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Magnetic ($2k_F$) and electronic ($4k_F$) Peierls transitions from a Hubbard Hamiltonian extended with intersite-dependent transfer

Sytze Huizinga, Jan Kommandeur, and Harry T. Jonkman
Laboratory for Physical Chemistry, Materials Science Center, University of Groningen, Nijenborgh 16, 9747 AG, Groningen, The Netherlands

Cornelis Haas
Laboratory for Inorganic Chemistry, Materials Science Center, University of Groningen, Nijenborgh 16, 9747 AG, Groningen, The Netherlands

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We report a model calculation with an intersite-dependent Hubbard Hamiltonian, showing that the well-known Peierls transition has a $2k_F$ and a $4k_F$ component when the intrasite Coulomb repulsion U is less than the transfer integral t. At higher values of U the two components are split and each forms a proper phase transition; the electronic Peierls transition ($4k_F$) remaining at about the same temperature while the magnetic Peierls transition ($2k_F$) is driven towards lower temperatures as U increases. For lower temperatures and lower U a new phase transition occurs, leading from a mixed ($2k_F+4k_F$) phase to a pure $2k_F$ phase. The calculation was performed for two electrons distributed over four sites, but group-theoretical arguments are put forward to show that one may expect an infinitely long chain with a quarter-filled band to show the same behavior.

I. INTRODUCTION

In 1955, Peierls[1] first predicted that one-dimensional metals would, at low temperatures, show a nuclear distortion of wave vector $2k_F$, where k_F is the Fermi momentum. Beni and Pincus[2] showed in 1972 that a transition with the same wave vector occurs in one-dimensional spin systems. Such $2k_F$ transitions are by now well known to occur in, for instance, the tetracyanoquinodimethane (TCNQ) salts. In tetrathiafulvalenium-tetracyanoquinodimethanide (TTF-TCNQ), a highly conductive compound, the Peierls instability manifests itself at first as a dynamic distortion, as observed in diffuse x-ray scattering for temperatures up to 150 K (Refs. 3 and 4). After a suggestion by Torrance, Pouget[3] and others[4] have investigated the $4k_F$ region of the diffuse x-ray reflectance and concluded a dynamic distortion of $4k_F$ as well, which persists up to room temperature. MEM$(TCNQ)_2$ (MEM stands for N-methyl-N-ethylmorpholinium) was found to have three distinct phases.[5] At high temperatures it has an (almost) uniform TCNQ chain, which at 335 K converts to a dimerized chain[6] ($4k_F$ for this quarter-filled band) while below 19 K the chain becomes tetramerized ($2k_F$).[7,8]

Some attempts have been made to explain the $4k_F$ distortions. Emery[9] showed with perturbation theory that, besides a $2k_F$ instability, a $4k_F$ instability is expected in a Hubbard system when $U \gtrsim 6t$, where U is the on-site electron-electron repulsion and t the electronic transfer integral. Bernasconi *et al.*[10] pointed out that for infinite U a Fermi wave vector exists that would be twice that of the electrons at $U=0$, and a "Peierls" transition would thus occur at $4k_F$. Torrance[11] suggested that the intersite Coulomb repulsion might be responsible for the formation of a Wigner lattice with wave vector $4k_F$, while Weger and Gutfreund in their small U approach also included an intersite Coulomb repulsion.[12]

Very recently Bray and coworkers[13,14] using a computer renormalization-group technique calculated retarded density autocorrelation functions for systems of 2, 4, 8, and 16 sites. From their results they conclude that an intersite Coulomb repulsion, in addition to the Hubbard Hamiltonian, is indispensable for obtaining a $4k_F$ transition.

It is the purpose of this paper to show that given a sufficiently steep exponential dependence of the transfer integral on intersite separation the extended Hubbard Hamiltonian contains a $2k_F$ as well as a $4k_F$ instability. We also find out how these instabilities depend on U/t.

II. QUALITATIVE INSIGHT

It is useful to gain some qualitative insight by considering the essential features of the $2k_F$ and $4k_F$ instabilities. Mechanisms have been proposed to explain the $2k_F$ transitions: in the low-U case electronic energy is gained by modifying the transfer integrals (t) in a chain (1), while in the other limit it is the exchange (proportional to t^2/U)[15] that is modified with wave vector $2k_F$ (2). Both mechanisms require the possibility of having two electrons share the same orbital when their spins are antiparallel. When U approaches infinity this double occupancy becomes prohibited, depressing the $2k_F$ transition temperature to zero, in agreement with Sokoloff's[16] statement that for infinite U the spins behave independently. Remaining, however, is the possibility of accomodating only one electron in the lowest energy orbital as, for instance, in the H_2^+ molecule. The bonding provided by this electron leads to a $4k_F$ nuclear distortion with one electron per unit cell, instead of two electrons per unit cell as is the case in a $2k_F$ distortion. This picture closely resembles that described by Beni *et al.*[17] for the infinite U limit. They show a system of ρN electrons (where ρ is the number of electrons per site and N is the number of sites) can be treated as consisting of $(1-\rho)N$ spinless fermions in a tight-binding band. Then the Fermi wave vector is doubled and the unit cell resulting from the "Peierls" instability is halved, corresponding to $4k_F$, with k_F defined for the $U=0$ system.

