PHYSICAL REVIEW B VOLUME 48, NUMBER 12 15 SEPTEMBER 1993-II

Quasiregular impurity distribution driven by a charge-density wave

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(Received 13 January 1993; revised manuscript received 18 May 1993)

The displacive motion of impurities immersed into a one-dimensional (1D) system has been studied in detail previously as one kind of quasiregularity driven by charge-density waves (CDW). As a further investigation of this problem we develop here a microscopic model for a different kind of quasiregular impurity distribution driven by the CDW, consisting of a modulation in the probability of occupied sites. The dependence on impurity concentration and temperature of relevant CDW quantities is obtained. Data reported in the quasi-1D materials $NbSe_3$ and Ta_2NiSe_7, in particular thermal hysteresis effects at the CDW transition, are interpreted in the framework of the present model. Possible similarities to other physical systems are also suggested.

I. INTRODUCTION

The charge-density-wave (CDW) state is a form of the two-fermion condensate consisting of a coherent superposition of electron-hole pairs having a given value Q of the total momentum. In the one-dimensional (1D) system, to which we restrict ourselves in this work, this value is twice the Fermi value reduced to the first Brillouin zone ($Q = 2k_F \bmod G$, where G is the basic wave vector of the reciprocal lattice). Let us now assume that we add impurities to this system. They will be supposed to be ordinary (nonmagnetic) and to have no internal degree of freedom. The electrons will then scatter on them. By assuming, furthermore, that the spatial distribution of impurities in the chains is perfectly random, the scattering processes will be incoherent, thereby yielding the breakup of the coherent superposition of electron-hole pairs of the CDW condensate. Actually, the assumption of perfect randomness of impurity distribution was made in most of the studies dealing with this problem (see, e.g., Refs. 1–4 for reviews). Moreover, it was assumed that the spatial distribution of impurities is the same in the normal state and in the CDW one. Such an impurity distribution may be termed perfectly random and rigid.[5] Its destructive effect, as mentioned above, has been studied by means of a multitude of methods.[6–10]

However, very simple electrostatic arguments can be invoked to show that—unlike in the normal state—the perfectly random and rigid impurity distribution does not correspond to the most stable state of the system in the CDW state. Once the static modulation of electron density and the accompanying Peierls distortion of the lattice are installed into the system, impurities will tend to adjust their positions so as to minimize the energy of their interaction with lattice and electrons. Consequently, a quasiregularity in their spatial distribution having the same wave vector Q is expected. In a series of papers,[11,12,5] the occurrence of a CDW-driven displacive motion of impurities has been discussed. It has been argued that this kind of Q quasiregularity, having a similar form to the Peierls lattice distortion itself, could be expected in the case of low-mobility impurities. Nontrivial effects could result from this displacive motion: a reentrant CDW at the increase of impurity concentration x, thermal hysteresis effects, and a sensible broadening of the range of x values compatible with a gapless CDW state.[5]

However, this does not represent the most-favored state for the energetics of the CDW impurity system. Most favorable would be that impurities could occupy those sites in the chain where they would take the maximum advantage from the presence of the CDW. This would correspond to a modulation in the probability of sites occupied by impurities.

One should argue that this modulation could effectively occur in two realistic cases. Firstly, this could happen in the case where impurities could migrate through the crystal, via atomic diffusion processes, towards those sites where the energy of their interaction with the CDW is minimum. Experimental data reported for deuterated thiourea,[13] blue bronze,[14] and (cf. the presently proposed interpretation, Sec. V) niobium triselenide[15] could be invoked in favor of such a modulation allowed for highly mobile impurities. Secondly, one may expect such a modulation in the distribution of impurities in connection with the manner in which a certain doped quasi-1D material is synthesized. If this preparation process yields a material whose stable state is a CDW one, one would expect that, in the case where the process is slow enough, impurities would have the possibility to drift towards those sites at which the minimization of the total energy occurs; thence, a Q modulation in the occupation probability. We argue that this is the case of the Krogmann salt potassium cyano-platinide (KCP) which possesses a Peierls CDW distortion whatever the value of temperature where this quasi-1D compound is stable; the microscopical description based on this assumption turned out to be successful in explaining a variety of experimental data reported for KCP.[16,17]

0163-1829/93/48(12)/8619(10)/$06.00

As stated previously,[5] this CDW-driven quasiregularity of impurity distribution has to be accounted for in parallel to the usual pair-breaking effect of impurities on the CDW condensate. The purpose of the present paper is to investigate this interplay between disorder and $2k_F$ quasiregularity associated with the impurity distribution in the 1D CDW system for the second type of regularity described above. This study is intended to be complimentary to that done previously for the case of the CDW-driven displacive motion of impurities.[5] Both the aims and methods we shall use here are borrowed from the aforementioned investigation. Therefore, in order to avoid any repetition we shall skip the computational details whenever possible and present only those calculations which are specific to this paper.

The remaining part of the paper is organized in the following manner. The precise statement of the modulated impurity distribution is made in Sec. II, where the description of the method of solution is also given. Two limiting models of the modulated impurity distributions are discussed in Secs. III and IV; there, the dependence on impurity concentration of the relevant CDW quantities is derived. The last part of the paper, Sec. V, is particularly devoted to the discussion of the experimental data reported in various quasi-1D CDW materials with impurities in the light of the results obtained within the assumption of quasiregular impurity distribution.

