Spin-Peierls transition in quasi-one-dimensional crystals

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A review is given of theoretical concepts and experimental data concerning the spin-Peierls transition in a one-dimensional spin system with antiferromagnetic exchange interaction (an analog of Peierls instability of a one-dimensional metal). Analysis of experimental data confirms the existence of the spin-Peierls transition in TTF-CuBDT, TTF-AuBDT, and MEM(TCNQ)$_2$ crystals. The magnitude of the spin-phonon interaction in crystals undergoing the spin-Peierls transition at low temperatures is discussed together with the role of fluctuations in transitions of this type. The influence of magnetic fields on spin-Peierls transitions is examined.

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CONTENTS

1. INTRODUCTION

Quasi-one-dimensional compounds have been attracting increasing attention of both experimenters and theoreticians. This has been largely due to the unusual properties of quasi-one-dimensional systems, an example of which is the low-temperature conductivity peak exhibited by compounds of the form TTF-TCNQ. It may now be regarded as firmly established that, as the temperature is reduced, many conducting quasi-one-dimensional crystals exhibit a Peierls transition to the dielectric state, which is accompanied by a charge-density wave. Many low-temperature properties of quasi-one-dimensional conductors are directly related to the Peierls transition. The transition is accompanied by static displacements of ions with wave vector $Q = 2k_F$, which gives rise to the splitting of the conduction band and a reduction in the energy of electrons occupying the lower band of the one-dimensional system by the amount $\Delta^2 \ln(W/\Delta)$, where Δ is the gap in the electron spectrum, which is proportional to the amplitude of the wave of static displacements of the ions, and W is the width of this conduction band; the increase in the elastic energy due to the deformation of the lattice is proportional to Δ^2, which favors displacements with $Q = 2k_F$ at zero temperature. We note that the ion displacements give rise to a redistribution of electron density along the chain which, in turn, produces the so-called charge-density wave (CDW). The CDW is, in fact, responsible for many of the unusual properties of quasi-one-dimensional conductors (the Peierls transition is reviewed, for example, in Refs. 1–3).

The magnetic analog of the Peierls instability is the so-called spin-Peierls (SP) transition of a homogeneous antiferromagnetic chain of spins to an alternated state, i.e., a state with twice the period. The SP transition in a Heisenberg chain of spins with $S = 1/2$ is a phase transition of the second kind to the singlet ground state. It is accompanied by the appearance of a gap in the spectrum of triplet magnetic excitations. The concept of the instability of a homogeneous chain of spins with $S = 1/2$ with respect to alternation was put forward more than fifteen years ago by McConnell *et al.*[4] and was subsequently developed elsewhere.[5-9] However, until quite recently, there was no experimental evidence confirming the existence of the SP transition despite the large number of known quasi-one-dimensional compounds that could satisfactorily be described by the Heisenberg spin chain (see the review in Ref. 10). However, the situation has changed in the last three years, following the discovery and then intensive investigation of two quasi-one-dimensional dielectric crystals whose properties can be satisfactorily explained within the framework of the theory of the SP transition.[11-17] These two crystals belong to a group of quasi-one-dimensional donor-acceptor compounds of the form TTF-$MS_4C_4(CF_3)_4$, where M is a metal atom. The SP transition has been found to occur in compounds with M = Cu and Au at temperatures of 12 °K and 2 °K, respectively, and may be regarded as firmly established for these compounds. There is also evidence that the SP transition occurs in certain other compounds, namely, MEM(TCNQ)$_2$ (Ref. 18), Li-TCNQ (Ref. 19), and K-TCNQ (Ref. 20). However, whether or not the phase transition in these compounds is due to the spin subsystem must, for the present, be regarded as an open question.

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The SP transition is a new type of magnetic transition which, apart from being interesting in itself, may also be useful in connection with the electron Peierls transition because it is analogous to the Peierls transition in a half-filled conduction band. There are, at present, no known conducting quasi-one-dimensional crystals with a half-filled band, but in a certain sense, this particular case is a special one because of the importance of commensurability effects that tend to suppress CDW phase excitations. Moreover, the effect of the magnetic field on the spin-Peierls transition corresponds to a change in the degree of filling of the conduction band in the Peierls system, so that the behavior of the SP system in a magnetic field is a source of information about the influence of commensurability effects on the Peierls transition. Thus, the close connection between SP transition and Peierls instability means that studies of this transition will be very important for a better understanding of the properties of quasi-one-dimensional systems generally (both magnetic dielectrics and conductors).

2. THEORY OF THE SPIN-PEIERLS TRANSITION

A quasi-one-dimensional antiferromagnetic compound is commonly modeled by a set of noninteracting spin chains with Heisenberg interaction between nearest-neighbor spins. The Hamiltonian for this system is

$$\mathscr{H}_S = \sum_{\mathbf{n}} \sum_{l=1}^{N} J_{\mathbf{n}}(l, l+1) \left(\mathbf{S}_{\mathbf{n},l}\mathbf{S}_{\mathbf{n},l+1} - \frac{1}{4}\right), \tag{2.1}$$

where $\mathbf{S}_{\mathbf{n},l}$ is the operator corresponding to the l-th spin in the chain $\mathbf{n}$, N is the number of spins in the chain, and $J_{\mathbf{n}}(l, l+1)$ is the exchange integral which is a linear function of the displacement $u_{\mathbf{n}}(l)$ of the magnetic ions:

$$J_{\mathbf{n}}(l, l+1) = J + [u_{\mathbf{n}}(l) - u_{\mathbf{n}}(l+1)]\nabla_l J(l, l+1). \tag{2.2}$$

Substituting (2.2) in (2.1), and adding the elastic energy associated with the displacement of the ions, $U = \sum_{\mathbf{n},l,\mathbf{n}',l'} K_{\mathbf{n}l,\mathbf{n}'l'} u_{\mathbf{n}l} u_{\mathbf{n}'l'}$, and their kinetic energy $T = \frac{1}{2}\sum_{\mathbf{n},l} M(u_{\mathbf{n}l})^2$, we obtain the complete Hamiltonian for the system of three-dimensional phonons, spins with one-dimensional Heisenberg interaction, and the spin-photon interaction. In principle, one should include the exchange and the dipole-dipole interaction between the spins in neighboring chains, but this is small and will be neglected. We can now transform in (2.1) from the spin operators $\mathbf{S}_l$ to the pseudofermion operators ψ_l with the aid of the Jordon-Wigner transformation:

$$\psi_l^{\pm} = 2^{l-1} S_1^z S_2^z \ldots S_{l-1}^z S_l^{\pm}, \tag{2.3}$$

where $S^{\pm} = S^x \pm iS_l^y$.[21,22] When there are no phonons, the Hamiltonian (2.1) can be written in terms of the pseudofermion operators ψ_k in the momentum representation[23]:

$$\mathscr{H}_s = \mathscr{H}_{s,0} + \mathscr{H}_{s,\mathrm{int}}, \quad \mathscr{H}_{s,0} = \sum_k E_0(k)\psi_k^+\psi_k,$$

$$\mathscr{H}_{s,\mathrm{int}} = \frac{1}{N}\sum_{k,k',q} V(q)\psi_{k+q}^+\psi_{k'-q}^+\psi_{k'}\psi_k, \tag{2.4}$$

where $E_0(k) = J(\cos k - 1)$ and $V(q) = J\cos q$. The Hamiltonian $\mathscr{H}_{s,0}$ describes noninteracting fermions. It corresponds to the spin XY interaction $J(S_l^x S_{l+1}^x + S^y S_{l+1}^y)$, and the XY model has an exact solution. The interaction $JS_l^z S_{l+1}^z$ can be written in the form of the four-fermion interaction $\mathscr{H}_{s,\mathrm{int}}$ after the transformation given by (2.3).

