

Substitutional impurities in a linear chain with Peierls instability: Single-impurity approach

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The effect of substitutional impurities on a half-occupied linear chain with Peierls instability is studied within a single-impurity approach. The change in energy due to the presence of impurities is calculated analytically assuming them to be independent. The evolution of the order parameter at $T=0$ K versus impurity concentration is investigated, showing an abrupt drop to zero and the possibility of metastable solutions. The approximation is tested by analyzing the effects of pair interaction on the single-impurity results. Finally, the finite-temperature case is investigated by considering the evolution of the transition temperature with impurity concentration.

I. INTRODUCTION

The presence of impurities has important effects on systems with Peierls instabilities,¹ altering the static, dynamic, and transport properties of both chainlike^{2,3} and layer compounds.⁴ In general, impurities weaken the Peierls instability smearing out the transition between the normal and distorted phases. This destructive mechanism of impurities has been studied theoretically under various different points of view.⁵⁻¹¹

In this paper we study the problem of substitutional impurities in a half-occupied linear chain with Peierls instability.¹² We use a local approach,¹³ analyzing exactly the change in energy due to a single impurity in a system with a spatially uniform distortion. In this approximation, the effect of N impurities is assumed to be N times that of an isolated impurity, neglecting mutual interaction. This approximation provides exact results in the limit of small concentration of impurities, its main shortcomings being the imposed condition of spatial uniformity of the order parameter and the neglect of the electron-electron interaction in the model Hamiltonian.

The paper is organized as follows: In Sec. II we establish the model and obtain the change in energy due to a single impurity at zero temperature. In Sec. III we consider the evolution of the order parameter with impurity concentration, showing a discontinuous drop to zero and the possibility of metastable states. In Sec. IV we test the single-impurity results by considering the interaction between pairs of impurities, and we show that it has small influence on the single-impurity results. In Sec. V we consider the finite-temperature case and analyze the transition temperature versus impurity concentration. In Sec. VI we summarize our work.

II. FORMALISM

We consider a half-occupied linear chain of orbitals described by the following model Hamiltonian:^{11,12}

$$H_0 = \sum_k \epsilon(k) c_k^\dagger c_k + \Delta \sum_k c_{k+Q}^\dagger c_k + \frac{1}{2\lambda} \Delta^2, \quad (1)$$

where c_k^\dagger (c_k) creates (destroys) an electron with wave

number k and energy $\epsilon(k)$, Δ is the order parameter (or gap), and λ is the electron-phonon coupling. The first term in (1) is the band-structure term, the second term represents the Peierls instability mechanism with Q corresponding to the perfect nesting wave number for the half-occupied band (i.e., $Q=2k_F$), and the third term is the restoring elastic energy. It has to be pointed out that the electron-electron interaction is not included in H_0 , this has important consequences as it will be discussed below. This Hamiltonian can be rewritten in the following local version:

$$H_0 = \sum_i V (c_i^\dagger c_{i+1} + \text{H.c.}) + \Delta \sum_m c_m^\dagger c_m - \Delta \sum_n c_n^\dagger c_n + \frac{1}{2\lambda} \Delta^2, \quad (2)$$

where V is the hopping parameter between nearest-neighbor sites and c_i^\dagger (c_i) runs over odd (even) sites, showing clearly the dimerized nature of the system which may be seen as a chain of alternating sites with orbital energy Δ and $-\Delta$, respectively.

The presence of substitutional impurities is modeled by the addition of the following term to the Hamiltonian H_0 :

$$H_{\text{imp}} = \sum_\alpha \epsilon c_\alpha^\dagger c_\alpha, \quad (3)$$

where α runs over the impurity sites, which are taken to be distributed at random. From (3) we see that the impurity shifts by ϵ the corresponding orbital level. In this paper we will explicitly consider the case of negative ϵ , although the analysis is exactly the same for a positive ϵ . Within the scheme of the single-impurity approach, we have to analyze how the impurity perturbs the system. The change in electronic energy can be written as¹⁴

$$U = \frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} \ln(1 - \epsilon g) dE, \quad (4)$$

where $g = \langle \alpha | (E - H_0)^{-1} | \alpha \rangle$ is the diagonal matrix element of the resolvent (Green's operator) corresponding to the unperturbed Hamiltonian taken at the site of the impurity, and E_F is the Fermi level. We have to consider the two possible kinds of sites in the dimerized chain and

we design by g_{\downarrow} and g_{\uparrow} the Green's-function elements corresponding to sites with orbital energy $-\Delta$ and $+\Delta$, respectively (Δ being positive).

