PHYSICAL REVIEW B VOLUME 20, NUMBER 9 1 NOVEMBER 1979

Gap equations of Peierls transitions

Y. Lépine
Département de Physique, Université de Montréal, Montréal, Québec, Canada H3C 3J7

C. Tannous and A. Caillé
Département de Physique et Groupe de Recherche sur les Semiconducteurs et les Diélectriques,
Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

(Received 8 May 1979)

The gap equations for the electronic Peierls transition, the XY spin-Peierls transition and the Heisenberg spin-Peierls transition are investigated. Conditions under which the dependence of the energy gap on temperature is of the BCS type are established. For realistic parameters, the BCS law is a good description for the electronic and the XY Peierls transitions. In the case of the Heisenberg spin-Peierls transition, we find that the approach of Beni is very different from the BCS-type behavior of Pytte. With the first approach, a first-order transition for any values of the parameters is obtained. Large fluctuations are expected near the critical point. The changes in the gap equation with magnetic field are also calculated and we show that the ordered phase can disappear for large enough fields. Finally, our results are compared with those of the recent theory of Cross and Fisher.

I. INTRODUCTION

The Peierls (or spin-Peierls) transition was predicted to occur in quasi-one-dimensional systems with a half-filled electron (quasifermion) band as a result of electron (spin)–phonon coupling.[1–4] The ordered state of these systems is characterized by an energy gap in the electronic (quasifermion) spectrum at $k = 2k_F$ (k_F is the Fermi wave vector for the half-filled band). This gap is associated to a dimerization of the chain. The purpose of this paper is the comparative study of this gap equation for three different cases: the electronic Peierls transition[1] and the spin-Peierls transition for the XY (Ref. 2) and Heisenberg chains (Refs. 3 and 4).

Since the energy gap may be considered as the order parameter for the Peierls transitions, it is essential to know its temperature variation to describe the temperature dependence of most measurable physical quantities associated to dimerization: magnetic susceptibility, EPR, specific heat, transport coefficients, optical absorption, and x-ray diffraction. Up to now, it has generally been assumed that the gap equations for Peierls-like transitions reduced to the BCS form to different levels of approximation. In particular, for the Heisenberg spin-Peierls transition, successful fitting of the magnetic susceptibility as a function of temperature has been realized with a BCS dependence of the degree of dimerization on temperature for (TTF)Cu(BDT) [tetrathiafulvalenium *bis-cis-*(1,2-perfluoromethylethylene-1,2-dithiolato)-copper][5] and K(TCNQ) (potassium-tetracyanoquinodimethanide).[6] However in the spin-Peierls case, as it will be shown, the band-gap behavior depends on the theory chosen to treat the quasifermion-quasifermion interaction, arising from the z coupling between the spins of the Heisenberg model.

Important similarities and differences exist between the BCS and the Peierls systems. In the former case, the ordered state is a condensate of Cooper pairs. Only electrons whose energy is within a shell of thickness $2\hbar\omega_D$ (ω_D is the Debye frequency) around the Fermi level participate. The electron-phonon interaction, binding the Cooper pairs is three dimensional. The Coulombic repulsive effects are generally neglected. The transition is always second order. However in Peierls systems, all the particles participate to the transition, the elementary excitations being of the particle-hole type. Moreover for the Peierls case, the electronic (quasifermion) system is one dimensional while the phonon system is three dimensional. For the Peierls systems, two limits are considered for half-filled bands. If $t >> U$ (where t is the transfer integral between two adjacent sites and U is the intrasite repulsive energy), an electronic Peierls transition results from an instability driven by the electron-phonon interaction. If $t << U$ (the atomic limit), the instability is driven by a spin-phonon interaction. It is the spin-Peierls transition. For the electronic Peierls transition, the electron-electron interaction is weak while for the Heisenberg spin-Peierls transition, the quasifermion-quasifermion interaction (arising from coupling of the z component of the spins) is of the same order of magnitude as the band energy.

The paper is organized as follows. First, the different gap equations are presented and we investigate under which conditions they reduce to the BCS one.

In particular, for the Heisenberg case, in the framework of Beni's theory[3] it is shown that the gap equation does not reduce to the BCS expression. Exact analytical arguments at $T=0$ K are given to support our conclusions. In Sec. III, we give numerical results for the XY interaction and we show that for a Heisenberg interaction the transition is of first order in the Beni's description. Next we investigate the effect of a magnetic field on the gap equation as an experimental means to check the theory: the magnetic field has a large effect on the critical temperature. Finally we conclude by a discussion of the results of Cross and Fisher[7] who used an original approach to this problem.