a) Hartree-Fock approximation

Bulaevskiĭ[23] considered the four-fermion interaction in a homogeneous magnetic chain in the Hartree-Fock approximation. Subsequently, Pytte[8] used this approximation to examine the bound spin-phonon system. In the Hartree-Fock approximation, the Hamiltonian for the system is

$$\mathscr{H} = \sum_{k,\mathbf{n}} E(k) a_{\mathbf{n}k}^+ a_{\mathbf{n}k} + \sum_{k,\mathbf{q},\mathbf{n}} \frac{g(k,\mathbf{q})}{\sqrt{N}} (b_{\mathbf{q}} + b_{-\mathbf{q}}^+) a_{\mathbf{n}k}^+ a_{\mathbf{n},k-q} + \sum_{\mathbf{q}} \omega_0(\mathbf{q}) b_{\mathbf{q}}^+ b_{\mathbf{q}}. \tag{2.5}$$

In the derivation of this expression, the displacements $u_{\mathbf{n}}(l)$ of the magentic ions in (2.2) were expressed in the usual way in terms of the phonon creation and annihilation operators $b_{\mathbf{q}}^+$ and $b_{\mathbf{q}}$, $\omega_0(\mathbf{q})$ is the phonon frequency corresponding to wave vector $\mathbf{q} = (q, \mathbf{q}_\perp)$, and $q, \mathbf{q}_\perp$ are the components of the phonon momentum, respectively parallel and perpendicular to the chain. Finally,

$$E(k) = pJ\cos k, \quad g(k,\mathbf{q}) = \frac{igp[\sin k - \sin(k-q)]}{\sqrt{2\omega_0(\mathbf{q})}}, \quad g = \frac{\nabla_l J(l, l+1)}{\sqrt{M}}, \tag{2.6}$$

where M is the mass of the magnetic ion or molecule. In the Hartree-Fock approximation, the constant p is determined from the equation

$$1 - p = \frac{2}{N}\sum_k \cos k \left[1 + \exp\left(\frac{Jp\cos k}{T}\right)\right]^{-1}, \tag{2.7}$$

which gives $p = 1 + (2/\pi)$ at low temperatures $T \ll J$. The Hamiltonian (2.5) is equivalent to the Hamiltonian for a one-dimensional electron-phonon system, whose susceptibility has a singularity at $q = 2k_F$, which is responsible for the Peierls transition. This equivalence has led to the designation "spin-Peierls transition" in the one-dimensional antiferromagnetic Heisenberg chain. Since the fermion band is half-filled in the absence of the magnetic field (the chemical potential is zero), the system will be unstable against doubling of the period with $q = 2k_F = \pi$, and static displacements of the ions, $\langle u_{\mathbf{n},l}\rangle = (-1)^l \cos(\mathbf{Q}_\perp \mathbf{n}) u_0$, will appear below the critical temperature T_c, where u_0 is the displacement amplitude. In the self-consistent field approximation, the transition temperature is given by[8]

$$T_c = 2.28pJe^{-1/\lambda_{s,\mathrm{ph}}}, \quad \lambda_{s,\mathrm{ph}} = \frac{4g^2p^2N(0)}{\omega_0^2(\mathbf{Q})}, \quad N(0) = \frac{1}{\pi pJ}, \tag{2.8}$$

where $N(0)$ is the density of states in the fermion band at the Fermi level, $\lambda_{s,\mathrm{ph}}$ is the spin-phonon interaction constant, and $\omega_0(2k_F, \mathbf{Q}_\perp)$ is the frequency of the nucleating phonons corresponding to the doubling of the period along the chain. The magnitude of the transverse momentum $\mathbf{Q}_\perp$ is determined from the condition that the phonon frequency $\omega_0(2k_F, \mathbf{q}_\perp)$ is a minimum as $\mathbf{q}_\perp$ is varied (phonons with $\mathbf{Q} = (2k_F, \mathbf{Q}_\perp)$ are found to condense during the SP transition). At the critical point T_c, the displacement amplitude is $u_0 = 0$, whereas, below T_c, the amplitude increases with decreasing temperature, and the function $u_0(T)$ in the Hartree-Fock approximation is the same as the temperature dependence of the gap in the BCS model. The increase in u_0 is accompanied by an increase in the gap Δ in the spectrum of triplet excitations. In the Hartree-Fock approximation, Δ

$=u_0\omega_0\sqrt{\lambda M/4N(0)}$. Near T_c, we can write down the Landau functional for the order parameter u_0 or Δ. If we take the Landau order parameter to be $\varphi=\Delta$, we obtain

$$\mathscr{F}=\frac{1}{2}a\varphi^2+\frac{1}{4}b\varphi^4,\quad a=\alpha\tau,\quad \tau=\frac{T}{T_c}-1, \tag{2.9}$$

where $\alpha=N(0)$ and $b=0.106N(0)(k_BT_c)^{-2}$. Since the Hartree-Fock approximation corresponds to the BCS model, the jump in the specific heat at T_c is given by the usual formula $\Delta c=1.43\gamma T_c$.[15] Gradient terms in the free energy $\mathscr{F}$ will be given below in Sec. 6. The increase in the gap width in the spectrum of triplet excitations below T_c gives rise to a rapid reduction in paramagnetic susceptibility with decreasing temperature.

We note that the predicted appearance of Peierls displacements below the critical temperature T_c, given by (2.8), was obtained in the self-consistent field approximation for the ion displacements, and in the Hartree-Fock approximation for the fermions. The self-consistent field approximation for the displacements does not take fluctuations into account, i.e., it ignores the presence of phonons in the system (except for condensed phonons with $\mathbf{q}=\mathbf{Q}$). In principle, this approximation may turn out to be too rough for the quasi-one-dimensional system. Its validity will be examined below. Here, we merely note that the three-dimensionality of the phonon system in real crystals is sufficient to suppress fluctuations everywhere with the exception of a narrow band around T_c.

