Effect of crystal lattice disorder on Peierls transitions

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The effect of disorder on Peierls structural transitions is considered for quasi-one-dimensional crystals of the $K_2Pt(CN)_4Br_{0.30}\cdot 3H_2O$ type and for salts based on TCNQ. The exactly solvable Lloyd disorder model and the "fragment" model are considered. It is shown that in both models disorder causes a strong suppression of the Peierls transition, and its effect is qualitatively similar to the effect of magnetic impurities on the superconducting transition. Possible experimental consequences are discussed.

The synthesis and study of physical properties of highly conducting quasi-one-dimensional crystals on bases of TCNQ salts[1] and of plane complexes of transition elements of the platinum group [the $K_2Pt(CN)_4Br_{0.33}\cdot 3H_2O$ type] raised the problem of applicability to those compounds of the Peierls argument on instability of one-dimensional electron systems with respect to a change in the lattice period. According to these concepts, a displacement by a wave vector $2k_F$ (k_F is the electron Fermi momentun) should appear at low temperatures in the original crystal lattice affected by the electron system, and below a temperature T_P the one-dimensional system must remain a dielectric, since a gap appears in the electron system at the Fermi surface. In $K_2PT(CN)_4Br_{0.30}\cdot 3H_2O$ compounds diffuse x-ray scattering[2,3] and inelastic neutron scattering[4] indicate that the Peierls instability is indeed observed. According to the data of ref. 3 a static displacement of atoms (a sixfold increase of the period) occurs at a temperature below 77°K, and at higher temperatures this static distortion is preceded by softening of phonon frequencies with quasimomentum $\approx 2k_F$. Obviously, a Peierls period occurs also in the highly conducting TTF–TCNQ salt,[5] while at the same time this transition has not been so far observed in magnetic data of other investigated TCNQ salts. Indeed, for a Peierls transition the paramagnetic susceptibility should fall with temperature lowered below T_P. Exactly such susceptibility behavior is observed[6] in TTF-TCNQ, but not in other highly conducting TCNQ salts.[7]

It is clear that crystal lattice disorder has a large effect on the Peierls transition. Indeed, disorder washes out those features in the density of states of one-dimensional electron bands which lead to lattice instability in the displacements with gap formation at the Fermi surface. An internal instability, however, is inherent in all quasi-one-dimensional crystals, besides TTF–TCNQ. In platinum complexes halogen ions fill only part of the sites which they can occupy, and their site distribution is random. In the highly conducting TCNQ salts disorder is related to a random orientational distribution of asymmetric cations. Only for the TTF–TCNQ complex is the TTF cation totally symmetric and lattice disorder can be related only to structure defects.

In this paper we consider the effect of lattice disorder on the temperature and the order parameter of the Peierls transition. The calculations indicate that this effect is as strong as the effect of magnetic impurities on the superconducting transition. The results obtained below explain why the Peierls transition is not observed in all quasi-one-dimensional crystals. We also discuss new properties added to this transition by lattice disorder.

1. INITIAL EQUATIONS AND DISORDER MODEL

We consider only the simplest example of a Peierls transition, one with a doubled period. Such a transition occurs if the original electron band is half full, and only in this case is a lattice change not accompanied by a redistribution of electron charge.[8] For this ratio a transition with a doubled period is simplest, and to evaluate the transition temperature T_P in the static approximation it is necessary to know only the dependence of the electronic density of states on the displacement of the lattice atoms and the degree of lattice disorder. In doubling the displacement u_n of atom n we use

$$u_n = (-1)^n u. \tag{1}$$

For a half-filled band the free energy of the electrons and the lattice is expressed in terms of the parameter u as

$$F(u, T) = -T\int_{-\infty}^{\infty} d\varepsilon\, \rho(u, \varepsilon) \ln\left(1 + e^{\varepsilon/T}\right) + \frac{1}{2} K u^2, \tag{2}$$

where K is the lattice elasticity coefficient with electrons localized at the sites,[8] and $\rho(u, E)$ is the electronic density of states for displacement u. We consider below only disorder models leading to $\rho(u, E)$ symmetric with respect to the energy $E = 0$, i.e., $\rho(u, E) = \rho(u, -E)$. In this case the electronic chemical potential is $\mu = 0$. Below the Peierls transition temperature T_P the free energy is lowered at $u \neq 0$, and T_P is the temperature for which the equation

$$\left.\frac{\partial E(u, T)}{\partial u}\right|_{u\to 0} = 0. \tag{3}$$

has a nontrivial solution $u \neq 0$ for the first time.