II. GAP EQUATIONS

First we give, for reference, the BCS gap equation:

$$1 = VN(0)\int_0^{\hbar\omega_D} \frac{d\zeta}{(\zeta^2+\Delta^2)^{1/2}} \tanh\tfrac{1}{2}\beta(\zeta^2+\Delta^2)^{1/2} \ , \quad (1)$$

where V is the electron-electron attractive potential ($V \sim g^2/\hbar\omega_D$ where g is the electron-phonon coupling constant), $N(0)$ is the density of states at the Fermi level, Δ is the energy gap, and $\beta=1/k_BT$. The free-energy lowering induced by this pairing is, at $T=0$ K,

$$F_s = -\tfrac{1}{2}N(0)\Delta^2 - N(0)\Delta^2 \ln\left(\frac{\Delta_0}{\Delta}\right) \ . \quad (2)$$

The main contribution is in $\Delta^2 \ln\Delta$. [$\Delta_0=\Delta(T=0)$.] The critical temperature is

$$k_BT_c = 1.13\hbar\omega_D \exp\left(-\frac{1}{N(0)V}\right)$$

and

$$\Delta_0 = 2\hbar\omega_D \exp\left(\frac{1}{N(0)V}\right) \ . \quad (3)$$

We give the gap at $T=0$ K (Δ_0) because it is an exact value (to order Δ^2) that can easily be compared with other cases.

For the electronic Peierls transition, the gap equation is obtained for a one-dimensional tight-binding half-filled electron band, coupled to the three-dimensional phonons using a mean-field theory.[1] The resulting gap equation is

$$b' = \epsilon_F \int_\Delta^{(\epsilon_F^2+\Delta^2)^{1/2}} \tanh(\tfrac{1}{2}\beta\epsilon) \times \frac{d\epsilon}{(\epsilon^2-\Delta^2)^{1/2}(\epsilon_F^2-\Delta^2-\epsilon^2)^{1/2}} \ , \quad (4)$$

where $b'=\hbar\omega/g^2N(0)$ and ϵ_F is the Fermi energy (it is equal to $2t$ for a half-filled band). ω is the frequency of the phonon which will be softened. Equation (4) is expanded for $k_BT/\epsilon_F \ll 1$ (a condition easily satisfied in conductors)

$$b' = \int_0^{\epsilon_F} \tanh(\tfrac{1}{2}\beta(\zeta^2+\Delta^2)^{1/2}) \frac{d\zeta}{(\zeta^2+\Delta^2)^{1/2}} + \ln 2 + O\left(\frac{\Delta^2}{\epsilon_F^2}\right) \ . \quad (5a)$$

For $T \lesssim T_c$, Eq. (5a) reduces to

$$b' = \int_0^{\epsilon_F} \frac{d\zeta}{\zeta} \tanh(\tfrac{1}{2}\beta\zeta) + \ln 2 - \frac{0.790}{\pi^2}\frac{\Delta^2}{T^2} + O\left(\frac{\Delta^2}{\epsilon_F^2}\right) \ . \quad (5b)$$

The free energy at $T=0$ K is (exact to order Δ^2)

$$F = N(0)\left\{\tfrac{1}{2}b'\Delta^2 - \tfrac{1}{4}\Delta^2\left[2\ln\left(\frac{4\epsilon_F}{\Delta}\right)+1\right]\right\} \ , \quad (6)$$

$$k_BT_c = 2.28\epsilon_F \exp(-2b')$$

and

$$\Delta_0 = 4\epsilon_F \exp(-2b') \ , \quad (7)$$

and Δ is directly proportional to δ (the degree of dimerization). For $k_BT_c \ll \epsilon_F$, the Δ^2/ϵ_F^2 term becomes negligible and Eq. (5b) reduces to the BCS form leading to a second-order phase transition.

For a spin-Peierls transition, the electrons are localized and the remaining degrees of freedom (the spins) are coupled to the phonons and between themselves through an antiferromagnetic interaction of strength J. When the interaction between the z components of the spins is absent (as in the XY model) the system of spins can be treated as a gas of free quasifermions. In this case, the formalism is equivalent to that of the electronic Peierls system.

The gap equation is[2]

$$b = \int_0^1 d\theta \frac{(1-\theta^2)^{1/2}}{[\delta^2+\theta^2(1-\delta^2)]^{1/2}} \times \tanh\beta J[\delta^2+\theta^2(1-\delta^2)]^{1/2} \ ; \quad (8)$$

if $k_BT \ll J$, it can be expanded to yield (with $\Delta=\delta J$)

$$b = \int_0^J \frac{\tanh(\frac{1}{2}\beta(\Delta^2+\zeta^2)^{1/2})\, d\zeta}{(\Delta^2+\zeta^2)^{1/2}} + \ln\left(\frac{2}{e}\right) + O\left(\frac{\Delta^2}{k_BTJ}\ln\beta J\right) + O\left(\frac{\Delta^2}{k_BTJ}\right) + O\left(\frac{\Delta^2}{J^2}\right) \ , \quad (9)$$

