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| Title | COMMENSURABILITY ENERGY IN A ONE DIMENSIONAL QUARTER-FILLED ELECTRON-PHONON SYSTEM(THEORIES ON CDW NONLINEAR DYNAMICS, International Symposium on NONLINEAR TRANSPORT AND RELATED PHENOMENA IN INORGANIC QUASI ONE DIMENSIONAL CONDUCTORS) |
| Author(s) | Ohfuti, Y.; Ono, Y. |
| Citation | 物性研究 (1984), 41(4): 32-40 |
| Issue Date | 1984-01-20 |
| URL | http://hdl.handle.net/2433/91177 |
| Right | |
| Type | Departmental Bulletin Paper |
| Textversion | publisher |

# COMMENSURABILITY ENERGY IN A ONE DIMENSIONAL QUARTER-FILLED ELECTRON-PHONON SYSTEM

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Abstract

The commensurability energy of a one dimensional quarter-filled electron-phonon system is evaluated by calculating the total energy as a function of the phase $\phi$ of the fundamental ($2k_F$) order parameter in the case where $\phi$ is uniformly changing. The role of the higher harmonic ($4k_F$) order parameter is also discussed.

## §1. Introduction

Several quasi-one dimensional inorganic materials are known to have a nearly quarter-filled electron band.[1,2] Some experiments performed on those materials suggest the existence of non-linear local excitations, the so-called solitons.[3,4] In order to discuss the properties of the solitons in such systems, it is inevitable to evaluate the commensurability energy. In this paper we show the calculation of the commensurability energy in a quasi-one dimensional quarter-filled electron-phonon system. The case of the quarter-filled band has not yet been investigated carefully enough in comparison with the half-filled and one-third-filled cases.[5-10] Several authors considered the quarter-filled case[9] or the 1/M-filled case with a general integer M.[10] They did not pay, however, any attention to the role of the higher harmonic order parameters. The higher harmonics need not be explicitly considered for $M \leq 3$. For example, in the one-third-filled case, the $4k_F$ order parameter is nothing but the complex conjugate of the $2k_F$ order parameter, and $6k_F$ is equal to the reciprocal lattice vector; here $k_F$ is the electron Fermi momentum. The quarter-filled case is the simplest where the higher harmonic order parameter has a non-trivial meaning.[11]

In the quarter-filled electron-phonon system, the state of the system is characterized by three parameters, namely the amplitude and the phase of the fundamental ($2k_F$) order parameter ($= \Delta_1 e^{i\phi}$) and the higher harmonic ($4k_F$) order parameter ($= \Delta_2$) which is a

real number. The ground state of the system has a four-fold degeneracy in general, and the denenerate ground states are specified by different values of $\phi$. The soliton in this system is a local excitation connecting two semi-infinite segments of the chain which are in different ground states and therefore have different values of $\phi$. The commensurability energy is defined as the energy barrier height to be overcome by the system when $\phi$ changes from one ground state value to another. In order to evaluate the commensurability energy, we calculate the total energy E of the system as a function of $\phi$ by assuming the order parameters are uniform and by minimizing E with respect to $\Delta_1$ and $\Delta_2$ for each fixed $\phi$. In this way it is possible to find a pass in the space of $\phi$, $\Delta_1$ and $\Delta_2$ with the minimum energy barrier. As will be seen in the following, the effect of $\Delta_2$ is not negligible as far as the commensurability energy concerns, though the absolute value of $\Delta_2$ is much smaller than $\Delta_1$.

## §2. Model and Ground States

As a model of the one dimensional coupled electron-phonon system, we take the Fröhlich Hamiltonian of the following form,

$$H = -\sum_{k,s} 2t_0 \cos ka\, c^+_{k,s} c_{k,s} + \frac{1}{\sqrt{N}} \sum_{k,q,s} g(q)\, c^+_{k+q,s} c_{k,s} (b_q + b^+_{-q}) + \sum_q \omega_q b^+_q b_q \quad , \tag{1}$$

where $c^+_{k,s}$ and $c_{k,s}$ are the creation and annihilation operators for an electron with spin s and wave vector k ($-\pi/a < k \leq \pi/a$), $b^+_q$ and $b_q$ the creation and annihilation operators for a phonon with wave vector q and frequency $\omega_q$, $t_0$ the nearest neighbour transfer integral, a the lattice constant, N the total number of lattice sites, and g(q) representing the strength of the electron-phonon coupling.