From (4) we can see that the change in energy due to a simple impurity is the integral of a phase shift of the perturbing potential. In order to evaluate (4) we should know the position of the localized states which appear with the impurity. These localized states satisfy the condition:¹⁵

$$\frac{1}{\epsilon} - \text{Re}(g) = 0. \quad (5)$$

This condition is illustrated in Figs. 1 and 2 in which the detailed form of g_{\uparrow} and g_{\downarrow} is shown. The unperturbed spectrum¹² shows the characteristic two bands with a gap of magnitude 2Δ separating the occupied and unoccupied parts. We see that there is only one localized state with energy E_1 below the H_0 spectrum if the impurity substitutes a site of kind \downarrow . On the other hand, if the impurity is placed on a site of kind \uparrow , two localized states appear with energies E_3 (below the spectrum) and E_2 (within the gap). The position of the localized states together with the form of the spectrum of the unperturbed Hamiltonian is analyzed in the Appendix. It should be pointed out that the localized state within the gap (E_2) "comes" from the upper band (see Fig. 2) and it remains unoccupied at zero temperature provided that the impurity does not carry any extra charge. In this case the Fermi level is always below this state.

Using Eq. (4), we obtain for the change in energy when the impurity is on site \downarrow the following expression:

$$U_{\downarrow} = E_1 - E_b + I_0, \quad (6)$$

where $E_b = -(1 + \Delta^2)^{1/2}$ is the lower edge of the spectrum in units of the half-bandwidth ($4V^2 = 1$); these units will be used in the rest of the paper. I_0 is the integral (4) in the lower band:

$$I_0 = + \frac{1}{\pi} \text{Im} \int_{E_b}^{-\Delta} \ln(1 - \epsilon g_{\downarrow}) dE. \quad (7)$$

A similar expression can be obtained for U_{\uparrow} :

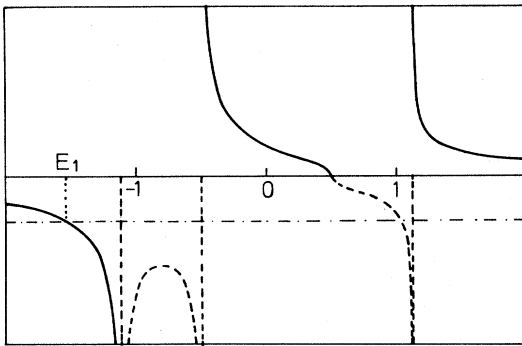


FIG. 1. Real (—) and imaginary (---) parts of the Green's function g_{\downarrow} for order parameter $\Delta = 0.5$ (half-bandwidth units). The condition for the appearance of the localized state and its position (E_1) are also illustrated.

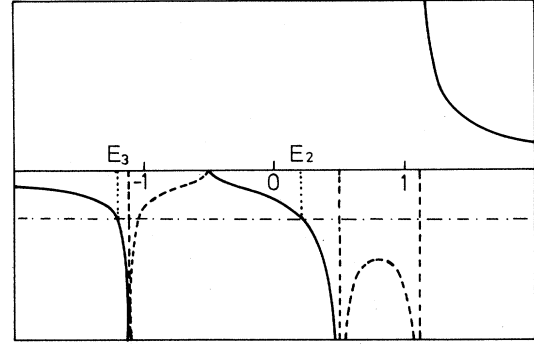


FIG. 2. Same as Fig. 1 for the Green's function g_{\uparrow} and its localized states (E_2 and E_3).

$$U_{\uparrow} = E_3 - E_b + I_1 \quad (8)$$

with

$$I_1 = \frac{1}{\pi} \text{Im} \int_{E_b}^{-\Delta} \ln(1 - \epsilon g_{\uparrow}) dE. \quad (9)$$

Bearing in mind that the impurity has the same probability of presence in both kinds of sites, the total energy change due to the presence of one impurity can be written as

$$U = \frac{1}{2}(U_{\downarrow} + U_{\uparrow}) = \frac{1}{2}(E_1 - E_b + E_3 - E_b + I_0 + I_1). \quad (10)$$

