(x)-q_l x\ , \tag{2}$$

leads to the double sine-Gordon equation

$$\frac{d^2\phi}{dx^2}=V_l\sin\phi+V_d\sin(\phi-q_0 x)\ . \tag{3}$$

This equation can be related to the spatial variations of the phase angle of an incommensurate modulation in the field of two lock-in potentials when the amplitude of the modulation is assumed to be homogeneous (phase-modulation-only approximation). V_l and V_d represent the amplitudes of the lattice potential and of the DDW potential, and

$$q_0=q_d-q_l\ , \tag{4}$$

the DDW wave vector, refers to the lock-in wave vector q_l of the pure crystal.

On the basis of general theoretical arguments, Aubry has shown that this continuous model is equivalent to the discrete Frenkel-Kontorowa problem (FKP).[5,6] As a consequence, the thermodynamically stable solutions neither correspond to the coexistence of several phases nor to chaotic states but to periodic phases. The variations of the modulation period as a function of the coefficients V_l or V_d are represented by a devil's staircase; the system undergoes a succession of transitions between phases whose wave vector is either commensurate or incommensurate with the DDW one. The existence of these periodic stable phases has been confirmed by the numerical work of Fradkin *et al.*[4] Using mapping technics, they found that the Fourier spectrum of the modulation is constituted by a finite (or a countable) number of δ functions at wave vectors either commensurate or incommensurate with q_0. Typical spectra were plotted by these authors. In some of

them, the Fourier components appear to be regularly spaced but possible relations between their wave vectors are not explicit. Besides, neither the structure of the modulation in real space nor the characteristics of the transitions between periodic phases are explicitly described in their work.

Here, we clarify these points by using an analytical approach to the problem in the case where the DDW potential has an amplitude much smaller than that of the lattice:

$$V_d \ll V_l \ . \tag{5}$$

From an experimental point of view, this condition is realized when the properties of the DDW-marked system are not too different from those of the pure crystal. This is the case in $SC(NH_2)_2$,[1] Rb_2ZnCl_4,[3] and perhaps also in $Ba_2NaNb_5O_{15}$.[2,7]

The paper is organized as follows. In Sec. II, we describe our model and show its equivalent with the FKP. We investigate the spatial structure of the modulation in the stable phases of the system in Sec. III and we calculate its Fourier spectrum in Sec. IV. Our results are then compared with available experimental data in Sec. V; the case of Rb_2ZnBr_4 is specially investigated.

II. THE PERTURBED SOLITON MODEL

The solutions of the sine-Gordon equation (3) in the pure crystal case ($V_d=0$) are well known:[8,9] $\phi(x)$ is a periodic function whose wave vector continuously decreases to zero as V_l increases. Near the lock-in transition, it describes a soliton (discommensuration) lattice. The solitons can be considered as domain walls where the phase undergoes a rapid 2π variation, which separate quasi-commensurate regions where $\phi(x)$ is nearly constant and equal to a multiple of 2π.

The basic point of our approach is to consider the so-called solitons as objects subject to their mutual interactions (as in the pure crystal case) and also subject to an "external" potential representing the DDW potential. Hence, we are led to a Frenkel-Kontorowa-type problem where the atoms of the usual FKP are replaced by the solitons.

For a crystal of length L, the free energy of N solitons in the field of the DDW potential $W(x)$ is,[8,9]

$$F=\sum_{i=1}^{N}[-\tau+U(x_{i+1}-x_i)+W(x_i)] \ , \tag{6}$$

where x_i is the position of the ith soliton, $-\tau$ its energy of creation, and $U(l)$ the interaction energy of a pair of solitons at a distance l. We assume that this interaction is repulsive, convex, and decreases with l, so that

$$U(l)>0, \quad U'(l)=\frac{dU}{dl}<0, \quad U''(l)=\frac{d^2U}{dl^2}>0 \ . \tag{7}$$

These conditions are verified by the interaction obtained in the classical treatment of an incommensurate modulation in a pure crystal; in the soliton regime, when the domains-wall fluctuations are neglected, we have[8]

$$\tau=\frac{\pi\delta_0}{2}-2(V_l)^{1/2} \tag{8}$$

and

$$U(l)=8(V_l)^{1/2}\exp[-4l(V_l)^{1/2}] \ . \tag{9}$$

For the sake of simplicity, we only retain the first harmonic of the DDW periodic potential:

$$W(x)=-w_0\cos(q_0x) \ , \tag{10}$$

with $w_0>0$, and we discard a possible spatial-independent term in $W(x)$ which only leads to a renormalization of τ. Besides, we neglect the temperature dependences of all the coefficients in the model except τ since this parameter vanishes at the lock-in transition of the pure crystal. Further on, we shall consider that τ represents the "temperature" of the system. $\tau=0$ is the lock-in transition temperature of the pure crystal.