We investigate the quarter-filled case and therefore $k_F = \pi/4a$. As is well known, the system described by the above Hamiltonian undergoes the Peierls transition due to the $2k_F$-singularity of the electron polarization function. Thus the condensation of phonons with wave vectors $Q(= 2k_F)$ and 2Q is expected; the condensation of the 2Q-phonon is due to the higher order effect of the electron-phonon coupling. Note that 3Q is equivalent to -Q and 4Q is equal to the reciprocal lattice vector. Within the mean-field approximation, we replace the phonon field operators by the following averages,

$$\langle b_Q \rangle = \langle b^{+}_{-Q} \rangle = \sqrt{N}\, t_0\, \Delta_1 e^{i\phi}/g_1 \quad , \tag{2.a}$$

$$\langle b_{2Q} \rangle = \sqrt{N}\, t_0 \Delta_2 / g_2 \quad , \tag{2.b}$$

and

$$\langle b_q \rangle = 0 \quad (q \neq \pm Q,\ 2Q) \quad , \tag{2.c}$$

where $g_1 = g(Q)$ and $g_2 = g(2Q)$, $\Delta_1 e^{i\phi}$ and $\Delta_2$ representing the fundamental and higher harmonic dimensionless order parameters respectively.

It is convenient to introduce the electron operators in the reduced zone $(-\pi/4a < k \leq \pi/4a)$ as $c^{(j)}_{k,s} = c_{k+jQ,s}$ with $j = 0,1,2,3$. The Hamiltonian $H$ (eq. (1)) where the phonon operators are replaced by the averages as eqs. (2.a-c) is not diagonal in the $c^{(j)}_{k,s}$-representation. The diagonalization of $H$ is straightforward and the result is

$$H = t_0 \sum_{j,k,s} \varepsilon^{(j)}_k\, a^{(j)+}_{k,s} a^{(j)}_{k,s} + \tfrac{1}{2} N t_0 (K_1 \Delta_1^2 + K_2 \Delta_2^2) \quad , \tag{3}$$

where $K_1$ $(= \omega_Q t_0 / g_1^2)$ and $K_2 (= 2\omega_{2Q} t_0 / g_2^2)$ are the inverse dimensionless coupling constants, and $\varepsilon^{(j)}_k$, the electronic energy normalized by $t_0$, is determined by the following fourth order equation,

$$\varepsilon_k^4 - 2(2 + 2\Delta_1^2 + \Delta_2^2)\varepsilon_k^2 - 8\Delta_1^2\Delta_2 \cos 2\phi\ \varepsilon_k + 4\sin^2 2ka$$

$$+ 4\Delta_2^2 + 2\Delta_1^2(1 - \cos 4\phi) - 4\Delta_1^2\Delta_2^2 + \Delta_2^4 = 0 \quad . \tag{4}$$

The field operators $\{a^{(j)}_{k,s}\}$ are related to the original operators $\{c^{(j)}_{k,s}\}$ through an appropriate unitary transformation. The lowest energy of the system for given values of $\phi$, $\Delta_1$ and $\Delta_2$ is obtained by summing up the electronic energy in the lowest band denoted by $j = 0$. Thus the total energy is written as follows,

$$E(\Delta_1, \Delta_2, \phi) = N t_0 \{ \frac{2a}{\pi} \int_0^{\pi/4a} \varepsilon^{(0)}_k\, dk + \tfrac{1}{2}(K_1 \Delta_1^2 + K_2 \Delta_2^2) \} \tag{5}$$

From the fact that $\varepsilon^{(0)}_k$ is the smallest solution of eq. (4), it is easy to see that E takes the lowest value when $\phi = n\pi/2$ and $\mathrm{sign}(\Delta_2) = (-)^{n+1}$ $(n = 0,1,2,3)$. The system has four-fold degenerate ground states, which are specified by $\phi = n\pi/2$, $\Delta_2 = (-)^{n+1}\Delta_{20}$ and $\Delta_1 = \Delta_{10}$ with $n = 0,1,2,3$. The values of $\Delta_{10}$ and $\Delta_{20}$ are calculated numericaly in general and depend on $K_1$ and $K_2$.