The problem thus reduces to the determination of the electronic density of states $\rho(u, E)$ in a disordered lattice. The possibility of applying approximate methods in determining the density of states in a one-dimensional system seems doubtful; therefore we consider disorder models which allow accurate determination of the density of states. Such are the Lloyd[9] and the "fragment"[10] models.

2. THE LLOYD MODEL

In this model it is assumed that the electrons are described in the tight binding approximation by means of the Hamiltonian

$$H=\sum_{n,\sigma}\{\varepsilon_n a^+_{n\sigma}a_{n\sigma}+b_{n,n+1}(a^+_{n\sigma}a_{n+1\sigma}+a^+_{n+1\sigma}a_{n\sigma})\}, \quad (4)$$

in which the transition parameter (the resonance integral) $b_{n,\,n+1}$ is not a random quantity, but the potentials ε_n are randomly distributed over the sites n. It is assumed that the distributions ε_n are independent for different sites, and are all described by a Lorentz distribution

$$P(\varepsilon)=\frac{1}{\pi}\frac{\varepsilon_1}{\varepsilon^2+\varepsilon_1^2}. \quad (5)$$

Obviously, this model is qualitatively adequate for the platinum complexes, in which disorder in the Br or Cl ion positions leads to a random potential, acting on the conduction electrons of the chain. For the distribution (5) the density of states $\rho(E)$ in the disordered lattice ($\varepsilon_1 \neq 0$) is expressed in terms of the density of states $\rho_0(E)$ in an ideal lattice ($\varepsilon_1 = 0$) by the relation

$$\rho(E)=\frac{\varepsilon_1}{\pi}\int_{-\infty}^{\infty}dx\,\frac{\rho_0(x)}{(E-x)^2+\varepsilon_1^2}. \quad (6)$$

In an ideal lattice with a doubled period the electron spectrum is of the form

$$\varepsilon(k)=\pm\sqrt{\Delta^2+4b^2\cos^2 k},\ k=\frac{2\pi n}{N},\ n=0,\pm1,\pm2,\ldots,\pm\frac{N}{2}, \quad (7)$$

where N is the number of atoms in the system, 2b is the half-width of the original band (the band without doubling) $2b = b_{n,\,n-1} + b_{n,\,n+1}$ and $\Delta = |b_{n,\,n+1} - b_{n,\,n-1}|$; $\Delta/2b \ll 1$ (we consider only the case of small atomic displacements, i.e., $T_P \ll 2b$). The plus sign in (7) corresponds to the upper part of the band, and the minus sign to the lower. The density of states, proportional to the derivative $dk/d\varepsilon$, is infinite at the band edges ($k = 0, 2\pi$) for $N \to \infty$. This feature also causes the Peierls instability of the original ideal lattice.

We notice that in the Lloyd model the electronic free energy is infinite due to the slow decrease of the Lorentzian distribution function (5) for $\varepsilon \to \infty$; this divergence, however, is not crucial for us since the part of the electronic free energy which depends on the displacements u, i.e., $\partial E(u,T)/\partial u$, is finite. Physically the divergence in (2) for large E is removed if the ion energy is included in the same potential field ε_n.