with $b=\pi C/J$ where C is the elastic constant for the potential between two ions. [b is also equal to $\hbar\omega/g^2N(0)$ where $N(0)=1/\pi J$ and g is the spin-phonon coupling constant.] This is an equation of the BCS type, but restricted to a smaller range of temperature whereas the former condition $k_BT \ll \epsilon_F$

was more easily satisfied [Eq. (5)] [the leading term is in $(\Delta^2/k_BTJ)\ln(J/k_BT)$ instead of Δ^2/J^2]. The free energy at $T=0$ K is

$$F=C\delta^2-\frac{2}{\pi}J(1+\delta^2\ln 2-\tfrac{1}{2}\delta^2\ln\delta-\tfrac{1}{4}\delta^2)+O(\delta^4)\ . \tag{10}$$

Δ_0 and T_c are given by

$$\Delta_0=1.47J\exp(-b)$$

and

$$k_BT_c=0.83J\exp(-b)\ . \tag{11}$$

Again, as in Eq. (5), the similarity with the BCS gap equation is clearly evident for $k_BT \ll J$. Numerical results will be given in Sec. III.

The Heisenberg spin-Peierls transition description differs from the XY case because of a large quasifermion-quasifermion interaction term arising from the coupling of the z components of the spins. Two different approaches have been used to treat this interaction. First, Pytte[4] treats this interaction in the Hartree-Fock approximation for a uniform chain and then uses the spin-phonon coupling to dimerize the chain at low temperature. Second, Beni[3] treats these interactions, again within the Hartree-Fock approximation, considering however already dimerized quasifermions. The two approaches give quite different results as it will be shown (see also Cross and Fisher[7]). Unfortunately it is difficult to know which approach is the best since in both cases we are working with approximate expressions. In our opinion the best approach is to go as far as we can exactly (Beni's point of view) and then to approximate, i.e., to treat in the Hartree-Fock approximation the interaction between *dimerized* quasifermions. Physically, this is appealing since, once the chain is in its thermodynamic equilibrium, it is the quasifermions corresponding to the dimerized lattice that interact. The quasifermions corresponding to the uniform chain no longer exist. Recent results (from numerical extrapolations on the exact eigenvalue spectrum of finite chains[8]) support this approach for the energy-gap calculation. Let us look first at the results of Pytte.[4] For a quasifermion interaction treated on the uniform chain, he showed that the spin-Peierls transition *essentially* reduces, when $k_BT_c \ll J$, to the XY Peierls transition[2] where J is replaced by pJ and g by gp with p given by the self-consistent equation

$$p=1-2\sum_k\frac{\cos ka}{\exp(E_k/k_BT)+1} \tag{12}$$

($E_k=pJ\cos ka$). As shown in Eq. (9), it also reduces, if $k_BT_c \ll J$, to the usual Peierls transition[1] once ϵ_F is replaced by pJ and g by pg. If $k_BT_c \ll J$, $p(T)$ is nearly a constant (1.637) and the transition follows a second-order BCS law [Eq. (9)]. The energy gap is related to the degree of dimerization by $\Delta=pJ\delta$. Δ_0 and T_c are given by

$$\Delta_0=1.47Jp\exp\left(-\frac{b}{p}\right)$$

and

$$k_BT_c=0.83Jp\exp\left(-\frac{b}{p}\right)\ . \tag{13}$$

Note that the proportionality constants are those of Eq. (11) instead of those of Eq. (7) as used by Pytte[4] and Bray *et al.*[5] The reason for this discrepancy is that they did not go far enough in the small k_BT_c/J expansion to obtain the BCS form.[7] This discrepancy originates from the slight differences between the gap equations of the Peierls and of the spin-Peierls transitions: the electron-phonon interaction is proportional to $\sin ka$ for the spin case.[4,5]

Let us now analyze Beni's approach where the quasifermion interaction is treated in the dimerized structure.[3] He argues that his theory reduces to that of Beni and Pincus[2] (XY model) if b is replaced by $\bar{b}$

$$\bar{b}=\frac{2b}{1+(1+8b/\pi)^{1/2}}\simeq(\tfrac{1}{2}\pi)^{1/2}b^{1/2}\ , \tag{14}$$

if b is large and if the occupation numbers of the dimerized quasifermions bands are replaced by those of noninteracting dimerized quasifermions (those of Beni and Pincus[2]). This approximation was assumed to be valid for $k_BT/J \ll 1$. One then expects a BCS law for the gap equation with b replaced by $\bar{b}$. However we will show that a more exact treatment and numerical calculations produce different results.