b) The Cross-Fisher approximation

The way in which the Hartree-Fock approximation for fermions takes into account the interaction between fermions is not completely correct. At the same time, the interaction is not small for the Heisenberg spin chain and may turn out to be even more important in the case of a one-dimensional system of fermions. Cross and Fisher[24] have taken the analysis outside the framework of the Hartree-Fock approximation and have replaced the four-fermion Hamiltonian $\mathscr{H}_{s,\mathrm{int}}$ in (2.4) with the Hamiltonian used in the Luttinger-Tomonaga model, which can be solved exactly. The exact cosinusoidal dispersion relation for pseudofermions, given in (2.4), is replaced by a linear function with the corresponding Fermi velocity, and the interaction $V(q)$ is replaced with $V(0)=J$ for forward scattering and $V(\pi)=-J$ for backscattering. It was assumed[24] that this procedure correctly reproduced the characteristic features of the response of the one-dimensional system of fermions with interaction to the appearance of periodic ion displacements. The reduction to a model that has an exact solution enables us to evaluate the spin (or fermion) polarization operator $\Pi(q,\omega)$, which determines the softening of the nucleating phonons due to the polarizability of the spin system:

$$\omega^2(\mathbf{q})=\omega_0^2(\mathbf{q})+g^2(\mathbf{q})\,\omega_0(\mathbf{q})\,\Pi(q,\omega),$$
$$\Pi(q,\omega)=\int_{-\infty}^{+\infty}dt\,e^{i\omega t}\sum_l e^{-iql}\{-i\theta(t)\langle[(\mathbf{S}_l\mathbf{S}_{l+1})_t\,(\mathbf{S}_0\mathbf{S}_1)_{t=0}]\rangle\}, \tag{2.10}$$

where $\theta(t)=1$ for $t>0$ and $\theta(t)=0$ for $t<0$.

The transition temperature T_c can be determined from the condition $\omega^2(\mathbf{q})=0$. Calculations show that, when the interaction is taken into account, the polarization operator $\Pi(2k_F,0)$ diverges as J/T for $T\ll J$ (and not logarithmically, as $\ln(J/T)$, as in the case of the Hartree-Fock approximation). This ensures that the transition temperature is a linear function of the coupling constant:

$$T_c=0.8\lambda_{s,\mathrm{ph}}\,J, \tag{2.11}$$

and data on T_c and J show that $\lambda_{s,\mathrm{ph}}=0.19$ in the case of TTF-CuBDT, whereas, in the Hartree-Fock approximation, the corresponding result is $\lambda_{s,\mathrm{ph}}=0.29$. At zero temperature, the variation in the energy of the spin system with the dimerization parameter u_0 is described by $\Delta E\propto -u_0^{4/3}$,[1)] which is different from the result $\Delta E\propto -u_0^2|\ln u_0|$, obtained in the Hartree-Fock approximation.[25] The former result was obtained by Cross and Fisher and is very similar to the exact upper limit for the dimerization energy obtained by van der Braak *et al.*,[26] namely, $-u_0^{1.377}$. Fields *et al.*[27] have compared different approximations used to calculate the alternated chain and have computed the gap in the spectrum of magnetic excitations as well as the ground-state energy of the alternated chain as functions of the alternation parameter u_0, using the renormalization group method in real space. This comparison has shown that the Cross-Fisher method is better than the Hartree-Fock method in describing the ground-state energy, but the dependence of the gap on the alternation parameter is better in the Hartree-Fock approximation.

So far, we have considered the spin-Peierls transition within the framework of the localized-spin concept. All the conclusions are, of course, valid for quasi-one-dimensional compounds described by the Hubbard model with strong Coulomb repulsion U between electrons on a single center and a half-filled band with gap W ($U\gg W$), since it is well known that, in this case, the ground state and all the low-lying states of the system can be described by the effective Hamiltonian (2.1) with $J\sim W^2/U$.

It is less obvious that systems with strong Coulomb repulsion on a single center and a band not half-filled can also be unstable with respect to the spin-Peierls transition. In such systems, the strong Coulomb repulsion ensures that two electrons with opposite spins will not be found in the same center in the limit as $W/U\to 0$, and their motion will be equivalent to the motion of spinless fermion particles.[28,29] The Fermi momentum of these particles is $2\pi\nu/a=2k_F$, where ν is the degree of filling of the band, a is the lattice period, k_F is the Fermi momentum of electrons in the system for $U=0$, and the system is unstable with respect to Peierls displacements with $q=2\times 2\pi\nu/a=4k_F$. Klein and Zeitz[30] have shown that the spin degrees of freedom of delocalized particles are then described by the Heisenberg spin Hamiltonian. The spin-Peierls instability then corresponds to $q=2\pi\nu/a=2k_F$, since a/ν is the mean separ-

1)This result was obtained by Cross and Fisher[24] on the basis of heuristic considerations. They have also obtained the value of the coefficient α in (2.9) but were unable to determine the parameter b of this Landau expansion.

ation between spins. It is not clear at present whether the SP transition will occur in this system of "delocalized spins" within the framework of the model with $U \gg W$. However, analysis of one-dimensional systems with interaction has shown that, under certain definite conditions, such systems do exhibit responses that diverge at low temperatures for wave numbers $q = 2k_F$ and $q = 4k_F$, but, so far, this cannot be regarded as an explanation of superstructures with $2k_F$ and $4k_F$ in TTF-TCNQ.

3. EXPERIMENTAL DATA

The SP transition can now be regarded as firmly demonstrated for the quasi-one-dimensional donor-acceptor compunds TTF-$CuS_4C_4(CF_3)_4$ and TTF-$AuS_4C_4(CF_3)_4$, and it may be assumed that it has also been observed in $MEM(TCNQ)_2$. The first two of these compounds have now been examined in greater detail, and we shall therefore begin with experimental data on compounds containing TTF. In crystals of these compounds, planes containing the donor molecules (TTF) and the acceptor molecules $[MS_4C_4(CF_3)_4]$ are practically parallel, so that alternating layers of donor and acceptor molecules form a stack along the c axis.[12] The unpaired spin 1/2 in these compounds occurs on the TTF^+. Bray *et al.*[11] have found that the paramagnetic susceptibility falls sharply to practically zero in the case of TTF-$CuS_4C_4(CF_3)_4$ (TTF-CuBDT) and TTF-$AuS_4C_4(CF_3)_4$(TTF-AuBDT) molecules at $T_c = 12$ and 2 °K, respectively (Fig. 1). They suggested that this fall was due to a phase transition of the second kind, namely, the SP transition. Above the transition temperature, the paramagnetic susceptibility is excellently described by the one-dimensional antiferromagnetic Heisenberg chain of $S = 1/2$ spins. Thus, the susceptibility is isotropic and shows a broad peak at low temperatures.[11,12] Below the critical temperature T_c, the paramagnetic susceptibility remains isotropic and falls sharply with decreasing temperature. The isotropic behavior of susceptibility below T_c precludes the possibility of three-dimensional antiferromagnetic order in the system. The EPR linewidth is also found to show a sharp reduction below T_c, which again points to the appearance of a gap in the spectrum of triplet excitations of the spins in the chain. Smith *et al.*[13] have shown that their NMR relaxation data are also in agreement with this assumption: as the temperature is reduced below T_c, the nuclear relaxation time increases exponentially and, as was shown by Ehrenfreund and Smith,[14] the temperature dependence of the rate of relaxation below T_c is reasonably well described by a theory involving relaxation in an alternated antiferromagnetic chain. Wei *et al.*[15] have also carried out calorimetric studies of the above compounds. They found a specific heat discontinuity Δc at T_c, indicating the occurrence of a phase transition of the second kind (Fig. 2). Moreover, the temperature dependence of the specific heat was found to contain the linear contribution γT above T_c, which is characteristic of one-dimensional homogeneous antiferromagnets with $\gamma = 2k_B^2/3J$, where the exchange integral J can be obtained independently from susceptibility data above T_c.