II. COEXISTING CDW AND MODULATED IMPURITY DISTRIBUTION

It is well known that the electron-lattice interaction causes the (Peierls) distortion of the 1D periodic lattice, $\delta X_n = A_L \cos(QX_n + \varphi_L)$, and the static modulation of the electron density. Let us now assume that N_i out of the N atoms (ions) of the lattice are replaced by impurities which could occupy the lattice sites: $Y_\nu = X_{\overline{n}}$ ($1 \leq \overline{n} \leq N$, $1 \leq \nu \leq N_i$).[18] As discussed in the Introduction, a modulation in the probability w_n of sites occupied by impurities is expected in the case where they could reach the positions where the total energy of the system is minimum. In view of the overall $2k_F$ periodicity of the Peierls CDW state, the most natural assumption to be made on this probability is that it also possesses a $2k_F$ modulation,

$$w_n = \frac{1}{N}[1 + w_1 \cos(QX_n + \varphi_i)]. \tag{1}$$

Its amplitude w_1 accounts for the fact that a (small) fraction of impurities is no more randomly distributed. For the moment, we can think that Eq. (1) is an ansatz for the present problem whose form is justified by the qualitative arguments presented above. Later on (Sec. IV) we shall return to this point in more detail. Equation (1) plays a basic role in the present approach: it incorporates both the regularity (via the nonvanishing value of w_1) and the disorder (via the distribution function w_n itself) related to the modulated impurity distribution we are going to study.[19]

As the presence of impurities is essential, a precise statement of the framework adopted in the present investigation should be in order. It has been pointed out that no long-range order could exist in the presence of disorder in space dimensions less than four;[20,21] impurities smear out the CDW transition. Practically this means that CDW ordering occurs in finite domains of the order of the correlation length. Insofar as the latest extends over many unit cells,[22] one can argue that treating impurity effects on the static CDW properties by employing the methods used for an infinite system is acceptable as a first-step investigation.[23] On the other hand, as usual in this kind of study, we shall keep the picture of extended electronic states and ignore localization effects. Furthermore, the pinning effect also will be disregarded throughout in the present study on the static CDW properties.[24]

Following Ref. 5, we can get the total Hamiltonian H of the electron-lattice-impurity system in the presence of an overall (incommensurate) Q distortion. It consists of three parts,

$$H \equiv H^0 + H_{\text{scatt}} + E_{\text{elastic}}. \tag{2}$$

The first part is diagonal(izable), the second corresponds to the incoherent electron-impurity scattering, and the third represents the elastic energy. The first term has the form

$$H^0 = \sum_p \hat{\psi}_p^\dagger \, v_F p \, \hat{\tau}_3 \, \hat{\psi}_p + \sum_p \hat{\psi}_p^\dagger \left(\Delta \hat{\tau}_+ + \Delta^* \hat{\tau}_-\right) \hat{\psi}_p. \tag{3}$$

Here $\hat{\psi}_p$, $\hat{\psi}_p^\dagger$ are the Nambu spinors, $\hat{\tau}_\pm \equiv (\hat{\tau}_1 \pm i\hat{\tau}_2)/2$ ($\hat{\tau}_{1,2,3}$ are Pauli matrices), and v_F is the Fermi velocity. The $2k_F$ potential Δ acting on electrons consists of two parts,

$$\Delta \equiv |\Delta| \exp(i\varphi) = \Delta_L + \Delta_i, \tag{4}$$

corresponding to the Peierls distorted lattice (Δ_L) and $2k_F$ coherent scattering by the $2k_F$ regularity embodied in the impurity distribution of Eq. (1). Their explicit forms read

$$\Delta_L = \frac{1-x}{2} \, A_L \, \sqrt{\pi v_F \lambda M \omega_Q^2 / d} \, \exp[i(\varphi_L + \varphi_g)], \tag{5}$$

$$\begin{aligned} \Delta_i &= \frac{x}{2d} w_1 \left[V_{e-i}(Q) - V_{e-L}(Q)\right] e^{i\varphi_i} \\ &\equiv \frac{x}{2d} w_1 \, U_B \, \exp\left[i\left(\varphi_i + \varphi_B\right)\right]. \end{aligned} \tag{6}$$

The following notations have been used above: $x \equiv N_i/N$ is the fractional impurity concentration, d is the lattice spacing, λ is the dimensionless electron-phonon coupling strength, M is the mass of host lattice atoms (ions), ω_Q is the frequency of the bare $2k_F$ phonons, φ_g is the phase of electron-phonon coupling constant, and $V_{e-L}(Q)$ and $V_{e-i}(Q)$ are Q Fourier components of electron-lattice and electron-impurity interactions, respectively.

The incoherent part H_{scatt} comprises both forward and backward scattering of electrons by the impurity random potential[5] ($L \equiv Nd$ is the chain length)

$$H_{\mathrm{scatt}} \equiv \sum_{p} \sum_{q\neq 0} \hat{\psi}^{\dagger}_{p+q/2}\, \hat{U}(q)\, \hat{\psi}_{p-q/2},$$
$$\hat{U}(q) = \mathcal{U}_F(q)\hat{1} + \mathcal{U}_B(Q+q)\hat{\tau}_+ + \mathcal{U}_B^*(Q-q)\hat{\tau}_- . \tag{7}$$

The elastic energy stored by the distorted lattice is a classical quantity having, in the harmonic approximation, the expression

$$E_{\mathrm{elastic}} \equiv \frac{|\Delta_L|^2}{\pi v_F \lambda_L}\, L = \frac{|\Delta_L|^2}{\pi v_F \lambda} \frac{1-2x(1-1/\alpha)}{(1-x)^2}\, L, \tag{8}$$

$\alpha \equiv 4\,(\kappa_{LL}/\kappa_{Li}) \sin^2(Qd/2)$ being a dimensionless quantity proportional to the ratio of lattice-lattice (κ_{LL}) and lattice-impurity (κ_{Li}) elastic strengths.

Three effects of impurities on the CDW system are taken into account in the total Hamiltonian written above.

(i) An extra $2k_F$ potential [Δ_i, Eqs. (4) and (6)] originating from the coherent scattering of electrons by the $2k_F$ regularity of impurity distribution [Eq. (1)].

(ii) The usual pair-breaking effect brought about by the incoherent electron-impurity scattering [Eq. (7)] via the finite electronic lifetime, included in the case of perfect randomness.[6–9]

(iii) The renormalization of elastic energy stored up by the Peierls distorted lattice.

The present Hamiltonian differs from that corresponding to the case of displacive motion (Ref. 5): Δ_i is no longer an independent variational parameter and E_{elastic} does not contain the interference term dependent on $\varphi_L - \varphi_i$ any more.

