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Effects of impurities on charge-density waves: A mean-field calculation

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The effect of substitutional impurities on systems that present a charge-density-wave (CDW) ground state induced by a Peierls distortion is studied within a mean-field approximation. The calculations have been performed for both one-dimensional and two-dimensional models. The results of the calculations indicate the following. (i) The presence of impurities weakens the CDW and eventually destroys it. (ii) A distinction is made between the two effects of doping that perturb the CDW, namely, the disorder and the shift of the band filling. (iii) In the case of disorder, the results are interpreted in terms of lack of coherence of the electronic states and the coherence length of the instability. (iv) The variations at $T=0$ of the CDW order parameter with the impurity concentration follows a square-root law. (v) The CDW transition temperature is reduced by the presence of impurities showing a critical behavior. (vi) Substitutional impurities in commensurate CDW systems have a similar effect as magnetic impurities in superconducting materials and normal impurities in the excitonic insulator.

I. INTRODUCTION

It is well known that impurities have important effects on charge-density waves (CDW's) in both chainlike[1] and layered compounds.[2] The problem of impurities in complex systems such as the quasi-one-dimensional tetrathiafulvalene-tetracyanoquinodimethane or the quasi-two-dimensional layered compound $1T$-TaS$_2$ is extremely complicated and can be considered under different points of view.[3–8] One is therefore forced to choose a particular aspect of the problem and focus attention on it, ignoring for the time being any other.

One of the more important consequences of the incorporation of certain impurities in some materials that present CDW instabilities is the weakening of the CDW amplitude as deduced from the decrease of the CDW transition temperature.[2,9]

In this work, we study the decrease of the CDW order parameter at $T=0$ with the addition of substitutional impurities as well as the reduction of the transition temperature. We model the problem by considering a Hamiltonian which includes electronic, vibrational, and electron-phonon (only a single phonon is considered) contributions. The effect of disorder is included via an electronic self-energy obtained by two different mean-field approximations, such as the coherent-potential approximation[10] (CPA) and the cluster-Bethe-lattice[11] model. The Hamiltonian is solved for both a one- and a two-dimensional model. It is shown that the main results obtained numerically with these ingredients are essentially reproduced by an oversimplified model described by a constant density of states and an energy-independent Lorentzian broadening of the electronic states. These results stress the general validity of our model calculation, at least for commensurate and fixed $\vec{q}$-vector CDW instabilities.

This paper is organized as follows. In Sec. II we discuss the model Hamiltonian and show how to solve it to get the order parameter and the transition temperature. In Sec. III we present the results for both one- and two-dimensional systems. The results of this section are interpreted in terms of simple physical concepts in Sec. IV. Finally, in Sec. V the conclusions of our work are presented.

II. MODEL

In this section we discuss the model Hamiltonian for the pure material, and in Secs. II A and II B we discuss its ground state. The effect of impurities in the Hamiltonian, and therefore in the ground state, is discussed in Sec. II C.

A. Model Hamiltonian

We consider a model of electrons in Bloch states in the presence of a static lattice distortion. The Hamiltonian therefore contains three terms[12]

$$H=H_e+H_{\mathrm{ph}}+H_{e\text{-ph}}\,. \tag{2.1}$$

The one-electron term H_e describes a collection of noninteracting electrons moving in the periodic potential of the undistorted lattice

$$H_e=\sum_{\vec{k}}E(\vec{k})C^{\dagger}_{\vec{k}}C_{\vec{k}}\,, \tag{2.2}$$

where $E(\vec{k})$ is the band dispersion relation and the operator $C^{\dagger}_{\vec{k}}$ ($C_{\vec{k}}$) creates (destroys) an electron of crystalline momentum $\vec{k}$. The sum in (2.2) is extended to the first Brillouin zone and includes spin index.

The phonon (elastic) part of the Hamiltonian H_{ph} is the elastic energy due to the restoring force acting on the ions in the distorted lattice. This part can therefore be written as

$$H_{\mathrm{ph}}=\tfrac{1}{2}\gamma u^2\,, \tag{2.3}$$

where u is the amplitude of the periodic distortion and γ is a constant which accounts for the rigidity of the lattice.

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The electron-phonon coupling term of the Hamiltonian $H_{e\text{-ph}}$ is intended to describe the perturbation of the one-electron states induced by the periodic lattice distortion of amplitude u and wave vector $\vec{q}$. This term can be written as

$$H_{e\text{-ph}} = -\alpha u \sum_{\vec{k}} C^{\dagger}_{\vec{k}+\vec{q}} C_{\vec{k}} \, . \tag{2.4}$$

The constant α describes the intensity of the deformation of the crystalline potential.

The appearance of a Peierls distortion[13] (PD) and, consequently, a CDW, depends critically on $H_{e\text{-ph}}$.[12] If the reduction of electronic energy due to the electron-phonon coupling is large enough to overcome the elastic term H_{ph}, the system is unstable against the periodic distortion and the ground state presents a CDW.

The following remarks concerning the Hamiltonian (2.1) are in order.

(i) The $H_{e\text{-ph}}$ term is restricted to a chosen distortion with periodicity given by $\cos(\vec{q}\cdot\vec{r})$. In our calculations the wave vector $\vec{q}$ has been taken to be commensurate with the undistorted lattice and equal to $2\vec{k}_F$.

(ii) The coupling between electron states mediated by the lattice is taken linearly in the amplitude of the ion displacement u, the structure factor being a constant independent of $\vec{k}$.