As was pointed out in the Introduction, our calculations use an exponential dependence of the transfer integral on intersite distance. This is an electron-phonon coupling quite different from that of other authors, who either use,[18] or imply,[13] a linear on-site coupling, while this dependence gives, following Madhukar,[19] a coupling:

$$H_{e-p} = -\sum_{q}\sum_{k\sigma} C^{\dagger}_{k\sigma} C_{k+q\sigma} u_q F(k,q) \ ,$$

with

$$F(k,q) = +2i \sum_{n=1} f_n [\sin n(k+q) - \sin nk] \ ,$$

where f_n is the nth derivative of t with respect to the intersite distance and k and q are the electron and phonon momenta. Using this exponential dependence in a calculation thus means that one treats the e-p coupling in all orders, and takes into account that it depends on both q and k.

These arguments lead to the conclusion that the simple Hubbard Hamiltonian with an exponential dependence of t should contain both the $2k_F$ and $4k_F$ instabilities.

Distortions are not uncommon for finite ring systems. Whether they always occur, however, depends on the number of electrons they contain. This follows directly from one-electron theory. Then $(U=0)$ the orbital energies are given by $E=2t_0\cos ka$, with $k=n\pi/Na$, with N the number of sites, and $n=-N, -N+1, 0\ldots(N-1)$. When the number of electrons on the ring does not equal $4m+2$, where m is an integer, the ground state will be electronically degenerate and show a Jahn-Teller distortion. The decrease in the electronic energy will then contain a linear term in the distortion parameter, and the distortion will always occur. On the other hand, if there are $4m+2$ electrons on the ring, the ground state is totally symmetric and a distortion can, but does not have to occur. Given a sufficiently strong "electron-phonon" interaction, however, it will.

This can most easily be seen for our case here of two electrons on four sites in the limit of $U=0$. The undistorted square has energy $-4t_0$. If we allow a distortion of the square to a rectangle the ground state has energy

$$-2(t_1+t_2) = -4t_0\cosh(cr_0\xi) \ ,$$

where ξ is the distortion and cr_0 describes the steepness of the variation of the transfer integral. This energy is lower by at least $2(cr_0\xi)^2$. If the lattice energy, written as $\frac{1}{2}\alpha\xi^2$ does not increase more than that, i.e., when $2(cr_0)^2 > \frac{1}{2}\alpha$ *then* and *only then* the system will distort. Note, that if only a linear dependence of t on r is used, no distortion would be observed. The exponential dependence of the transfer integral is now of crucial importance!

For infinitely large rings, as for instance Rice and Strässler[20] have shown, this difference between $4m+2$ and other numbers of electrons is of course lost and the electronic energy is lowered by a term proportional to $\xi^2\ln\xi$, which is indeed between the two previously discussed dependencies, and will always lead to a phase transition. We feel confident therefore that our calculations will carry over to an infinite chain, as long as we make sure that the electron-phonon coupling (in this case the steepness of the transfer integral) is larger than the threshold value set by the $(4m+2)$ systems.

III. GROUP-THEORETICAL APPROACH

For classifying the symmetries of the distortions along a chain and finding general expressions for the free energies of the various phases group theory can be helpful. The symmetry operators for a regular one-dimensional chain with intersite spacing a are the sets $\{ET_n\}$ and $\{iT_n\}$, where E is the identity, i is the inversion, and T_n is the translation operator over n sites. Since we will only deal with the $4k_F$ and $2k_F$ distortions for a quarter-filled system, we can limit the translations to T_0, T_1, T_2, and T_3, a translation T_{n+4} yielding the same result as T_n. The sets $\{ET_n\}$ and $\{iT_n\}$, where $n=0$, 1, 2, or 3 then form a subgroup of the space group for the chain.

By letting the elements of the subgroup operate on a function with the symmetry of our problem we can find the transformation matrices corresponding to these elements, and reduce these to find the irreducible representations (I.R.). Since we have taken $T_{n+4}=T_n$ four functions with wave vectors, $0, +\pi/2a$, and π/a suffice to generate all I.R. From $k=0$ we obtain Γ_1 and Γ_2, from $k=\pi/a$ we find Γ_3

TABLE I. The subgroup G of the space group of a regular one-dimensional lattice, describing functions with wave vector 0, $\pm\pi/2a$, and π/a. As indicated, there is a one-to-one correspondence between the elements and I.R.'s of G and C_{4v}.

G	ET_0	ET_2	ET_1, ET_3	iT_0, iT_2	iT_1, iT_3	
Γ_1 ($k=0$)	1	1	1	1	1	A_1
Γ_2 ($k=0$)	1	1	1	−1	−1	A_2
Γ_3 ($k=\pi/a$)	1	1	−1	−1	1	B_1
Γ_4 ($k=\pi/a$)	1	1	−1	1	−1	B_2
Γ_5, Γ_6 ($k=\pm\pi/2a$)	2	−2	0	0	0	E
	E	C_2	$2C_4$	$2\sigma_d$	$2\sigma_v$	C_{4v}

and Γ_4, and from $k=\pm\pi/2a$ we find the two-dimensional Γ_5. The character table of this group is given in Table I, where we have ordered the elements in classes.