In Beni's theory, the gap equation is given by

$$\bar{b}\delta=\int_0^{\pi/2}\frac{dk}{J}\left(\frac{\partial J_k}{\partial\delta}\right)\tanh(\tfrac{1}{2}\beta\epsilon_k)\ , \tag{15}$$

where $J_k=J[1-(1-\delta^2)\sin^2 k]^{1/2}$. ϵ_k is a sum of J_k and of other terms coming from the quasifermion interactions.[3] If ϵ_k is approximated by J_k, a BCS law is obtained (the same as Beni and Pincus[2]). The lower the temperature is, the better the approximation is satisfied. Consequently, the approximation is at its best for $T=0$ K where

$$\begin{aligned}F={}&C\delta^2-1.339J-0.492J\delta^2+0.677\delta^2J\ln\delta\\&-0.203\delta^2J\ln^2\delta+O(\delta^4)\ .\end{aligned} \tag{16}$$

The term in $\delta^2\ln^2\delta$ makes the behavior different from a typical BCS one which is in $\delta^2\ln\delta$ [Eq. (2)]. The zero-temperature degree of dimerization is

$$\begin{aligned}\delta(0)&=3.227\exp[-\tfrac{1}{4}(\pi^2+8\pi b)^{1/2}]\\&\simeq 3.227\exp[-(\tfrac{1}{2}\pi)^{1/2}b^{1/2}]\end{aligned} \tag{17}$$

for large b and $\delta(0)$ is related to the gap Δ_0 by

$$\Delta_0 = J\delta\left(1+\frac{4}{\pi}\ln 2-\frac{2}{\pi}\ln\delta\right) \ . \tag{18}$$

Equations (16)–(18) show that the behavior of the $T=0$ K Beni's Heisenberg spin-Peierls phase is appreciably different from a BCS or a usual Peierls phase [Eqs. (2) and (3) or (6) and (7)]. An extra term in $(\delta\ln\delta)^2$ appears in the free energy, $\delta(0)$ is proportional to $\exp(-\sqrt{b})$, and Δ_0 is no more directly proportional to $\delta(0)$. Unfortunately no analytical expression for T_c is available due to the complexity of the quasifermion interaction term. In Sec. III, numerical results will confirm that in the Beni's description, the phase transition is not of the BCS type.

III. NUMERICAL CALCULATIONS

In this section, numerical results concerning the gap equation are given. All numerical calculations have been checked against the exact limiting values at $T=0$ K and agreement is found to a high degree of accuracy. Figure 1 shows the normalized energy gap $\Delta(T)/\Delta(0)$ as a function of T/T_c for the XY spin-Peierls transition. For $k_BT_c << J$, we expect a BCS behavior [Eq. (9)]. Results are given for $C/J=1$ $(k_BT_c/J=0.036)$ and $C/J=0.3$ $(k_BT_c/J=0.369)$ and are compared with the BCS gap equation (full drawn curve). Larger values of k_BT_c/J could not be used because of the large dimerization implied. (The approximation of a linear dependence of the exchange parameters on dimerization and of a quadratic repulsive interionic potential would be no longer valid.) It can be seen that all the curves are of the BCS type and depart only slightly from the full drawn curve. Thus we conclude that for small dimerization a BCS dependence of the XY spin-Peierls energy gap is appropriate.

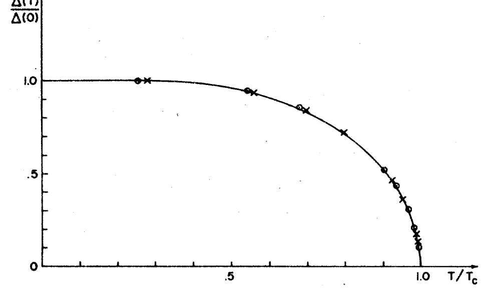

FIG. 1. Gap equations for XY spin-Peierls transition. Full drawn curve is the BCS gap equation. Crosses are obtained from XY model for $C/J=1$ $(k_BT_c/J=0.036)$ and circles are for $C/J=0.3$ $(k_BT/J=0.369)$.

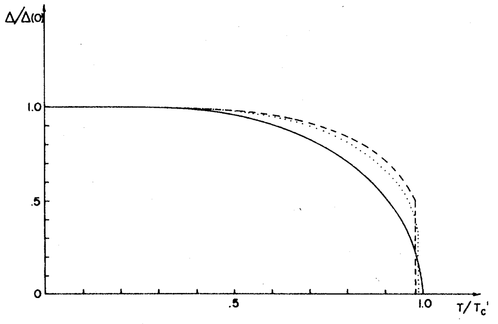

FIG. 2. Gap equations for Heisenberg spin-Peierls transition. Full drawn curve is the BCS gap equation. Dotted line is obtained from the Heisenberg model for $C/J=1$ $k_BT_c/J=0.382$, $k_BT_c'=0.387$. Dashed line is obtained for $C/J=3$, $k_BT_c/J=0.093$, and $k_BT_c'/J=0.095$.