(iii) The Coulomb electron-electron interaction is not taken into account. We therefore do not discuss possible magnetic ordering of the system.[14]

B. Ground state

The stable solution of the coupled electron-phonon system is found by minimizing the total energy [expectation value of (2.1)] with respect to the lattice deformation parameter u:[12]

$$\frac{\partial}{\partial u}\langle H(u)\rangle = 0 \, . \tag{2.5}$$

This stationary condition leads to the following equation:

$$-\alpha \sum_{\vec{k}} \langle C^{\dagger}_{\vec{k}+\vec{q}} C_{\vec{k}} \rangle + \gamma u = 0 \, . \tag{2.6}$$

The angular brackets in the above equations indicate the expectation value in the ground state.

The condition (2.6) is equivalent to solving the following Hartree-Fock (HF) self-consistent Hamiltonian:[15]

$$H_{\text{HF}} = \sum_{\vec{k}} E(\vec{k}) C^{\dagger}_{\vec{k}} C_{\vec{k}} - \lambda\zeta \sum_{\vec{k}} C^{\dagger}_{\vec{k}+\vec{q}} C_{\vec{k}} + \tfrac{1}{2}\lambda\zeta^2 \, , \tag{2.7}$$

where

$$\zeta \equiv \left\langle \sum_{\vec{k}} C^{\dagger}_{\vec{k}+\vec{q}} C_{\vec{k}} \right\rangle \tag{2.8a}$$

and

$$\lambda \equiv \alpha^2/\gamma \, . \tag{2.8b}$$

The average ζ plays the role of the order parameter of the system. If the solution of (2.7) gives $\zeta = 0$, the system is stable in the undistorted phase. However, if $\zeta \neq 0$ the ground state presents a lattice distortion of amplitude $u = (\alpha/\gamma)\zeta$ and the electronic spectrum displays a gap of halfwidth $\Delta \equiv \lambda\zeta$.

To get an idea of the relationship between ζ and λ and to characterize the condensed state one can assume a rectangular density of states ρ of bandwidth $2W$. If perfect nesting at half-band filling [i.e., $E(\vec{k}) = -E(\vec{k}+\vec{q})$] is assumed, it can easily be shown (see Appendix for details) that

$$\zeta = \frac{2W}{\lambda} e^{-1/\rho\lambda} \, , \tag{2.9}$$

where W is the half-bandwidth.

Therefore, we obtain a BCS-type equation[16] for the band gap,

$$\Delta = 2W e^{-1/\rho\lambda} \, . \tag{2.10}$$

Also the transition temperature behaves as in the BCS theory.[12] It is important to indicate that for more realistic electronic structures the functional relation (2.10) between Δ and λ remains valid.[12,15]

C. Effect of substitutional impurities

To study the effect on the CDW transition of substitutional impurities, we assume that only the electronic part of the Hamiltonian (2.1) is affected by the presence of impurities. Accordingly, the Hamiltonian H_e (2.2) takes the following form:

$$H_e' = \sum_i \epsilon_i C_i^{\dagger} C_i + V \sum_{\langle i,j \rangle} C_i^{\dagger} C_j + \text{H.c.} \, , \tag{2.11}$$

where $C_i^{\dagger}$ (C_i) creates (destroys) and electron at site i. The second sum in H_e' is restricted to nearest-neighbor atoms. The diagonal term ϵ_i is a random quantity whose probability distribution is

$$P(\epsilon_i) = x\delta(\epsilon_i - \epsilon_B) + (1-x)\delta(\epsilon_i - \epsilon_A) \, , \tag{2.12}$$

x being the concentration of impurities. ϵ_A and ϵ_B stand for the atomic energy levels of the host material (A component) and the impurities (B component), respectively. It is assumed that in absence of impurities the pure A component has perfect nesting of the Fermi surface at half-filled band.

The presence of impurities destroys the periodicity of the system and the elementary excitations are no longer Bloch-type waves. Therefore, the $E(\vec{k})$ dispersion relation is not well defined. It is clear that under these circumstances for a given concentration of impurities, the Peierls condition may not be satisfied, and therefore the CDW ground state is destroyed.

In order to handle the Hamiltonian (2.11) we replace the exact H_e' by an effective one in which the effect of disorder has been included in an average way,

$$H_e' \cong H_e^{\text{eff}}(\Sigma) \, . \tag{2.13}$$

This Hamiltonian is formally identical to the periodic one (2.2), but it is characterized by an energy-dependent self-energy Σ which in some way takes account of the effect of the disorder. The effective Hamiltonian is intended to reproduce the configurational-average electronic properties of the alloy.

In our calculations, and to characterize the effective Hamiltonian (2.13), we have used the CPA (Ref. 10) self-energy in the one-dimensional calculations. In the two-dimensional calculations we have used the self-energy obtained by means of a modified version[11] of a method[17,18] based on the cluster-Bethe-lattice model.

Once the electron Hamiltonian has been replaced by the effective one, the problem is formally identical to the perfect periodic one described above. The energy minimization equation is the same, but in this case the self-consistent equation for the order parameter is

$$\zeta \equiv \left\langle \sum_{\vec{k}} C^{\dagger}_{\vec{k}+\vec{q}} C_{\vec{k}} \right\rangle = -\frac{1}{\pi}\,\mathrm{Im} \int_{-\infty}^{+\infty} d\epsilon\, f(\epsilon) \sum_{\vec{k}} \frac{-\lambda\zeta}{[\epsilon-\Sigma(\vec{k},\epsilon)][\epsilon-\Sigma(\vec{k}+\vec{q},\epsilon)]-(\lambda\zeta)^2}\,, \tag{2.14}$$

where $\Sigma(\vec{k},\epsilon)$ is the complex dispersion relation of the effective electron Hamiltonian $H^{\mathrm{eff}}(\Sigma)$ describing the alloy. The function $f(\epsilon)$ is indeed the Fermi-Dirac distribution function. The sum in (2.14) is extended to the first Brillouin zone.