In contrast to the works of Aubry[5] and Fradkin *et al.*,[4] our procedure destroys the symmetry between the two lock-in potentials of Eq. (3). The number of characteristic lengths of the system is reduced from 3 (the period of the incommensurate modulation in absence of the two lock-in potentials and the periods of these potentials) to 2 (the spacing between neighboring solitons in the pure crystal without any DDW and the period of the DDW). In fact, our model can be considered as a perturbation of the pure crystal case valid when the strength of the DDW potential is much smaller than the lattice one:

$$V_d \ll V_l \ . \tag{11}$$

To emphasize the analogy between our model and the FKP, we put

$$x_i=il+u_i \ , \tag{12}$$

where l is the spacing between the solitons in the pure crystal and we expand $(x_{i+1}-x_i)$ around l up to the second order. l is deduced from the minimization equation of F when $w_0=0$:

$$\tau=U(l)-lU'(l) \ . \tag{13}$$

Using this equation and the relation

$$x_N-x_0=L \ , \tag{14}$$

a straightforward calculation leads to

$$F=U'(l)+\sum_{i=1}^{N}\left[\frac{U''(l)}{2}(u_{i+1}-u_i)^2-w_0\cos q_0(il+u_i)\right] \ . \tag{15}$$

This expression looks like that of the Hamiltonian used by Pokrovski and Talapov[10] in their study of the FKP. A slight difference exists in the expression of the term $U'(l)$. However, this term does not depend on the u_i displacements and it only acts as a chemical potential determining the number of solitons in the system. Hence, the general results of Aubry[6] on the FKP can be applied to our model with the following consequences.

(i) The stable phases of our model are periodic.

(ii) Three kinds of stable phases can be distinguished:

(1) The commensurate phase locked on the underlying lattice. (2) The phases incommensurate with the lattice but locked on the DDW. Their period $\mathscr{L}$, as well as the average spacing $\langle l \rangle$ between neighboring solitons, is commensurate with the DDW period

$$l_0 = \frac{2\pi}{q_0} . \tag{16}$$

(3) The unlocked incommensurate phases for which $\mathscr{L}$ and $\langle l \rangle$ are incommensurate with l_0.

(iii) The temperature dependence of $\langle l \rangle$ is represented by a devil's staircase. Its completeness depends on the value of the coefficient

$$\epsilon_l = \frac{w_0}{U''(l)} \left[\frac{2\pi}{l_0} \right]^2 . \tag{17}$$

On cooling towards the lock-in transition, the spacing between solitons increases to infinity and so does ϵ_l. When ϵ_l is larger than a critical value ϵ_c, the staircase is complete; the system only passes through phases locked on the DDW as the temperature is varied. When ϵ is smaller than ϵ_c, the staircase is incomplete and the system also exhibits incommensurate unlocked phases.

This analysis shows that our model presents the same general properties (i) to (iii) as the continuous biperiodic model [Eq. (1)] studied by Aubry[5] and by Fradkin *et al.*[4] As we shall see, now one can take advantage of its greater simplicity to investigate with more detail the properties of the stable phases introduced above.

III. PROPERTIES OF THE MODEL

First, we shall discuss the structure and the stability of two kinds of phases composing the devil's staircase: the phases for which the average distance between solitons is equal to or near a multiple of l_0. The other phases will be briefly investigated at the end of this section.

A. Structure of the modulation

1. pl_0 locked phases

It is obvious that the phases locked on the DDW with $\langle l \rangle$ just equal to pl_0 (p integer) are composed of regularly spaced solitons located in the minima of the DDW potential wells ($x_i = ipl_0$). Hereafter, we shall refer to them as pl_0 phases. Their free energy is easily derived from Eq. (6):

$$F(pl_0) = \frac{-\tau - w_0 + U_p}{pl_0} , \tag{18}$$

with

$$U_p = U(pl_0) . \tag{19}$$

2. *Surrounding incommensurate phases*

To determine the structure of the unlocked phases surrounding the pl_0 phases in the devil's staircase, we start from the free energy (6) and we use the transformation of variables:

$$x_i = ipl_0 + l_0 \frac{\theta_i}{2\pi} . \tag{20}$$

Using an expansion of $U(x_{i+1} - x_i)$ around pl_0 up to the second order, we obtain

$$F = \sum_{i=1}^{N} -\tau + U_p + U_p' \frac{l_0}{2\pi}(\theta_{i+1} - \theta_i) + \tfrac{1}{2} U_p'' \left[\frac{l_0}{2\pi} \right]^2 (\theta_{i+1} - \theta_i)^2 - w_0 \cos\theta_i , \tag{21}$$

with

$$U_p' = \frac{dU}{dx}(pl_0) , \qquad U_p'' = \frac{d^2U}{dx^2}(pl_0) . \tag{22}$$

If the spatial variations of θ_i are smooth (see the end of Sec. III B), we can use the continuous approximation

$$\theta_i = \theta(i) , \qquad \theta_{i+1} - \theta_i = \theta'(i) , \tag{23}$$

which leads to

$$F = N(-\tau - w_0 + U_p - pl_0 U_p') + LU_p' + \frac{U_p''}{L} \left[\frac{l_0}{2\pi} \right]^2 \int_0^N \left[\frac{(\theta')^2}{2} + \epsilon_p (1 - \cos\theta) \right] di , \tag{24}$$

where

$$\epsilon_p = \frac{w_0}{U_p''} \left[\frac{2\pi}{l_0} \right]^2 . \tag{25}$$

The minimization of F with respect to $\theta(i)$ leads now to a simple sine-Gordon equation,