The case of the Heisenberg spin-Peierls transition is quite different within the approach of Beni.[3] Numerical calculations show that the transition is of first order. Let us call T_c the first-order transition temperature and T_c' the temperature at which a second-order transition would be predicted to occur, by extrapolation, in the absence of the first-order transition. Figure 2 shows $\Delta(T)/\Delta(0)$ vs T/T_c' for $C/J=1$ $(k_BT_c/J=0.382$ and $k_BT_c'/J=0.387)$ and for $C/J=3$ $(k_BT_c/J=0.093$ and $k_BT_c'/J=0.095)$. It is observed that the transition is first order and, compared to the BCS behavior, the order parameter Δ reaches its saturation value at a higher temperature. Moreover, the universality is not obeyed.

Additionally this first-order transition is characterized by a very small energy barrier separating the ordered (dimerized) state from the unform phase: It is of the order of 10^{-5} J near T_c. The free energy near the transition temperature is thus nearly flat so that large thermal fluctuations of δ are expected. The jump in the energy gap is however quite large [of the order of 0.3 to 0.5 $\Delta(0)$]. All these results are significantly different from those of Beni who approximated ϵ_k by J_k and found a second-order behavior.

IV. EFFECT OF THE MAGNETIC FIELD ON THE GAP EQUATION

Clearly, a controversy exists about the way of treating the Heisenberg spin-Peierls system since many papers[3–5] considered the problem from different points of view resulting in different behavior of the gap with the temperature. Only the experiments can settle this controversy by indicating which model is closest to the real physical situation. Obviously, since we have a spin system, the most natural way to probe it in order to study its excitations is the application of a magnetic field. Hence, the aim of Sec. IV is to study the effect of the magnetic field on the transition in order to compare directly with experiments on systems like (TTF)Cu(BDT).[5,9] It is to be noted that we will only consider the instability from the uniform to the dimerized phase of the spin system. Hence we will not consider the possibility of incommensurability. This is justified since at least in one system of interest, (TTF)(Cu)(BDT), it is now well established that the phonon which softens and shepherds the quasifermion instability has a commensurate wave vector.[10] In other words the considered spin-Peierls instability is guided by this commensurate phonon which was on the verge of becoming soft by itself.

We recall that a magnetic field has a drastic effect[11] on the spin-Peierls transition for the XY model in which the interactions between quasifermions are totally absent. For the Heisenberg model these interactions are large and modify the spectrum of the free quasifermions of the XY model. Let us consider a dimerized antiferromagnetic chain consisting of $2N$ spins ($S=\frac{1}{2}$) or N dimers. The Hamiltonian of this chain, specified by two exchange constants J_1 (intradimer) and J (interdimer), with an external magnetic field H along the z direction is

$$H=\sum_{j=1}^{N} J_1(\vec{S}_{j,1}\cdot\vec{S}_{j,2}-\tfrac{1}{4})+J_2(\vec{S}_{j,2}\cdot\vec{S}_{j+1,1}-\tfrac{1}{4})$$

$$+\mu H\sum_{j=1}^{N}(S^z_{j,1}+S^z_{j,2})+NC\delta^2 \quad , \tag{19}$$

where $\vec{S}_{j,1}$ and $\vec{S}_{j,2}$ represent the first and second electron spin in the j th dimer; $\mu=2\mu_B$ where μ_B is the Bohr magneton and $NC\delta^2$ is the elastic energy of the N dimers in the one-phonon approximation of mean-field theory.[3] Proceeding as usual[3,4,12] in the Hartree-Fock approximation and in the linear approximation $[J_{1,2}=J(1\pm\delta)]$ we obtain expressions similar to those of Beni[3] with additional terms arising from the magnetic field. The latter modifies the occupation numbers and the energy spectrum. Following the notation of Beni[3] these are given respectively by

$$n_k^{\alpha,\beta}=\left[1+\exp\left(\frac{\epsilon_k^{\alpha,\beta}+\mu H}{k_BT}\right)\right]^{-1}$$

and

$$\epsilon_k^{\alpha,\beta}=\omega_k^{\alpha,\beta}+\tfrac{1}{2}(J_1+J_2)\sum_k(n_k^\alpha+n_k^\beta)$$

$$\pm\frac{1}{N}\sum_{k_1}v(k_1,k)(n_{k_1}^\beta-n_{k_1}^\alpha) \quad , \tag{20}$$