At this point, we will simplify the expression (10) using the symmetry of the unperturbed spectrum and a sum rule. Looking at Figs. 1 and 2, we observe that I_0 and I_1 are related to each other: I_1 is the integral of $\ln(1 - \epsilon g_{\downarrow})$ in the upper band and vice versa. On the other hand, if the spectrum is completely occupied, the change in energy is simply the change in the trace of the Hamiltonian, which in this case is ϵ . Using this sum rule and the symmetry previously indicated, we can write

$$\epsilon = E_1 - E_b + I_0 + I_1, \quad (11a)$$

$$\epsilon = E_3 - E_b + E_2 - \Delta + I_1 + I_0. \quad (11b)$$

Equations (11) provide us with a relation between the three localized states and also allow us to write Eq. (10) in a simpler way:

$$U = \frac{1}{2}(\epsilon + E_3 - E_b). \quad (12)$$

The simple expression (12) is the change in energy due to a single impurity (after taking into account the two possible choices of site) when the impurity does not modify the electronic content of the system.

III. ORDER PARAMETER

Our basic assumption is to consider the effect of N impurities as if they were independent (infinitely apart from each other), so that, the total energy (per site) of the system can be expressed as

$$F = F_0 + xU, \quad (13)$$

where x is the concentration (per site) of impurities, U is given by (12) and F_0 is the energy of the unperturbed Hamiltonian, given by (see Appendix)

$$F_0 = \frac{1}{2\lambda} \Delta^2 - \frac{1}{\pi} \frac{\mathbf{E}(k)}{k}, \quad (14)$$

where $k \equiv (1 + \Delta^2)^{-1/2}$ and $\mathbf{E}(k)$ is the complete elliptic integral of the second kind.¹⁶

In Fig. 3 we can see a plot of the total energy F versus the order parameter Δ for various concentrations and a given set of parameters. We observe that the minimum energy position shifts downward with the increase of impurity concentration and eventually disappears. We can also see that the order parameter drops to zero abruptly and the minimum in the total energy can be above the energy of the nondimerized ($\Delta=0$) lattice giving rise to hysteresis in the order parameter. This behavior is shown in Fig. 4 where we have plotted the order parameter versus impurity concentration for the same set of parameters. The abrupt drop to zero and the hysteresis are clearly shown. It should be pointed out that the discontinuous drop to zero of the order parameter is a consequence of the behavior of the first derivative of U versus Δ , which does not vanish at $\Delta=0$. The linear behavior of the order parameter in the vicinity of $x=0$ is also found when the disorder is treated in a mean-field approximation¹¹ (although the slope is different), while the discontinuous drop to zero and the hysteresis are novel features associated with the single-impurity approach.

Leaving aside the problem of the validity of the previous results beyond the noninteracting impurities approximation, this approach is indeed correct in the limit $x \rightarrow 0$. In this limit we can analyze the evolution of the order parameter versus impurity concentration. The stability condition reads as follows:

$$\frac{dF}{d\Delta} = \frac{dF_0}{d\Delta} + x \frac{dU}{d\Delta} = 0. \quad (15)$$

Equation (15) implies that, in the limit $x \rightarrow 0$, the order parameter decreases linearly with the impurity concentration

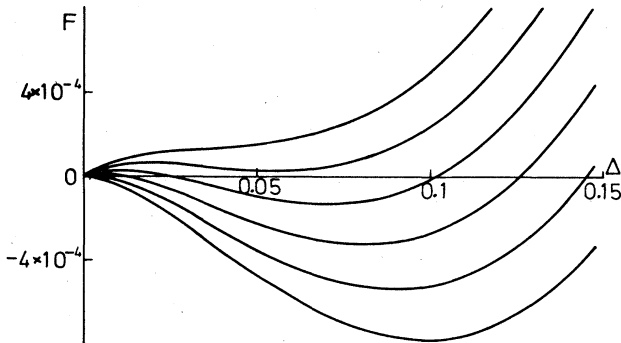


FIG. 3. Total energy versus order parameter for various impurity concentrations ($x=0, 0.005, 0.01, 0.015, 0.02, 0.025$) with $\lambda=0.85$ and $\epsilon=-6$.

$$\Delta = \Delta_0 - mx, \quad (16)$$

where Δ_0 is the order parameter in absence of impurities and m is given by

$$m = \left[\frac{dU/d\Delta}{d^2F_0/d\Delta^2} \right]_{\Delta=\Delta_0}. \quad (17)$$

From (12) and (14) we can obtain an explicit expression for m . With the results of the Appendix, we can write the following expression for m in the limit $\Delta_0 \rightarrow 0$:

$$m = \frac{\pi}{2} \left[\frac{dE_3}{d\Delta} \right]_{\Delta_0} = \frac{\pi}{2} \frac{\epsilon^2}{\epsilon^2 + 1}. \quad (18)$$

The value of m versus ϵ is plotted in Fig. 5. We see a quadratic behavior near the origin and a saturation¹¹ for large ϵ . The quadratic behavior corresponds to the Born approximation for the scattering by impurities while the saturation implies that, once the impurity is sufficiently different from the host lattice, a further increase of the perturbing potential is completely irrelevant. In analogy with the theory of magnetic impurities¹⁷ in superconductors, m can be thought of as the breaking parameter (per impurity) of the Peierls instability.