The effect of H_{scatt} [Eq. (7)] will be taken into account by computing the electron self-energy and vertex corrections (averaged over the impurity configuration) within the self-consistent Born approximation and ladder approximation, respectively.[25,9,5] Besides the diagonal terms, the following nondiagonal term survives after averaging by means of Eq. (1),

$$\langle \mathcal{U}_F(q)\mathcal{U}_B^*(Q+q)\rangle \simeq \frac{x}{2dL}\, w_1\, U_F\, U_B\, e^{-i(\varphi_i+\varphi_B)}.$$

It is the direct consequence of the $2k_F$ modulated impurity distribution which mixes the forward- and backward-scattering processes which have the difference of momentum transfers equal to Q. This term prevents us from obtaining an analytic solution of the Dyson equations in the general case. Therefore we shall discuss below only the case $U_F = 0$; it has the advantage that the impurity modulation is still retained in a reasonable manner and a solution in closed analytic form could also be given. Following the standard method,[25,9,5] the thermodynamic potential Ω could easily have been obtained as

$$\Omega - \Omega_0 = -2k_B T \sum_p \sum_{i\epsilon} \int_0^{|\Delta|^2} \frac{d\xi}{\tilde{\epsilon}^2 + v_F^2 p^2 + \xi} + \frac{L}{\pi v_F \lambda_L}|\Delta_L|^2, \tag{9}$$

where Ω_0 corresponds to the normal state with perfectly random distribution of impurities, $\tilde{\epsilon} = \epsilon + (\tilde{\epsilon}\Gamma_B/2)\left(\tilde{\epsilon}^2 + |\Delta|^2\right)^{-1/2}$, $\Gamma_B \equiv xU_B^2/v_F d$. Within the variational approach one has to minimize the above expression with respect to both A_L and $\varphi_L - \varphi_i$.

III. CDW DRIVEN BY MODULATED IMPURITY DISTRIBUTION

So far, we have not made any assumption on the fractional modulation amplitude w_1. We shall assume in this section that w_1 is independent of A_L. The reason why we first adopted this model is twofold. Firstly, the variational procedure is simpler for this model of w_1. Secondly, although it no longer corresponds to a CDW-driven impurity regularity (see, however, the last part of Sec. IV), but rather to a converse situation where the CDW is driven by the modulated impurity distribution, this situation could also have its own relevance.[26] The minimization with respect to A_L and $\varphi_L - \varphi_i$ then yields a simple phase matching $\varphi_i - \varphi_L = \varphi_g - \varphi_B$ (φ_g is the phase of the electron-phonon coupling constant) (corresponding to $|\Delta| = |\Delta_L| + |\Delta_i|$) and the following equation for the CDW order parameter:

$$\frac{1}{\lambda_L}\left(1 - \frac{|\Delta_i|}{|\Delta|}\right) = B \equiv 2\frac{\pi v_F k_B T}{L} \sum_p \sum_{i\epsilon} \frac{1}{\tilde{\epsilon}^2 + v_F^2 p^2 + |\tilde{\Delta}_\epsilon|^2}. \tag{10}$$

The dependence on x of Δ at $T=0$ can be immediately obtained

$$\log\frac{|\Delta_0|}{|\Delta|} - \frac{\pi\zeta}{4} + \theta(\zeta-1)\left\{\frac{1}{2}\left[\sqrt{1-\zeta^{-2}} + \zeta \arctan\sqrt{\zeta^2-1}\right] - \log\left(\zeta + \sqrt{\zeta^2-1}\right)\right\} = \frac{1}{\lambda_L}\left(1 - \frac{|\Delta_i|}{|\Delta|}\right) - \frac{1}{\lambda}, \tag{11}$$

where $\zeta \equiv \Gamma_B/(2|\Delta|)$ and Δ_0 corresponds to the clean system. The nonvanishing expression in the right-hand side of the above equation reveals the difference between the present result and that derived within the Abrikosov-Gorkov-type approach.[6–10] On one hand there is the contribution of the impurity modulation, reflected in the presence of Δ_i. On the other hand, there is the effect of impurity renormalization of elastic energy, manifested in the difference between λ_L and λ [cf. Eq. (8)]. Figure 1 shows the dependence of A_L on impurity concentrations for various input parameter values at $T = 0$. Because of the model we have chosen in this section (CDW is now driven by impurity modulation), the quantity Δ does not vanish at increasing x. The true order parameter is now A_L and it vanishes beyond a certain critical concentration x_c, which is easily obtained by imposing $A_L = 0$ in Eq. (11),

$$\log \frac{x_c}{x_{c,0}} = \frac{1}{\lambda} + \log\left(2\overline{\zeta}\right) - \frac{\pi\overline{\zeta}}{4} + \theta\left(\overline{\zeta} - 1\right)\left[\frac{1}{2}\sqrt{1-\overline{\zeta}^{-2}} + \frac{\overline{\zeta}}{2}\arctan\sqrt{\overline{\zeta}^{2}-1} - \log\left(\overline{\zeta} + \sqrt{\overline{\zeta}^{2}-1}\right)\right] . \tag{12}$$

Here $x_{c,0}$ is the critical concentration value in the absence of both impurity modulation and impurity renormalization[6,8] and $\overline{\zeta} \equiv U_B/(v_F w_1)$.

A nonmonotonic behavior of A_L with increasing x could occur in the present case for certain values of the input parameters, contrasting with the overall monotonic decreasing in the perfectly random case. This behavior, which is sketched in Fig. 1, could reflect itself in elastic (x-ray, neutron, electron) $2k_F$ scattering data. Similar to other situations,[5,9,25] one finds an expression of the gap parameter $\Omega_g = \theta(\zeta - 1)|\Delta|\left(1 - \zeta^{2/3}\right)^{3/2}$ $(< |\Delta|)$ which shows that a *gapless* CDW regime can occur in the present model. As compared to the Abrikosov-Gorkov-type calculation,[9] the range of x compatible to the gapless regime $(0.912 < x/x_{c,0} < 1)$ is considerably enlarged; this is illustrated in Fig. 2. As a way to herald experimentally the gapless regime, the spin susceptibility χ can be computed within the ladder approximation for the vertex function.[5,9] Particularly simple is this expression for $T = 0$ $(\chi_P \equiv 2\mu_B^2/\pi v_F)$,