Since Eq. (2.14) is the core of this work, several remarks concerning the procedure for obtaining it are in order at this point.

(i) The disorder is only included in the electronic part of the Hamiltonian although it also perturbs the phonon and the electron-phonon terms. This is a good approximation, since we are mainly interested in the effect of the lack of the electron coherence on the CDW state.

(ii) Since we are using a mean-field approximation, statistical fluctuations are ignored. Spatial variations of the order parameter (phase or amplitude) are not included in the calculation.

(iii) The electron Hamiltonian has been replaced by an effective one before applying the electron-phonon mechanism. This implies a performing of the configurational average over electrons moving in the undistorted lattice potential. In terms of the Green's-function formalism this is equivalent to the following decoupling procedure:

$$\langle G\rangle = \langle G_0\rangle + \langle G_0 H_{e\text{-ph}} G\rangle \cong \langle G_0\rangle + \langle G_0\rangle H_{e\text{-ph}} \langle G\rangle\,, \tag{2.15}$$

where $G \equiv (z-H)^{-1}$ and $G_0 \equiv (z-H_e)^{-1}$. The angular brackets in (2.15) indicate configurational average.

III. RESULTS

In this section we present the results on the effect of substitutional impurities in the PD in the following different situations. (a) In the case of the one-dimensional lattice the effect of impurities is considered within the CPA. (b) In the case of the two-dimensional square lattice the alloy is treated using a reciprocal-space version[11] of the cluster-Bethe-lattice approximation.

In both (a) and (b) the electronic Hamiltonian is approximated by a tight-binding one which represents one orthogonal orbital per site with interactions between nearest-neighbor sites only. Also, in both cases we assume that the host atoms carry one electron per site (half-occupation). This band filling gives, for the pure material, a 2×1 superlattice in the one-dimensional case and a $C(2\times 2)$ in the two-dimensional case. In the case of the alloy the Fermi level has been adjusted in order to accommodate the following number of electrons n per site:

$$n = (1-x)n_A + x n_B\,, \tag{3.1}$$

with $n_A = 1$ (half-occupation) and $n_B = 2$ (full occupation). We now discuss the two cases separately.

A. One-dimensional case

With the above-indicated prescriptions the only parameter left to characterize the system is the energy difference between the atomic levels of the host and impurity atoms, respectively. In this section we illustrate the results for well-separated bands, i.e.,

$$\epsilon_A - \epsilon_B = 6W\,, \tag{3.2}$$

where $2W = 4V$ is the pure material's bandwidth.

We have performed the following calculations.

(i) *Phase diagram* $\lambda_m(x)(T=0)$. To obtain the phase diagram we find the minimum value of λ (λ_m) which gives a nontrivial solution of (2.14) for each impurity concentration. The results of the calculation are shown in Fig. 1. It is important to note the well-characterized logarithmic behavior near $x=0$,

$$\lambda_m \to 1/|\ln x| \quad \text{as } x \to 0\,. \tag{3.3}$$

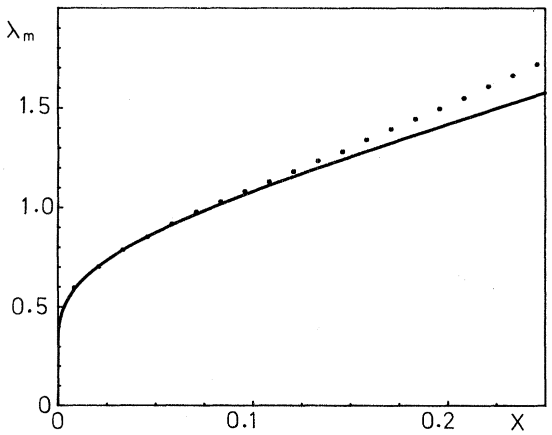

FIG. 1. Phase diagram for the one-dimensional system. The variation with impurity concentration of the minimum value of λ (λ_m) required to the appearance of the instability is shown. Dots indicate the results of the calculations. The continuous line represents the logarithmic fit of the results in the limit $x \to 0$ [see Eq. (3.3)].

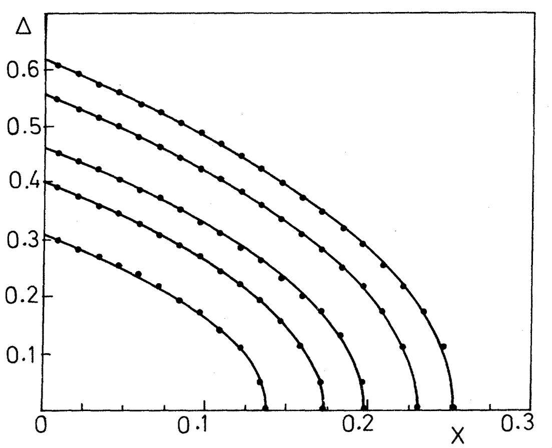

FIG. 2. Order parameter ($\Delta \equiv \lambda\zeta$) vs impurity concentration for five different values of λ/W (1.25, 1.40, 1.50, 1.65, and 1.75) in the one-dimensional system. Dots indicate the results of the calculations. The solid line is the square-root fit [Eq. (3.4)].

