(1975).
[9]R. Peters and H. Meissner, Phys. Rev. Lett. 30, 965 (1973).
[10]This is probably due to grains with slightly different T_c. See D. H. Douglass, Jr., and R. Meservey, Phys. Rev. 135, A19 (1964). Calculations show that fluctuations cannot produce such a large effect in clean, 1000-Å-thick aluminum films. See M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975), p. 238.
[11]L. P. Gor'kov and G. M. Eliashberg, Zh. Eksp. Teor. Fiz. 54, 612 (1968) [Sov. Phys. JETP 27, 328 (1968)].
[12]W. A. Little, Can. J. Phys. 37, 334 (1959).
[13]A. Schmid, Phys. Rev. 186, 420 (1969).
[14]J. Clarke, Phys. Rev. Lett. 28, 1363 (1972).
[15]M. Tinkham and J. Clarke, Phys. Rev. Lett. 28, 1366 (1972).

Weakly Pinned Fröhlich Charge-Density-Wave Condensates: A New, Nonlinear, Current-Carrying Elementary Excitation

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New, nonlinear, charged elementary excitations are predicted to occur for weakly pinned Fröhlich charge-density-wave condensates at low temperatures.

The existence at low temperatures of a pinned Fröhlich charge-density-wave (CDW) condensate[1,2] in the interesting linear-chain conductors tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) and $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ (KCP) now seems to be fairly well established.[3,4]

On the basis of a phenomenological theory, we have been able to investigate the *nonlinear* phase dynamics of weakly pinned CDW condensates. We wish to report here the following most interesting theoretical finding: As a specific consequence of nonlinearity and the periodicity of the potential $V_p(\varphi)$ by which the condensate is pinned, an altogether new type of mobile, current-carrying, elementary excitation of the condensate occurs. These new, nonlinear, charged excitations arise, formally, from "solitary wave" or elementary-particle-like solutions[5] of a nonlinear wave equation for the local phase $\varphi(x,t)$. We shall refer to them here as "φ particles." Physically, they correspond to propagating *localized* compressions (φ particles) or rarefactions (anti φ particles) in the local condensed electron density $n_s(x,t)$. They separate segments of the condensate having common uniform phase and may therefore be viewed as mobile domain walls. A finite threshold energy, E_0, is required for their creation and they can thus only be thermally excited at finite T. Furthermore, since the charges on the φ and anti φ particles are equal and opposite, the number of φ and anti φ particles present at any given T must necessarily be the same. In this respect the φ particles may be regarded as the inevitable Schottky defects of the perfect "ionic crystal" of which the condensate with completely uniform phase at $T=0$ is representative.

It is interesting that although the condensate is pinned, and therefore unable to contribute a collective Fröhlich conductivity,[1,2] the charged φ particles now render it conducting.

In general, local deformations of an otherwise perfectly uniform Fröhlich CDW condensate may result from local variations in either the condensate's amplitude or phase. The linear dynamics of such deformations (amplitude and phase "phonons") have been discussed in an elegant paper by Lee, Rice, and Anderson[6] (LRA). Sufficiently weak pinning, however, implies a comparatively *much softer* force constant for phase deformations, with the result that at low temperatures spontaneous local deformations in the phase will dominate those occurring in the amplitude.[7] Since the local phase variations involved need not necessarily be small, a nonlinear treatment of their dynamics is called for.

The latter may be studied on the basis of a straightforward generalization of a phenomenological theory of the linear phase dynamics given by Rice, Strässler, and Schneider.[2,8] Allowing for a spatially dependent phase, the classical Lagrangian density $\mathcal{L}$ for the condensate is postulated to be

$$\mathcal{L} = \mathcal{L}(\varphi_0) + n_s m^* q_0^{-2}\{\tfrac{1}{2}\dot{\varphi}^2 - \tfrac{1}{2}c_0^2(\nabla_x\varphi)^2 - \omega_F^2 V(\varphi)\}, \quad (1)$$