$$\chi/\chi_P = \theta(\zeta - 1)\ \sqrt{1-\zeta^{-2}}\ , \tag{13}$$

showing that nonvanishing values of the spin susceptibility in the CDW state exist only in the gapless regime. This is also displayed in Fig. 2. The temperature dependence of the order parameter (A_L in the present case) could be found by solving numerically Eqs. (4)–(6) and (10) for various values of the impurity concentration x.[27] Although, as we have just mentioned, there is no CDW-to-normal transition in this model; the actual order parameter A_L displays a monotonic decrease with increasing T. Unlike Δ, it eventually vanishes at a temperature $T_{c,L}$, whose equation can be straightforwardly obtained by imposing $A_L = 0$. Because $\Delta\ (= \Delta_i) \neq 0$, its x dependence can be only numerically found. Although it will be not given here, one should mention the large values of $T_{c,L}$ obtained in this case and the possible relation to the physical situations of fictitiously critical temperature: besides the compound pioneering the field of quasi-1D materials, KCP, already mentioned (cf. Ref. 17 and references therein), this situation reminds us of polyacetylene and $(BEDT\text{-}TTF)_2X$, where the dimerization (rather of chemical origin, which could be accounted for within the present model for Δ_i) is not a conventional Peierls distortion (see, e.g., Ref. 28).

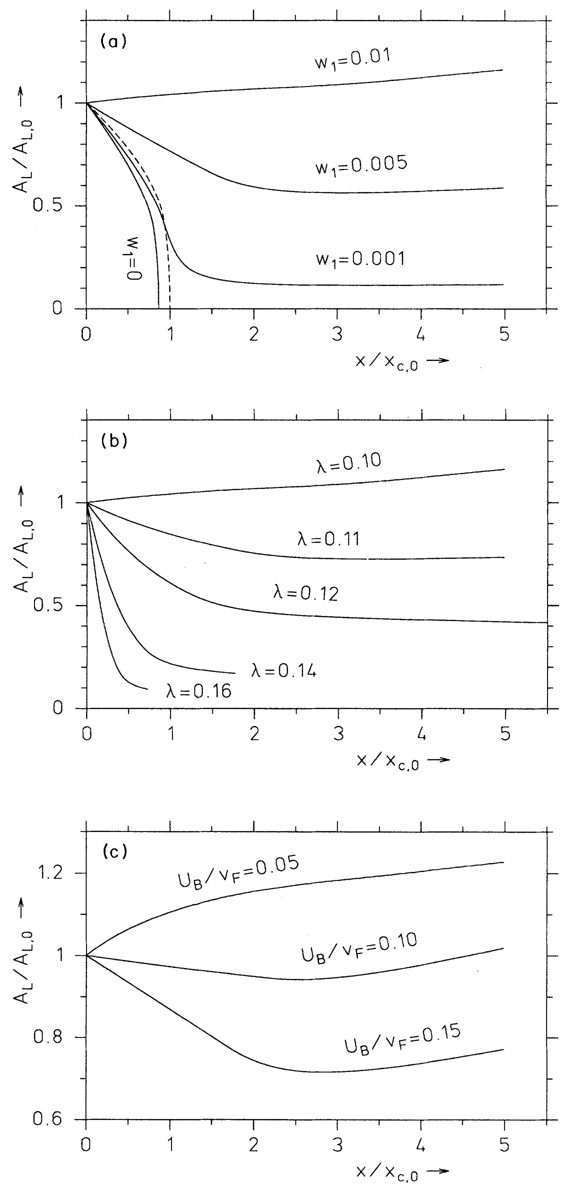

FIG. 1. Amplitude of the lattice distortion A_L normalized to that of the clean system $A_{L,0}$ plotted vs the impurity concentration (x) at $T = 0$ for $\alpha = 1$, $2Wd/v_F = 1$, and several values of (a) the fractional impurity modulation w_1 and $\lambda = 0.1$, $U_B/v_F = 0.075$ (the dashed curve, obtained in the absence of modulation and elastic energy renormalization by impurities, is different from the curve for $w_1 = 0$, including the latter effect); (b) the electron-phonon coupling strength λ and $w_1 = 0.01$, $U_B/v_F = 0.075$; (c) the scattering parameter U_B/v_F and $w_1 = 0.1$, $\lambda = 0.1$. Notice the x nonmonotonic behavior of A_L for certain values of input parameters.

IV. MODULATED IMPURITY DISTRIBUTION DRIVEN BY CDW

The present section is devoted to the discussion of the physical situation—which is more interesting in the light of what was stated in the Introduction—where the modulated impurity distribution is driven by the CDW. Then, the quantity w_1 [Eq. (1)] is no longer a free input parameter, but depends on the CDW properties. As discussed in the Introduction, if the impurity distribution is very flexible, impurities could migrate through the crystal to reach those positions which are most favored energetically. The energy of electron-impurity interaction can be easily evaluated, yielding[24]

$$w_n \propto \exp\left[\frac{2\beta|\Delta|}{\pi v_F}\; B\; U_B\; \cos\left(QX_n + \varphi_L + \varphi_g - \varphi_B\right)\right] .$$

By means of the above expression of w_n, and ignoring the higher-order harmonics of the quasiregular impurity distribution, one recovers the results of Sec. II. In the present case of CDW-driven modulated impurity distribution Δ_i can be entirely specified in terms of the CDW properties

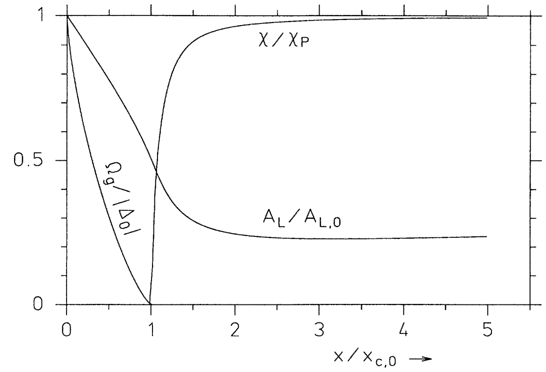

FIG. 2. Normalized order parameter ($A_L/A_{L,0}$), gap parameter ($\Omega_g/|\Delta_0|$), and spin susceptibility (χ/χ_P) plotted vs reduced concentration ($x/x_{c,0}$) at $T = 0$. The values of the input parameter are $\alpha = 1$, $2Wd/v_F = 1$, $\lambda = 0.1$, $w_1 = 0.001$, and $U_B/v_F = 0.075$.