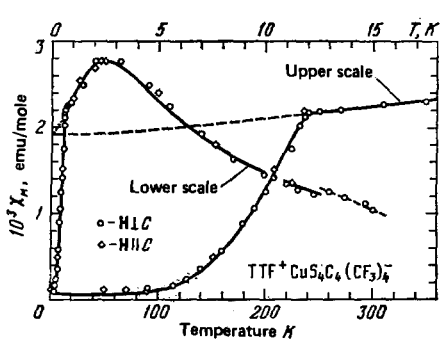

FIG. 1. Magnetic susceptibility of TTF-CuBDT as a function of temperature.[11,12] Solid lines-calculated for antiferromagnetic Heisenberg chain with homogeneous exchange integral above 12 °K and with temperature-dependent alternative exchange below 12 °K.

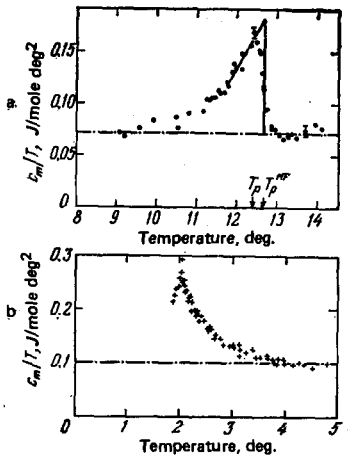

FIG. 2. a—Magnetic specific heat (c_m/T) of TTF-CuBDT as a function of temperature[15] (the dot-dash curve corresponds to the specific heat of the homogeneous chain with $J = 77$ °K), b—magnetic specific heat (c_m/T) of TTF-AuBDT as a function of temperature.[15]

Experimental data are in good agreement with the theoretical prediction $\Delta c = 1.43\gamma T_c$, obtained in the Hartree-Fock approximation.[2)] Thus, in the case of TTF-CuBDT, the theoretical prediction is 1.31 J/mol.deg, whereas the experimental result is $\Delta c = 1.41 \pm 0.2$ J/mol.deg.[15] X-ray studies of TTF-CuBDT, performed by Moncton *et al.*,[31] provide direct evidence for the doubling of the unit cell below $T_c = 12$ °K, and the temperature dependence of the displacement amplitude u_0 is satisfactorily described by the function characteristic for the BCS model (Fig. 3). The origin of the anisotropy in the interaction between spins in TTF-CuBDT and the nature of the displacement of the TTF molecules during the SP transition will be discussed in greater detail below.

Let us now consider experimental data[18] on the quasi-one-dimensional crystal $MEM(TCNQ)_2$. In these crystals, the molecules of the acceptor TCNQ and the donor MEM form donor and acceptor stacks and the TCNQ and

[2)] As noted above, the coefficient b in the Landau expansion for the Cross-Fisher approximation is unknown so that one cannot predict the specific heat discontinuity at the transition temperature in this approximation.

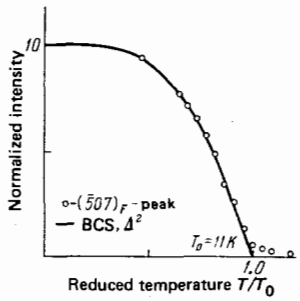

FIG. 3. Temperature dependence of the intensity of new Bragg peaks appearing as a result of dimerization.[31] The intensity is proportional to the square of the amplitude of the ion displacement u_0^2 or the square of the order parameter φ^2. Solid line-square of gap as a function of temperature in the BCS model.

MEM stacks are found to alternate in the crystal. Unpaired electrons occur in the TCNQ stack and two molecules of TCNQ correspond to one conduction electron, which corresponds to a quarter-filled band with $k_F = \pi/4a$, where a is the separation between molecules in the stack. At high temperatures, MEM(TCNQ)$_2$ is satisfactorily described by the Hubbard model with strong Coulomb repulsion $U \gg W$. At 335 °K, a phase transition of the first kind to a strongly dimerized state, i.e., a transition with wave vector $q = 4k_F$, is observed in MEM (TCNQ)$_2$. This is accompanied by a reduction in conductivity by three orders of magnitude, which is clear evidence for the appearance of a gap in the spectrum of electron excitations. The phase transition with $q = 4k_F$ can be explained within the framework of the model with $U \gg W$ as a Peierls transition in a system of spinless particles. Below 335 °K, the paramagnetic susceptibility and the magnetic part of the specific heat of MEM (TCNQ)$_2$ are satisfactorily described by a model involving a one-dimensional spin chain with the Heisenberg interaction and $J = 106$ °K.[18] A jump in specific heat occurs at $T_c = 19$ °K and further reduction in temperature produces a sharp fall in the paramagnetic susceptibility, i.e., its behavior in the case of MEM(TCNQ)$_2$ below T_c is similar to that shown in Fig. 1 for TTF-CuBDT. The jump in specific heat at T_c in the case of MEM (TCNQ)$_2$ is 2.5 ± 0.4 J/mol·deg, whereas the estimate based on the Landau theory is 1.84 J/mol·deg. X-ray analysis below T_c shows that additional dimerization along the TCNQ chain occurs in this compound below T_c, i.e., the lattice of dimers that appears after the first transition (at 335 °K) doubles the period below T_c.

All existing experimental data on TTF-CuBDT, TTF-AuBDT, and MEM(TCNQ)$_2$ turn out to be satisfactorily interpreted in terms of the SP transition.

4. THE SPIN-PHONON INTERACTION CONSTANT

At first sight, there are serious objections to the SP transition as a way of explaining the properties of the above crystals. The point is that, under ordinary conditions, crystals with exchange interaction parameter $J \approx 100$ °K have a very small spin-phonon interaction constant. Indeed, for a given rigidity of the lattice with respect to the Peierls displacements, the fermion-phonon interaction constant λ, which determines the transition temperature, is proportional to the width of the fermion band [see (2.6)]. For the electron-phonon Peierls transition in compounds such as TTF-TCNQ, the electron-band width is about eV and $\lambda_{1,ph} \approx 0.5$.[3] For one-dimensional magnetic systems, the pseudofermion band width is $2pJ \approx 3J$ ($J = 77$ °K in TTF-CuBDT, 68 °K in TTF-AuBDT,[11] and 106 °K in MEM(TCNQ)$_2$). Thus, for roughly equal crystal stiffness, the constant $\lambda_{s,ph}$ should be roughly 0.01–0.02 for the SP transition. This is lower by at least an order of magnitude than the values of $\lambda_{s,ph}$ obtained from data on T_c and J in the case of TTF-CuBDT (0.19 according to Cross and Fisher and 0.29 according to the Hartree-Fock approximation). When $\lambda_{s,ph} \approx 0.01$, the SP transition temperature should not exceed 1 °K in the case of TTF-MBDT and 2 °K in the case of MEM (TCNQ)$_2$. There is now a large number of organic and inorganic compounds whose magnetic properties can be described within the framework of the homogeneous spin chain model with exchange interaction $J \leq 100$ °K and all the crystals that have been investigated (with the exception of the three mentioned above) remain homogeneous down to very low temperatures.[10] Serious doubts have, therefore, arisen as to whether the doubling of the period of the low-temperature phase of the above three compounds is, in fact, due to the spin-Peierls instability. In principle, the usual structural transition with the doubling of the lattice period can occur at T_c and the alternation of the exchange interaction in the spin chain can be a subsidiary consequence of this transition. However, the size of the jump in the specific heat, namely, $\Delta c = 1.43\gamma T_c$, observed during the transition, corresponds to the magnetic parameters of the crystal ($\gamma = 2k_B^2/3J$), and this practically precludes the interpretation of existing experimental data outside the framework of the SP transition theory. However, once the SP transition model is adopted, we must be able to explain why the constant $\lambda_{s,ph}$ for the above crystals is higher by at least an order of magnitude than expected.