Inspection shows that the $4k_F$ and $2k_F$ distortions form bases for Γ_3 and Γ_5, respectively (see Fig. 1). We will therefore call the normal modes giving the distortions Q_3 and Q_5, Q_6, respectively, where Q_5 and Q_6 are degenerate. A Landau series expansion of the free energy (F) in terms of these modes can only contain powers of Q_i that transform like the totally symmetric Γ_1 representation.[21] An analysis of the terms up to fourth order shows that F must be of the following form:

$$
\begin{aligned}
F(Q_3,Q_5,Q_6) = {} & AQ_3^2 + B(Q_5^2+Q_6^2) \\
& + CQ_3(Q_5^2-Q_6^2) + DQ_3^4 \\
& + E(Q_5^4+Q_6^4) + FQ_5^2Q_6^2 \\
& + GQ_3^2(Q_5^2+Q_6^2) \ .
\end{aligned}
$$

The possible phases of the linear chain correspond to minima in $F(Q_3,Q_5,Q_6)$ given by the conditions:

$$
\begin{aligned}
\frac{\partial F}{\partial Q_3} = {} & 2AQ_3 + C(Q_5^2-Q_6^2) + 4DQ_3^2 \\
& + 2GQ_3(Q_5^2+Q_6^2) = 0 \ ,
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial F}{\partial Q_5} = {} & 2BQ_5 + 2CQ_3Q_5 + 4EQ_5^3 \\
& + 2FQ_5Q_6^2 + 2GQ_3^2Q_5 = 0 \ ,
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial F}{\partial Q_6} = {} & 2BQ_6 - 2CQ_3Q_6 + 4EQ_6^3 \\
& + 2FQ_5^2Q_6 + 2Q_3^2Q_6 = 0 \ ,
\end{aligned}
$$

which admit the following solutions (see Fig. 1):

(I) $Q_3=Q_5=Q_6=0$ the undistorted chain ($8k_F$);

(II) $Q_5=Q_6=0$ and $Q_3\neq 0$, a purely $4k_F$ distorted chain (dimers);

(III) Two degenerate solutions with $Q_3\neq 0$ and either Q_5 or $Q_6=0$, a mixed $2k_F+4k_F$ distorted chain (dimerized dimers);

(IV) $Q_3=0$ and $Q_5=\pm Q_6$, the purely $2k_F$ distorted chain (trimers). Other solutions lead to maxima of $F(Q_3,Q_5,Q_6)$.

Especially note that a purely Q_5 or Q_6 distorted phase does not exist. On the introduction of such a distortion in the uniform chain the term $CQ_3(Q_5^2-Q_6^2)$ in F will cause Q_3 to become finite as well, and in addition to a purely $4k_F$ distorted chain the mixed phase (III) is obtained.

The transitions between the various phases can have the following order (16):

$8k_F \rightarrow 2k_F$. No third-order term in Q_5 or Q_6, i.e., first or second order;

$8k_F \rightarrow 2k_F+4k_F$. Q_5 is the order parameter for this

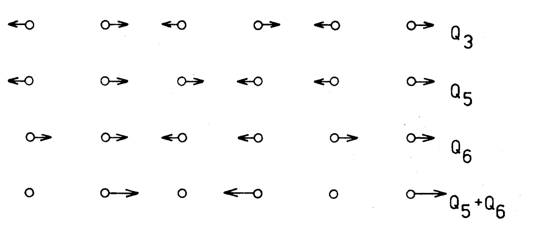

FIG. 1. The $4k_F$ and the $2k_F$ distortions for a quarter-filled one-dimensional chain. Q_3 denotes the $4k_F$ distortion, Q_5 and Q_6 the degenerate $2k_F$ distortions, and Q_5+Q_6 and Q_5-Q_6 are different linear combinations of the $2k_F$ distortions.

transition because Q_3 is determined by it and not the other way around. Near the transition temperature Q_3 contains only even-order terms in Q_5 and therefore F will contain only even-order terms in Q_5. The transition can then be first or second order;

$8k_F \rightarrow 4k_F$. No third-order term in Q_3, i.e., first or second order;

$4k_F \rightarrow 2k_F + 4k_F$. No third-order term in Q_5, i.e., first or second order;

$2k_F + 4k_F \rightarrow 2k_F$. The symmetry group of one phase is not a subgroup of that of the other, i.e., first order only.

Which phases are stable at what temperatures will, of course, depend on the values of the coefficients A, B, C, etc., which in their turn depend on the electronic and lattice properties of the chain, as well as on their coupling. To come to any predictions a calculation, including the electron-electron repulson has to be performed. It is well known that even the simplest model taking this repulsion into account (the Hubbard model) cannot be solved analytically for a quarter-filled infinitely long chain. Therefore recourse was taken to a simple model, which does, however, conserve all the symmetry properties outlined above.

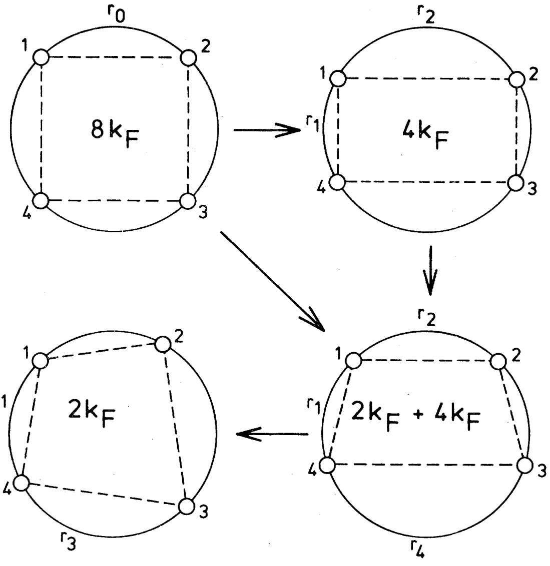

FIG. 2. Conformations of the four sites. The square ($8k_F$) has no distortion, the rectangle ($4k_F$) has distortion Q_3, the trapezoid ($2k_F + 4k_F$) has Q_3 and Q_5 or Q_6, while the kite ($2k_F$) has $Q_5 + Q_6$ or $Q_5 - Q_6$ as a distortion. The possible phase transitions are indicated by the arrows.