$$\Delta_i = f_T\,\frac{x}{d}\,U_B\,e^{i(\varphi_i+\varphi_B)}\,\frac{\displaystyle\sum_{n=1}^{N}\exp\left[\frac{2\beta|\Delta|}{\pi v_F}\;B\;U_B\;\cos\left(QX_n+\varphi_i\right)\right]\cos\left(QX_n+\varphi_i\right)}{\displaystyle\sum_{n=1}^{N}\exp\left[\frac{2\beta|\Delta|}{\pi v_F}\;B\;U_B\;\cos\left(QX_n+\varphi_i\right)\right]}\,, \tag{14}$$

where $\varphi_i \equiv \varphi_L + \varphi_g - \varphi_L$. The numerical factor f_T ($\ll 1$) accounts for the physical fact that only a (small, presumably temperature-dependent) fraction of impurity atoms (ions) could follow the CDW and be distributed quasiregularly. More complicated now because of Eq. (14), the minimization of the thermodynamic potential yields an equation giving the T dependence of Δ whose solution can be obtained only numerically. However, no special feature is associated with this overall monotonic decrease with increasing T. Therefore we shall limit ourselves to discuss only the cases of high (i.e., near the critical) and low temperatures.

Close to the CDW-to-normal transition, the first-order expansion leads to distribution which is exactly of the form of the ansatz [Eq. (1)] we made in Sec. II with

$$w_1 = 2f_c\,\frac{\beta U_B}{\pi v_F}|\Delta|B. \tag{15}$$

Then the minimization of Eq. (9) yields the following self-consistency condition

$$B = \frac{1}{\lambda_L}\left(1 - f_c\,\frac{\beta\Gamma_B}{\pi}B\right)\left[1 - f_c\,\frac{\beta\Gamma_B}{\pi}\left(B - |\Delta|^2 C\right)\right], \tag{16}$$

$$C = \frac{1}{2}\pi k_B T \sum_{\epsilon}\frac{1}{\left(\tilde{\epsilon}^2 + |\Delta|^2\right)^{3/2}}\,\frac{1 - \frac{\Gamma_B}{2}\frac{1}{(\tilde{\epsilon}^2+|\Delta|^2)^{1/2}}}{1 - \frac{\Gamma_B}{2}\frac{|\Delta|^2}{(\tilde{\epsilon}^2+|\Delta|^2)^{3/2}}}\,.$$

Equation (16), along with Eqs. (10), provides the T and x dependence of the CDW order parameter Δ in the high-temperature limit. The equation for the critical temperature in the present model is obtained by imposing $A_L \to 0$ in Eqs. (10) and (16) as (ψ is the digamma function)

$$\log\frac{T_{c,0}}{T_c} - \psi\left(\frac{1}{2} + \frac{\Gamma_B}{4\pi k_B T_c}\right) + \psi\left(\frac{1}{2}\right) = \frac{1}{\lambda_L}\left(\frac{2}{1 + \sqrt{1 + f_c\,\frac{4\Gamma_B}{\pi\lambda_L k_B T_c}}}\right)^2 - \frac{1}{\lambda}. \tag{17}$$

The dependence on the impurity concentration of T_c is displayed in Fig. 3 for various input parameter values. It is worthwhile to note again the nonmonotonical dependence on x obtained in this model. It contrasts to the overall decreasing CDW critical temperature in the perfectly disordered case with increasing impurity content, vanishing beyond $x_{c,0}$ (a value considerably lower than the critical value of the present model, see below).[6–10] So, similar to the case of displacive motion,[5] the value of the CDW critical temperature is *higher* when a CDW-driven quasiregularity is allowed for. By imposing $T_c \to 0$, the present approach gives a critical value $\Gamma_B^c = 2W$, much larger than that obtained in the case of perfect randomness,[29] $\Gamma_B^{c,\,0} = |\Delta_0| = 2W\exp(-1/\lambda)$.[6,8,10] Although the corresponding value of impurity concentration $x_c = (2W/v_F)\,(v_F/U_B)^2$ is outside the range $x \ll 1$ compatible to the employed approximations, this result could be taken as indicating a sensible enhancement of

x_c caused by the CDW-driven impurity modulation.

In the low-T limit, one straightforwardly gets $|\Delta_i| = f_0 x U_B/d$. Now the quantity Δ_i does not depend on Δ any more and we recover the results of the preceding section if we formally set $w_1 = 2f_0$. This was an extra reason for discussing in detail the rather simpler model of Sec. III, whose main shortcoming, insofar as the CDW-driven modulation of impurities is intended, is the fact that the CDW does not disappear by increasing either x or T. Unlike that situation, a transition from the CDW to the normal state occurs in the present model by the increase of either x or T. We therefore argue that the CDW-driven modulated impurity distribution can realistically be described at low temperatures by the model with constant w_1 (Sec. III), whereas the high-temperature properties can be accounted for within the assumption (15), simpler than Eq. (14).

In the continuum limit, Eq. (14) yields $|\Delta_i| = (f_T x U_B/d)\,[\log\, I_0(z)]'$, where $z \equiv 2\beta U_B|\Delta|B/(\pi v_F)$ and $I_0(z)$ is the modified Bessel function. The behavior of the latter ($1 + \mathcal{O}(z^2)$ and $\exp(z)/\sqrt{2\pi z}\,[1 + \mathcal{O}(z^{-2})]$ (Ref. 30)) reveals the similarity of the results obtained for continuous and discrete distributions in high- and low-temperature limits.