$$\frac{d^2\theta}{di^2} = \epsilon_p \sin\theta . \tag{26}$$

Its solutions describe a lattice of discommensurations whose period $\mathscr{L}$ is generally incommensurate with l_0. Between the discommensurations, $\theta(x)$ is nearly constant and equal to a multiple of 2π; the related solitons are located in the minima of the DDW potential wells, distant by pl_0, as in the locked pl_0 phase. At each discommensuration $\theta(x)$ undergoes a rapid $\pm 2\pi$ variation which corresponds to a $\pm l_0$ shift of the soliton positions from a DDW potential well to the next well. Hereafter, we shall call supersolitons those intrinsic defects of the ordinary soliton pattern. A positive (negative) shift $+l_0$ ($-l_0$) corresponds to an advanced (retarded) supersoliton for which the average distance between two neighboring solitons is larger (smaller) than pl_0. An example of the soliton pattern and of the related spatial variations of the phase of the modulation $\phi(x)$ is schematized in Fig. 1.

The number P of supersolitons per length L of the crystal is defined by

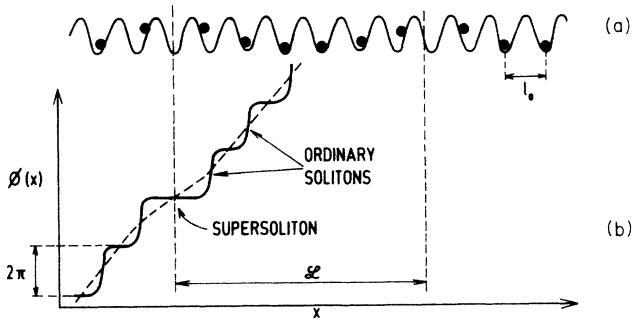

FIG. 1. (a) Example of the soliton distribution in an incommensurate phase with an average soliton spacing $\approx pl_0$. The sinusoid represents the DDW potential. (b) Spatial variations of the phase of the modulation related to the soliton pattern. The dashed curve is an approximation of $\phi(x)$ used to calculate the Fourier spectrum of the modulation (see Sec. IV).

$$\theta_N-\theta_0=2\pi P\ . \tag{27}$$

P is positive for advanced supersolitons and negative for retarded ones.

Taking into account the relations between the various lengths of the problem

$$L=\mathscr{N}l_0=N\langle l\rangle=|P|\mathscr{L}\ , \tag{28}$$

where $\mathscr{N}$ is the number of wells of the DDW potential per length L of the crystal, one finds that P is related to the number of solitons N through the relation

$$P+Np=\mathscr{N}\ , \tag{29}$$

and that the period $\mathscr{L}$, of the incommensurate phase is given by

$$\mathscr{L}^{-1}=|l_0^{-1}-p\langle l\rangle^{-1}|\ . \tag{30}$$

Hence, the unlocked phase with an average distance $\langle l\rangle\gtrsim pl_0$ ($\langle l\rangle\lesssim pl_0$) between neighboring solitons is obtained from the pl_0 phase by the introduction in the soliton pattern of

$$P=\mathscr{N}\left[1-\frac{pl_0}{\langle l\rangle}\right] \tag{31}$$

advanced (retarded) supersolitons and the simultaneous vanishing (creation) of $|P|/p$ ordinary solitons.

To derive its free energy, we substitute $\theta_P(x)$ [the solution of Eq. (26) containing P supersolitons] into (24). Following the soliton formalism of Bak and Emery,[9] we obtain

$$F_{P,p}=F(pl_0)+P(\mathscr{E}_{P,p}+\mathscr{U}_{P,p})\ , \tag{32}$$

where

$$\mathscr{E}_{P,p}=\frac{\tau+w_0-U_p}{p}+l_0U_p'+8\,\mathrm{sgn}(P)\left[\frac{l_0}{2\pi}\right]^2(\epsilon_p)^{1/2}U_p'' \tag{33}$$

and

$$\mathscr{U}_{P,p}=32\frac{l_0}{2\pi}(w_0U_p'')^{1/2}\exp\left[-\frac{(\epsilon_p)^{1/2}}{|P|}\frac{L}{l_0}\right]\mathrm{sgn}(P)\ , \tag{34}$$

with

$$\mathrm{sgn}(P)=+1\ \text{ if } P>0$$

and

$$-1\ \text{ if } P<0\ . \tag{35}$$

$\mathscr{U}_{P,p}$ is a repulsive interaction between two neighboring supersolitons spaced by $\mathscr{L}=L/|P|$ and whose width is $l_0\epsilon_p^{-1/2}$, while $\mathscr{E}_{P,p}$ can be interpreted as the energy necessary to create an advanced or a retarded supersoliton. The first term in the right-hand side of Eq. (33) corresponds to the disappearance of a $1/p$ ordinary soliton which occurs for each creation of one supersoliton [see Eq. (29)], the last terms correspond to a remodeling of the soliton pattern around the created supersoliton.

B. Description of the devil's staircase

Let us discuss now the stability of the locked pl_0 phase against (a) the surrounding unlocked phases, (b) the locked $(p\pm1)l_0$ phases, and (c) the phase locked on the underlying lattice.