IV. PAIR APPROXIMATION

In this section we test the validity of the single-impurity (i.e., noninteracting impurities) approximation, considering the interaction between impurities. We restrict ourselves to the case of pairs of impurities. In other words, we consider each impurity added to the system as experiencing the field of another impurity at a given distance. Therefore, we compute the change in electronic energy of the system when adding an impurity in the presence of a previous one. The expression (4) for the change in energy remains valid, but in this case, g is the diagonal matrix element at the impurity site of the Green's operator of the system with one impurity at a distance n of the site where we include the new impurity. The change in energy per impurity in this approximation, U , is obtained by averaging over the distribution of distances corresponding to a given concentration of impurities:

$$U = \sum_{n=1}^{\infty} P_n U_n, \quad (19)$$

where U_n is the energy per impurity when two impurities are at a distance n and P_n is the probability corresponding to that separation:

$$P_n = x(1-x)^{n-1}. \quad (20)$$

Once U is known, the problem is, as in the preceding section, to minimize the total energy, which is also given by

$$F = F_0 + xU. \quad (21)$$

In this case, unlike the preceding section, U also depends on the impurity concentration through Eqs. (19) and (20).

We have therefore evaluated numerically the change in energy U for the value $\epsilon = -6$ which corresponds to a strong perturbing impurity (see Fig. 5). In practice, we

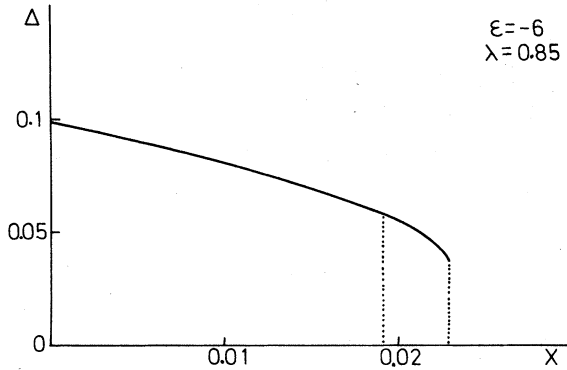


FIG. 4. Order parameter versus impurity concentration with $\lambda=0.85$ and $\epsilon=-6$. The dotted vertical lines indicate the concentration at which the energy minimum passes from absolute to local minimum (first dotted vertical line) and the concentration at which this local minimum disappears (second dotted vertical line).

have calculated the correction to the single-impurity energy up to 20 lattice site distances in Eq. (19). For larger distances, the corrections to the single-impurity value are negligibly small. The order parameter obtained by minimization of Eq. (21) is shown in Fig. 6 for various values of λ . The corresponding values for the single-impurity approach are also shown for the sake of comparison. We observe small changes in the order parameter as compared with the single-impurity case, and the discontinuous drop to zero is preserved in the pair approximation. The same applies to the appearance of a local minimum with energy higher than the nondimerized chain (hysteresis) as can be seen in Fig. 7, which is the corresponding version of Fig. 4 in the pair approximation. The origin of the small influence of the impurity interaction on the single-impurity results comes from the fact that the correction is a weakly dependent function of the order parameter, although the correction itself is far from

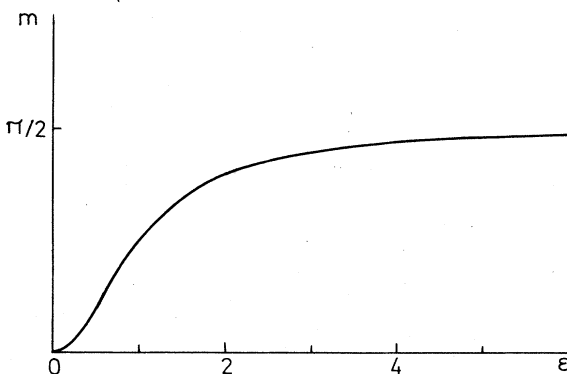


FIG. 5. Absolute value of the slope of the order parameter versus impurity concentration at $x=0$ plotted against the intensity of the impurity potential.

being negligible. We conclude that the single-impurity approach can be considered as a good approximation in the studied case of strong perturbing potential.