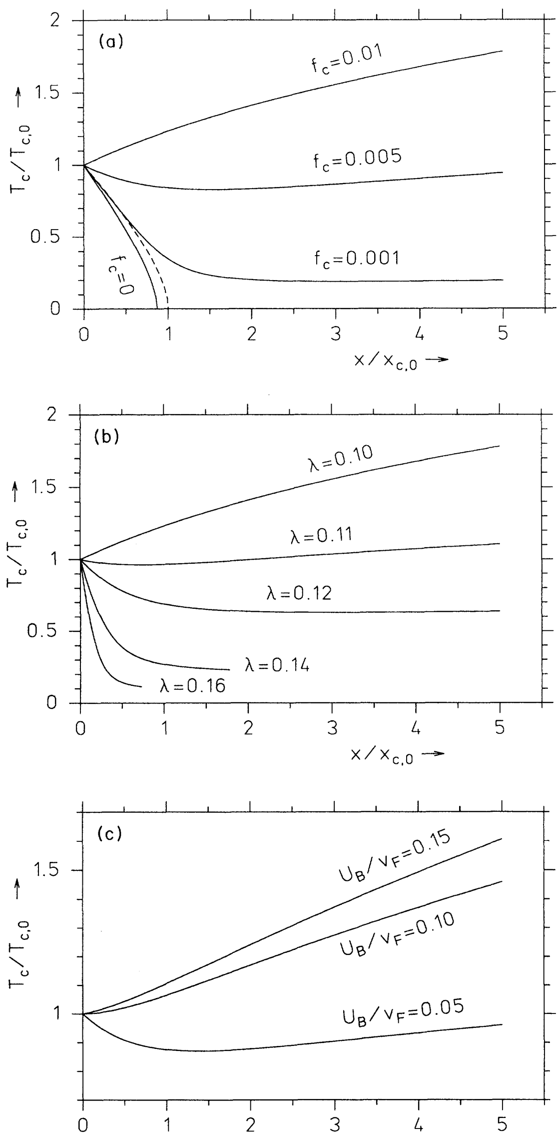

FIG. 3. Normalized critical temperature $T_c/T_{c,0}$ of the CDW-to-normal transition occurring in the case of the CDW-driven modulation of impurity distribution plotted vs the impurity concentration for $\alpha = 1$, $2Wd/v_F = 1$, and several values of (a) the fractional impurity modulation f_c and $\lambda = 0.1$, $U_B/v_F = 0.075$; (b) the electron-phonon coupling strength λ and $f_c = 0.01$, $U_B/v_F = 0.075$; (c) the scattering parameter U_B/v_F and $f_c = 0.007$, $\lambda = 0.1$. Notice the *nonmonotonical* x dependence of the critical temperature for certain input parameter values. The dashed curve in (a) has been obtained similarly to the dashed curve of Fig. 1(a).

V. DISCUSSIONS AND CONCLUSIONS

As a complimentary study to the displacive motion of impurities brought about by the CDW,[5] we have investigated here the modulated impurity distribution[16,17,31,32] as another kind of quasiregularity of impurities embeded into the 1D CDW system. This section will be devoted to the discussion of several experimental findings which do not fit the frame provided by the theory based on the assumption of perfectly random and rigid distribution of impurities, but in agreement with the results obtained in the case of quasiregular impurity distribution. While they clearly reveal a *qualitative* agreement with the theoretical predictions based on the assumption of quasiregular impurity distributions, one should also mention that the incomplete picture emerging from the experiments reported to date as well the limitations of the theoretical investigation—essentially: weak-coupling and weak-scattering[24] limits (λ, $U_B/v_F \ll 1$), the difficulty to evaluate microscopically the impurity fraction f—worsen the task of a quantitative comparison, or preclude to rule out alternative explanations.

A. Nonmonotonical CDW behavior

As a rule one can state that, whichever the type of $2k_F$ quasiregularity in the impurity distributions—of either Ref. 5, Sec. III, or Sec. IV—, the CDW correlations are enhanced with respect to the case of perfectly random distribution. As discussed previously,[5] universal curves for, e.g., the reduced order parameter, the critical temperature and the gap parameter as overall *decreasing* functions of reduced impurity concentration have been found in the latter case ("law of corresponding states"). Actually, even for perfect randomness, this universality is lost if the impurity renormalization effect is accounted for: it is reflected in the presence of the quantity α in Eq. (8). Perhaps the most spectacular manifestation of this loss of universality is the reentrant CDW regime obtained in the case of CDW-driven displacive motion of impurities.[5] Neither the model of Sec. III nor that of Sec. IV displays a reentrant CDW behavior. However, a nonmonotonical behavior of various quantities with increasing x could occur in either case of $2k_F$ modulated impurity distribution (cf. Figs. 1 and 2). Experimentally, one observed an upturn in the resistive anomaly associated with the upper CDW transition occurring in the linear chain compound $Nb_{1-x}Ta_xSe_3$ at the increase of x beyond $\approx 4.5\%$.[33] An analysis of the physical situation in this alloyed quasi-1D compound has already been made.[5] We should only remark here that the possible explanation given there by invoking a CDW-driven quasiregularity of tantalum atoms could comprise either the displacive motion or the modulated distribution. One should also notice at this point that a nonmonotonical change at the variation of impurity content in a physical system, where coexisting ordered phases influence each other, is also encountered in the heavy fermion superconductor $Th_xU_{1-x}Be_{13}$ (see, e.g., Ref. 34, for a recent review). There, a nonmonotonical drop of the superconducting critical temperature at the increase of the Th content has been observed.

B. Broad impurity range for the gapless CDW regime

Another similarity with the case of CDW-driven impurity displacive motion is the possibility of considerably broadening the impurity concentration range for the gapless CDW regime. A gapless CDW state has been observed in heavily ClO_4-doped polyacetylene,[35,28] but the range of the dopant concentration which is experimentally compatible to the gapless regime is much broader than that obtained for the case of perfect randomness.[5] To assign this broadening to a modulated distribution is particularly tempting in the case of polyacetylene in view of its fictitious critical temperature (cf. Sec. III).

C. Thermal anomalies at the CDW transition

A nontrivial issue of these investigations of CDW-driven quasiregularities in the spatial distribution of impurities is the possibility of a thermal hysteretic behavior at the CDW transition. This behavior is related to the fact that, when studying the instability of the normal state of the system containing impurities upon cooling, this critical temperature coincides with that of suppressing (by heating) the CDW state in the case of *perfectly random* distributed impurities.[36] As already mentioned (see Sec. IV and also Ref. 5), the CDW critical temperature is higher in the case of quasiregular impurity distribution (either displacive motion or modulated distribution): $T_{c,\mathrm{heating}} > T_{c,\mathrm{cooling}}$.[37] In addition, a finite difference exists at a given temperature T between the values of various quantities computed in the cases where the impurity distribution is quasiregular and perfectly random.