The unexpected data obtained from x-ray studies of TTF-CuBDT[31] provide the explanation as to why the parameter $\lambda_{s,ph}$ has the anomalously high value in this compound. At 225 °K, a transition of the first kind occurs in TTF-CuBDT and gives rise to the appearance of a one-dimensional chain of spins in the crystal. Figure 4a (solid line) shows the disposition of the magnetic molecules of TTF in the crystal above 225 °K. The broken line shows their disposition at temperatures between 12 and 225 °K. The transition of the first kind at

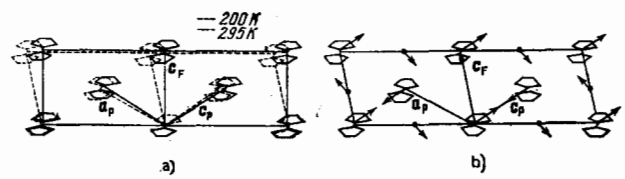

FIG. 4. a—Structural transition of the first kind in TTF-CuBDT at 225 °K (solid lines show the position of the TTF molecules above the transition point and broken lines show their position below this temperature[31]; for simplicity, the CuBDT molecules are not shown), b—displacements of molecules in TTF-CuBDT below the SP transition temperature ($T_c = 12$ °K).[17] Arrows show the directions of displacement for the TTF$^+$ and CuBDT molecules (points) as the temperature is reduced below T_c.

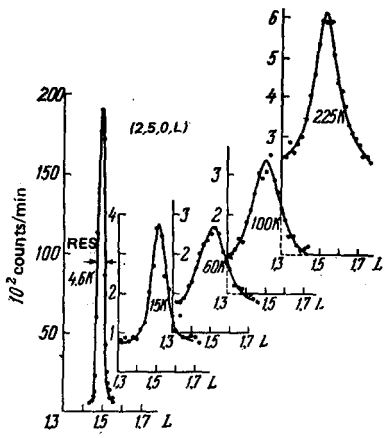

FIG. 5. Scattering of x rays along $Q = (2, 5, 0, L)$P in TTF-CuBDT as a function of temperature above and below the SP transition.[31]

225 °K produces a reduction in the separation between the molecules along the $\mathbf{c}_P$ axis and an increased separation along the $\mathbf{a}_P$ axis. The net result is that the difference $\mathbf{a}_P - \mathbf{c}_P$ changes from 0.3 Å to 1.4 Å after the transition. The arrows in Fig. 4b indicate the motion of the molecules below 12 °K that leads to the alternation of the chain of spins along the $\mathbf{c}_P$ axis (the separation between the TTF molecules along the stacks, i.e., along the **c** axis, does not then change). Thus, the TTF molecules lying along the $\mathbf{c}_P$ axis (but not along the stacks) form a one-dimensional chain of spins, and the transition at 225 °K leads to the monomerization of the interaction in the system of spins because, above 225 °K, the interaction between spins along the $\mathbf{a}_P$ and $\mathbf{c}_P$ axes is practically the same. A recent neutron diffraction study of the SP transition in TTF-CuBDT, performed by Kasper and Moncton,[38] has completely confirmed the picture of this transition deduced from data on x-ray scattering, and has resulted in a direct determination of the displacement of the TTF molecules during the SP transition. However, from our point of view, the most interesting fact is that, below 225 °K, x-ray scattering by TTF-CuBDT exhibits a strong peak near $\mathbf{q} = \mathbf{Q}$, which corresponds precisely to phonons that have condensed down below the SP transition temperature[31] (Fig. 5). This peak shows that the frequency of these phonons well above T_c is anomalously low. Cross and Fisher[24] estimate that it amounts to roughly one-third of the frequency of typical phonons. As $T \to T_c$, there is an additional softening of these phonons, in this case, due to the spin-Peierls instability, and this is clearly seen in Fig. 5. Preliminary softening of phonons produces an increase in the constant describing the interaction between pseudofermions from (2.5) and phonons with wave vector $q = 2k_F$ by roughly an order of magnitude [see Eq. (2.8)], and the value $\lambda_{s,ph} \approx 0.2$ becomes realistically possible. We are thus forced to the conclusion that the SP transition can be observed in typical quasi-one-dimensional compounds with exchange interaction parameter $J \leq 100$ °K but only in the case of preliminary strong softening of phonons corresponding to the doubling of the period of the chain. There is no connection between the softening and the existence of one-dimensional magnetic chains in TTF-CuBDT, and this presents us with a considerable problem. However, there are reasons for supposing that the softening is a relatively rare phenomenon. It would appear that this is the reason why the SP transition has not been seen in the large number of known compounds with $J \leq 100$ °K, which can be described by the Heisenberg model with one-dimensional antiferromagnetic interaction.[10]

We do not as yet know whether the corresponding soft mode is present in TTF-AuBDT and MEM(TCNQ)$_2$. There is no reason to doubt that the properties of TTF-AuBDT are similar to those of TTF-CuBDT. However, if the transition at $T_c = 19$ °K in MEM(TCNQ)$_2$ is interpreted within the framework of the SP transition model, we are forced to the conclusion that the soft mode corresponding to alternation in the chain of spins should exist in this crystal also at temperatures well above 19 °K (this mode should correspond to dimerization in the TCNQ stacks in this crystal).

5. EFFECT OF A MAGNETIC FIELD ON THE SPIN-PEIERLS TRANSITION

There is one further decisive possible verification of the validity of the interpretation of experimental data in terms of the SP transition model in the case of TTF-CuBDT, TTF-AuBDT, and MEM(TCNQ)$_2$. In contrast to the usual structural transition, the SP transition is characterized by its considerable sensitivity to a magnetic field.[32,33] The point is that the SP transition, being a period doubling transition, is very sensitive, because of commensurability effects, to the degree of filling of the pseudofermion band (2.5), which is governed by the magnetic field. In fact, to take the magnetic field into account in the Hamiltonian $\mathscr{H}_{s,0}$, given by (2.4), we must add the term $\mu_B H \sum_k \psi_k^* \psi_k$, i.e., the inclusion of the magnetic field shifts the chemical potential of the system and modifies the magnitude of $2k_F$. In the state with twice the period, the commensurability energy of the Peierls displacements and of the initial lattice is high, i.e., of the order of the total energy of the Peierls displacements. The shift of $2k_F$ from π, which corresponds to twice the period, takes the system away from the commensurate state, and the commensurability energy falls sharply. It follows that, for small deviations of $2k_F$ from π (low magnetic fields $H < H^*$), the system prefers to remain in the state with twice the period although the wave vector associated with the displacements Q is then not equal to $2k_F$.