V. FINITE-TEMPERATURE RESULTS

The single-impurity approach can be used to analyze the finite-temperature situation without taking into account the phonon entropy. In this case, we have to calculate the change in the free energy when adding a single impurity and from this result we can study the change in the transition temperature with impurity concentration. The change in free energy due to a single impurity can be written as follows:¹⁸

$$U(T) = -\frac{1}{\beta} \int_{-\infty}^{+\infty} \delta\rho(E) \ln(1 + e^{-\beta E}) dE, \quad (22)$$

where $\beta \equiv 1/kT$ and $\delta\rho(E)$ is the change in the density of states due to the impurity:¹⁴

$$\delta\rho(E) = -\frac{1}{\pi} \text{Im} \frac{\partial}{\partial E} \ln(1 - \epsilon g), \quad (23)$$

where g represents the diagonal matrix element of the unperturbed Hamiltonian in the site of the impurity.

In expression (22) it has been implicitly assumed that the Fermi level remains at the unperturbed energy ($\mu=0$). This is true in the limit of small concentration of impurities ($x \rightarrow 0$) and finite temperature. The reason is that at small concentration, the condition that fixes the Fermi level is dominated by the unperturbed spectrum, so it remains at $\mu=0$. It also requires the temperature not to be too low because, in that case, the Fermi level would be dominated by the position of the localized state in the gap (which should be unoccupied in the limit $T \rightarrow 0$ K).

Performing a partial integration in (22) and taking into account that the total change in the integrated density of states is zero, we can write the following expression for U :

$$U = \frac{1}{\pi} \text{Im} \int_{-\infty}^{+\infty} dE f(E) \ln(1 - \epsilon g), \quad (24)$$

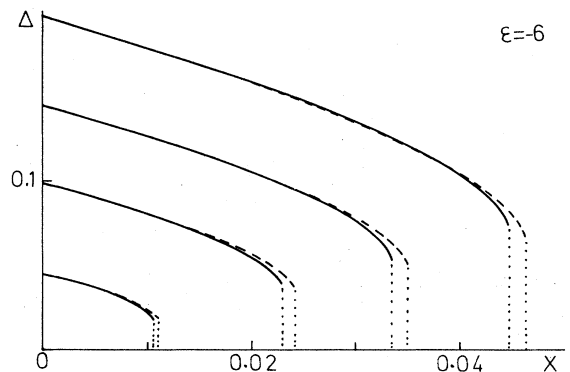


FIG. 6. Order parameter versus impurity concentration for various values of λ (0.7, 0.85, 0.95, 1.05) comparing the single-impurity results (—) and the pair approximation (---).

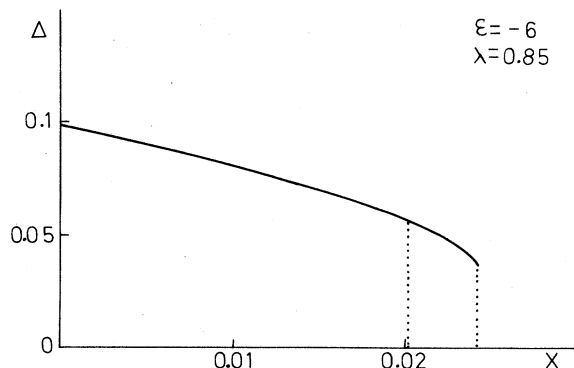


FIG. 7. Same as in Fig. 4 in the pair approximation.

where $f(E)$ is the Fermi-Dirac occupation factor.

Taking into account the two possible choices of site, the total energy can be written as

$$U = \frac{1}{2}(U_{\uparrow} + U_{\downarrow}), \quad (25)$$

where U_{\uparrow} (U_{\downarrow}) is calculated from (24) with the use of g_{\uparrow}

We can carry out an analysis completely similar to that of the zero-temperature case and making use of the symmetry of the unperturbed spectrum we arrive at the following expression for U :

$$U = \frac{1}{2}[\epsilon - (E_1 - E_b)] + \frac{1}{2\beta} \ln \left[\frac{(1 + e^{-\beta E_b})(1 + e^{-\beta E_b})(1 + e^{-\beta \Delta})}{(1 + e^{-\beta E_1})(1 + e^{-\beta E_2})(1 + e^{-\beta E_3})} \right]. \quad (26)$$

It is easily shown that Eq. (26) reduces to expression (12) in the limit $T \rightarrow 0$ (provided $E_2 > 0$ and therefore the corresponding localized state is unoccupied in that limit).