Within this interpretation, the results of Sec. IV allow us to evaluate the fractional change of, e.g., the critical temperature and the low-T distortion amplitude in the low-x limit,

$$r_T = f_c\, x\, (v_F/\gamma W d)\, (U_B/\lambda v_F)^2 \exp(1/\lambda)\,,$$

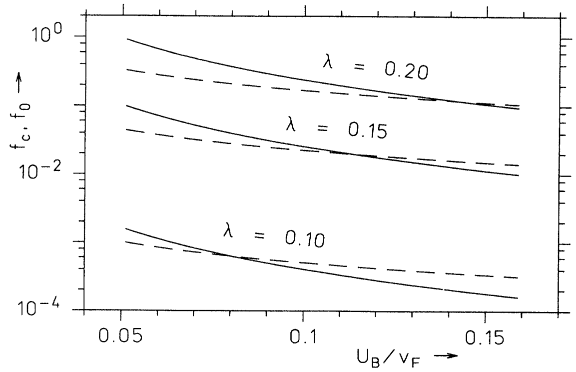

FIG. 4. The λ and (U_B/v_F) dependence of the impurity fractions f_c (solid line) and f_0 (dashed line) corresponding to $r_T = 1\%$ and $r_A = 1\%$ (i.e., observable thermal hysteresis) at an impurity content $x = 1000$ ppm ($2Wd/v_F = 1$).

and

$$r_A = f_0\, x\, (v_F/2Wd)\, (1-\lambda)\, (U_B/\lambda v_F) \exp(1/\lambda),$$

respectively ($\gamma \simeq 1.78$). As shown in Fig. 4, the values of f_c and f_0 which render the thermal hysteresis observable strongly depend on λ and U_B/v_F; hence, there is a strong material dependence of the observability of this effect. Notice that the ratio r_T/r_A is also λ and (U_B/v_F) dependent, a fact which could explain why, even in a given material, a thermal hysteretic behavior could be exhibited by a certain quantity, whereas it could be absent in another quantity.

1. Case of $NbSe_3$

Whether the CDW transition displays a thermal hysteresis is effectively observed or not in a system with a presumable modulated impurity distribution strongly depends on at least two things. Firstly, the impurities have to be sufficiently mobile in the host lattice to be able to migrate towards the most favored positions. To this aim, one needs a time scale for changing the temperature slower than the time of (atomic) diffusion. Secondly, it is related to the magnitude of critical fluctuations. It seems likely that when they are large, they would reflect themselves in significant *pretransitional* effects along with short CDW correlation length. With this in mind, let us proceed by analyzing the thermal study on $NbSe_3$ of Ref. 15. Although not very recent and performed on a material not *intentionally* doped,[38,39] its salient feature is the fact that this experiment has been conducted with an extremely slow variation of temperature ($\sim$ 1 K/h). At such low values of temperature variation, two specific heat anomalies, associated with the partial removal of the Fermi surface of this quasi-1D compound due to formations of two CDW gaps,[1] have been found.[15] The large pretransitional effects at the upper CDW transition of $NbSe_3$ (up to $\sim$ 7 K) above the critical temperature T_{c1} = 145 K (Ref. 15) combined with the (lower bound) estimation of intrachain CDW coherence length, $\xi_1 \approx 50$ Å (Ref. 40) could be inferred to explain why no difference in the critical temperature during heating and cooling has been detected in Ref. 15. Fortunately, the lower CDW transition of $NbSe_3$ displays no pretransitional effects[15] and the (lower bound) estimate for the intrachain CDW coherence length is much larger ($\xi_2 \approx 3000$ Å).[41] One should therefore expect an experimentally detectable difference in the critical temperature at the lower CDW transition. The actual experimental data, $T_{c2,\text{heating}} = 59$ K and $T_{c2,\text{cooling}} = 58$ K (Ref. 15), support the proposed picture. As already mentioned, a finite difference exists at a given temperature T between the values of various quantities (for instance, Δ, A_L, Ω_g) computed in the cases where the impurity distribution is quasiregular and perfectly random. In the case where the physical conditions allow a quasiregular impurity distribution this difference should yield a first-order character (finite latent heat) of the CDW transition upon cooling down at the value $T = T_{c,\text{cooling}}$. It is just the behavior observed in Ref. 15. The fact that the observed latent heats were much larger than those expected from an incommensurate-commensurate CDW transition is related to the much larger energy scale involved in the presently proposed mechanism.[42] So, we suggest that the anomalous thermal behavior (both the hysteresis in the critical temperature T_c and latent heats) seen in Ref. 15 is due to the fact that the extremely slow change of temperature allows the spatial distribution of defects to follow the CDW and become modulated.

2. Case of Ta_2NiSe_7

More recently, thermal hysteresis in resistivity and order parameters extracted from x-ray scattering data has been reported in the chainlike compound Ta_2NiSe_7.[43] It is beyond the scope of the present paper to give a definite picture of the physical behavior of this material. For this, much more work has to be done from both theoretical and experimental sides. Nevertheless, we think that the present paper, along with the previous ones on quasiregular impurity distributions,[5,36] could provide some insight into the unusual features reported in Ta_2NiSe_7. This is why we shall discuss below in some detail the physical picture emerging from the aforementioned study.[43] The experimental findings can be summarized as follows.[43] An electronic anomaly and an incommensurate modulation have been observed in Ta_2NiSe_3. It has been concluded that the structural distortion is of electronic origin, although some unusual features found there do not rule out a chemical origin of the distortion. It has been also claimed that the much more ordered structure of Ta_2NiSe_7 with respect to its structurally similar compound $FeNb_3Se_{10}$ drastically reduces the magnitude of the random potential present in the latter. Consequently, one may expect a metallic behavior of Ta_2NiSe_7 over a broad temperature range starting from room temperature and extending down to liquid helium. However, from these measurements it was inferred that the ordering (of Ni and Ta on the octahedral chains) is incomplete. As such, a weak localization remains at low temperatures. As in $FeNb_3Se_{10}$, the disorder present in Ta_2NiSe_7 affects the formation of true long-range order below the CDW onset temperature as well as the amplitude of the CDW, not only the phase as in other compounds with a chain or layered structure.