where the local phase $\varphi = \varphi(x,t)$ is measured relative to the uniform phase φ_0 of the undeformed condensate, the latter's (constant) Lagrangian density being $\mathcal{L}(\varphi_0)$. The quantities[2] n_s, m^*, and $q_0 = 2k_F$ denote, respectively, the density of condensed conduction electrons, the condensed electron effective mass, and the fundamental periodicity wave vector of the undeformed condensate; $k_F = (\pi/2)n$ is the Fermi wave vector of the original uncondensed metallic system of n conduction electrons per unit length, and ω_F is the pinning frequency.[2] The second term in (1) is the local kinetic energy while the third and fourth terms are, respectively, the potential energies (PE) resulting from local strain and from displacement of the condensate. We have assumed that while local variations in the magnitude of φ may be arbitrarily large, spatial gradients in φ are *small*. Consequently, we have taken (a) the strain PE density to be proportional to the square of the local strain, $q_0^{-1}\nabla_x\varphi$, and have introduced the corresponding linear force constant K in (1) in the form $K = m^* c_0^2$, where c_0, a characteristic velocity, is a property of the undeformed condensate. Inspection of the paper by LRA reveals that, for the particular microscopic model of the condensate employed by these authors, $c_0 = v_F(m/m^*)^{1/2}$, where $v_F = \hbar k_F/m$ and m denote, respectively, the Fermi velocity and effective electronic mass in the uncondensed metallic state. We have also taken (b) the displacement PE density to be $n_s V_p(\varphi)$, where $V_p(Q) = V_p(-\varphi)$ is a periodic model potential[2] assumed to be responsible for the pinning of the undeformed condensate. In its present form our theory is not applicable if the functional form of V depends strongly on x, e.g., if the pinning is dominated by defects. For φ close to φ_0, $V_p(\varphi)$ is assumed to possess the scaled harmonic form[2,8] $V_p(\varphi) = m^*\omega_F^2 q_0^{-2}\varphi^2/2$ and in (1) we have introduced the dimensionless potential $V(\varphi) = V_p(\varphi) q_0^2/m^*\omega_F^2$. In the following we take 2π to be the minimum periodicity in $V(\varphi)$. This assumption is readily relaxed to include higher symmetry, as required, for instance, in N-fold commensurability potential models[6] where[9] $V(\varphi) = N^{-2}(1 - \cos N\varphi)$.

It follows from (1) that the equation of motion for the local phase is the nonlinear "relativistic" wave equation:

$$\ddot{\varphi} - c_0^2\nabla_x^2\varphi + \omega_F^2 dV/d\varphi = 0. \quad (2)$$

Approximate, small-amplitude, extended wave solutions of (2) may be obtained by linearizing according to the substitution $V(\varphi) \to \varphi^2/2$, and they correspond to the phase phonons found by LRA. This Letter, however, is concerned with the recognition that [when $V(\varphi)$ is not explicitly x-dependent] there exists a class of *exact* (nonlinear) wave solutions of (2). These are solitary wave solutions,[5] $\varphi_\pm(x - vt)$, given by

$$\pm(x - vt)/(1 - v^2/c_0^2)^{1/2} = (d/\sqrt{2})\int_{\pm\pi}^{\varphi_\pm} d\varphi\, V(\varphi)^{-1/2}, \quad (3)$$

which formally describe a local shift in phase of $\pm 2\pi$ propagating at uniform velocity v ($|v| < c_0$). In the rest frame the wave profile is localized over a distance of order twice the characteristic length $d = c_0/\omega_F$; $\nabla_x\varphi_\pm$ is symmetric about $x = 0$. These solutions will be consistent with the small-strain assumption in (1) if $2\pi/2dq_0 \ll 1$, i.e., if d is large by comparison to an intermolecular spacing. We now briefly develop the interpretation of these solutions described in the introduction.

The classical excitation energies $E_\pm(v)$ associated with the solutions (3) may be calculated by substituting the latter into the Hamiltonian density obtained from (1) and integrating over the length L ($\to \infty$) of the system. We find $E_\pm(v) = Mc_0^2/(1 - v^2/c_0^2)^{1/2}$, the form of a relativistic particle, where the rest mass M is given by

$$M = (8n_s/q_0^2 d)m^* G, \quad G = 8^{-1/2}\int_0^\pi d\varphi\, V(\varphi)^{1/2}, \quad (4)$$

where G has been defined so that $G = 1$ if $V(\varphi) = 1 - \cos\varphi$ (sine-Gordon potential[5]).

According to the phenomenological theory[2,8] a time-dependent phase generates the local current density $j_s(x,t) = n_s e q_0^{-1}\dot{\varphi}(x,t)$. Consequently, the mean current density due to a φ particle is

$$j_\pm = e n_s q_0^{-1}\int dx\, \dot{\varphi}_\pm(x,t)/\int dx,$$

which, on using (3), yields $j_\pm = L^{-1}(\mp 2en_s/n)v$, indicating that the particles carry negative or positive charge of magnitude $e^* = 2en_s/n$. This may also be seen by noting from the phenomenological theory[2,8] that gradients in φ imply a modulation in the local condensed electron density according to[10] $\delta n_s(x,t) = n_s q_0^{-1}\nabla_x\varphi$ [evidently, the local conservation law $\nabla_x j_s(x,t) - e\delta\dot{n}_s(x,t) = 0$ is obeyed].