The total free energy (per site) of the system with a concentration x of impurities can be written as follows:

$$F = F_0 + xU, \quad (27)$$

where F_0 represents the free energy of the unperturbed system. The equilibrium position corresponds to the minimization of F versus the order parameter which can be easily performed using the expression of F_0 (Ref. 12) and U [Eq. (26)]. The first comment concerns the nature of the transition, which remains continuous as in the unperturbed case. This relies on the fact that the first derivative of the impurity contribution versus the order parameter vanishes at $\Delta = 0$.

We now focus our attention on the evolution of the transition temperature (T_c) versus impurity concentration. The stability condition is

$$\frac{dF}{d\Delta} = \frac{dF_0}{d\Delta} + x \frac{dU}{d\Delta} = 0. \quad (28)$$

We can write¹² (in the limit $\Delta \ll 1$)

$$\frac{dF_0}{d\Delta} = \frac{\Delta}{\lambda} - \frac{\Delta}{\pi} \ln \left[\frac{2.28}{kT} \right]. \quad (29)$$

Expanding U in powers of Δ and taking into account that the first derivative vanishes, we can write

$$\frac{dU}{d\Delta} \simeq U_0'' \Delta \quad (30)$$

with

$$U_0'' \equiv \left[\frac{d^2 U}{d\Delta^2} \right]_{\Delta=0}. \quad (31)$$

Using (29) and (30) in (28) we arrive at the following solution for the transition temperature:

$$kT_c = 2.28 e^{-\pi/\lambda} e^{-\pi U_0'' x} \simeq kT_0 (1 - \pi U_0'' x), \quad (32)$$

where $kT_0 = 2.28 e^{-\pi/\lambda}$ is the transition temperature for the unperturbed system.¹² From (32) we observe that the transition temperature decreases linearly with the impurity concentration in the limit of small concentration. We can analyze the slope of this decrease by noting that, in the limit of small T_c , we can approximate U_0'' in the following way (see the Appendix):

$$U_0'' \simeq \frac{\beta}{2} \frac{\epsilon^2}{(\epsilon^2 + 1)^2}. \quad (33)$$

Therefore, we can write the following expression for the transition temperature (with $kT \ll 1$):

$$kT = kT_0 - \frac{\pi}{2} \frac{\epsilon^2}{(\epsilon^2 + 1)^2} x. \quad (34)$$

It is interesting to note that in the limit $\epsilon \rightarrow 0$, this expression becomes identical to that of the order parameter versus concentration at $T = 0$ K, so that the ratio Δ/kT_c remains at the value obtained in absence of impurities. This is also the behavior obtained in the case of magnetic impurities in superconductors stressing the analogy between the two problems.¹⁷

VI. SUMMARY

The problem of impurities in a linear chain of atoms with Peierls instability has been studied within the framework of a single-impurity approach. In this model, the effect of N impurities is approximated by simply adding the change due to a single impurity introduced in a system with a spatially uniform Peierls distortion. This approximation yields exact results in the limit of small concentrations of impurities. The presence of impurities always tends to destroy the instability. We have studied this decrease of the order parameter in terms of the perturbing potential. Interesting aspects of the evolution of the order parameter with impurity concentration are the abrupt drop to zero and the possibility of metastable states. The single-impurity results have been tested by explicitly considering the interaction between pairs of impurities in the limit of strong perturbing potential. The single-impurity results are scarcely affected by the inclusion of pair interaction. Finally, we have studied the problem at finite temperature in the limit of a very small concentration of impurities. We have shown that the transition remains continuous and the transition temperature decreases with

impurity concentration. This decrease has been analyzed in terms of the perturbing potential showing that, in the limit of small perturbing potential, it is the same as that of the order parameter versus impurity concentration at zero temperature.

Before we conclude, we comment on the two main shortcomings of this model calculation, namely the neglect of (i) the electron-electron interaction and (ii) the phonon entropy at $T \neq 0$.

