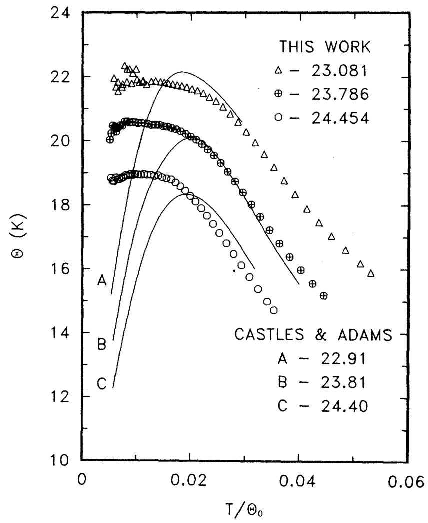

FIG. 2. The Debye thetas for bcc ^{3}He versus reduced temperature. The numbers are the molar volumes in cubic centimeters. The smooth curves were determined using the data of Castles and Adams tabulated in Ref. 4 with Θ_0 set equal to the maximum value of $\Theta(T)$.

ture that has been reported on the basis of all of the previous C_V measurements[1-4] on bcc ^{3}He. The small decrease in $\Theta(T)$ in the present data for $T/\Theta_0 \lesssim 0.008$ is within experimental uncertainty. Also shown in the figure are the smoothed results of Castles and Adams which are qualitatively typical of the earlier measurements.

It is concluded that the present specific heat data are inconsistent with the existence of the long-standing low-temperature specific-heat anomaly in bcc ^{3}He and thus that the anomaly observed by others is not due to some intrinsic property of this quantum solid.

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New Mechanism for a Phonon Anomaly and Lattice Distortion in Quasi One-Dimensional Conductors*

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It is shown that for sufficiently strong repulsive electron-electron interactions a quasi one-dimensional conductor has a phonon anomaly with wave vector component $4k_F$ and an associated phase transition to a new kind of correlated charge-density wave state and lattice distortion, which can account for recent x-ray experiments on tetrathiafulvalene-tetracyanoquinodimethane. In the ordered state, the charge-density excitations are solitons and there is a gap in their spectrum.

In this Letter, it is shown that there is a new kind of correlated electron-phonon state in quasi one-dimensional conductors which may explain the $4k_F$ phonon anomaly discovered by Pouget *et al.*[1] by x-ray scattering from tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ). These experiments found one-dimensional scattering at two wave vectors with components $0.295\vec{b}^*$ and $0.59\vec{b}^*$, respectively. The first of these, which had been observed previously,[2-4] appeared below 150 K whereas the second was still visible at room temperature. In both cases there were superlattice reflections at low temperatures.[1,2,5]

Since a quasi one-dimensional conductor is expected to have a Kohn anomaly and a Peierls transition[6] for phonons with wave vector $2k_F$ (where k_F is the Fermi wave vector), it is *a priori* possible to imagine that either $2k_F = 0.295b^*$ and the new scattering is at $4k_F$ or, alternatively, $2k_F = 0.59b^*$ and the original scattering was at k_F. The explanation proposed here adopts the former point of view and is consistent with the usual interpretation of the earlier experiments. It involves a correlated state of electron *charge-density waves,* which is similar to the correlated state of *electrons* occurring in the usual Peierls transition.[6] It differs from a previous suggestion of Torrance,[7] that in the strong-coupling limit, there will be two phonon anomalies associated with correlated *electron* states, one (at $0.295b^*$) leading to a modulation of the spin density, and the other to a modulation of the charge density.

The physical picture is as follows. In the usual Peierls transition, a lattice distortion produces a superlattice with reciprocal vector $2k_F$ which allows an electron to undergo umklapp scattering from one Fermi point to the other. This process mixes nearly degenerate states and the consequent decrease in electron energy more than compensates the increase in the elastic energy of the lattice. There is a gap in the single-particle spectrum. In a similar way, a $4k_F$ lattice distortion allows umklapp scattering of *two* electrons across the Fermi sea, and it will be shown that this produces a correlated state of the electron charge-density waves and a gap in their energy spectrum. Such a state is known to occur in the case of a half-filled band[8,9] for which the reciprocal vector of the *original* lattice is $4k_F$. The new feature is that the same effect may be achieved by means of a lattice distortion provided there is a sufficiently strong repulsive interaction between the electrons. Coupling to the lattice is through phonon modulation of the intersite Coulomb matrix elements and the transition is preceded by a phonon softening in the disordered state analogous to the Kohn anomaly[6] at $2k_F$. The exclusion principle forbids a similar process for $6k_F$, $8k_F$, etc.