(a) By analogy with the classical treatment[8] (within the continuous approximation) of the lock-in transition between an incommensurate phase and a locked phase, the minimization of $F_{P,p}$ with respect to P leads to a continuous transition between the locked pl_0 phase (which corresponds to $P=0$) and the surrounding incommensurate phases. The transition temperatures are determined by the cancellation of $\mathscr{E}_{P,p}$; the pl_0 phase is stable against the creation of advanced supersolitons when

$$\tau\geq\tau_p-w_0-8p\frac{l_0}{2\pi}(w_0U_p'')^{1/2}\ , \tag{36a}$$

and against the creation of retarded supersolitons when

$$\tau\leq\tau_p-w_0+8p\frac{l_0}{2\pi}(w_0U_p'')^{1/2}\ , \tag{36b}$$

where

$$\tau_p=U_p-pl_0U_p' \tag{37}$$

is the temperature related to the pl_0 phase in the pure crystal [see Eq. (13)].

(b) The comparison of the free energies of the $(p-1)l_0$, pl_0, and $(p+1)l_0$ locked phases given by Eq. (18) shows that (i) the transitions between these phases are discontinuous and (ii) the pl_0 phase is stable when

$$\tau_p-w_0+p(U_p-U_{p+1}+l_0U_p')\leq\tau\leq\tau_p-w_0+p(U_{p-1}-U_p+l_0U_p')\ . \tag{38a}$$

When $p\gg1$, these inequalities can be approximated by

$$\tau_p-w_0-\frac{pl_0^2}{2}U_p''\leq\tau\leq\tau_p-w_0+\frac{pl_0^2}{2}U_p''\ . \tag{38b}$$

(c) The free energy of the phase locked on the underlying lattice is zero since there are no solitons in this phase. As U_p decreases to zero when p goes to infinity, Eq. (18) shows that this phase is stable against the creation of ordinary solitons when $\tau < -w_0$. Hence, in our model, the temperature of the lock-in transition between the modulated phase and the phase locked on the lattice is shifted from 0 for a pure crystal to

$$\tau_L = -w_0 \tag{39}$$

for the DDW marked crystal.

The above analysis leads to an approximate determination of the devil's staircase which describes the temperature dependence of $\langle l \rangle^{-1}$. The staircase is an increasing curve starting from $\tau_L = -w_0$, composed of plateaus related to the pl_0 phases locked on the DDW and of smoothly varying curves joining the plateaus related to the phases incommensurate with the DDW (see Fig. 2).

The comparison of Eqs. (36) and (38) shows that two regimes can be distinguished. The lower part of the staircase, obtained for

$$-w_0 \leq \tau \leq \tau_{p_0} ,$$

with p_0 defined by

$$\epsilon_{p_0} = \frac{\pi^4}{16} , \tag{40}$$

is only composed of plateaus (complete staircase); the system undergoes discontinuous transitions between the successive pl_0 phases (with $p > p_0$); their stability range is given by

$$(\Delta\tau)_p = p(U_{p+1} + U_{p-1} - 2U_p) \approx pl_0^2 U_p'' . \tag{41a}$$

By contrast, the upper part of the staircase, when $\tau \geq \tau_{p_0}$, is incomplete: the system undergoes continuous transitions between the pl_0 phases and the surrounding unlocked phases described above. The stability range of the pl_0 phase is now given by

$$(\Delta\tau)_p = 16p \frac{l_0}{2\pi} (w_0 U_p'')^{1/2} . \tag{41b}$$

In both cases, $(\Delta\tau)_p$ becomes exponentially smaller and smaller as p increases if we assume for $U(x)$ the classical law (9).

However, this analysis is approximate for two reasons. On the one hand, the continuous approximation (23), used to determine the structure of the unlocked phases, is only valid when the width of the supersoliton is much larger than the period of the DDW, i.e., when

$$\epsilon_p \ll 1 . \tag{42}$$

This condition is not verified in the lower part of the incomplete staircase (whose lower bound is $\epsilon_{p_0} = \pi^4/16$). In this range, one has to consider discreteness effects which increase the stability of the locked phases against the unlocked ones.

On the other hand, up to now we only considered the simplest locked phases whose period is a multiple of l_0. It is not easy to determine the free energy and the structure of higher-order locked phases [with $\langle l \rangle = (p/q) l_0$ with $q > 1$] and of the related unlocked phases. However, because of the correspondence between our model and the FKP considered by Pokrovski and Talapov,[10] we know that their smoothed structures (i.e., the structures composed with the barycenters of q successive solitons) are similar to the structures of the simplest phases considered here above with $\langle l \rangle = pl_0$ or $\langle l \rangle \approx pl_0$. Their free energies are similar to the expressions (18) and (32) with renormalized τ, U, and w_0 coefficients. Of course, the consideration of these higher-order phases leads to a much more complicated structure of the devil's staircase which cannot be easily derived using analytical methods.

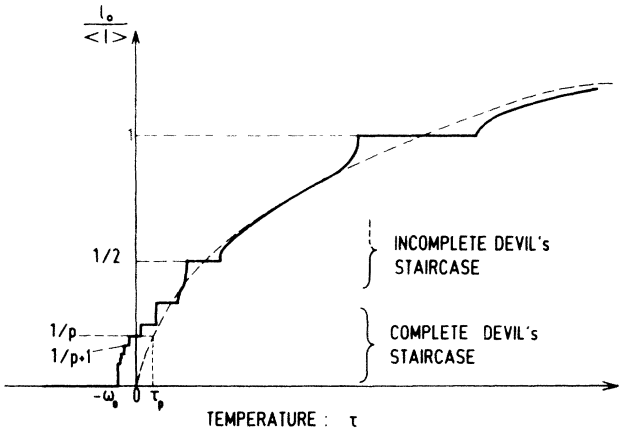

FIG. 2. Temperature dependence of the average soliton spacing in a pure crystal (dashed curve) and in a crystal marked by a DDW (solid curve). In the latter case, commensurate phases with a p/ql_0 period ($q > 1$) are not considered.