(i) The electron-electron interaction weakens the formation of the Peierls gap.¹⁹⁻²¹ If the electron-electron interaction is included via a Hubbard-type Hamiltonian, complex ground states with magnetic order can take place,²⁰ making the analysis very complicated in a nonuniform system. Nevertheless, there are regions in the phase diagram²⁰ where the ground state is a pure charge-density-wave (CDW) state. In this case the main effect of the electron-electron interaction is to reduce the charge

fluctuations and therefore the above reported values of Δ should be smaller, in general, and the analytic expression (14) would no longer be valid.

(ii) In the calculation of T_c we have neglected the contribution of the phonon entropy since in our mode we have only considered the destruction of the CDW due to the weakening of the electron coherence. This is a limitation of the model²² and therefore the calculated critical temperature can only be considered as an approximated one.

APPENDIX

We give in this Appendix the expressions for the unperturbed Green's function, the total energy in absence of impurities, and the position and derivatives of the localized states. The real and imaginary part of the diagonal element of the Green's operator in a site of kind \downarrow are given by the following expressions (see Fig. 1):

$$\text{Reg}_1(E) = \begin{cases} - \left[\frac{E + \Delta}{E - \Delta} (E^2 - \Delta^2 - 1) \right]^{-1/2}, & -\infty < E < -(1 + \Delta^2)^{1/2} \\ \left[\frac{\Delta + E}{\Delta - E} (1 + \Delta^2 - E^2) \right]^{-1/2}, & -\Delta < E < \Delta \\ \left[\frac{\Delta + E}{\Delta - E} (E^2 - \Delta^2 - 1) \right]^{-1/2}, & (1 + \Delta^2)^{1/2} < E < \infty \\ 0 & \text{otherwise,} \end{cases} \quad (\text{A1})$$

$$\text{Im}g_1(E) = \begin{cases} - \left[\frac{E + \Delta}{E - \Delta} (1 + \Delta^2 - E^2) \right]^{-1/2}, & -(1 + \Delta^2)^{1/2} < E < -\Delta \\ - \left[\frac{E + \Delta}{E - \Delta} (1 + \Delta^2 - E^2) \right]^{-1/2}, & \Delta < E < (1 + \Delta^2)^{1/2} \\ 0 & \text{otherwise,} \end{cases}$$

where Δ is the gap in the spectrum and the energy E is measured in units of the half-bandwidth.

The corresponding expressions for g_{\uparrow} are the symmetric and antisymmetric versions of g_{\downarrow} (see Fig. 2). The condition (5) for the appearance of localized states gives the following equation for E_1 (see Fig. 1):

$$P(\Delta, E_1) \equiv a_3 E_1^3 + a_2 E_1^2 + a_1 E_1 + a_0 = 0 \quad (\text{A2})$$

with

$$a_3 = 1, \quad a_2 = \Delta, \quad a_1 = (-\epsilon^2 - \Delta^2 - 1), \\ a_0 = \Delta \epsilon^2 - \Delta - \Delta^3.$$

The first and second derivatives of E_1 versus the order parameter are [from (A2)]

$$\frac{dE_1}{d\Delta} = - \frac{\frac{\partial P}{\partial \Delta}}{\frac{\partial P}{\partial E_1}}, \quad (\text{A3})$$

$$\frac{d^2 E_1}{d\Delta^2} = - \frac{\frac{\partial^2 P}{\partial \Delta^2} + 2 \left[\frac{\partial^2 P}{\partial \Delta \partial E_1} \right] \frac{dE_1}{d\Delta} + \left[\frac{\partial^2 P}{\partial E_1^2} \right] \left[\frac{dE_1}{d\Delta} \right]^2}{\frac{\partial P}{\partial E_1}}.$$

Applying Eq. (5) to g_{\uparrow} , we obtain the following equation for E_2 and E_3 (see Fig. 2):

$$Q(\Delta, E) \equiv b_3 E^3 + b_2 E^2 + b_1 E + b_0 = 0, \quad (\text{A4})$$

where E represents both E_2 and E_3 , and the coefficients are given by

$$b_3 = 1, \quad b_2 = -\Delta, \quad b_1 = -\epsilon^2 - 1 - \Delta^2, \\ b_0 = -\Delta(\epsilon^2 - 1) + \Delta^3.$$

The first and second derivatives of E_2 and E_3 versus the order parameter are given by expression (A3) with $P(\Delta, E)$ substituted for by $Q(\Delta, E)$. Explicit expressions for the first derivative of the localized states for $\Delta=0$ are the following:

$$\left[\frac{dE_1}{d\Delta} \right]_{\Delta=0} = \frac{-\epsilon^2}{\epsilon^2 + 1}, \\ \left[\frac{dE_2}{d\Delta} \right]_{\Delta=0} = \frac{1 - \epsilon^2}{1 + \epsilon^2}, \\ \left[\frac{dE_3}{d\Delta} \right]_{\Delta=0} = \frac{\epsilon^2}{\epsilon^2 + 1}. \quad (\text{A5})$$