These ideas will now be expanded by considering an extension of the model of Luther and Emery.[10] First it will be shown that for independent chains, the relevant four-particle correlation functions diverge at low frequencies for zero temperature and momentum transfer $4k_F$. This indicates that there will be a phase transition in a system of coupled chains[11] and a phonon condensation when coupling to the lattice is introduced. To explore the nature of the condensed state, it will be shown that the Hamiltonian may be transformed to a Fröhlich Hamiltonian which forms the basis for the discussion of the usual Peierls transition.[6] In this way the $2k_F$ and $4k_F$ transitions will be put on the same mathematical footing. It will be seen that the charge-density wave excitations in the condensed state are quantized solitons. Finally, the application to TTF-TCNQ will be discussed.

The Hamiltonian is

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_L + \mathcal{H}_P + \mathcal{H}_{ep} + \mathcal{H}_{ic}, \tag{1}$$

where the first two terms,

$$\mathcal{H}_S = v_F \sum_{k,s,\lambda} k(a_{k,s,\lambda}{}^\dagger a_{k,s,\lambda} - b_{k,s,\lambda}{}^\dagger b_{k,s,\lambda}) + 2L^{-1}\sum_k V\rho_{1\lambda}(k)\rho_{2\lambda}(-k) \tag{2}$$

and

$$\mathcal{H}_L = \sum_{s,s'\lambda} \int dx\, \psi_{1s\lambda}{}^\dagger(x)\psi_{2s'\lambda}{}^\dagger(x)\psi_{1s'\lambda}(x)\psi_{2s\lambda}(x) \times (U_\parallel \delta_{s,s'} + U_\perp \delta_{s,-s'}), \tag{3}$$

constitute the model of Luther and Emery[10] for uncoupled chains. Here v_F is the Fermi velocity, $a_{k,s,\lambda}$ and $b_{k,s,\lambda}$ annihilate spin-$\frac{1}{2}$ fermions with momentum k on the λth chain, and $[\rho_{1\lambda}(k), \psi_{1s\lambda}(x)]$ and $[\rho_{2\lambda}(k), \psi_{2s\lambda}(x)]$ are the corresponding electron density and field operators defined in Ref. 10. The third term in $\mathcal{H}$ is the free-phonon Hamiltonian and the fourth is the large-momentum part of the electron-phonon coupling which may be imagined to arise from phonon modulation of hopping and intersite Coulomb interactions:

$$\mathcal{H}_{ep} = g_2 \sum\nolimits_\lambda \int dx\, \Psi_{2\lambda}(x)\varphi(x) + g_4 \sum\nolimits_\lambda \int dx\, \Psi_{4\lambda}(x)\varphi(x) + \text{H.c.} \tag{4}$$

Here $\varphi(x)$ is the phonon field,[12] and

$$\Psi_{2\lambda}(x) = \sum\nolimits_s \psi_{1s\lambda}{}^\dagger(x)\psi_{2s\lambda}(x) \tag{5}$$

and

$$\Psi_{4\lambda}(x) = \psi_{1s\lambda}{}^\dagger(x)\psi_{1,-s,\lambda}{}^\dagger(x)\psi_{2,-s,\lambda}(x)\psi_{2s\lambda}(x), \tag{6}$$

are operators which take one or two particles across the Fermi sea. To simplify the discussion, umklapp processes and small-momentum phonons have been omitted and the electron-phonon coupling is taken to be constant in momentum space. The Coulomb interaction between electrons on different chains is given by $\mathcal{H}_{ic}$.

First consider the possibility of phase transitions in the coupled chains in the absence of phonons. This requires[11] divergences in the Fourier transforms of the correlation functions $C_{2\lambda} = \langle \Psi_{2\lambda}^{\dagger}(x,t)\Psi_{2\lambda}\rangle$ and $C_{4\lambda} = \langle \Psi_{4\lambda}^{\dagger}(x,t)\Psi_{4\lambda}\rangle$ of the individual chains ($\mathcal{H}_{ep}=0$ and $\mathcal{H}_{ic}=0$). These functions may be evaluated directly by the use of a boson representation of $\Psi_{2\lambda}$ and $\Psi_{4\lambda}$ as described in Refs. 8, 10, and 13. Since $\Psi_{4\lambda}(x)$ contains the spins in a symmetric way, $C_{4\lambda}(\omega, 4k_{\mathrm{F}})$ involves only charge-density wave excitations and, if the band is not half-filled, it is a Luttinger-model correlation function[13] given by