IV. MODEL CALCULATION

In order to gain quantitative insight in the phase transitions one would like to exactly calculate the free energy of an infinite one-dimensional chain using the Hubbard Hamiltonian extended with a lattice term. Since this is as yet impossible we have calculated the properties of a simple model system, consisting of two electrons distributed over four sites, each carrying one orbital and arranged in a square. This is the simplest model of a quarter-filled band system that can show $2k_F$ and $4k_F$ distortions.

Of course, such a finite system by itself will not show a phase transition. We therefore consider an ensemble of these squares for which we require that all squares show the same distortions at the same temperatures. The "cooperativeness" of the phase transition is simulated in this manner and phase transitions are indeed obtained.

This model may seem to be an oversimplification but, as we will show, the relevant symmetries are in fact the same as derived in the previous section for the infinite chain. The four sites transform according to the C_{4v} group, which is isomorphous with the group given in Table I: there is a one-to-one correspondence between the symmetry elements and the I.R.'s, as is indicated in the same table. A dimerization (Q_3), tetramerization (Q_5), and trimerization ($Q_5 + Q_6$) of the square are depicted in Fig. 2, the former transforming in C_{4v} as B_1 and the latter two as E. If we expand the free energy in the normal modes we find the same general expression as for an infinite chain. Of course, the magnitude of the free energy will differ between a square and a chain, but the conclusions of the previous section will still hold.

We now proceed with a more detailed description of the model and report the quantitative results of the computation in Sec. V.

The four sites are arranged on a circle as depicted in Fig. 2 and are connected by one-electron transfer integrals t_i, which are taken to depend on the intersite distances along the circle r_i as[22]

$$t(:)r^3e^{-cr} \tag{1}$$

with

$$c = Z'/2a_0 ,$$

where Z' is the effective nuclear charge ($Z' \approx 3.4$ in use for TCNQ salts) and a_0 the Bohr radius. To conveniently describe the $4k_F$, $2k_F + 4k_F$, and $2k_F$ distortions we introduce the parameters ξ, η_1, and η_2, defined in the following equations:

$$\begin{aligned} r_{1,3} &= (1-\xi)(1 \mp \eta_1) r_0 , \\ r_{2,4} &= (1+\xi)(1 \mp \eta_2) r_0 . \end{aligned} \tag{2}$$

The various distortions of the square as depicted in

Fig. 2 are then given by

$$\xi=\eta_1=\eta_2=0 \quad (\text{square, } 8k_F) \ ,$$

$$\xi\neq 0,\quad \eta_1=\eta_2=0 \quad (\text{rectangle, } 4k_F) \ ,$$

$$\xi\neq 0,\quad \eta_1=0,\quad \eta_2\neq 0 \quad (\text{trapezoid, } 2k_F+4k_F) \ ,$$

$$\xi=0,\quad \eta_1=\eta_2\neq 0 \quad (\text{kite, } 2k_F) \ .$$

By keeping r_0 fixed the perimeter of the ring is kept constant, forbidding lattice expansion or contraction. For the transfer integrals we then obtain

$$t_{1,3}=t_0(1-\xi)^3(1\mp\eta_1)^3\exp\{-cr_0[\mp\eta_1(1-\xi)-\xi]\} \ ,$$
$$t_{2,4}=t_0(1+\xi)^3(1\mp\eta_2)^3\exp\{-cr_0[\mp\eta_2(1+\xi)+\xi]\} \ , \tag{3}$$

where cr_0 can be treated as a single parameter with a value of about 10 for the TCNQ salts.[19] The electronic system is described by the Hubbard Hamiltonian:

$$H=-\sum_{\substack{1\neq m\\ \sigma}} t_{1m}c^{\dagger}_{1,\sigma}c_{m,\sigma}+\sum_{1} Un_{1,\sigma}n_{1,-\sigma} \ , \tag{4}$$

where 1 and m label the sites, $c^{\dagger}_{1,\sigma}$ and $c_{1,\sigma}$ are the usual creation and annihilation operators for an electron with spin σ at site 1, and $n_{i,\sigma}$ is the number operator $c^{\dagger}_{i,\sigma}c_{i,\sigma}$. As a basis set we take the $m_s=0$ two electron states $c^{\dagger}_{1,\sigma}c^{\dagger}_{m,-\sigma}|0\rangle$, which is permitted in the absence of a magnetic field and spin-orbit coupling. To facilitate the calculation we formed linear combinations which were bases for the irreducible representations of the group C_{2v}, appropriate for the rectangle. Inspection of the parity of the spin part of the linear combinations divides these up in ten singlet states and six triplet states.

Some lattice terms should also be included. The aim of this paper was to show the effect of the electron-electron repulsion on the phase transitions. The lattice entropy can therefore be neglected, since it will only affect the value of the phase-transition temperatures, but not the general behavior of the system as a function of U.