IV. FOURIER SPECTRUM OF THE MODULATION

Let us investigate now the structure of the incommensurate modulation in reciprocal space.

A. Splitting of the soliton-pattern spectrum

First, we shall focus our attention on the spectrum of the soliton distribution, with the solitons considered as objects of zero width, since this approach of the problem leads to a qualitative understanding of the modulation spectrum without any calculation.

In the locked pl_0 phases, the solitons are equally spaced as in a usual incommensurate phase and the Fourier spectrum contains only one component (whose wave vector is $2\pi/pl_0$) and its harmonics ($n2\pi/pl_0$, n integer). By contrast, we showed in the preceding section that the spacing between neighboring solitons is not constant but periodic in the unlocked incommensurate phases. This is also verified in the high-order locked phases (containing q solitons per p periods of the DDW), since in these phases the soliton density is higher in the lower arches of the DDW potential than in the upper ones. Hence, for both the latter cases, the soliton spacing can be written

$$x_{i+1} - x_i = \langle l \rangle + f(i) , \tag{43}$$

where f is a periodic function whose period $\mathscr{L}$, as well as $\langle l \rangle$, is commensurate with respect to l_0 in the locked $(p/q)l_0$ phase and incommensurate with l_0 in the unlocked phases.

This situation is qualitatively similar to the case of a displacive incommensurate phase in which the atomic spacing is modulated. As a consequence, the Fourier spectrum of the soliton pattern displays several satellite components around the main harmonic. Their wave vectors are

$$q_m = \frac{2\pi}{\langle l \rangle} + m\frac{2\pi}{\mathscr{L}} \tag{44}$$

for integer m.

However, both problems are different from a quantitative point of view because of the magnitude of the modulation amplitude. Actually, in a displacive incommensurate phase, the atomic displacements are generally much smaller than the cell parameters; the amplitudes of the incommensurate satellites exponentially decrease[11] with m so that the number of observable scattering orders is small (generally $m = \pm 1$). By contrast, the amplitude of the spacing modulation $f(i)$ is not necessarily much smaller than the average soliton spacing $\langle l \rangle$. On cooling, it increases in the unlocked phases since the width of the supersolitons ($\sim U_p''^{1/2}$) rapidly decreases with p. Hence the number of relevant Fourier components of the soliton pattern may be fairly large. In order to make this statement clearer, let us investigate now the amplitude of the components of the modulation spectrum.

B. Fourier spectrum of the incommensurate modulation

We show in the Appendix that the amplitude scattered by a displacive modulation in an elastic neutron or an x-ray scattering experiment can be approximated by a linear combination of the Fourier transformed (FT) of the order-parameter components: $\rho\cos\phi$ and $\rho\sin\phi$. To calculate these FT, we assume that the amplitude of the modulation is homogeneous (phase-modulation-only approximation[8]) and we use a Fourier expansion of the periodic phase $\phi(x)$. Within a continuous approximation, $\phi(x)$ is written as

$$\phi(x) = \frac{2\pi}{\langle l \rangle}x + \sum_{m=1}^{\infty} a_m \sin\left[\frac{2\pi m x}{\mathscr{L}}\right] + b_m \cos\left[\frac{2\pi m x}{\mathscr{L}}\right], \tag{45}$$

in the more general case where it does not possess any particular symmetry. The first term in the right-hand side is related to the average spatial variations of $\phi(x)$ and the summation describes the anharmonicity of the incommensurate modulation. With the help of the identity

$$\exp(iz\cos\theta) = \sum_{n=-\infty}^{+\infty} i^n J_n(z)\exp(in\theta), \tag{46}$$

a straightforward calculation leads to

$$\rho\cos\phi(x) = \frac{\rho}{2}\sum_{(m,m')}\left[(i)^{m_1'+\cdots+m_n'+\cdots} J_{m_1}(a_1)\cdots J_{m_n}(a_n)\cdots J_{m_1'}(b_1)\cdots J_{m_n'}(b_n)\cdots \right.$$
$$\left. \times \exp i2\pi x\left[\frac{1}{\langle l \rangle} + \frac{m_1+\cdots+m_n+\cdots+m_1'+\cdots+m_n'+\cdots}{\mathscr{L}}\right] + \text{c.c.}\right] \tag{47a}$$

and

$$\rho\sin\phi(x) = \frac{\rho}{2i}\sum_{(m,m')}\left[(i)^{m_1'+\cdots+m_n'+\cdots} J_{m_1}(a_1)\cdots J_{m_n}(a_n)\cdots J_{m_1'}(b_1)\cdots J_{m_n'}(b_n)\cdots \right.$$
$$\left. \times \exp i2\pi x\left[\frac{1}{\langle l \rangle} + \frac{m_1+\cdots+m_n+\cdots m_1'+\cdots m_n'+\cdots}{\mathscr{L}}\right] - \text{c.c.}\right], \tag{47b}$$

where $J_m(x)$ is the mth-order Bessel function and $\sum_{(m,m')}$ is a summation over all the integer values of the m_n and m_n' coefficients.