Here we should mention about the inverse dimensionless coupling constants $K_1$ and $K_2$. Usually $K_1$ can be estimated from the experimentally measured value of the energy gap in the electronic energy spectre. As for $K_2$, however, we have few information, and therefore we have to determine the ratio $K_2/K_1$ by assuming a proper model. Here we take the Debye model for the phonon frequency $\omega_q \propto q$ and assume the dilation type interaction for the electron-phonon coupling, i.e., $g(q) \propto q/\sqrt{\omega_q}$. This model yields $K_2/K_1 = 2$ and in the following we use this ratio.

## §3. Commensurability Energy

Using eqs. (4) and (5), we can calculate the total energy $E(\phi)$, which is minimized with respect to $\Delta_1$ and $\Delta_2$ for each fixed $\phi$. In Fig. 1, the curve 1 shows the minimized total energy as a function

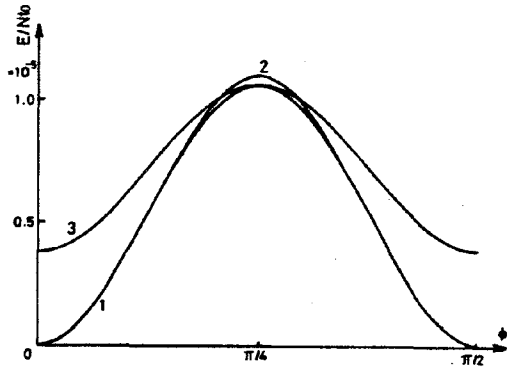


Fig.1; Dependence of the total energy E on $\phi$ for $K_1 = 2$ and $K_2 = 4$. Meaning of the three curves is explained in the text. Note that $E(\Delta_1,\Delta_2,\phi) = E(\Delta_1,-\Delta_2,\phi+\pi/2)$.

of $\phi$ for $K_1 = 2$ and $K_2 = 4$, which are chosen as typical values and for which the weak coupling approximation is thought to be valid. The origin of the energy is taken at the ground state energy, and therefore the curve 1 is nothing but the commensurability energy scaled by $t_0$. For comparison, two other curves are shown in the same figure: The curve 2 represents the total energy as a function of $\phi$ which is minimized only with respect to $\Delta_2$ with $\Delta_1$ fixed at $\Delta_{10}$ (the ground state value), and the curve 3 is obtained by putting $\Delta_2 = 0$ and minimizing with respect to $\Delta_1$. From Fig. 1, we find that the change of $\Delta_1$ with $\phi$ is not essential in determining the commensurability energy and that the effect of $\Delta_2$ is not negligible quantitatively. The higher harmonic order parameter $\Delta_2$ lowers the ground state energy and as a result raises the commensurability energy.