The CDW formation in Ta_2NiSe_7 can be inferred from three main observations: a resistive anomaly, a magnetic susceptibility anomaly, and x-ray-scattering satellite intensities. Roughly, all these anomalies develop in the same temperature region. The resistive anomaly, whose shape is qualitatively similar to that of $NbSe_3$, though of smaller magnitude, has its upturn at the temperature $T_o = 52.5$ K, suggesting the CDW onset at that temperature. The anomaly in magnetic susceptibility data is even smaller than that in resistivity. The smallness of these anomalies witnesses the fact that the CDW formation removes but a small part of the Fermi surface. This CDW picture is further supported by the recent scanning transmission microscope images,[44] which revealed a complex electronic rearrangement below the temperature $T = 52.5$ K, a value which agrees with the CDW onset temperature extracted from the aforementioned anomalies. The T-dependent integrated intensity of the x-ray (incommensurate) CDW satellite displays a number of unusual features.[45] What matters at the present stage of discussion is that, essentially, it accompanies the aforementioned anomalies in the same temperature range.

More interesting for the present purpose is the clear observation of a thermal hysteresis. The resistivity is larger upon warming than upon cooling, implying thereby a *larger* CDW gap during *warming*: exactly the behavior we expect in the case of a quasiregular impurity distribution (of either the kind presently discussed or that of the displacive motion kind[5]). Most encouraging for such an interpretation is the fact that a hysteresis in the very x-ray scattering intensities—thus *directly* associated with a *modulated* structure—accompanies the thermal hysteresis in resistivity. In addition, the coincidence of temperature ranges rules out the possibility to ascribe the latter to the difference in local readjustment of the CDW phase during warming and cooling. Moreover, the attempts to detect nonlinear conduction below the CDW transition region failed.[43] On this basis, one should claim that the phason contribution to the conductivity is altogether ineffective. Furthermore, this feature could be interpreted as an indirect evidence for a Q quasiregular impurity distribution: as shown previously,[17] the latest could considerably increase the pinning frequency of the phase mode. The large value of the pinning frequency in KCP, explained by such a quasiregularity,[17] pushes the threshold field of nonlinear conduction up to ~ 2000 V/cm.[46]

More generally, one can assign the present work as investigating the possibility of a CDW-driven ordering in a system which is manifestly disordered. We mention in this context a recent study[47] which fits well this more general framework. There, by employing high-resolution electron microscopy in investigating the Ag-Mg alloys near Ag_3Mg, the formation of long-period superlattice structures from the disordered phase has been observed. A CDW-driven ordering process has been suggested, related to the nesting property of the Fermi surface. In light of the present study, a search for possible thermal anomalies could give further insight into the nature of the ordering process observed in this system.

In these phenomena involving quasiregularities induced by an ordered (CDW) phase, the explicit inclusion of impurity kinetics (diffusion processes) in order to derive a microscopic expression for the parameter f—in the manner discussed in Ref. 48—would be a desirable next step.

ACKNOWLEDGMENTS

One of the authors (I.B.) wishes to thank the hospitality extended to him at Universität Ulm, where the main work related to this paper has been carried out. The financial support which made this possible, provided by the Alexander von Humboldt Foundation, is most gratefully acknowledged. He wants to thank Professor W. Wonneberger for valuable discussions, helpful suggestions to organize the material, and the critical reading of the manuscript, and Mr. W. Aichmann for computer assistance and carefully reading the manuscript. Part of this work has been done when I.B. was visiting the International Centre for Theoretical Physics, Trieste. The financial support provided by ICTP Trieste is also gratefully acknowledged. Further thanks are due to Professor P. Monceau for bringing Ref. 15 to his attention and for a helpful discussion related to it, to Professor P. N. Butcher for making him aware on the terminology used in doped systems, and to Professor A. Ruckenstein for stimulating discussions and drawing his attention to Ref. 48.

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[18]This choice, which corresponds to the case of substitutional impurities, is made only for simplicity; calculations could be done also for $Y_\nu = X_{\bar{n}} +$ const or for a continuous distribution ($0 \leq Y_\nu \leq L$).

[19]The term *modulated impurity distribution*, which we use here, was put forward in connection with the quasi-1D compound KCP (Refs. 16 and 17); simultaneously but independently a somewhat similar physical situation in deuterated thiourea has also been discussed and termed a *defect density wave* [P. Lederer, G. Montambaux, and J. P. Jamet, Mol. Cryst. Liq. Cryst. **121**, 99 (1985)].

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[23]Actually, this restriction is less severe in the present case; one would expect an enhancement in the correlation length by allowing a quasiregularity of impurity distribution, Eq. (1), as compared to the case of perfect randomness.

[24]We neglect throughout the pinning effect, i.e., we allow no space and time dependence of the phase parameters characterizing the Q distortions. Actually, in the weak-scattering limit ($U_B/v_F \ll 1$) the CDW is only weakly perturbed [cf. I. Tüttó and A. Zawadowski, Phys. Rev. B **32**, 2449 (1985)]. The study of the pinning effect, which plays an essential role for the CDW dynamical properties, along with the electron lifetime effect, is deferred to a subsequent publication. Actually, the quasiregularity in the distribution of impurities should have important effects on the CDW dynamics of the CDW transport. We mention for illustration the enhancement in the pinning frequency of the phase mode (Refs. 16 and 17).

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[37]One may think that the inequality in the text is questionable; as for its derivation, mean-field-like approximations have been employed. We argue, however, that the physical reason for this inequality goes well beyond these approximations. The mechanism raising $T_{c,\text{heating}}$ above the value of $T_{c,\text{cooling}}$ is the CDW-driven quasiregularity; consequently, it acts only when approaching the transition from the CDW side.

[38]P. Monceau (private communication).

[39]The thermal anomalies we are going to discuss in the framework of the proposed model of modulated impurity and/or defect distributions in these "pure" samples of $NbSe_3$—which contained, however, a certain amount of intrinsic disorder (Ref. 38)—are only related to the latest; one would expect larger effects in samples with appropriate (for the present purpose) *intentional* doping.

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