$$\begin{aligned} C_{4\lambda}(\omega,4k_{\mathrm{F}}) &\sim \omega^{4R-2}, \quad R<\tfrac{1}{2}, \\ &\sim \text{constant}, \quad R>\tfrac{1}{2}, \end{aligned} \tag{7}$$

for low frequency and $T=0$. Here $R=(2-\overline{W}_{\parallel})^{1/2}/(2+\overline{W}_{\parallel})^{1/2}$, $\overline{W}=(2V-U_{\parallel})/\pi v_{\mathrm{F}}$ (in the notation of Ref. 8). The evaluation of $C_{2\gamma}(\omega, 2k_{\mathrm{F}})$ is described in Refs. 8 and 10 and yields

$$\begin{aligned} C_{2\lambda}(\omega,2k_{\mathrm{F}}) &\sim \omega^{R-1}, \quad R<1, \\ &\sim \text{constant}, \quad R>1, \end{aligned} \tag{8}$$

when $|U_{\perp}| \leq U_{\parallel}$, for which $U_{\parallel}$ and $U_{\perp}$ renormalize to zero[14] at $T=0$. [This is the case of interest when $U_{\parallel} \sim W_{\parallel}$ since $W_{\parallel}>0$ if $C_{4\lambda}(\omega,4k_{\mathrm{F}})$ diverges. A full discussion of the singularities of $C_{2\lambda}(\omega,2k_{\mathrm{F}})$ for different values of $W_{\parallel}$, $U_{\parallel}$, and $U_{\perp}$ will not be given here.]

Equation (8) shows that $C_{2\lambda}(\omega,2k_{\mathrm{F}})$ diverges and there is a $2k_{\mathrm{F}}$ phase transition for arbitrarily weak interchain coupling when $R<1$ (i.e., when $\overline{W}_{\parallel} \geq 0$). Similarly $C_{4\lambda}(\omega,4k_{\mathrm{F}})$ diverges and there is a $4k_{\mathrm{F}}$ phase transition when $R<\frac{1}{2}$ (i.e., when $\overline{W}_{\parallel}>\frac{6}{5}$) and it diverges more strongly than $C_{2\lambda}(\omega, 2k_{\mathrm{F}})$ when $R<\frac{1}{3}$, i.e., when $\overline{W}_{\parallel}>\frac{8}{5}$. (In either case there can be transitions when the correlation functions do not diverge if the coupling is strong enough.) It is important to realize that, even if $\overline{W}_{\parallel}>\frac{8}{5}$, the $2k_{\mathrm{F}}$ transition may well take place at a higher temperature since the $\Psi_{2\lambda}$ order parameters are coupled in lowest order in the interchain Coulomb interaction whereas the $\Psi_{4\lambda}$ order parameters are not.

A divergence in $C_4(\omega,2k_{\mathrm{F}})$ will also give rise to a lattice distortion when the electron-phonon coupling is taken into account. In order to see this without relying on any particular approximate method of solving the coupled electron-phonon Hamiltonian, it will now be shown that the $4k_{\mathrm{F}}$ instability problem can be transformed into an effective Fröhlich Hamiltonian for spinless fermions. In this way, the complete analogy between the $2k_{\mathrm{F}}$ and $4k_{\mathrm{F}}$ instabilities will become clear and any method of calculating the properties of one can be applied to the other. To simplify the discussion, set $g_2=0$ in Eq. (4) and omit $\mathcal{H}_{ic}$ for the time being.

If $\varphi(x)$ were replaced by e^{-iGx}, which is a c-number, $\mathcal{H}_{ep}$ [defined in Eq. (4)] would become identical to the umklapp-scattering part $\mathcal{H}_u$ of the Hamiltonian solved by Emery, Luther, and Peschel[8] [see Eq. (4) of Ref. 8]. The method of solution was to use a boson representation of fermion operators to show that the charge and spin-density parts of $\mathcal{H}_S + \mathcal{H}_L$ could be diagonalized separately by means of a canonical transformation. For $\overline{W}_{\parallel}=\frac{6}{5}$, $\Psi_{4\lambda}$ became a bilinear form in spinless-pseudofermion operators which were constructed from charge-density waves. This entire argument made no use of the fact that $\varphi(x)$ was a c-number and it can be carried through in the same way when $\varphi(x)$ is a phonon field as in Eq. (4). Following the steps which led to Eq. (9) of Ref. 8, the charge-density wave part of $\mathcal{H}$ (which contains $\mathcal{H}_{ep}$) may be written

$$\begin{aligned} \mathcal{H}_{FC} = v_{\mathrm{F}}' \sum_{k,\lambda} k(c_{k\lambda}^{\dagger}c_{k\lambda} - d_{k\lambda}^{\dagger}d_{k\lambda}) + \mathcal{H}_p \\ + \frac{g_4}{2\pi r}\int dx\, \psi_{c\lambda}^{\dagger}(x)\psi_{d\lambda}(x)\varphi(x)\exp(2ik_{\mathrm{F}}x) \\ + \mathrm{H.c.} \end{aligned} \tag{9}$$