Thus, the imposition of a sufficiently weak magnetic field will not change the structure of the Peierls displacements at the transition point, but it will reduce T_c, which, in the Hartree-Fock approximation, is determined from the equation

$$\omega_0(\mathrm{Q}) + g^2(\mathrm{Q})\,\Pi(T, \pi, 0) = 0$$

or

$$\frac{1}{\lambda_{s,\,ph}} = \int_0^{pJ/T} \frac{dx\,\mathrm{sh}\,x}{x\sqrt{1-(xT/pJ)^2}\,[\mathrm{ch}\,x + \mathrm{ch}\,(\varepsilon_F/T)]}, \tag{5.1}$$

where $\varepsilon_F = 2\mu_B H(\pi+2)/(\pi+4)$ in the Hartree-Fock approximation. Equation (5.1) can be rewritten in the form

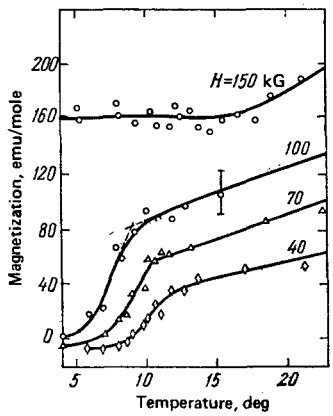

FIG. 6. Temperature dependence of magnetizability of TTF-CuBDT in different magnetic fields.[16] Broken line shows the method used to determine the critical temperature T_c.

$$\ln \frac{T_c(H)}{T_c(0)} = \mathrm{Re}\,\psi\left[\frac{1}{2} + \frac{\varepsilon_F}{2\pi T_c(H)}\right] - \psi\left(\frac{1}{2}\right), \tag{5.2}$$

where $\psi(x)$ is the diagram function. This result was obtained by Leung[34] for the usual Peierls transition and was extended to the SP transition by Bray,[32] and by Khomskiĭ *et al.*[33] within the framework of the Hartree-Fock approximation and by Cross[35] within the framework of a more accurate inclusion of the fermion interaction (the two approaches result in qualitatively similar conslusions). In low fields H, the theory predicts that T_c should fall by the amount $\Delta T_c/T_c = \eta(\mu_B H/T_c)^2$ and that the magnetizability should be a highly nonlinear function of the field. Both effects have been confirmed experimentally[16,17] in the case of TTF-CuBDT. Figure 6 shows the magnetizability as a function of temperature in the case of TTF-CuBDT at low temperatures and in different magnetic fields.[16] For $T > T_c$, the temperature dependence of magnetizability is characteristic for a homogeneous chain of spins. Below T_c, the magnetizability decreases with decreasing temperature because of the appearance of the gap in the spectrum of magnetic excitations. It is clear from Fig. 6 that the critical temperature T_c decreases with increasing magnetic field. The experimental function $T_c(H)$ is shown in Fig. 7 (points) together with the theoretical results (solid curve) for the transition of the second kind in $H < H^* = 0.72T_c/\mu_B$ (Hartree-Fock approximation). It is clear from Fig. 7 that the experimentally determined coefficient η is higher than the theoretical value. The experimental result $\eta = 0.82 \pm 0.05$ may be compared with the Hartree-Fock approximation which yields $\eta = 0.44$ and the Luther-Peschel model used by Cross and Fisher, which yields $\eta = 0.35$. The origin of this discrepancy between experimental and theoretical estimates is still not clear. For $H > H^*$, the model with $\lambda_{s,ph}$ independent of q predicts that the superstructure period should depend on H at the transition point T_c. However, in practise, $\lambda_{s,ph}$ decreases rapidly as q departs from π in the case of the SP transition (because of the increase in ω_0), and a more realistic situation is that in which the superstructure corresponds to twice the period even for $H > H^*$ and the superstructure is the result of a transition of the first kind for $H > H^*$. The corresponding critical

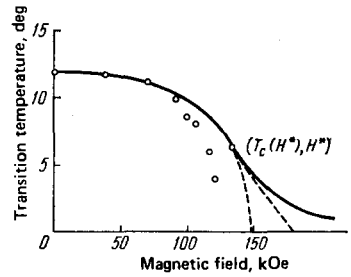

FIG. 7. The SP transition temperature T_c as a function of the magnetic field: open circles—experimental,[16] solid curve—theoretical results obtained in the Hartree-Fock approximation,[32,33] broken curve—transition of the first kind (the precise shape of this curve is not known).

field H_c $(T = 0)$ for the SP transition is then T_c/μ_B in the Hartree-Fock approximation (the field is determined from the condition $N(0)\Delta_0^2/2 = \chi_0 H_c^2/2$, where χ_0 is the paramagnetic susceptibility of the homogeneous chain, which is equal to $4\mu_B^2/(\pi + 4)$ in the Hartree-Fock approximation, and $\Delta_0 = 1.76T_c$). Recent experimental data[39] suggest the possibility of a noncommensurate phase in strong magnetic fields in TTF-CuBDT.

Thus, the occurrence of the SP transition in TTF-CuBDT and in its isostructural analog TTF-AuBDT may be regarded as established. This follows from the totality of experimental data that are excellently described by the SP transition model and cannot be explained in terms of alternative theories. However, the situation is less definite in the case of MEM(TCNQ)$_2$ and will remain so until experiments are performed in strong magnetic fields, or the soft mode is verified at temperatures well above $T_c = 19$ °K.

6. FLUCTUATION REGION AND TYPE OF SPIN-PEIERLS TRANSITION

As already noted, the SP transition in TTF-CuBDT is described with high precision by the self-consistent field approximation. TTF-AuBDT exhibits some deviations from the predictions of this approximation but they are small.[15] On the other hand, the interaction between spins in the compounds under consideration can confidently be regarded as one-dimensional because spins belonging to different chains experience weak interaction which is not experimentally detectable in the temperature range in which we are interested. However, the self-consistent field approximation does not, in general, apply to a purely one-dimensional system.