where

$$\omega_k^{\alpha,\beta}=-\tfrac{1}{2}(J_1+J_2)\pm\tfrac{1}{2}(J_1^2+J_2^2+2J_1J_2\cos k)^{1/2} \quad ,$$

and $k=2\pi n/N$ with $n=1,2,\ldots,N$. Furthermore we have[3]

$$v(k_1,k_2)=\tfrac{1}{2}J_1\cos 2(\phi_{k_1}-\phi_{k_2})$$

$$+\tfrac{1}{2}J_2\cos(k_2-k_1-2\phi_{k_1}+2\phi_{k_2}) \quad ,$$

where

$$\phi_k=-\tfrac{1}{2}\tan^{-1}[\gamma\sin k/(1+\gamma\cos k)]$$

and $\gamma=J_2/J_1$. Note that in the presence of a magnetic field the symmetry $\epsilon_k^\alpha=-\epsilon_k^\beta$ is broken and consequently $n_k^\alpha+n_k^\beta\neq 1$. Thus the free energy per link is written

$$\frac{F}{N}=J[\tfrac{1}{2}E_S^2+(h-1)E_S+h+E_L+(h+\eta)E_H$$

$$+\tfrac{1}{4}(1+\delta)(A^2+\gamma C^2)]+C\delta^2 \quad , \tag{21}$$

where

$$E_S=\frac{2}{\pi}\int_0^\pi dk\,\frac{1+\lambda\cosh\beta\epsilon_k}{1+\lambda^2+2\lambda\cosh\beta\epsilon_k} \quad , \qquad E_L=-\frac{1}{\pi J\beta}\int_0^\pi dk\,\ln(1+\lambda^2+2\lambda\cosh\beta\epsilon_k) \quad ,$$

$$E_H=\frac{2\lambda}{\pi}\int_0^\pi dk\frac{\lambda+\cosh\beta\epsilon_k}{1+\lambda^2+2\lambda\cosh\beta\epsilon_k} \quad , \qquad A=\frac{2\lambda}{\pi}\int_0^\pi dk\,\frac{(1+\gamma\cos k)\sinh\beta\epsilon_k}{(1+\gamma^2+2\gamma\cos k)^{1/2}(1+\lambda^2+2\lambda\cosh\beta\epsilon_k)} \quad ,$$

and

$$C=\frac{2\lambda}{\pi}\int_0^\pi dk\,\frac{(\gamma+\cos k)\sinh\beta\epsilon_k}{(1+\gamma^2+2\gamma\cos k)^{1/2}(1+\lambda^2+2\lambda\cosh\beta\epsilon_k)} \quad ,$$

with a dimensionless magnetic field $h=\mu H/J$. Besides we have used the following definitions:

$$\eta=E_S-1 \quad , \qquad \lambda=\exp\beta J(\eta+h) \quad ,$$

and

$$\epsilon_k/J=\tfrac{1}{2}(1+\delta)(1+\gamma^2+2\gamma\cos k)^{1/2}+(1-\delta)(A+C)\cos k/2(1+\gamma^2+2\gamma\cos k)^{1/2}$$

$$+(1+\delta)(A+\gamma^2C)/2(1+\gamma^2+2\gamma\cos k)^{1/2} \quad .$$

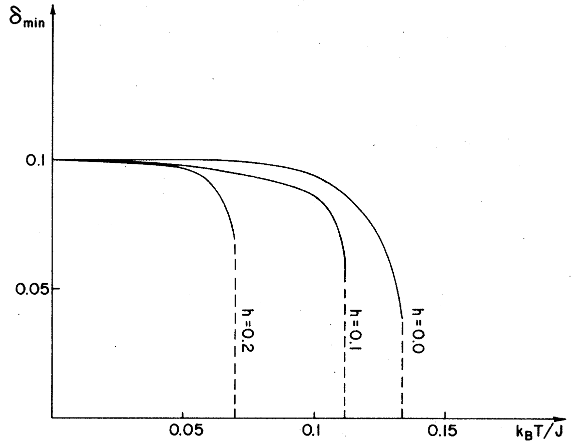

FIG. 3. Variation of the dimerization parameter as a function of temperature for the Heisenberg spin-Peierls transition. The curves are given for different magnetic fields, for $\pi C/2J = 3.6$.