To allow for distortions, as Vegter[22] already pointed out a steep lattice repulsion is needed, counteracting the exponential dependence of the electron transfer on intersite distance. We therefore, in our calculation, use the Born expression for the lattice free energy, neglecting the dynamics of the lattice and hence the vibronic entropy thereof:

$$F_{\text{lat}}=B\sum_{j} r_j^{-n} \ , \tag{5}$$

where B is a proportionality constant, n is the repulsive exponent, and the summation runs over all four bonds. By rewriting this in terms of ξ, η_1, and η_2, substituting $\alpha/4n(n+1)$ for Br_0^{-n}, and expanding in a power series up to quadratic terms we obtain the form

$$F_{\text{lat}}=\alpha/n(n+1)+\tfrac{1}{2}\alpha[\xi^2+\tfrac{1}{2}(\eta_1^2+\eta_2^2)] \ , \tag{6}$$

which enables us to relate α to the linear lattice compressibility. The restriction of the displacements to a constant perimeter, implicitly included in Eq. (5) by substituting ξ, η_1, and η_2 from Eq. (2), acts as an attractive interaction counteracting the Born repulsion, and thus obviates the need for an extra attractive term.

The value chosen for n in our calculations is 12, which is sufficiently strong to limit the distortions to reasonable fractions of the intersite distance. For α we take 160 in units of t_0, which is in accordance with for instance a compressibility of $4\times 10^{-11}\,\text{cm}^2/\text{dyne}$ and a one electron transfer integral t_0 of 0.1 eV. These numbers are comparable to those found for instance RbTCNQ.[22] Because the electronic system we consider has a nondegenerate ground state the Jahn-Teller argument does not apply, and it is possible to choose a set of parameters for which no distortion of the square will occur even at very low temperature. The numbers we have introduced above (10, 12, and 160 for cr_0, n, and α, respectively) are such that for a wide range of U/t_0 values reasonable distortions occur. Since the Hamiltonian matrix can only be analytically diagonalized for zero and infinite U, we use computer procedures to obtain eigenvalues and eigenfunctions for a large set of ξ, η_1, and η_2 values at varying values of U. As a function of temperature (T) the free energy is then obtained for each set of eigenvalues. We are thus able to find the most favorable conformation of the four sites for any U and T. The magnetic susceptibility was obtained by multiplying the triplet occupancy by the appropriate Curie constant, while the charge densities were calculated from the wave functions.

V. RESULTS

In Fig. 3 we show contour plots of the free energy as a function of the distortion parameters $\xi(4k_F)$ and $\eta_2(2k_F)$ for $U=6t_0$ at three different temperatures. At $T=0.002t_0$ a minimum is found at nonzero ξ and η_2, meaning that the trapezoid is the stable configuration. At $T=1.2t_0$ we find a minimum at $\xi=0.093$ and $\eta_2=0$ (the rectangle), while at $T=1.8t_0$ the undistorted square has the lowest free energy. η_1 remains zero at all temperatures.

In Fig. 4(a) the complete temperature dependence of ξ and η_2 for $U=6t_0$ is displayed. At $T=1.66t_0$, the $4k_F$ transition occurs (ξ) while at $T=0.65t_0$, η_2 becomes nonzero in the $2k_F$ transition. For $U=0$, Fig. 5(a) gives the temperature dependence of γ[equal to $\frac{1}{2}(\eta_1+\eta_2)$], being the $2k_F$ distortion parameter leading to the kite (trimers and monomers