Our final conclusion must therefore be that, if our model includes spin interactions, it is only along chains that fluctuations can be suppressed by the three-dimensionality of the phonon system. Let us therefore estimate the size of the fluctuation region for the SP transition. To do this, we must determine the Ginzburg-Landau functional for the order parameter corresponding to the spin-Peierls transition, and then use the Ginzburg-Levanyuk criterion to estimate the temperature range $\tau = (T_c - T)/T_c$ in which the fluctuations are not small. The displacements of molecules during the SP transition will be written in the form

$$u_n(l)=\omega_0^{-1}Q\sqrt{\frac{2+(4/\pi)}{\lambda MJ}}(-1)^l\cos(Q_\perp n)\,\varphi_{l,n},$$

where $\varphi_{l,n}$ is a slowly-varying function of coordinates ($\varphi_{l,n}$ is equal to the gap Δ in the spectrum of single-fermion excitations in the homogeneous case). We shall look upon it as the order parameter in the Ginzburg-Landau functional. The coefficients $a=\alpha\tau$ and b in front of φ^2 and φ^4 were given above [see Eq. (2.9)]. All that remains is to determine the coefficients of the gradient terms. In the Fourier expansion of the free-energy functional, the gradient terms have the form $C_\parallel p^2\varphi_p^2/2$ and $C_\perp p_\perp^2\varphi_p^2/2$ and, to determine the coefficients $C_\parallel$ and $C_\perp$, we must calculate the temperature variation of the SP transition as the wave vector $\mathbf{q}$ departs from the value $\mathbf{Q}=(\pi,\mathbf{Q}_\perp)$. Within the framework of the Ginzburg-Landau functional, this change is $\Delta\tau=|T(\mathbf{q})-T(\mathbf{Q})|/T(\mathbf{Q})=-(C_\parallel p^2+C_\perp p_\perp^2)/$, where $\mathbf{p}=(\mathbf{q}-\mathbf{Q})/d_\parallel$ and $d_\parallel$ is the period of the spin chain above T_c.

On the other hand, in the microscopic theory, the temperature $T(\mathbf{q})$ is determined from [see (2.6) and (2.9)]

$$\frac{1}{\lambda_{s,\,ph}}=\frac{\omega_0^2(\mathbf{Q})}{\omega_0^2(\mathbf{q})}\,\Pi(T,\,q=\pi+pd_\parallel,\,\omega=0)\cos^2\frac{pd_\parallel}{2},\tag{6.1}$$

whereas, in the Hartree-Fock approximation, the polarization operator has the form[1]

$$\Pi(T,\,\pi+pd_\parallel,\,0)=\int_0^{W/T}\frac{d\varepsilon\,\mathrm{sh}\,[\varepsilon\cos(d_\parallel p/2)]}{\varepsilon\sqrt{1-(\varepsilon T/W)^2}\left\{\mathrm{ch}\left(\varepsilon\cos\frac{pd_\parallel}{2}\right)+\mathrm{ch}\left[\frac{W}{T}\sqrt{1-\left(\frac{\varepsilon T}{W}\right)^2}\sin\frac{pd_\parallel}{2}\right]\right\}},\tag{6.2}$$

where $W=(1+2/\pi)J$.

Expanding the right-hand sides of (6.1) and (6.2) in powers of p for $W\gg T$, we have

$$\frac{1}{\lambda_{s,\,ph}}=\Pi(T,\,\pi,\,0)-\left[\beta\frac{W^2}{8T_c^2}d_\parallel^2+\left(\frac{1}{\omega_0}\frac{\partial^2\omega_0}{\partial p^2}\right)_{p=0}\times\Pi(T,\pi,0)\right]p^2-\Pi(T,\,\pi,\,0)\sum_i\left(\frac{1}{\omega_0}\frac{\partial^2\omega_0}{\partial p_{\perp i}^2}\right)_{p=0}p_{\perp i}^2,\quad\beta=\int_0^\infty\frac{\mathrm{sh}\,\varepsilon\,d\varepsilon}{\varepsilon(1+\mathrm{ch}\,\varepsilon)^2}=0.462.\tag{6.3}$$

where p, $p_{\perp i}$ are the components of the vector $\mathbf{p}$ along and at right-angles to the chain.[3)] From (6.3), we have

$$c_\parallel=\alpha\left[\frac{\beta W^2d_\parallel^2}{8T_c^2}+\frac{1}{\lambda_{s,\,ph}}\left(\frac{1}{\omega_0}\frac{\partial^2\omega_0}{\partial p^2}\right)_{p=0}\right]=\alpha\xi_\parallel^2,\qquad c_\perp=\frac{\alpha}{\lambda_{s,\,ph}}\left(\frac{1}{\omega_0}\frac{\partial^2\omega_0}{\partial p_{\perp i}^2}\right)_{p=0}=\alpha\xi_\perp^2.\tag{6.4}$$

[3)] We note that the presence of only quadratic terms in (6.3) is due to the particular feature of the SP transition, namely, the doubling of the period. In the case of the Peierls transition, the linear dispersion of phonons and the electron-phonon interaction constant near $Q_0=2k_F$ in (6.3) are responsible for the appearance of additional terms that are proportional to $qd_\parallel\Pi(T,0,2k_F)$. This ensures that as the temperature is reduced the phonons that condense in the system are not those with $Q_0=2k_F$ but those with $Q_0=2k_F+q_0$ is given by the minimum of the expression $\beta(W^2/T_c^2)(1/8)p^2d_\parallel^2+pd_\parallel/\lambda$. Hence, $q_0\sim T_c^2/(d_\parallel W^2\lambda\beta)$, which shifts the wave vector away from $2k_F$. For example, in the case of TTF-TCNQ, this shift amounts to a few percent. As the temperature is lowered further Q_0 tends to $2k_F$ and for $T_c-T\approx T_c$ the structure with $Q_0=2k_F$ is found to emerge.

The increase in free energy due to the appearance of a fluctuation field with Fourier components φ_p below T_c is given by

$$\delta F=\frac{1}{2}\sum_p(c_\parallel p^2+c_\perp p_\perp^2+a+3b\varphi_0^2)\,\varphi_p^2,\tag{6.5}$$

where $\varphi_0^2=a/b$ is the equilibrium value of the order parameter. The ratio of the fluctuation increment in the specific heat c_{fl} to the jump in specific heat at the SP transition point can be found with the aid of (6.5):

$$\frac{c_{fl}}{\Delta C}=\frac{T_cbd_\parallel d_\perp^2}{\pi^2}\int p_\perp\,dp_\perp\int dp\,\frac{1}{(c_\parallel p^2+c_\perp p_\perp^2+2\,|a|)^2}=\sqrt{\frac{\tau_G}{\tau}},\qquad\tau_G=\left(\frac{T_cbd_\perp^2d_\parallel}{2\sqrt{2}\,\pi\xi_\parallel\xi_\perp^2\alpha^2}\right)^2,\tag{6.6}$$

where $d_\perp$ is the separation between the spin chains. The self-consistent field approximation breaks down for $\tau\leqslant\tau_G$. Thus, the condition for the validity of this theory is $\tau_G\ll1$.

The quantity τ_G can be estimated for TTF-CuBDT. Experimental data on the width of the scattered x-ray peak[31] can be used to show that the softening of the nucleating phonons (roughly up to 1/3 of the initial value) above T_c is isotropic and occurs in a narrow region of radius $p_c\approx0.2/d_\parallel$ around $\mathbf{Q}$ (see Fig. 5). Hence, it follows that $(\omega_0^{-1}\partial^2\omega_0/\partial p^2)_{p=0}\approx4p_c^{-2}$ and, using the largest value of $\lambda_{s,ph}$, namely, $\lambda_{s,ph}=0.3$, we can determine the transverse and longitudinal correlation lengths from (6.4) and then use (6.6) to find τ_G. The result is that τ_G does not exceed 10^{-4}. This very small size of the critical region in the case of TTF-CuBDT explains why the mean-field approximation is satisfactory for the SP transition in this compound. Thus, the absence of phase fluctuations in the order parameter and the three-dimensionality of the phonon system together ensure the validity of the mean-field approximation in the description of the SP transition.