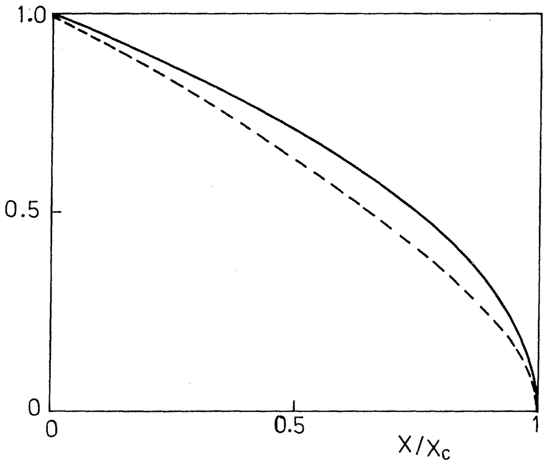

FIG. 4. Reduced values of the order parameter (Δ/Δ_0) (solid line) and the transition temperature (T/T_c) (dashed line) vs reduced impurity concentration (x/x_c) in the one-dimensional system.

(ii) *Evolution of the order parameter at zero temperature.* The numerical solution of Eq. (2.14) gives the order parameter $\zeta(x)$ (or equivalently $\Delta \equiv \lambda\zeta$) as a function of the impurity concentration x. Results of the calculations for different values of λ are shown in Fig. 2. A critical square-root behavior is clearly obtained. The numerical results can be fitted by the expression

$$\Delta(x) \propto (1-x/x_c)^{1/2}, \tag{3.4}$$

where x_c is the critical impurity concentration at which the order parameter vanishes, i.e., the condensed ground state is not stable.

(iii) *Transition temperature $T_c(x)$.* The self-consistent solution of the model Hamiltonian can also be obtained at finite temperatures. In the case of the dirty material as in the pure one there is a critical temperature $T_c(x)$ at which the CDW order parameter vanishes. Results of the calculations are shown in Fig. 3 for different values of the parameter λ. We also obtain a critical behavior for $T_c(x)$ which, indeed, is not of the square-root type such as $\Delta(x)$, indicating the different mechanism involved in the destruction of the CDW.

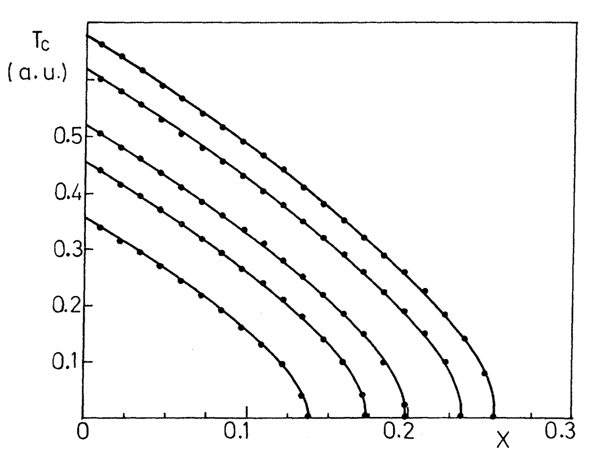

FIG. 3. Transition temperature T_c vs impurity concentration for five different values of λ/W (as in Fig. 2) in the one-dimensional system. Dots indicate results of the calculations. The solid line is a guide for the eye.

In Fig. 4 we have plotted results of the calculations for a given λ of the reduced order parameter and transition temperature in terms of the respective reduced concentration x/x_c. It is important to note that the BCS value for the ratio[12] Δ/T_c does not hold for impurity concentrations other than $x=0$.[4] This behavior is similar to that found in the problem of magnetic impurities in superconductors.[19,20]

In order to illustrate how the presence of impurities perturbs the electronic spectrum in the condensed phase we have calculated the density of electronic states for different values of $x<x_c$ for a given λ. Results of the calculation are shown in Fig. 5. In the case of pure material, ($x=0$), the lattice distortion is reflected in the existence of an energy gap whose magnitude 2Δ plays the role of the order parameter. In the concentration range $0<x<x_c$ the disorder has the effect of filling the gap with electronic states. However, as a result of the lattice distortion a dip in the energy spectrum is present. This depletion of states vanishes at the critical concentration. These results show that a lattice distortion can take place even if no absolute gap is present in the energy spectrum.[19]

B. Two-dimensional case

With the specifications indicated at the beginning of this section we have calculated the effect of substitutional impurities on the periodic-distorted-lattice state in the two-dimensional square lattice. In this case and in order to study how the results depend on the approximation involved in treating H_e', we present results in which the self-energy $\Sigma(\vec{k},\epsilon)$ is calculated in an approximation other than the CPA based on the cluster-Bethe-lattice approach. Details of this method and its relation with the single-site CPA can be found elsewhere.[11,21]

We have performed the same calculation as in the one-dimensional case. In this case we have taken

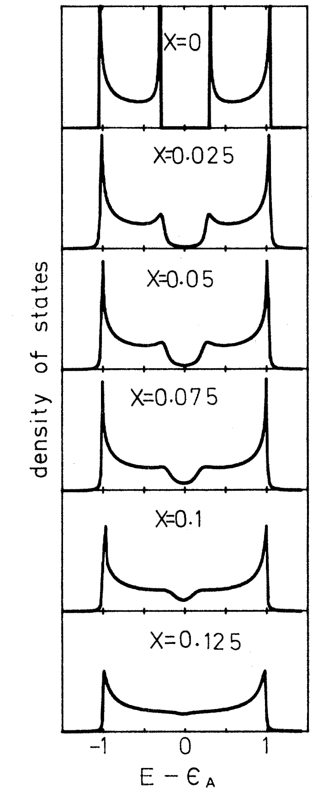

FIG. 5. Majority-band density of states for the one-dimensional system. The results are for five different values of the impurity concentration. In all cases a fixed value of λ ($\lambda=1.25W$) is taken.