Since in the rest frame a net change in phase of $\pm 2\pi$ is generated by the phase profile $\varphi_\pm(x)$, the net excess charge accumulated within the profile is $\Delta e = \mp e n_s q_0^{-1} 2\pi = \mp e^*$. To ensure that the total number of condensed electrons, Ln_s, is conserved, the integral over $\delta n_s(x,t)$ must vanish at all times, giving immediately the condition $\varphi(-\infty, t) - \varphi(\infty, t) = 0$ on $\varphi(x,t)$. This implies that the particles must always be created in *pairs* of positively and negatively charged particles, i.e., φ- and anti-φ-particle pairs.

In order to verify our proposition that the φ particles constitute an independent type of *elementary excitation* of the condensate at low temperatures, we have employed the functional integral technique[11] to investigate the classical free energy F of the Lagrangian field (1). The so-called "tunneling" contribution to F, ΔF_t, which appears in this method,[12] may be evaluated exactly in the low-temperature limit; it is

$$\Delta F_t = -2k_B T (L/2d) \exp(-Mc_0^2/k_B T). \qquad (5)$$

This is precisely the low-temperature ($k_B T \ll Mc_0^2$) free energy of a dilute "lattice gas" consisting of an average number of φ-particle pairs $N(T) = (L/2d)\exp(-Mc_0^2/k_B T)$ distributed at random over a total of $L/2d$ available φ-particle "sites" and $L/2d$ anti-φ-particle "sites" each of extent $2d$. The analogy with Schottky defects is apparent.

What are representative values of the φ-particle parameters e^*, $2d$, $E_0 = Mc_0^2$, and M/m for the systems of experimental interest? With $n_s = n$, appropriate for a nongapless[2] condensate at $T=0$, and $c_0 = v_F(m/m^*)^{1/2}$, and using the values[4,13] $v_F \simeq 1\times 10^7$ cm sec^{-1}, $m^*/m \simeq 10^2$, $\hbar\omega_F \simeq 1$ MeV, and[14] $q_0 \simeq 5\times 10^7$ cm^{-1}, assumed representative of TTF-TCNQ, we obtain the estimates shown in Table I. We see that if the angular-average G is approximately 1, $E_0 \sim 10^2$ °K, M is a light mass by comparison to m^*, and $2d$ is ~ 35 intermolecular spacings. A larger value of E_0 results for KCP.

We note that if E_0 is smaller than half the threshold energy for single-electron excitation, E_g, a situation which is favored by weak pinning ($E_0 \to 0$, as $\omega_F \to 0$), φ particles will be the dominant current-carrying excitations at low temperatures. Although a calculation of the φ-particle conductivity σ is beyond the scope of the present model, one would expect for $k_B T \ll Mc_0^2$ the form $\sigma = L^{-1}N(T)(e_+^2 + e_-^2) l/(k_B T M)^{1/2}$, where $e_+^2 = e_-^2 = e^{*2}$ and l is a phenomenological mean free path assumed to be the same for φ and anti φ particles. More explicitly,

$$\sigma = [4e^2 \omega_F l/(E_0 k_B T)^{1/2}](n_s/n)^2 \exp(-E_0/k_B T). \quad (6)$$

The observed[15] activation energy, $\epsilon_0 \sim 10^2$ °K, for the limiting low-temperature conductivity of TTF-TCNQ is indeed significantly smaller than the value[4] of $E_g/2 \simeq 800$°K reported from optical studies. The magnitude of ϵ_0, which is consistent with the above estimate of E_0, suggests that an interpretation in terms of φ-particle transport is not unfeasible. Similar remarks may also be made for KCP. It is possible that (modified) φ particles are more readily excited from a uniformly polarized condensate, so that a strong field dependence of the conductivity (as observed for both TTF-TCNQ[16] and KCP[17]) may result. Shot noise should be sensitive to the presence of φ particles, since it depends on the charge magnitude of the current-carrying entity. Further discussion of these and related topics will appear in a detailed account of the present work.

Stimulating discussions with P. A. Lee, G. D. Mahan, and S. Strässler are gratefully acknowledged. S. Strässler has attempted to investigate nonlinear aspects of the phase dynamics on the basis of a variational approach.[18] This work was stimulated by lectures presented at the Aspen Institute for Physics, summer 1975.

TABLE I. Estimated parameters for φ particles (see text).

Charge	$2d$ (Å)	M/m	E_0 (°K)
$\mp 2e$	130	$7.6G$	$140G$

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[1]H. Fröhlich, Proc. Roy. Soc. London, Ser. A 223, 296 (1954).

[2]For a review, see M. J. Rice, S. Strässler, and W. R. Schneider, in *One-Dimensional Conductors*, edited by H. G. Schuster (Springer, Berlin, 1975), p. 282.