Equations (47a), (47b), and (A4) confirm the result of Sec. V A. The first-order scattering spectrum of the modulation has a "comb" structure: its components wave vectors q_m are given by Eq. (44), while their intensities are proportional to

$$\mathscr{I}_m = B^2(q_m)\left|\sum (i)^{m_1'+\cdots m_n'+\cdots} J_{m_1}(a_1)\cdots J_{m_n}(a_n)\cdots J_{m_1'}(b_1)\cdots J_{m_n'}(b_m)\cdots\right|^2, \tag{48}$$

where $B(q)$ is a structure factor defined in the Appendix and where the summation must be done on all the m_n and m_n' integer values, such that

$$\sum_{n=1}^{\infty} n(m_n + m_n') = m. \tag{49}$$

Let us discuss now the following properties of the spectrum.

(i) It is symmetrical with respect to the origin of the wave vectors, since it is determined by the FT of a real quantity. Moreover, for each half spectrum the com-

ponent wave vectors are symmetrically located on both sides of the main harmonic.

$$\pm q_c = \pm \frac{2\pi}{\langle l \rangle} . \tag{50}$$

However, when intensities are considered, the half spectra are not symmetrical. Actually, the various terms composing the summation of Eq. (48) do not possess the same symmetry properties with regard to a reverse of sign of the m_i and m_i' coefficients since these coefficients do not play analog roles in Eq. (48) (the exponent of the complex symbol i does not depend on the m_i). Hence, the $\mathcal{I}_m$ and $\mathcal{I}_{-m}$ intensities are different.[12]

(ii) The spectrum of the incommensurate phases with $\langle l \rangle \approx l_0$ always contains a component whose wave vector is equal to the DDW wave vector. Actually, using Eqs. (30) and (44) with $p=1$, one obtains

$$q_1 \text{ or } q_{-1} = \frac{2\pi}{l_0} = q_0 . \tag{51}$$

(iii) The number of relevant components in the scattering spectrum depends on the magnitude of the Fourier coefficients a_n and b_n. Since $J_m(x)$ increases with x (for $0 \le x \le 2$ and $m > 0$), the stronger the anharmonicity of the phase $\phi(x)$; the wider the spectrum of the modulation.

(iv) Because of the finite resolution of scattering experiments or of the intrinsic linewidth of the components, the spectrum of the modulation will not necessarily appear as a comb structure. When the resultant linewidth is larger than $\mathscr{L}^{-1}$, the comb interval, one will only observe the envelope of the spectrum. According to the relative intensities of the components, the envelope may display one or several peaks.

To be more specific on these two last points, we have to consider the explicit form of the phase of modulation.

C. Examples of spectra

Let us consider, for example, the unlocked phases with $\langle l \rangle \approx l_0$ represented Fig. 1. For the sake of simplicity, we shall make two assumptions on the structure of the solitons and of the supersolitons. First, we assume that $\phi(x)$ varies linearly around each soliton, as is the case for a sinusoidal modulation.[8] This approximation is not good near the lock-in transition when the discommensurations are steep. However, from an experimental point of view, this case does not often occur since the intensity measurements of the satellites generally show that the anharmonicity of the modulation is weak. Second, we assume that the soliton spacing is equal to l_0 in the areas of the crystal where the solitons are quasilocked on the DDW and l_1 in the supersolitons areas.

Within both approximations, the spatial variations of the phase of the modulation are represented by a zig-zag line [dashed line of Fig. 1(b)]. When the origin of the coordinates is located at the center of a supersoliton, $\phi(x)$ is an odd function defined by

$$\phi(x) = 2\pi \frac{x}{l_1} \tag{52a}$$

in the supersoliton area $[-(\lambda/2) \le x \le (\lambda/2)]$, and

$$\phi(x) = \pm\pi + 2\pi \frac{x}{l_0} \tag{52b}$$

in the quasilocked area $[(\lambda/2) \le x \le \mathscr{L} - (\lambda/2)]$, where

$$\lambda = \frac{l_1 l_0}{l_1 - l_0} \tag{53}$$

is the width of the supersoliton and the $+$ and $-$ signs in (52b) are, respectively, related to a delayed or an advanced supersoliton.

The Fourier coefficients of $\phi(x)$ [see Eq. (30)] defined in Eq. (45) are

$$\langle l \rangle = \frac{\mathscr{L} l_0}{\mathscr{L} \mp l_0} ,$$

$$a_m = \pm \frac{2}{m} \frac{1}{1 - \frac{\lambda}{\mathscr{L}}} \frac{\sin(\pi m \lambda / \mathscr{L})}{\pi m \lambda / \mathscr{L}} , \tag{54}$$

$$b_m = 0 .$$

Hence, the wave vectors and the relative intensities of the components of the spectra related to the unlocked phases with $\langle l \rangle \approx l_0$ are approximately given by

$$q_m = 2\pi \left[\frac{1}{l_0} \pm \frac{1}{\mathscr{L}} \right] + \frac{m}{\mathscr{L}} , \tag{55a}$$

$$\mathcal{I}_m \propto \left| \sum_{m_1 \cdots m_n \cdots} J_{m_1}(a_1) \cdots J_{m_n}(a_n) \cdots \right|^2 , \tag{55b}$$

with

$$\sum_{n=1}^{\infty} n m_n = m , \tag{55c}$$

where the q dependence of the structure factor has been discarded.