$\epsilon_A-\epsilon_B=\frac{5}{2}W$, where $W=4V$ is the pure material's half-bandwidth. The results of the calculations are similar to those obtained in the one-dimensional case. In Figs. 6 and 7 we have plotted the phase diagram and variation of the order parameter with concentration, respectively. In these figures, we note that the logarithmic critical behavior of $\lambda_m(x)$ and the square-root behavior of the order parameter $\Delta(x)$ found in the one-dimensional case are also present in the two-dimensional calculation.[22] This clearly means that, within the mean-field approximation, the main features involved in the disappearance of the PD when impurities are present are independent of the dimensionality of the problem so long as the pure material presents a CDW ground state.

IV. DISCUSSION

In this section we interpret the results obtained in Sec. III in terms of simple physical ideas. It should be indicated that the most salient results reported above are valid for both the one- and two-dimensional calculations. We therefore address ourselves to generic systems that present CDW instabilities irrespective of the dimensionality of the problem. When the specific results have only been tested in the one-dimensional case, it will be indicated.

The effect of impurities (or any other kind of disorder) on the CDW ground state is that of destroying the coherence of the original Bloch electronic states near the Fermi level coupled by the instability [see Eq. (2.4)]. The lack of coherence is reflected in the fact that the electronic states are no longer eigenstates of the Hamiltonian, producing, therefore, an incertitude in energy δE which is somehow proportional to the amount of disorder. It is then reasonable to think that an instability involving the opening of an energy gap at the Fermi level is destroyed if δE is of the order of magnitude of the energy gap. If the gap behaves as $\exp(-1/\rho\lambda)$ [see Eq. (2.10)] we expect the parameter λ to behave as

$$\lambda \rightarrow 1/|\ln\delta E| \ . \tag{4.1}$$

This is what we have found in our calculations [see Eq. (2.3)], since, for low concentrations, δE is proportional to the impurity concentration x.[10]

To understand the problem more clearly, we have solved an oversimplified model in the Appendix which involved a constant density of states $\rho_0=\frac{1}{2}W$ where the disorder is simulated by adding a constant imaginary part Γ

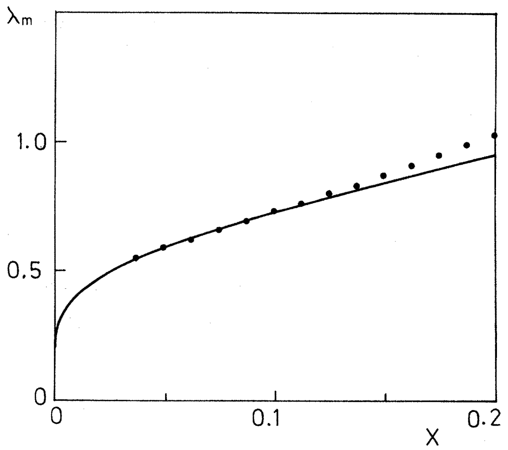

FIG. 6. Phase diagram for the two-dimensional system. The variation with impurity concentration of the minimum value of λ (λ_m) required to the appearance of the instability is shown. Dots indicate the results of the calculations. The continuous line represents the logarithmic fit of the results in the limit $x\rightarrow 0$ [see Eq. (3.3)].

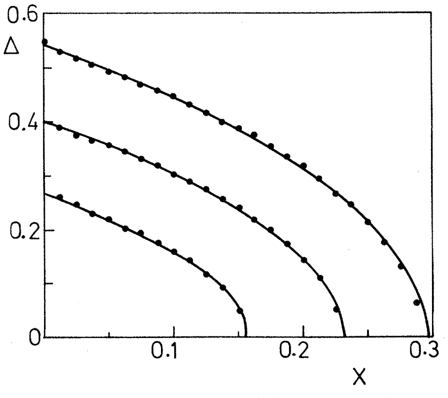

FIG. 7. Order parameter ($\Delta\equiv\lambda\xi$) vs impurity concentration for three values of λ/W (0.83, 1.04, and 1.25) in the two-dimensional system. The dots indicate the results of the calculations. The solid line is the square-root fit [Eq. (3.4)].

to the energy. The new electronic states are, therefore, Lorentzians characterized by a halfwidth at half maximum of Γ. We obtain for λ_m a critical logarithmic behavior [see Eq. (A11)], and for the gap we obtain a square-root variation with Γ of the form

$$\Delta/\Delta_0=(1-2\Gamma/\Delta_0)^{1/2}\ , \tag{4.2}$$

where Δ_0 is the energy gap in absence of impurities. The square-root variation of Δ is what we obtained in our numerical calculations in the preceding section, since, in the limit of low impurity concentration, Γ is proportional to x.

It is important to note that the relation (4.1) allows us to obtain a relation between Γ and Δ_0 of the form (see Appendix)

$$2\Gamma=\Delta_0\ . \tag{A12}$$

This relation is closely satisfied in the one-dimensional calculations in the limit of small energy gap, i.e., $\Delta_0 \ll W$ (see Fig. 8). Although we have not performed this calculation for the two-dimensional model, we believe it is still valid since in the way (A12) is derived the details of the density of states are unimportant. We are going to use Eq. (A12) to define, properly, the coherence length of the electrons in the condensed phase. As mentioned before, the reduction in the coherence of the electronic states gives rise to a finite lifetime τ, which is related to the energy incertitude by

$$\delta E\,\tau\sim\hbar\ . \tag{4.3}$$

We can then define the electronic mean free path l in the form

$$l=v_F\tau\ , \tag{4.4}$$

where v_F is the Fermi velocity.