We further choose for the transition parameter not the displacement u, but the quantity Δ proportional to it, which determines the gap in the electronic spectrum of an ideal lattice with the doubled period. We introduce also the dimensionless electron–lattice interaction constant g by means of the relation $Ku^2 = \Delta^2/\pi g^2 2b$. Taking into account the condition $\Delta/2b \ll 1$ for weak disorder $\varepsilon_1/2b \ll 1$, we obtain from (2), (3), (6), (7) for an infinite system the following equation for the transition temperature:

$$1=g^2\int_0^{2b}\frac{d\varepsilon}{\sqrt{1-\left(\frac{\varepsilon}{2b}\right)^2}}\frac{\varepsilon}{\varepsilon^2+\varepsilon_1^2}\operatorname{th}\frac{\varepsilon}{2T}. \quad (8)$$

For an ideal lattice ($\varepsilon_1 = 0$) Eq. (8) differs from the BCS equation for the superconducting transition temperature by the factor $[1-(\varepsilon/2b)^2]^{-1/2}$ only. This factor describes the electronic density of states in the tight binding approximation, and its appearance in (8) is related to the fact that the whole electron band contributes to the Peierls instability, while in a superconductor the electron–phonon interation differs from zero only in an energy interval of the order of the Debye frequency $\omega_D \ll 2b$ around the Fermi surface. In this narrow energy interval the density of states can be considered constant. The features of the density of states at the band edges, washed out by disorder, leads to the appearance in (8) of the factor $\varepsilon/(\varepsilon^2+\varepsilon_1^2)$, regular for $\varepsilon \to 0$, which decreases the transition temperature T_P.

Equation (8) is easily transformed into the form

$$\ln\frac{T_P}{T_{P_0}}=\psi\left(\frac{1}{2}+\frac{\varepsilon_1}{2\pi T}\right)-\psi\left(\frac{1}{2}\right);\ T_{P_0}=\frac{8\gamma b}{\pi}e^{-\frac{1}{g^2}}, \quad (9)$$

where $\ln\gamma = C$ is the Euler constant, and $\psi(x)$ is the digamma function. In (9) we see the full analogy between the effect of lattice disorder on the Peierls transition and the effect of magnetic impurities on the superconducting transition.[11] For increasing ε_1 the transition temperature T_P drops and the Peierls instability disappears when $\varepsilon_1 = \varepsilon_{1c} = \Delta_0/2$, where Δ_0 is the Peierls gap of an ideal crystal at T = 0, equal $\pi T_{P0}/\gamma$.

The dependence of the parameter Δ on the instability ε_1 is determined for T = 0 from the equation

$$\ln\frac{\Delta_0}{\varepsilon_1}=\frac{2}{\pi}\int_0^{\infty}dx\,\frac{\ln\left\{1+\sqrt{\left(\frac{x\Delta}{\varepsilon_1}\right)^2+1}\right\}}{1+x^2}. \quad (10)$$

For small disorder ($\varepsilon_1 \ll \Delta_0$) we obtain from (9), (10)

$$T_P=T_{P_0}\left\{1-\frac{\pi^2}{4\gamma}\frac{\varepsilon_1}{\Delta_0}\right\};\ \Delta=\Delta_0\left\{1-\frac{\varepsilon_1}{\Delta_0}\ln\frac{2e\Delta_0}{\varepsilon_1}\right\}, \quad (11)$$

and close to ε_{1c}, when the temperature T_P is low ($T_P \ll T_{P_0}$),

$$T_P=\frac{T_{P_0}}{4\gamma}\ln\frac{\Delta_0}{2\varepsilon_1};\ \frac{\Delta}{\varepsilon_1}\ln\frac{2e\varepsilon_1}{\Delta}=\frac{\pi}{4}\ln\frac{\Delta_0}{2\varepsilon_1}. \quad (12)$$

It is seen from (11) and (12) that in the Lloyd model the ratio Δ/T_P varies from π/γ (the BCS value) to zero for ε_1 varying from zero to ε_{1c}.