The wave vector of the mth component only depends on the value of the incommensurate period, while its intensity is only determined by the ratio $\lambda/\mathscr{L}$. Hence the spectra related to the same $\lambda/\mathscr{L}$ ratio are homothetical with respect to the component located at l_0^{-1}; to determine the influence of both parameters on the spectra shape, one can fix the λ value and one observes the $\mathscr{L}$ dependence.

Typical spectra computed for $\lambda = 4l_0$ and for various $\mathscr{L}$ values are plotted in Fig. 3(a). Their envelope exhibits two peaks. The first one is located at $2\pi/l_0$, the DDW wave vector. When $\langle l \rangle$ increases from l_0, it broadens and its intensity decreases, while a second peak develops on its left side which progressively shifts towards the small wave-vector area. Between the two peaks the envelope exhibits a very weak minimum related to the central component at $2\pi/\langle l \rangle$. Spectra with $\langle l \rangle / l_0 \ge 1.25$ have not been computed since our assumptions on the structure of the modulation [Eqs. (52)] become less valid as a measure as the soliton spacing increases; in particular, commensurate locked phases such as $\frac{4}{3} l_0, \frac{3}{2} l_0$ phases cannot be described with the help of the supersoliton concept.

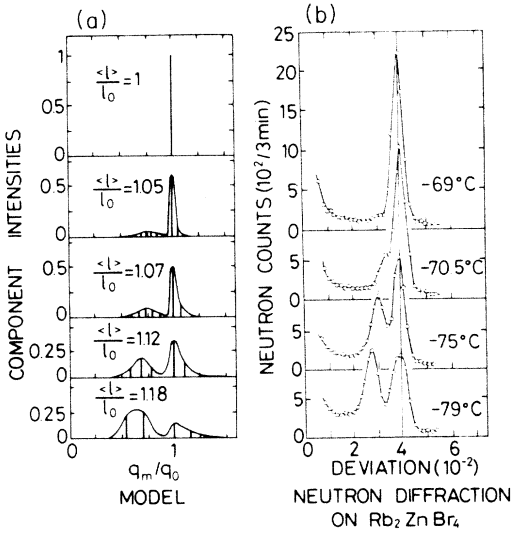

FIG. 3. (a) Calculated Fourier spectra of the modulation obtained for $\lambda=4l_0$ and for various values of the average soliton spacing. They are in good qualitative agreement with the experimental spectra shown on right. (b) Neutron scattering spectra of Rb_2ZnBr_4 (from Ref. 21).

V. DISCUSSION

Let us discuss now from an experimental point of view two significant results of the preceding sections.

(i) The existence of plateaus in the temperature dependence of the modulation wave vector.

(ii) The multipeaked shape of the envelope of the modulation spectrum.

In regard to the first point, a lock-in of the modulation on a DDW has indeed been observed directly or indirectly in several materials displaying the DDW-induced-memory effect. Actually, γ-ray and x-ray scattering experiments performed on quartz[13] and on $Ba_2NaNb_5O_{15}$,[14] after an annealing inside their incommensurate phase, showed that the modulation wave vector remains locked on the value realized at the annealing temperature when the sample temperature is varied. Typical orders of magnitude of the temperature width of the plateaus related to the l_0 locked phase are 0.2 K for quartz and 20 K for $Ba_2NaNb_5O_{15}$. In thiourea and in A_2BX_4 compounds, no direct observations of the lock-in of the modulation on the DDW are available up to now. However, birefringence[1] and dielectric susceptibility[1,3] measurements have been interpreted by assuming the existence of such lock-ins.

By contrast, the plateaus related to high-order $(p/q)l_0$ locked phases do not seem to have been observed up to now. Two types of explanations can be given. First, we saw that the stability range of the pl_0 locked phases rapidly vanishes when p increases; the width of the plateaus may become smaller than the temperature resolution of the experiment. Second, throughout this paper, we were interested in the thermodynamic ground state of the model (the absolute minimum of the free energy), while the experimental studies[1-3] of the DDW-induced memory effect exhibit a thermal hysteresis of a specific type demonstrating the metastable character of the investigated systems. Hence, experimental results correspond to somewhat disordered materials and one may expect to observe broadened incommensurate satellites which hide the stepwise temperature dependence of the modulation wave vector. Hence, the situation with respect to the observation of a devil's staircase in DDW marked crystals is similar to the one in pure incommensurate crystals for which, up to now, there has been little experimental evidence of plateaus related to a high-order lock-in on the underlying lattice.[15-17]

Let us discuss now the second result, i.e., the multipeaked shape of the envelope of the modulation spectrum. A splitting of an incommensurate satellite into several components has been observed in various materials, namely, $[N(CH_3)_4]_2XCl_4$ with X=Zn (Refs. 17 and 18), Fe (Ref. 19) or Co (Ref. 20), Rb_2ZnBr_4 (Ref. 21), and $Ba_2NaNb_5O_{15}$ (Ref. 14). Up to now, no confirmed explanation of this phenomenon has been given. We suggest that for the two last compounds in which a DDW-induced memory effect has been reported, such an apparent splitting corresponds in fact to the observation of the envelope of the Fourier spectrum calculated here above.