The coherence length ξ is defined as the shortest mean free path required to allow the condensation to take place.

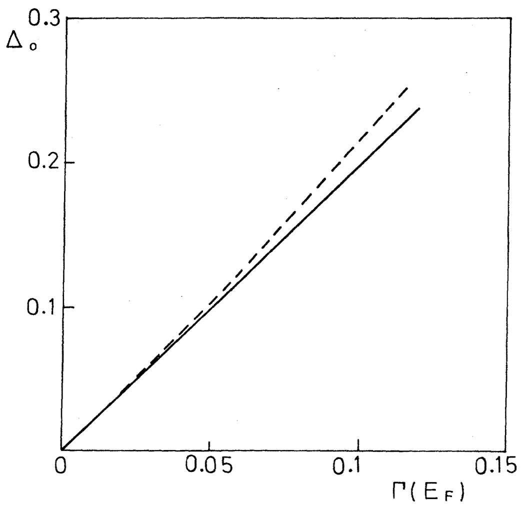

FIG. 8. Order parameter in absence of impurities (Δ_0) vs the imaginary part of the self-energy at the Fermi level (see text). Solid line: straight line corresponding to Eq. (A12). Dashed line: results of the calculation in the one-dimensional system.

It can therefore be written in the form

$$\xi=v_F\tau=v_F\hbar/\delta E\ . \tag{4.5}$$

If we take $2\Gamma=\delta E$ and make use of (A12), we end up with

$$\xi=\hbar v_F/\Delta_0\ , \tag{4.6}$$

which is analogous with what is found in superconductivity.[23] Therefore, the CDW disappears when the mean free path of the Fermi electrons is shorter than the coherence length.

So far we have only discussed the effect of the disorder in the CDW state. Impurities have another important effect on the CDW state that also weakens its magnitude, namely, they may change the position of the Fermi level. So far we have studied the case in which the host and impurity bands are well separated and the Fermi level meets the nesting condition in the majority (host) band. If, in the other extreme case, we assume that the only effect of the impurities is to change the total number of electrons in the system, the Fermi level is shifted and the nesting condition is not satisfied any longer, weakening (and eventually destroying) the CDW. By using the model of the Appendix it can be seen that in this case, the minimum λ (λ_m) required to produce a CDW of a given $\vec{q}$ vector is given by

$$\lambda_m=\frac{1}{\rho_0\ln|W/E_F|}\ , \tag{4.7}$$

where E_F is the shift of the Fermi level with respect to the perfect nesting condition. In (4.7) we see that the shift in the Fermi level has a similar effect on the CDW to that of the disorder [compare with Eq. (A11)].

To study the interplay between these two mechanisms of weakening of the CDW ground state, we have analyzed, in the one-dimensional model, the variation of λ_m with the separation in energy of the host and impurity atomic orbitals. We characterize this separation by the parameter

$$\delta=(\epsilon_A-\epsilon_B)/W\ , \tag{4.8}$$

and the calculations have been performed at a fixed concentration ($x=0.125$). We have considered two different forms of filling of the energy levels.[3]

(i) *Homopolar case.* In this case both components have the same valence and provide the same number of electrons per atom to the material. We have taken the half-filled-band case.

(ii) *Heteropolar case.* In this case the two kinds of atoms have different valence and for our particular example we have assumed that the host and impurity atoms carry one and two electrons, respectively.

We have calculated for each value of the parameter δ the two different values of λ_m corresponding to cases (i) and (ii). Since we are interested in distinguishing between the two CDW-weakening mechanisms discussed above, we have plotted, in Fig. 9, the two values of Δ_0 corresponding to the calculated λ_m. In the same figure we also show the imaginary part of the self-energy at the Fermi level $\Gamma(E_F)$ which is essentially the same in both cases. It should be noted that the quadratic behavior of Γ near $\delta=0$ corresponds to the Born approximation. Figure 9 allows us to

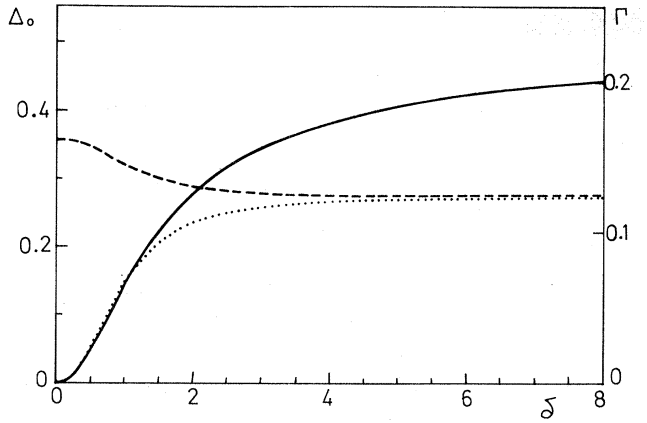

FIG. 9. Relationship between the imaginary part of the self-energy at the Fermi level and the order parameter in absence of impurities (Δ_0) for the one-dimensional system. The results for two different kinds of band filling are plotted vs the separation of atomic levels (see text). Dotted line: imaginary part of the self-energy at the Fermi level. Dashed line: Δ_0 for the heteropolar case. Solid line: Δ_0 for the homopolar case. The scales of Δ_0 and Γ are shifted to satisfy the calculated condition $\Delta_0 \cong 2.18\Gamma$ (see Fig. 8).

separate the two effects under discussion since, if only the disorder were important, the relation (A12) would be satisfied. Looking at Fig. 9 we conclude that the relation (A12) is satisfied, and therefore the disorder is the dominant mechanism in the CDW weakening in the following cases.