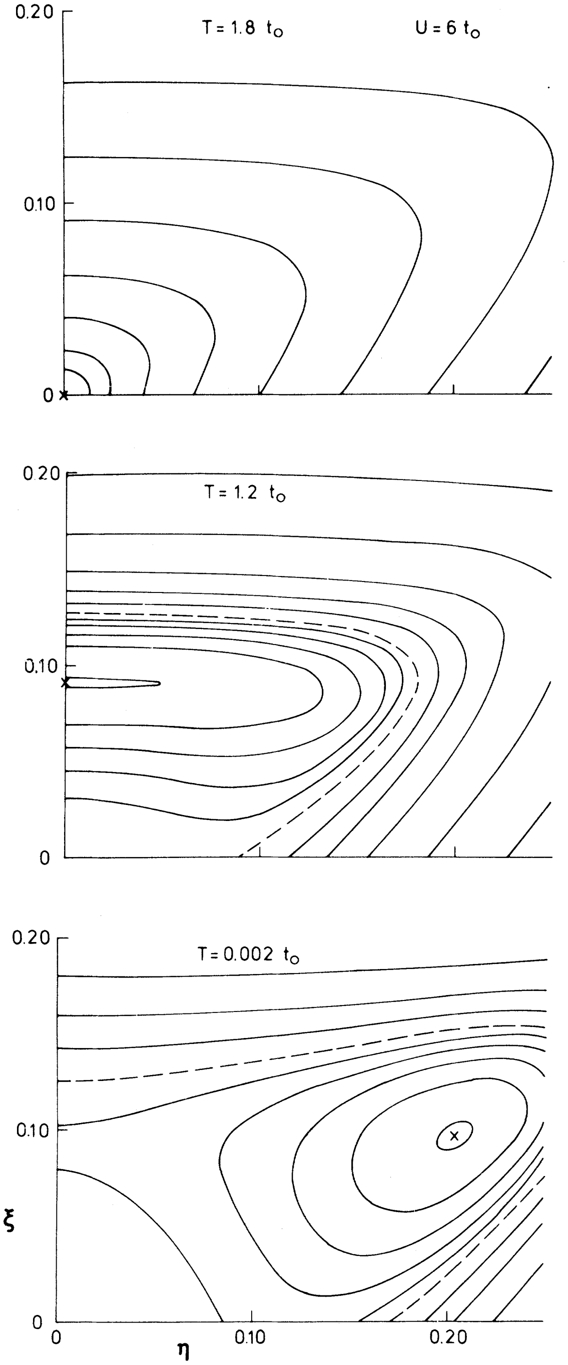

FIG. 3. Contour plots of the free energy vs $4k_F(\xi)$ and $2k_F(\eta_2)$ distortions for $U=6t_0$ at $T=0.002t_0$, $1.2t_0$, and $1.8t_0$. The levels of free energy indicated are chosen to show the important features; the broken line has the same free energy as the square ($\xi=\eta_2=0$). The X indicates the minimum of the free energy: for $T=0.002t_0$ it is at $\xi=0.098$ and $\eta_2=0.0204$ (trapezoid); for $T=1.2t_0$ at $\xi=0.093$ and $\eta_2=0$ (rectangle); and for $T=1.8t_0$ at $\xi=\eta_2=0$ (square).

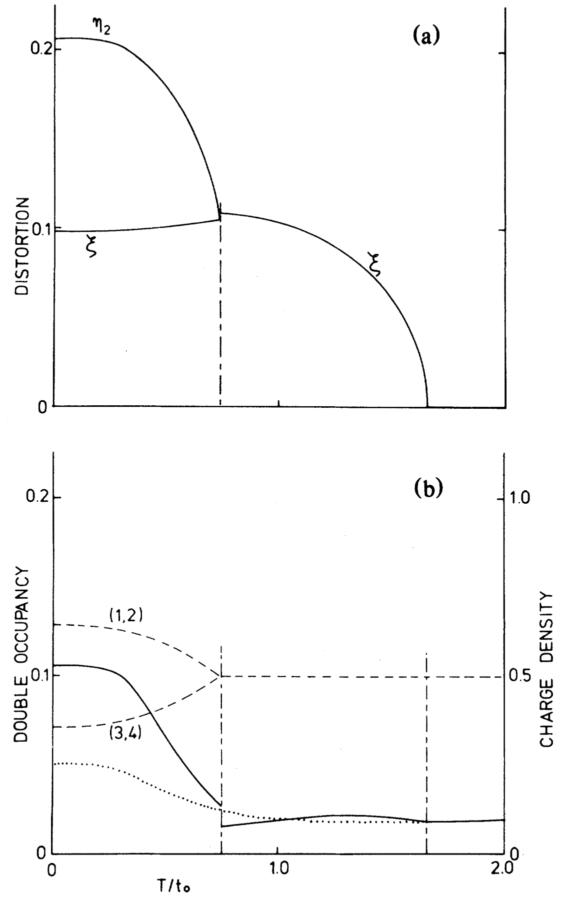

FIG. 4. Phase transitions at $U=6t_0$. Temperature dependences of (a) the $2k_F$ parameter η_2 and the $4k_F$ parameter ξ, and (b) the charge densities (broken lines, site numbering as in Fig. 2) and the double occupancy in the distorted (solid line) and undistorted (dotted line) system.

of Fig. 1). Here we only find a $2k_F$ transition at $T=1.85t_0$.

Figures 4(b) and 5(b) show the behavior of charge densities (broken lines) and double occupancy (solid lines) as a function of temperature. In the square ($8k_F$) and rectangle ($4k_F$) each site of course has the same charge density, but in the trapezoid ($2k_F+4k_F$) charge is concentrated on the sites labeled 1 and 2 in Fig. 2, and in the kite ($2k_F$) it is concentrated on the sites encompassing the two shorter bonds (trimer) at $T=0$, leaving the "faraway" site (3) completely unbound. The double occupancy, defined by $\sum_l n_{l,\sigma}n_{l,-\sigma}$, measures the correlation energy in the system when multiplied by U. In Fig. 4 ($U=6t_0$), we see that at the $4k_F$ transition it is hardly affected, but below the $2k_F$ transition it rises sharply relative to the value for the undistorted system (dotted line). Also in Fig. 5, the double occupancy rises below the