We notice that in a disordered system the Peierls transition does not cause a gap appearance in the electronic spectrum, since in this case the density of states remains nonzero in the energy interval from $-\Delta$ to Δ, although a pseudogap occurs in this region. Thus, in the center of the original band we have for E = 0

$$\rho(0)=\frac{\varepsilon_1}{b\Delta}<\rho_0(0)=\frac{1}{2b}.$$

3. THE "FRAGMENT" MODEL

The "fragment" model is realized if a quasi-one-dimensional crystal has structural defects or impurity atoms, through which conduction electrons with energies Around the Fermi surface cannot pass (for example, closed-shell impurity molecules). In the Hamiltonian (4)

744

this situation corresponds to the case $\varepsilon_n = 0$, but the resonant integral $b_{n,n+1}$ is a random quantity, vanishing for several neighboring atoms n, n + 1, while having for other neighboring atoms the ideal lattice value. The linear system of atoms is then decomposed into a number of "fragments" and the Peierls transition in each of these fragments takes place independently at a temperature T_P depending on the number of atoms in the fragment. In a system of N atoms the electronic spectrum in the tight binding approximation is described, after doubling the period by Eq. (7). For finite N the discrete nature of the spectrum causes a weakening of the Peierls instability, and for decreasing N the transition temperature $T_P \to 0$.

For the density of states we have from (7)

$$\rho(E) = \sum_{n=-N/2}^{N/2} \delta\left(E \pm \sqrt{\Delta^2 + 4b^2 \cos^2 \frac{2\pi n}{N}}\right). \qquad (13)$$

Further, let N be twice an odd number. The chemical potential is then $\mu = 0$, and this simplifies the calculations considerably (the final results are, obviously, independent of the choice of N). From (2), (3), and (11) we obtain the T dependence of Δ,

$$1 = g^2 \sum_{n=-N/2}^{N/2} \mathrm{th} \frac{\sqrt{\Delta^2 + 4b^2 \cos^2 \frac{2\pi n}{N}}}{2T} \frac{1}{\sqrt{\Delta^2 + 4b^2 \cos^2 \frac{2\pi n}{N}}}. \qquad (14)$$

The Poisson summation equation allows to write (12) in the form

$$1 = g^2 \int_0^1 \frac{dx}{\sqrt{1-x^2}} \frac{\mathrm{th}\left(\frac{1}{2T}\sqrt{\frac{\Delta^2}{4b^2} + x^2}\right)}{\sqrt{\frac{\Delta^2}{4b^2} + x^2}} \left(1 + 2\sum_{n=1}^{\infty} \cos Nn \arccos x\right). \qquad (15)$$

Using the condition $T_{P0} \ll 2b$ and choosing N as twice an odd number, we obtain from (15) an equation for the transition temperature:

$$\ln \frac{T_{P_0}}{T} = 4 \sum_{n=1}^{\infty} \frac{1}{2n-1} \frac{1}{e^{(2n-1)\frac{\pi T}{\varepsilon_N}} + 1}; \quad \varepsilon_N = \frac{2b}{N}. \qquad (16)$$

For the order parameter Δ at T = 0 we have

$$\ln \frac{\Delta}{\Delta_0} = 2 \sum_{n=1}^{\infty} (-1)^n K_0\left(n \frac{\Delta}{\varepsilon_N}\right), \qquad (17)$$

where $K_0(x)$ is the modified Bessel function. From (16), (17) we obtain for large N (when $\varepsilon_n \ll \Delta_0$)

$$T_P = T_{P_0}\left(1 - e^{-\frac{\gamma\Delta_0}{\varepsilon_N}}\right); \quad \Delta = \Delta_0\left(1 - \sqrt{\frac{\pi\varepsilon_N}{\Delta_0}} e^{-\frac{\Delta_0}{\varepsilon_N}}\right), \qquad (18)$$

and for small $T_P \ll T_{P0}$ we have

$$T = \frac{6T_{P_0}}{\pi} \ln \frac{T_{P_0}}{\varepsilon_N}; \quad \Delta = \frac{\pi T_{P_0}}{\sqrt{7\zeta(3)}} \sqrt{8 \ln \frac{T_{P_0}}{\varepsilon_N}}, \qquad (19)$$

where $\zeta(x)$ is the Riemann function. A Peierls transition does not occur if $N < N_c = 2b/T_{P0}$. In this model the ratio Δ/T_P varies from π/γ to ∞ for N varying from ∞ to N_c.