(a) Heteropolar case and very different species, i.e., δ very large (this is the case studied in this work).

(b) Homopolar case and very similar species, i.e., $\delta \rightarrow 0$.

Away from these two limits the disorder and the filling of the bands cooperate to perturb the CDW.

Around $\delta = 0$ the interpretation is specially simple. In the homopolar case the disorder results produce the dominant effect, whereas in the heteropolar case in the limit of no disorder $\delta = 0$, the only way to weaken the CDW is by shifting the Fermi level and destroying the Fermi-surface nesting condition.

V. CONCLUDING REMARKS

The main conclusion that can be drawn from the model developed in this work is that the presence of substitutional impurities weakens the CDW and eventually destroys it. The reduction of the CDW order parameter at $T=0$ is such that it varies with the concentration of impurities following a square-root law. The CDW transition temperature is reduced by the presence of impurities in agreement with previous theories. In our theory we can distinguish between the two processes that destroy the CDW when impurities are incorporated. Firstly, the lack of coherence of the electrons which is interpreted in terms of the energy-time incertitude principle, and, secondly, the shift of the Fermi level that does not meet the original perfect nesting condition.

We believe that the model we have presented incorporates the main physical ingredient of the problem treated, i.e., the effect of impurities in the Peierls instability. However, in order to make it feasible we have introduced some approximations which limit the validity of the results. Among the limitations we can include the following.

(i) The problem is treated within the mean-field approximation. We therefore ignore spatial fluctuations of the order parameter. These fluctuations are related to the impurity configurational fluctuations[8] that are ignored in single-site calculations. The main effect of the fluctuations in the alloy density of states is to introduce small exponential tails, we therefore believe that its effect in the CDW is to smooth the critical behavior of the order parameter around the critical concentration.

(ii) The effect of impurities is included only in the electronic part of the Hamiltonian. This approximation does not seem to be very restrictive since the destruction of the CDW is caused by the lack of coherence of the electronic states. A more sophisticated treatment would change the square-root behavior but not the overall picture.

(iii) We assume that only one phonon of a well-defined $\vec{q}$ vector is involved in the electron-phonon coupling. We are also limited to dealing with a CDW with a commensurate wave vector. This constrains us to consider only one specific kind of CDW instability. The variation of the CDW $\vec{q}$ vector with the filling of the band may have important consequences. Our model is intended to study mainly the effect of the disorder with a constant filling of the host band.

(iv) We have assumed that the impurities do not destroy the symmetry of the problem. This implies that the dispersionless constant energy contour related to the nesting of the Fermi surface is not destroyed. This is not a major effect, although in a realistic calculation it should be incorporated.

(v) We have not included the Coulomb electron-electron interaction. If it is included via a Hubbard-type Hamiltonian, complex ground states with magnetic order can take place,[14] making the analysis very complicated. However, if the electron-electron repulsion does not destroy the pure CDW ground state, its main effect is to reduce the amplitude of the CDW, and therefore, Eq. (2.9) is no longer valid.

(vi) In the calculation of T_c we have neglected the contribution of the phonon entropy. The calculated critical temperature can therefore be considered only as a lower bound.[24]

In spite of the above shortcomings of the work we can conclude that impurities in systems which present a phonon-induced CDW have similar effects as charged impurities in excitonic insulators[25] or magnetic impurities in superconductors.[19] These similarities arise from the fact that impurities in these systems have a pair-breaking effect due to the finite lifetime of the coupled electronic states. Work to improve this model is in progress. The microscopic study of impurities seems to be the right direction for the future.

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APPENDIX

In this appendix we obtain analytical solutions of the CDW order-parameter equation (2.14) after making some simplifying assumptions. The following analysis, in spite of its conceptual simplicity, retains most of the physical ingredients of the problem treated in this work.

We assume a single band of Bloch electrons with a dispersion relation satisfying the nesting condition $E(\vec{k}) = -E(\vec{k}+\vec{q})$. We also assume a constant density of states ρ normalized to 1 as

$$\rho(E) = \begin{cases} \rho_0 \equiv 1/(2W), & |E| < W \\ 0, & |E| > W . \end{cases} \tag{A1}$$

The effect of the disorder is simply introduced by means of an energy-independent imaginary contribution Γ to the energy. If $G(\epsilon)$ is the Green's function for Bloch states, for its diagonal matrix elements when disorder is present we can write

$$\langle \vec{k} \,|\, G(\epsilon) \,|\, \vec{k} \rangle = [\epsilon - E(\vec{k}) + i\Gamma]^{-1} . \tag{A2}$$

Within these simplifications Eq. (2.14) can be written as follows:

$$\lambda^{-1} = \int_{-\infty}^{\infty} d\epsilon\, f(\epsilon) \int_{-W}^{W} dE\, g(\epsilon, E, \Gamma, \Delta) \rho(E) , \tag{A3}$$

where

$$g(\epsilon, E, \Gamma, \Delta) \equiv -\pi^{-1} \frac{2\Gamma\epsilon}{[\epsilon^2 - E^2 - \Gamma^2 - \Delta^2]^2 + 4\Gamma^2\epsilon^2} \tag{A4}$$

and $\Delta \equiv \lambda\xi$.