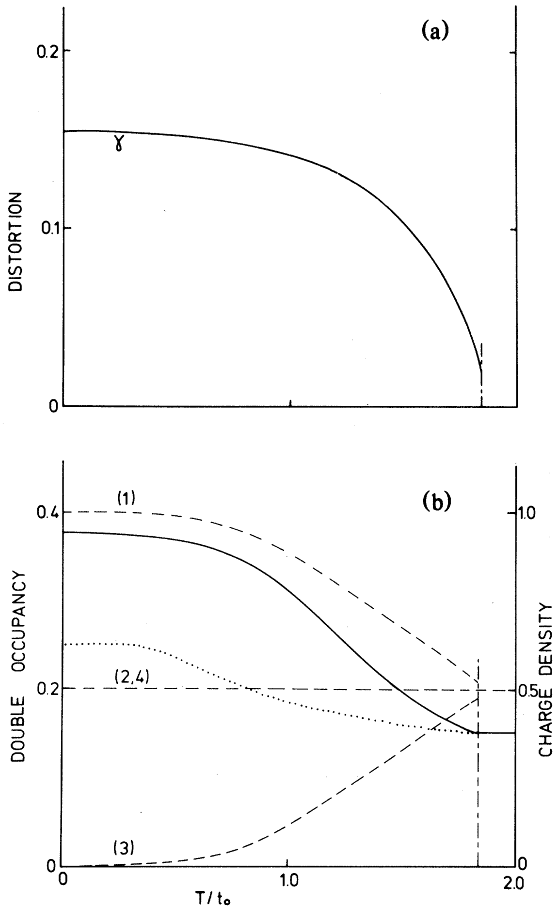

FIG. 5. Phase transition at $U=0$. Temperature dependences of (a) the $2k_F$ parameter γ [equal to $\frac{1}{2}(\eta_1+\eta_2)$], and (b) the charge densities (broken lines, site numbering as in Fig. 2) and the double occupancy in the distorted (solid line) and undistorted (dotted line) system.

$2k_F$ transition, but there is no energy associated with this rise because $U=0$.

As pointed out before, the $4k_F$ transition retains the spin entropy, while the $2k_F$ transitions remove it. We illustrate this in Fig. 6 where we give the calculated magnetic susceptibility versus the temperature for a set of U/t_0 values. At the $4k_F$ transition temperature no considerable change in χ occurs, but below $T(2k_F)$ χ drops sharply for the larger U values. Although the curves have the general shape found experimentally, it does not seem worthwhile to compare them to experiment in great detail, because our model contains only two spins. Moreover the actual transition temperatures depend on the stiffness of the lattice, which then also determines details of these curves.

Finally, in Fig. 7 we give the phase diagram for the various phases as a function of U/t_0. It is seen that

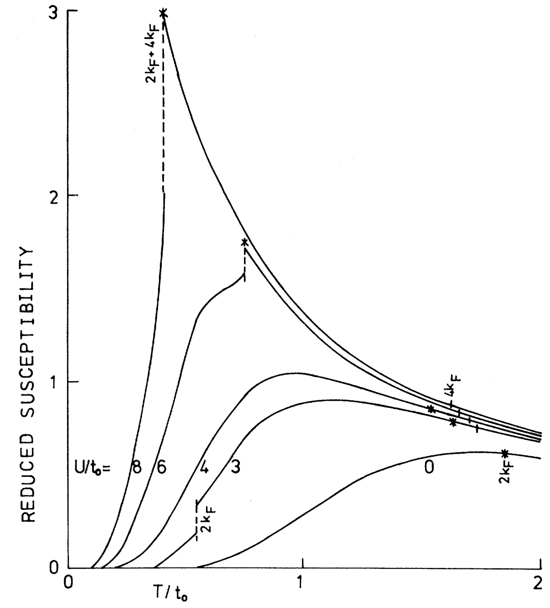

FIG. 6. Temperature dependence of the reduced magnetic susceptibility $(\chi 6t_0/Ng^2\beta^2)$ for a set of U/t_0 values. The vertical bars denote the $4k_F$ transitions, the asterisks the $2k_F$ transitions to the mixed $(2k_F+4k_F)$ phase. At $U/t_0=3$ we have in addition the transition to the pure $2k_F$ phase.

at low U the $8k_F$, the $2k_F$, and the $2k_F+4k_F$ phases occur, the pure $2k_F$ phase always being the lowest in energy. At $U\approx t_0$ the $4k_F$ component is split off from the $2k_F+4k_F$ phase, yielding the pure $4k_F$ phase over a considerable temperature range. At still higher U the pure $2k_F$ to the $2k_F+4k_F$ phase drops

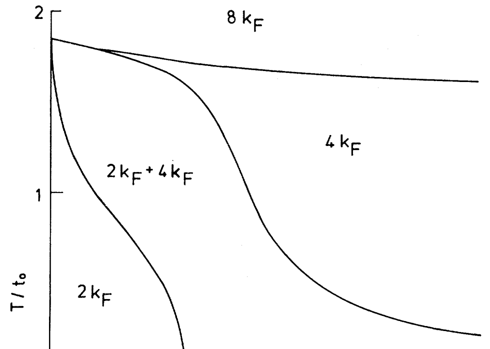

FIG. 7. The transition temperatures between the various phases of a quarter-filled one-dimensional chain as a function of the reduced correlation energy U/t_0. $8k_F$ denotes the regular chain, $4k_F$ the dimers, $2k_F+4k_F$ the dimerized dimers, and $2k_F$ the chain of trimers and monomers. At $U/t_0\approx 1$ a tricritical point between the $8k_F$, the $4k_F$, and the $2k_F+4k_F$ phases occurs.

sharply. The transition temperature from the regular ($8k_F$) to the dimerized chain ($4k_F$) is hardly affected by U.

VI. DISCUSSION

Our model calculation appears to mimic very well the behavior of a one-dimensional quarter-filled band as a function of temperature and on-site repulsion U. Both a $4k_F$ and a $2k_F$ phase transition occur, indeed all the phases predicted by the Landau expansion are found at some range of U/t_0 and temperature.