The above system of coupled self-consistent equations was solved numerically for the quasifermion energy bands ϵ_k (containing the interacting part) allowing us to calculate the free energy which must be minimized in order to get the value of the equilibrium order parameter δ. The whole procedure of self-consistency and minimization has been undertaken for different temperatures and fields. The results are displayed on Fig. 3 (for $\pi C/2J = 3.6$) on which one notes a jump in the order parameter for all the considered fields including $h = 0$. The transition stays first order until its destruction by a critical field $h \simeq 0.3$. This behavior is different from that of the XY model where the magnetic field progressively changes[11] the nature of the transition from a second (at $h = 0$) to a first order until its destruction which comes up at lower critical fields. (The comparison is made in the case where the degree of dimerization at zero temperature is the same for both cases.) This difference in behavior stems from the additional quasifermions interaction contribution which is temperature and magnetic field dependent (this term is present even at $T = 0$ K). In Fig. 4 the variations of the Fermi wave vector k_F with respect to the dimensionless magnetic field h are given. Note the drastic effect for the XY model and a smoother effect in the Heisenberg case. Moreover, on the same figure, we see that at $T = 0$ K a magnetic field $h = 1$ is sufficient to destroy in XY model all the quasifermions, i.e., by making $k_F = 0$, whereas we need twice[3] this value in order to depopulate thoroughly the quasifermion bands in the Heisenberg model.

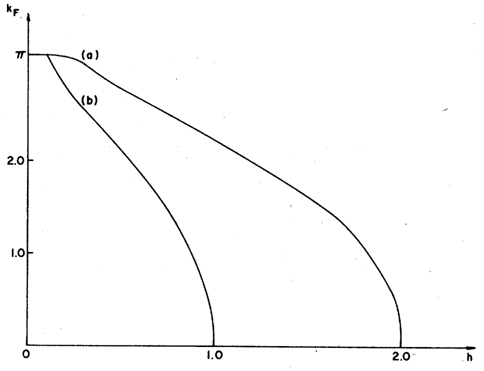

FIG. 4. Variation of the Fermi wave number at $T = 0$ K for the quasifermion bands as a function of magnetic field. (a) Heisenberg case, (b) XY case.

From Fig. 3 a rough estimate of the reduction of the critical temperature as a function of the applied magnetic field is obtained. We find a reduction in critical temperature T_c of the order of 2.4 K for a magnetic field of 8 T and $k_B T_c/J \approx 0.14$. For (TTF)Cu(BDT), $k_B T_c/J = 0.16$ a value close to that considered in Fig. 3; consequently we predict good agreement with recent experimental results: 2 K for 8 T.[9]

V. CONCLUSIONS

In this article, we have shown that the Peierls degree of dimerization and the energy gap usually followed a BCS-type law if $k_B T_c/\epsilon_F$ $(k_B T_c/J)$ is small enough. For the electronic Peierls transition, the lowest-order correction terms to the BCS behavior is in Δ^2/ϵ_F^2 while for the XY spin-Peierls transition, it is in $\Delta^2/(k_B TJ)\ln(J/k_B T)$. For systems of interest the above correction terms may be neglected leading to a second-order transition. We have shown that for the Heisenberg spin-Peierls transition, the behavior is substantially different. Two existing approaches have been investigated: that of Pytte who treats the interaction between the quasifermions (associated to the spin system) of the uniform chain and that of Beni who rather treats this interaction between already dimerized quasifermions. In the first case the transition is of the BCS type with a renormalization of the exchange (J) and of the quasifermion-phonon interactions. In contrast, the second case results in a first-order transition. The energy-gap curve as a function of temperature departs significantly from the BCS law even though the energy barrier separating the two phases near the transition point is very small (of the order of 10^{-5} J) allowing for large fluctuations around the transition point. We have also shown, as in the XY case, that the effect of the magnetic field was to move the Fermi level with respect to the energy bands (destroying quasifermions). This effect is less pronounced than in the XY case because of the coupling of the z components of the spins. However a sufficiently large magnetic field can decrease the transition temperature and can even destroy the transition. This effect is important as being a characterization of the transition. Good agreement with recent experimental results on (TTF)Cu(BDT) was also obtained.

The quasifermion interaction term is responsible for the peculiar behavior of the Heisenberg spin-Peierls transition. When the quasifermion-quasifermion interaction is treated in the Hartree-Fock approximation, neglecting fluctuations, the cooperativeness of the spin system is enhanced and accompanied by an increase in the jump of δ at a higher T_c. Such an increase in the value of δ at the minimum ($\delta_{\min}$) near the critical temperature, favors the retention of a potential barrier for small δ, allowing a first-order phase transition. Incidentally for $\delta \approx \delta_{\min}$ the energy gap varies the most rapidly with the degree of dimerization when the temperature of the system is closed to T_c. Thus for $\delta \approx \delta_{\min}$ the energy gained from the spin system per unit of δ is maximum for small changes in δ. The enhancement in cooperativeness arising from quasifermion interactions also results in larger critical magnetic fields for the Heisenberg model compared to the XY case.