In the absence of disorder, $\Gamma = 0^+$, and the solution of (A3) at $T=0$ gives the usual BCS-type gap equation

$$\Delta_0 = 2We^{-1/\rho_0\lambda} . \tag{A5}$$

In order to obtain the phase diagrams we have to solve (A3) for $\Delta = 0$. If we define

$$F(\epsilon, \Gamma) \equiv \int_{-W}^{W} dE\, g(\epsilon, E, \Gamma, \Delta = 0) \rho(E) , \tag{A6}$$

obtaining the following expression for $F(\epsilon, \Gamma)$ is straightforward:[26]

$$F(\epsilon,\Gamma) = -\frac{\rho_0}{\pi} \frac{1}{4(\epsilon^2+\Gamma^2)^{1/2}} \left[\frac{2\Gamma}{(\epsilon^2+\Gamma^2)^{1/2}} \ln \frac{(W+\epsilon)^2+\Gamma^2}{(W-\epsilon)^2+\Gamma^2} + \frac{4\epsilon}{(\epsilon^2+\Gamma^2)^{1/2}} \left[\arctan \frac{W^2-\epsilon^2-\Gamma^2}{2\Gamma W} + \frac{\pi}{2} \right] \right] . \tag{A7}$$

In the limit $\Gamma \ll W$, we can neglect the first term of the right-hand side. We can also make the following approximation:

$$\arctan \frac{W^2-\epsilon^2-\Gamma^2}{2\Gamma W} = \begin{cases} \pi/2, & |\epsilon| < W \\ -\pi/2, & |\epsilon| > W . \end{cases} \tag{A8}$$

Equation (A3) now reads as follows:

$$\frac{1}{\lambda_m} = -\int_{-W}^{W} d\epsilon\, f(\epsilon) \frac{\rho_0 \epsilon}{\epsilon^2+\Gamma^2} . \tag{A9}$$

For $T=0$ we obtain

$$\frac{1}{\lambda_m} = \rho_0 \int_0^W d\epsilon \frac{\epsilon}{\epsilon^2+\Gamma^2} = \frac{\rho_0}{2} \ln \frac{W^2+\Gamma^2}{\Gamma^2} . \tag{A10}$$

In the limit $\Gamma \ll W$, λ_m finally has the following form:

$$\lambda_m = \frac{1}{\rho_0 \ln(W/\Gamma)} . \tag{A11}$$

By using Eq. (A5) this equation can be expressed in a clearer form,

$$2\Gamma = \Delta_0 . \tag{A12}$$

This equation provides us with the amount of disorder (2Γ) needed to destroy a CDW instability characterized by a gap parameter Δ_0 in absence of disorder.

In order to solve Eq. (A3) for $\Delta \neq 0$, we change the order of integration,

$$\lambda^{-1} = \int_{-W}^{W} \rho(E) dE \int_{-\infty}^{\infty} f(\epsilon) g(\epsilon, E, \Gamma, \Delta) d\epsilon . \tag{A13}$$

For $T=0$ we obtain[26]

$$\int_{-\infty}^{0} g(\epsilon, E, \Gamma, \Delta) d\epsilon = \frac{1}{2\pi(E^2+\Delta^2)^{1/2}} \times \left[\arctan \frac{E^2+\Delta^2-\Gamma^2}{2\Gamma(E^2+\Delta^2)^{1/2}} + \frac{\pi}{2} \right] . \tag{A14}$$

Therefore, Eq. (A13) can be expressed as

$$\frac{1}{\rho_0 \lambda} = \int_{-W}^{W} \frac{dE}{2\pi(E^2+\Delta^2)^{1/2}} \times \left[\arctan \frac{E^2+\Delta^2-\Gamma^2}{2\Gamma(E^2+\Delta^2)^{1/2}} + \frac{\pi}{2} \right] . \tag{A15}$$

In the limit $\Gamma \ll \Delta \ll W$, Eq. (A15) can be solved performing the change of variable $U^2 = E^2 + \Delta^2$ and using the approximation

$$\arctan \frac{U^2-\Gamma^2}{2\Gamma U} \approx \frac{\pi}{2} - \frac{2\Gamma U}{U^2-\Gamma^2} . \tag{A16}$$

Equation (A15) now reads

$$\frac{1}{\rho_0 \lambda} = \ln\{ W/\Delta + [1+(W/\Delta)^2]^{1/2} \} - \frac{2\Gamma}{\pi(\Delta^2-\Gamma^2)^{1/2}} \arctan \frac{W}{(\Delta^2-\Gamma^2)^{1/2}} , \tag{A17}$$

which in the considered limit can be approximated by

$$\frac{1}{\rho_0\lambda} \cong \ln\frac{2W}{\Delta} - \Gamma/\Delta \ . \tag{A18}$$

Using (A5) we obtain

$$\Delta/\Delta_0 = e^{-\Gamma/\Delta} \cong 1 - \Gamma/\Delta \ . \tag{A19}$$

Solving (A19) for Δ^2 to first order in Γ/Δ_0 we obtain

$$\Delta^2 = \Delta_0^2 - 2\Delta_0\Gamma \ . \tag{A20}$$

It is worth mentioning that although Eq. (A20) has been obtained in the limit $\Gamma \ll \Delta \ll W$, numerical solutions of (A14) have approximately the same behavior as (A20) for a much wider range of Γ. In fact the solution of (A20) for $\Delta = 0$ gives us the same condition for the disappearance of the instability as in Eq. (A12).

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