The electronic energy of the unperturbed Hamiltonian at $T=0$ K is given by

$$I = - \int_{\Delta}^{(1+\Delta^2)^{1/2}} E \rho(E) dE, \quad (\text{A6})$$

where $\rho(E)$, the total density of states, has the following expression:

$$\rho(E) = \frac{1}{\pi} \frac{E}{(1 + \Delta^2 - E^2)^{1/2} (E^2 - \Delta^2)^{1/2}}. \quad (\text{A7})$$

The integral (A6) can be calculated exactly¹⁶ with the following result:

$$I = - \frac{1}{\pi} \frac{\mathbf{E}(k)}{k}, \quad k = (1 + \Delta^2)^{-1/2} \quad (\text{A8})$$

where $\mathbf{E}(k)$ is the complete elliptic integral of the second kind. The total energy of the unperturbed Hamiltonian is obtained by adding to (A8) the elastic term

$$F_0 = \frac{1}{2\lambda} \Delta^2 - \frac{1}{\pi} \frac{\mathbf{E}(k)}{k}. \quad (\text{A9})$$

Expanding $\mathbf{E}(k)$ in the vicinity of $\Delta \rightarrow 0$,¹⁶ we obtain the following expression for the total energy and its derivatives:

$$F_0 \approx \frac{1}{2\lambda} \Delta^2 - \frac{\Delta^2}{4\pi} \left[2 \ln \left[\frac{4}{\Delta} \right] + 1 \right], \quad (\text{A10})$$

$$\frac{dF_0}{d\Delta} \approx \frac{\Delta}{\lambda} - \frac{\Delta}{\pi} \ln \left[\frac{4}{\Delta} \right], \quad (\text{A11})$$

$$\frac{d^2 F_0}{d\Delta^2} \approx \left[\frac{1}{\lambda} - \frac{1}{\pi} \ln \left[\frac{4}{\Delta} \right] \right] + \frac{1}{\pi}. \quad (\text{A12})$$

Finally, we consider the single-impurity change in energy at finite temperature. The first derivative of expression (26) versus the order parameter can be written as follows:

$$U' = \frac{1}{2}(E'_b - E'_1) + \frac{1}{2}[f(E_1)E'_1 + f(E_2)E'_2 + f(E_3)E'_3] \\ - \frac{1}{2}[2f(E_b)E'_b + f(\Delta)], \quad (\text{A13})$$

where the prime means derivative versus Δ and $f(E)$ is the Fermi-Dirac factor. Using the expressions for the corresponding derivatives, it can be shown that U' vanishes at $\Delta=0$. When the temperature is small compared with the half-bandwidth, we can approximate (A13) in the following way:

$$U' \approx \frac{1}{2}(E'_3 - E'_b) + \frac{1}{2}f(E_2)E'_2 - \frac{1}{2}f(\Delta), \quad (\text{A14})$$

where we have made use of the relation (11) between the three localized states. The second derivative of U is, from (A14),

$$U'' \approx \frac{1}{2}(E''_3 - E''_b) + \frac{1}{2}f'(E_2)(E'_2)^2 + \frac{1}{2}f(E_2)E''_2 - \frac{1}{2}f'(\Delta), \quad (\text{A15})$$

where the double prime means second derivative versus order parameter and $f'(E)$ is the first derivative versus energy of the Fermi-Dirac factor:

$$f'(E) = \frac{-\beta e^{\beta E}}{(1 + e^{\beta E})^2}. \quad (\text{A16})$$

Using expression (A5) for E'_2 and the fact that $E'_2=0$ [Eq. (A3)], we obtain for U'' in the limit $\Delta=0$:

$$U''(\Delta=0) \equiv U''_0 = \frac{1}{2}(E''_3 - E''_b) + \frac{\beta}{2} \frac{\epsilon^2}{(\epsilon^2 + 1)^2}. \quad (\text{A17})$$

In the limit of low temperature, the second term of the right-hand side of (A17) becomes dominant and we obtain for U'' expression (33) of Sec. V:

$$U''_0 = \frac{\beta}{2} \frac{\epsilon^2}{(\epsilon^2 + 1)^2}. \quad (\text{A18})$$

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