Recently, Cross and Fisher approached the Heisenberg spin-Peierls transition from a new point of view.[7] They chose to approximate the quasifermion Hamiltonian to a point where it can be exactly diagonalized under the form of the Luttinger-Tomonaga model. This theory should give a better treatment of the quasifermion interaction term even if the approximations done to obtain the appropriate form implied adjustable parameters. These authors compare their results with the numerical calculation of Duffy and Barr[13] concerning the dependence of the ground-state energy per spin on the degree of dimerization. These appear on Fig. 5 as a $\delta^{4/3}$ law where the magnetic energy per pair is plotted as a function of δ at $T=0$ K (the energy reference is taken at $\delta=0.0$). Note that they had to fit the proportionality constant. On the same figure our results appear, with no adjustable parameter. It is seen that even if the $\delta^{4/3}$ dependence seems more appropriate to describe the data, the results of the Hartree-Fock approximates of Beni follow very closely the other curves. An approach that combines the exact critical behavior of Cross and Fisher with the good order-of-magnitude prediction of mean-field theory would be highly desirable.

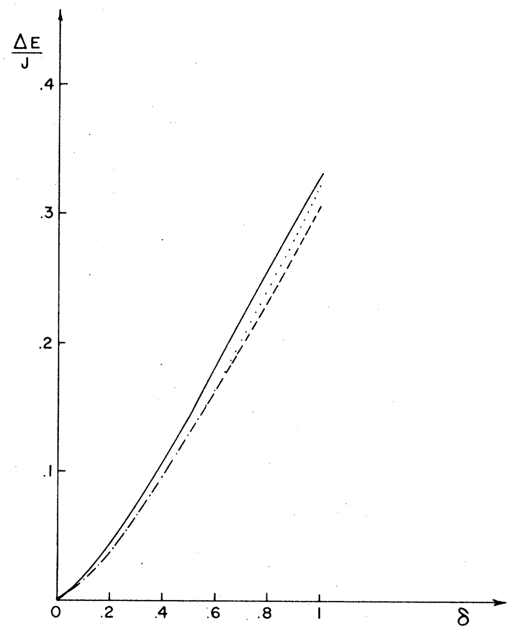

FIG. 5. Magnetic energy of a pair of spin (measured with respect to the zero-dimerization case) as a function of the degree of dimerization δ. Full drawn curve is data coming from Beni's theory (Ref. 3), dashed curve represents the numerical results of Duffy and Barr (Ref. 13) and the dots are the results of Cross and Fisher (Ref. 7).

ACKNOWLEDGMENTS

This research was partially supported by the Natural Sciences and Engineering Research Council of Canada and le ministère de l'Education du Québec (F.C.A.C.). One of us (Y.L.) would like to thank the Natural Sciences and Engineering Research Council of Canada for financial support.

---

[1] M. J. Rice and S. Strässler, Solid State Commun. 13, 125 (1973); G. J. Vegter and J. Kommandeur, Phys. Rev. B 8, 2887 (1973).

[2] G. Beni and P. Pincus, J. Chem. Phys. 57, 3531 (1972).

[3] G. Beni, J. Chem. Phys. 58, 3200 (1973); L. N. Bulaevskii, Zh. Eksp. Teor. Fiz 44, 1008 (1963) [Sov. Phys. JETP 17, 684 (1963)].

[4] E. Pytte, Phys. Rev. B 10, 4637 (1974).

[5] J. W. Bray, H. R. Hart, L. V. Interrante, I. S. Jacobs, J. S. Kasper, G. D. Watkins, S. H. Wee, and J. C. Bonner,

Phys. Rev. Lett. 35, 744 (1975); I. S. Jacobs, J. W. Bray, H. R. Hart, L. V. Interrante, J. S. Kasper, G. D. Watkins, D. E. Prober, and J. C. Bonner, Phys. Rev. B 14, 3036 (1976).

[6] Y. Lépine, A. Caillé, and V. Larochelle, Phys. Rev. B 18, 3585 (1978).

[7] M. C. Cross and D. S. Fisher, Phys. Rev. B 19, 402 (1979).

[8] J. N. Fields, H. W. J. Blöte, and J. C. Bonner, J. Appl. Phys. (to be published).

[9] I. S. Jacobs, J. W. Bray, L. V. Interrante, J. S. Kasper, H. R. Hart, Jr., D. Bloch, D. E. Moncton, G. Shirane, and J. C. Bonner, Bull. Am. Phys. Soc. 24, 354 (1979).

[10] D. E. Moncton, R. J. Birgeneau, L. V. Interrante, and F. Wudl, Phys. Rev. Lett. 39, 507 (1977).

[11] C. Tannous and A. Caillé, Can. J. Phys. 57, 508 (1979).

[12] Y. Lépine and A. Caillé, J. Chem. Phys. 67, 5598 (1977).

[13] W. Duffy and P. K. Barr, Phys. Rev. 165, 647 (1968).