4. DISCUSSION

The models considered by us differ in the nature of their instability. To compare their results and to compare, in particular, the Peierls transition critieria, we introduce a universal quantity for one-dimensional disordered systems, such as the electron localization length, which can be calculated if the density of states is known.[12] This quantity replaces in the one-dimensional case the mean free path and is essentially of similar nature. Clearly, in the "fragment" model the localization length l, expressed in interatomic distances, equals N. In the Lloyd model the localization length was calculated by Thouless,[12] and in the center of the original band at electron energies $E = 0$ and $\varepsilon_1 \ll 2b$ it equals $2b/\varepsilon_1$ (at the edge of the original band it is twice as large). Expressed in terms of the localization length l the parameters ε_1 and ε_N, characterizing disorder in the Lloyd and "fragment" models, coincide and equal $2b/l$. For the critical localization lengths in these models we obtain the very close values $(2\gamma/\pi)(2b/T_{P0}) = 1.13\,(2b/T_{P0})$ and $2b/T_{P0}$, respectively.

Thus, the criterion of Peierls transition appearance, expressed in terms of the localization length

$$l > l_c \approx \frac{2b}{T_{P_0}}, \qquad (20)$$

is, obviously, useful for any disorder. At the same time the ratio Δ/T_P can vary from π/γ to either side, depending on the nature of the disorder.

Applied to the platinum complexes, the results obtained allow us to assume that the smallness of the ratio $T_P/2B$ in $K_2Pt(CN)_4Br_{0.30} \cdot 3H_2O$ ($T_P \lesssim 77$°K; $2b \sim 2$ eV) be related to disorder in their Br ions. We notice that a suppression of Peierls instability is also caused by electron transitions between chains, which destroy the symmetry condition of the electron spectrum

$$\varepsilon(\mathbf{k}) - \mu = -\varepsilon(\mathbf{k} + \mathbf{q}) + \mu \qquad (21)$$

($\mathbf{q}$ is the wave vector of Peierls deformation), necessary for the occurrence of lattice instability[13,14] in a three-dimensional crystal [in a one-dimensional system Eq. (21) is always satisfied at least for electrons around the Fermi surface for $q = 2k_F$]. If the resonance integral of interchain transitions leading to violation of (21) is denoted by b_1, the transition temperature T_P is reduced[14] by about b_1/T_{P0}. At room temperature the conductivity anisotropy[15] in $K_2Pt(CN)_4Br_{0.30} \cdot 3H_2O$ exceeds 10^4, and for this compound $b_1 \ll T_{P0}$.

An attempt has been made[15] to explain the drop in conductivity in $K_2Pt(CN)_4Br_{0.30} \cdot 3H_2O$ by the appearance of a Peierls gap. As noted above, in a disordered system the gap is replaced by a "pseudogap," so that the appearance of an order parameter Δ does not, generally speaking, cause an exponential decrease of conductivity with temperature. The low-temperature conductivity is determined in this case by electron jumps over the energy levels inside the pseudogap. At the same time the electronic specific heat at low temperatures, proportional to the density of states at the Fermi surface, is strongly suppressed if the system undergoes a Peierls transition. Therefore, the small magnitude of electronic heat ca-

pacity in $K_2Pt(CN)_4Cl_{0.3} \cdot 3H_2O$ at low temperatures, measured by Greene and Little,[16] can be explained by the occurrence of a Peierls transition in this crystal, as well as in $K_2Pt(CN)_4Br_{0.30} \cdot 3H_2O$.

According to the results of ref. 7, in highly conducting crystals on a TCNQ base with asymmetric cations the transition resonance integral is a random quantity and can acquire arbitrarily small values. In this case the localization length is small and the Peierls transition can indeed be totally suppressed.

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