Here $v_{\mathrm{F}}'=\frac{4}{5}v_{\mathrm{F}}$; $c_{k\lambda}$ and $d_{k\lambda}$ are annihilation operators for the pseudofermions and $\psi_{c\lambda}(x)$ and $\psi_{d\lambda}(x)$ are their respective Fourier transforms, and r is a cutoff. In Eq. (9), $\mathcal{H}_{FC}$ is the Frölich Hamiltonian for spinless fermions with a linear spectrum, and it leads to a Kohn anomaly and a Peierls transition in the usual way,[6] except that the additional factor[15] $\exp(2ik_{\mathrm{F}}x)$ shifts the singularities to phonons of wave vector $4k_{\mathrm{F}}$. Physically, the condensation and the energy gap refer to the charge-density waves rather than the original fermions. In the mean-field theory of this transition, the charge-density waves satisfy the quantized sine-Gordon equation and the energy gap is the mass associated with the soliton excitations.[8,10,16]

When $\overline{W}_{\parallel} \neq \frac{6}{5}$, it is possible to carry out the same transformation but, in $\mathcal{H}_{FC}$, the Fermi velocity becomes $v_{\mathrm{F}}' + (\frac{5}{4} - 3W_{\parallel}/8\pi v_{\mathrm{F}})v_{\mathrm{F}}$ and there is an additional small-momentum-transfer interaction

$$\tfrac{5}{8}L^{-1}(W_{\parallel} - 6\pi V_F/5)\sum_k \rho_{c\lambda}(k)\rho_{d\lambda}(-k).$$

For $g_4=0$, the correlation function of $\psi_{c\lambda}^{\dagger}(x,t) \times\psi_{d\lambda}(x,t)$ is identical to C_4 (as it should be) and the previous conclusion that the $4k_F$ instability occurs when $\overline{W}_{\parallel} > \frac{6}{5}$ is equivalent to the statement that the Peierls instability requires repulsive interactions in the Luttinger model.[17]

Thus it appears that the existence of phonon anomalies at $2k_F$ and $4k_F$ have a similar mathematical basis and both should be seen if the electron interaction is sufficiently repulsive. The mechanism for a $4k_F$ phonon anomaly and lattice distortion which has been described here may account for the recent x-ray experiments[1] on TTF-TCNQ. In any case it might manifest itself in other quasi one-dimensional conductors. For TTF-TCNQ, measurements of the susceptibilities of the individual chains[18] suggest that the electron interactions are repulsive on TTF and attractive on TCNQ (extrapolating χ_F and χ_Q from $T > 54$ K gives χ_F finite and $\chi_Q \approx 0$ at $T=0$). If so, the $4k_F$ anomaly would appear only on the TTF chains and would be related to a correlated hole-phonon state. Since the $4k_F$ anomaly appears at the higher temperature, the interaction is quite strong.

Ultimately, both $2k_F$ and $4k_F$ phonons should condense although, as mentioned earlier, the $2k_F$ transition may well occur at a higher temperature. At present it is not easy to carry out a reliable microscopic calculation of the circumstances in which the distortions coexist. If symmetry allows, the $2k_F$ distortion will act as an external field driving the $4k_F$ mode and, in that case, as the temperature is lowered, the development of intrinsic $4k_F$ order will be similar to that of a ferromagnet in a magnetic field.[19]

Other four-particle correlation functions generated by $\psi_{1,s}{}^{\dagger}\psi_{2,s'}{}^{\dagger}\psi_{1,s'}\psi_{2,s}$ and by $\psi_{1,s}{}^{\dagger}\psi_{1,-s}{}^{\dagger} \times\psi_{2,-s}{}^{\dagger}\psi_{2,s}{}^{\dagger}$ have been evaluated[20] and implications of divergences have been worked out along the lines described here for Ψ_4. This will be described in a separate publication.

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