Actually, in Rb_2ZnBr_4, M. Iizumi and K. Gesi[21] observed a splitting of the modulation in the lower stability range of the incommensurate phase (between -63 and $-87\,^\circ$C). This compound pertains to the A_2BX_4 family in which the defects are assumed[3,22] to interact with the modulation, giving rise to relaxation and memory effects. Iizumi does not mention any annealing of the sample preceding the splitting observation, but in Rb_2ZnBr_4 the period of the modulation does not depend on the temperature in the upper range of the incommensurate phase between $+77$ and $-63\,^\circ$C. Hence, the cooling of a sample in this temperature range is equivalent to an annealing at a given temperature; the defects can order in the field of the modulation with constant wavelength. We claim that the origin of the satellite splitting observed below $-63\,^\circ$C lies in the effect discussed in this paper when the modulation has to reconcile the wave-vector temperature dependence and the interaction with the frozen DDW. The neutron diffraction spectra measured by Iizumi are plotted in Fig. 3(b). They are in good qualitative and quantitative agreement with the calculated spectra of Fig. 3(a) between -69 and $-79\,^\circ$C when $\langle l\rangle \lesssim 1.25l_0$. Beyond this value, the agreement becomes poorer since the assumptions (52a) and (52b) on the spatial variations of the modulation phase are no longer valid. One has to look for a more realistic description of the soliton pattern in the incommensurate phases surrounding the $\frac{4}{3}l_0$ or $\frac{3}{2}l_0$ locked phases.

$Ba_2NaNb_5O_{15}$ constitutes an other example.[2,14] After an annealing in its incommensurate phase (during which the DDW onsets), J. M. Kiat *et al.* have observed, on cooling, first a freezing of the modulation wave vector (interpreted as a locking on the DDW) followed by a splitting of the incommensurate modulation into two components. The temperature dependence of the scattering spectra (Fig. 2 of Ref. 14) is qualitatively similar to the one of Fig. 3(a) of this paper.

VI. CONCLUSION

In this paper, we have investigated the properties of an incommensurate modulation subject to two competing potentials with different periodicities: the potential of the underlying lattice and the potential induced by a frozen DDW. We used a perturbative model valid when the lattice potential is much stronger than the DDW one. In our model, the discommensurations of the modulation (solitons) are considered as material objects subject to their mutual interactions and to the DDW potential.

First, we have shown the equivalence of the model with the Frenkel-Kontorowa problem. As a consequence, and in agreement with the model of Aubry[5] and Fradkin[4] *et al.* on systems with competing periodicities, the soliton system undergoes, between the normal-incommensurate transition and the lock-in transition on the lattice, a succession of transitions between two kinds of periodic phases either locked or unlocked on the DDW; the temperature dependence of the average soliton spacing is represented by a devil's staircase.

Second, the structure, the free energy, and the stability of the unlocked phases with $\langle l \rangle \approx p l_0$ (p integer) have been determined with the help of the supersoliton concept. The supersoliton is an intrinsic defect of the soliton pattern which is the analog of a discommensuration for the atoms of the FKP.

Third, the Fourier spectrum of the modulation has been computed. Since the soliton spacing is not constant but modulated, the spectrum has a comb structure whose envelope can be adjusted to the type of multisatellite spectra observed in Rb_2ZnBr_4 (Ref. 20) and in $Ba_2NaNb_5O_{15}$ (Ref. 14). We suggest that our model provides the underlying explanation for these observations, unexplained until now.

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APPENDIX

In this appendix, we show that the amplitude scattered by the atoms of a displacive incommensurate material in a diffraction experiment can be approximated by a linear combination of the order-parameter components when the atomic displacements are small. Actually, the scattered amplitude is written as

$$A(q) \propto \sum_{n,p} b_p \exp(iqx_{n,p}) , \tag{A1}$$

where $x_{n,p}$ and b_p are, respectively, the coordinate and the form factor of the pth atom in the nth cell of the modulated phase. The main contribution to $A(q)$ comes for the atoms whose displacements are proportional to the order-parameter components. For a two-dimensional order parameter,

$$x_{n,p} - (x_p^0 + na) = \alpha_p \rho \cos(\phi_n - \phi_p) , \tag{A2}$$

where α_p is a proportionality constant, ϕ_p the relative phase of the displacements of the pth atoms with respect to the modulation, and $x_p^0 + na$ the coordinate of the pth atom of the nth cell in the unmodulated phase. When the atomic displacements are small, i.e.,

$$q\rho\alpha_p \ll 1 , \tag{A3}$$

and after elimination of the Bragg components, one derives for the first-order scattered amplitude

$$A(q) \propto B(q) \sum_n \exp(iqna)(\cos\psi \rho \cos\phi_n + \sin\psi \rho \sin\phi_n) , \tag{A4}$$

with

$$B(q)\exp i\psi = \sum_p \alpha_p b_p \exp(iqx_p^0)\exp(i\phi_p) . \tag{A5}$$

Equation (A4) is the expected result.

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