These results should be contrasted with the calculations of Bray and co-workers,[13,14] who found for instance the $4k_F$ instability too weak compared to the $2k_F$ instability, to allow the $4k_F$ transition to occur at a higher temperature than the $2k_F$ transition. We want to point out, however, that in their calculation they did not explicitly consider the electron-phonon coupling. They calculated (retarded) density autocorrelation functions, implicitly assuming on-site coupling only. Similarly, analytical work by Chui, Rice, and Varma[18] take the electron-phonon coupling to be independent of electron momentum; it is therefore the same for all electron wave vectors, and therefore also exclusively on site. But soon after, Madhukar[19] maintained that such an electron-phonon coupling cannot lead to a Peierls transition, and that is indeed true if internal degrees of freedom of the sites are not taken into account.

In contrast, in the present calculations we let the transfer integral depend on intersite distance in an exponential manner. This implies an electron-phonon coupling strongly varying as a function of both electron and phonon wave vectors, as well as coupling to all orders. For instance, the $4k_F$ phase transition does *not* occur in *these* calculations if only a linear dependence of the transfer integral on intersite distance is used, i.e., when the electron-phonon coupling is treated in first order. This is also clear when one realizes that in a quarter-filled band a $4k_F$ instability amounts to a dimerization. A linear dependence then means, that whatever is gained in energy on one side is lost on the other. Such arguments do not apply to the $2k_F$ transition, since the bonds between the sites are then somewhat inequivalent to start with, but again higher-order terms are very important.

In summary, therefore, previous calculations were aiming for *on-site* charge-density waves, while this calculation yields *intersite* charge density waves, or simply bond alternations. Of course, these are the only Peierls transitions one can expect, if internal site structure is not considered. Also, it appears to us that the distortions actually observed in, for instance, MEM(TCNQ)$_2$,[6] indeed amount to modulations of the transfer integral. To illustrate these "intersite charge-density waves", we show their electron density distribution in Fig. 8. This figure also shows how the sites in the $4k_F$ phase are still connected by inversion centers, forbidding on-site charge-density waves, unless these inversion centers are lost through an internal structural change of the site.

Figure 8 also shows how the microscopic mechanisms for the two phase transitions can be viewed. The $4k_F$ transition amounts to the alternate weakening and strengthening of the one-electron bonds between the sites. The $2k_F$ transition can be seen as the alternate strengthening and weakening of the two-electron character of the bonds between the sites that were least bound in the $4k_F$ phase. In agreement with this picture, U strongly affects the $2k_F$ transition temperature, while it leaves the $4k_F$ transition temperature essentially unchanged. When there is no energetic difference between a one-electron and half of a two-electron bond, i.e., when $U=0$, the two transitions occur together. It can be said that for $U > t_0$ it is the electron-electron repulsion that splits the transition into a $2k_F$ and a $4k_F$ component.

At sufficiently high U/t a distinction can be made into charge-density and spin-density waves (CDW and SDW) since the charge and spin can be considered almost independently. In this particular case the $4k_F$ distortion can be dynamically considered as a CDW, while the $2k_F$ distortion is then, similarly, a SDW. At low U/t this distinction becomes unclear, both waves consisting of mixtures, while at $U/t \lesssim 1$ the two types of waves merge completely.

Finally, it appears worthwhile to register some

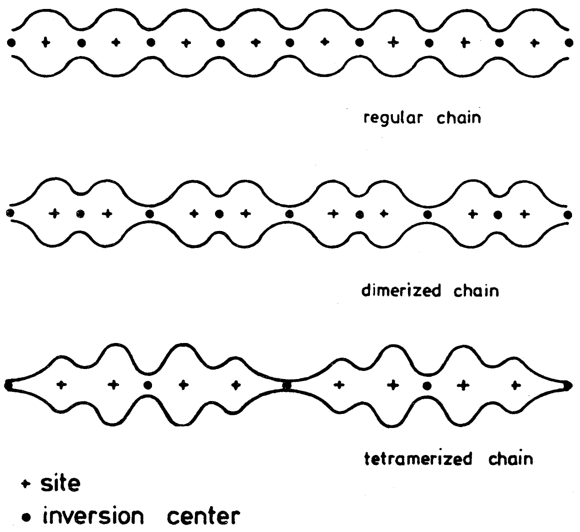

FIG. 8. Schematic representation of electron densities of a quarter-filled band system in the regular ($8k_F$), the dimerized ($4k_F$), and the tetramerized ($2k_F+4k_F$) phase. Note that in the dimerized phase all inversion centers are retained.

surprise that such meaningful results can be obtained from a calculation on such a small system that consists of only two electrons on four sites. It should be pointed out, however, that a total of 28 states (10 singlets and 6 triplets) is calculated and that for phase transitions one compares energies of two closely similar systems calculated in the same approximation. Although the absolute energies will be in error, in the energy differences the errors appear to cancel. So far, the calculation finds its justification in the results, which do indeed clarify the effect of the on-site electron-electron repulsion on the $4k_F$ and $2k_F$ phase transitions.

Both transitions are contained in the original Peierls transition, in which electron-electron repulsion was not considered. It seems appropriate therefore, to call the $4k_F$ transition in which the electronic degrees of freedom are lost the *electronic Peierls* transition, while the $2k_F$ transition in which the spin degrees of freedom are lost can be called the *spin Peierls* transition. These are both contained in the Hubbard Hamiltonian as long as a lattice term is added and the transfer integral is made to depend on the inter-site separation.

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