[3]H. R. Zeller, in *Low-Dimensional Cooperative Phenomena*, edited by H. J. Keller (Plenum, New York, 1975), pp. 215–233.

[4]A. J. Heeger and A. F. Garito, in *Low-Dimensional Cooperative Phenomena*, edited by H. J. Keller (Plenum, New York, 1975), pp. 89–123.

[5]For a review, see A. C. Scott, F. Y. F. Chu, and D. W. McLaughlin, Proc. IEEE 61, 1443 (1973). In

some cases, the solitary waves are "solitons."

[6]P. A. Lee, T. M. Rice, and P. W. Anderson, Solid State Commun. 14, 703 (1974).

[7]The derivation of the physical criteria for the existence of such a regime is nontrivial for it entails an appropriate consideration of the general nonlinear coupled phase-amplitude problem. The results which we have obtained in this regard {which, interestingly, are particularly favorable for TTF-TCNQ because of dominant [M. J. Rice, C. B. Duke, and N. O. Lipari, Solid State Commun. 17, 1089 (1975)] *intra*molecular electron-phonon interaction} will be published in a subsequent paper.

[8]M. J. Rice, in *Low-Dimensional Cooperative Phenomena,* edited by H. J. Keller (Plenum, New York, 1975), pp. 23–24.

[9]Very interestingly, for this potential the complete spectrum of *quantized* "particle" excitations of the Lagrangian field (1) is known *exactly.* [R. F. Dashen *et al.*, Phys. Rev. D 11, 3424 (1975)].

[10]Note that the weak Coulomb interaction between such charge accumulations has not been incorporated into Eq. (1).

[11]D. J. Scalapino, M. Sears, and R. S. Ferrell, Phys. Rev. B 6, 3409 (1972).

[12]See J. A. Krumhansl and J. R. Schrieffer, Phys. Rev. B 11, 3535 (1975). We have rigorously extended the philosophy of this paper to a wide class of potentials; the sine-Gordon case is exactly solvable using the Mathieu equation.

[13]Rice, Duke, and Lipari, Ref. 7.

[14]F. Denoyer *et al.*, Phys. Rev. Lett. 35, 445 (1975).

[15]S. Etemad, Phys. Rev. B (to be published).

[16]H. Kahlert, Solid State Commun. 17, 1161 (1975); K. H. Seeger, private communication.

[17]D. Kuse and H. R. Zeller, unpublished.

[18]L. Pietronero, S. Strässler, and G. A. Toombs, Phys. Rev. B 12, 5213 (1975).

Direct Observation of the Optical Plasma Resonance of Ag by Photon-Assisted Tunneling*

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Photon-assisted tunneling is proposed for the investigation of optical plasma resonances; this is demonstrated by the direct observation of the Ag resonance in appropriate Ag-Al_2O_3-Al structures. A spectral scan of the ratio of the signals photoinduced by the p and s polarizations shows a large enhancement corresponding to the plasma resonance of Ag.

The optical excitation of plasmons, achieved by irradiating thin films[1] of a solid with p-polarized light at oblique incidence, has provided a relatively accurate means of studying the detailed character of these collective electron oscillations.[2] That such thin-film oscillations are radiative was first proposed by Ferrell,[3] and was later demonstrated[4,5] to result in characteristic peaks in the absorption and reflection spectra (and a dip in the transmission spectrum) at the plasma frequency ω_p. The decay of these optically excited plasmons into single-electron excitations has been conclusively established by the observation of peaks—corresponding to the plasma-resonance absorption—in the photoelectric yield from thin metallic films.[6-8] In fact, since the photoemission peaks themselves constitute a direct observation of the optical plasma resonances, they have been used to obtain accurate estimates of the plasmon energies and lifetimes[7] in Cd, Mg, and Zn, and the experimental dispersion relation[8] for K. However no such direct observation of the photoelectric plasma resonance has been reported for Ag, which has otherwise been used very extensively in the study of optical plasma resonances. This is because of the inapplicability of photoemission for the study of a plasma resonance (for Ag, $\hbar\omega_p = 3.78$ eV) whose energy is less than the metal's work function ($\chi_{Ag} \gtrsim 4.31$ eV).[9]

Photon-assisted tunneling is not limited by such a constraint on photon energy, and is thus applicable even for $\hbar\omega_p < \chi$. This is demonstrated in the present Letter by the direct observation of the Ag plasma resonance in appropriate Ag-Al_2O_3-Al tunnel-junction structures. Spectral data for the ratio of the voltages photoinduced by p and s polarizations, respectively, are presented. As expected for a photoelectric plasma resonance, this ratio shows a distinct peak at the plasma frequency (of Ag).

The Ag-Al_2O_3-Al tunnel-junction structure[10]