Let us now briefly consider the nature of the SP transition. Penson *et al.*[36] have shown that the SP transition occurs for definite values of the parameters even in the case of a chain of classical spins in which it can be a transition of the first kind. An analogous conclusion for the Heisenberg $S=1/2$ chain was reported by Lepin and Caillé,[37] who carried out a numerical investigation of the possibility of a transition of the first kind within the framework of the Hartree-Fock approximation. They found that the system was unstable against the SP transition of the first kind over a broad range of parameter values and that the temperature of this transition exceeded the temperature T_c at which the transition of the second kind occurred. If this is correct, we must explain why it is the SP transition of the second kind that is observed experimentally in the compounds discussed above.

We note, in connection with the results reported by Lepin and Caillé, that the transition of the first kind to the dimerized state at $T_c=396$ °K was observed in the case of K-TCNQ. Lepin *et al.*[20] have analyzed experimental data for this compound and have shown that the Hubbard model with strong Coulomb repulsion provides a satisfactory explanation of the properties of these crystals. Since, in this case, the system can be de-

scribed by the effective Hamiltonian given by (2.1), the transition in K-TCNQ at $T_c = 396\,°K$ was interpreted[20] as the SP transition.

7. CONCLUSIONS

We have already noted that the Spin-Peierls transition can be observed in compounds with exchange integral $J \leq 100\,°K$, but only if the phonons that must condense during the SP transition undergo preliminary strong softening. This softening must be due to some other mechanisms unrelated to the SP transition. The very existence of the preliminary softening is a kind of "miracle" but it has, in fact, been detected in TTF-CuBDT. Moreover, it is clear from the foregoing that, if the SP transition is observed in TTF-AuBDT and $MUM(TCNQ)_2$, these materials should exhibit the preliminary softening of the "required" phonons. Experimental verification of this conclusion would be very interesting for MEM $(TCNQ)_2$ because the reality of the softening process cannot be deduced from other considerations.

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[1] L. N. Bulaevskiĭ, Usp. Fiz. Nauk 115, 263 (1975) [Sov. Phys. Usp. 18, 131 (1975)].
[2] G. A. Toombs, Phys. Rep. 40, 182 (1978).
[3] A. J. Berlinsky, Rep. Prog. Phys. 42, 1243 (1979).
[4] H. M. McConnell and R. J. Lynden-Bell, J. Chem. Phys. 36, 2392 (1962); D. D. Thomas, H. Keller, and H. McConnell, ibid. 38, 2321 (1963).
[5] D. B. Chestnut, *ibid.* 45, 4677 (1966).
[6] P. Pincus, Solid State Commun. 9, 1971 (1971).
[7] G. Beni and P. Pincus, J. Chem. Phys. 57, 3531 (1972); G. Beni, *ibid.* 58, 3200 (1973).
[8] E. Pytte, Phys. Rev. B 10, 2039 (1974).
[9] J. Y. Dubois and J. B. Carton, J. Phys. 35, 371 (1974).
[10] M. Steiner, J. Villain, and C. G. Windsor, Adv. Phys. 25, 87 (1976).
[11] 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).
[12] 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).
[13] L. S. Smith, E. Ehrenfreund, A. J. Heeger, L. V. Interrante, J. W. Bray, H. R. Hart, I. S. Jacobs and Jacobs Jr., Solid State Commun. 19, 377 (1976).
[14] E. Ehrenfreund and L. S. Smith, Phys. Rev. B 16, 1870 (1977).
[15] T. Wei, A. J. Heeger, M. B. Salamon, and G. E. Delker, S Solid State Commun. 21, 595 (1977).
[16] J. W. Bray, L. V. Interrante, I. S. Jacobs, D. Bloch, D. E. Moncton, G. Shirane, and J. C. Bonner, Phys. Rev. B 20, 2067 (1979).
[17] L. V. Interrante, J. W. Bray, H. R. Hart, I. S. Jacobs, Jacobs Jr., J. S. Kasper, and P. A. Piancente, in: Proc. Conf. on Quasi-One-Dimensional Conductors, Dubrovnik, Vol. 2, 1978, p. 55.
[18] S. Huizinga, J. Komandeur, G. A. Sawatzky, B. T. Thole, K. Kopinga, W. J. M. de Jonge, and J. Roos, Phys. Rev. B 19, 4723 (1979).
[19] A. Holz and K. H. Bennemann, *ibid.* 16, 3999 (1977).
[20] Y. Lépine, A. Caillé, and V. Laroohelle, *ibid.* 18, 3585 (1978).
[21] S. Rodriguez, *ibid.* 116, 1474 (1959).
[22] T. D. Schultz, D. C. Mattis, and E. H. Lieb, Rev. Mod. Phys. 36, 856 (1964).
[23] L. N. Bulaevskiĭ, Zh. Eksp. Teor. Fiz. 43, 968 (1962) [Sov. Phys. JETP 16, 685 (1963)].
[24] M. C. Cross and D. S. Fisher, Phys. Rev. B 19, 402 (1979).
[25] L. N. Bulaevskiĭ, Zh. Eksp. Teor. Fiz. 44, 1008 (1963) [Sov. Phys. JETP 17, 684 (1963)].
[26] H. P. Van der Braak, W. J. Caspers, F. W. Wiegel, and M. W. M. Willemse, J. Stat. Phys. 18, 577 (1978).
[27] J. N. Fields, H. W. J. Blöte, and J. C. Bonner, J. Appl. Phys. Phys. 50, 1807 (1979).
[28] J. Bernasconi, M. J. Rice, W. R. Schneider, and S. Strässler, Phys. Rev. B 12, 1090 (1975).
[29] V. Emery, Phys. Rev. Lett. 37, 107 (1976).
[30] D. J. Klein and W. A. Zeitz, Phys. Rev. B 10, 3217 (1974).
[31] D. E. Moncton, R. J. Birgeneau, L. V. Interrante, and F. W F. Wudl, Phys. Rev. Lett. 39, 507 (1977).
[32] J. W. Bray, Solid State Commun. 26, 771 (1978).
[33] L. N. Bulaevskiĭ, A. I. Buzdin, and D. I. Khomskiĭ, *ibid.* 27, 5 (1978).
[34] M. C. Leung, *ibid.* 15, 879 (1974).
[35] M. C. Cross, Preprint (1979).
[36] K. A. Penson, A. Holz, and K. H. Bennemann, J. Chem. Phys. 65, 5024 (1976).
[37] Y. Lépine and A. Caillé, J. Chem. Phys. 67, 5598 (1977).
[38] J. S. Kasper and D. E. Moncton, Phys. Rev. B 20, 2341 (1979). (1979).
[39] D. Bloch, J. Voiron, J. C. Bonner, J. W. Bray, I. S. Jacobs, and L. V. Interrante, Phys. Rev. Lett. 44, 294 (1980).

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