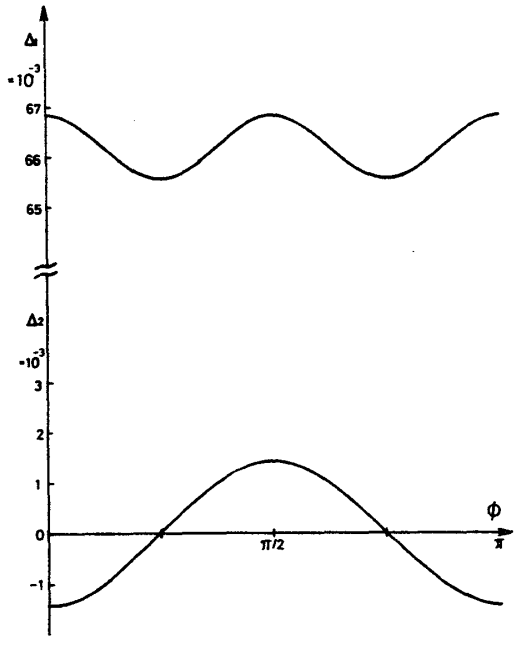


Fig.2; $\phi$-dependence of $\Delta_1$ and $\Delta_2$ minimizing the total energy E ($K_1$=2 and $K_2$=4). Note that $\Delta_1(\phi+\pi/2)=\Delta_1(\phi)$ and $\Delta_2(\phi+\pi/2)=-\Delta_2(\phi)$.

Figure 2 shows the values of $\Delta_1$ (the upper curve) and $\Delta_2$ (the lower curve) minimizing the total energy for each $\phi$ in the case where $K_1 = 2$ and $K_2 = 4$. The relative change of $\Delta_1$ is in fact small and it is reasonable that the change of $\Delta_1$ did not affect so much the commensurability energy. This conclusion is expected to be valid for the weak coupling case, where $\Delta_1 << 1$. In the weak coupling case, we can derive an analytic expression for the commensurability energy to some extent.

Assuming $\Delta_2 \sim o(\Delta_1)$ and neglecting terms higher order than $\Delta_1^2$ in eq. (4), we obtain

$$\varepsilon_k^{(0)} = -\sqrt{2}\{1+\Delta_1^2+[(1-\Delta_1^2)^2-\sin^2 2ka]^{1/2}\}^{1/2} \quad . \tag{6}$$

Substituting this expression into eq. (5) and differentiating E with respect to $\Delta_1$, we have the equation determining the ground state value of $\Delta_1$, denoted by $\Delta_1^{(0)}$,

$$K_1 - C = \frac{8a}{\pi}\int_0^{\pi/4a}\{|\varepsilon_k^{(0)}|[(\varepsilon_k^{(0)})^2-2(1-\Delta_1^2)]\}^{-1}dk \tag{7}$$

$$\equiv 8I_1(\Delta_1) \quad .$$

where $C = (2/\pi)\ln[\cot(\pi/8)] \simeq 0.24$. Within this lowest approximation, the commensurability energy does not appear. The commensurability energy is obtained by treating higher order terms in eq. (4) perturbationally. Retaining only relevant terms to determine the commensurability energy, we have the following expression for the contribution of the higher order terms to the total energy,

$$\delta E(\Delta_1^{(0)},\Delta_2,\phi)/Nt_0 = I_1(\Delta_1^{(0)})(\Delta_1^{(0)})^4(1-\cos 4\phi)$$
$$+ I_2(\Delta_1^{(0)})(\Delta_1^{(0)})^2\Delta_2\cos 2\phi + \tfrac{1}{2}K_2\Delta_2^2 \quad , \tag{8}$$

where $I_2$ is expressed in terms of the complete elliptic integral of the first kind, $K(z)$, as follows,

$$I_2(x) = \frac{1}{\pi}\frac{1}{1+x^2}K\left(\frac{1}{1+x^2}\right) \quad , \tag{9}$$

and a small correction to the last term on the r.h.s. of eq. (8) arising from the electronic energy is neglected. From eq. (8), $\delta E$ is found to be minimized as a function of $\Delta_2$ at $\Delta_2 = -[I_2(\Delta_1^{(0)})(\Delta_1^{(0)})^2/K_2]\cos 2\phi$. Thus we obtain the following expression for the commensurability energy scaled by $t_0$,

$$E_{com}(\phi) = (\Delta_1^{(0)})^4[(K_1-C)/8+(I_2(\Delta_1^{(0)}))^2/4K_2](1-\cos 4\phi) \quad , \tag{10}$$

where we have used the relation between $I_1(\Delta_1^{(0)})$ and $K_1$ (eq. (7)), and other $\phi$-independent contributions to $\delta E$ are disregarded. The second term in the square bracket is due to the appearance of $\Delta_2$ and gives a contribution of the same order as the first term. Numerical estimation shows that eq. (10) explains the curves in Fig. 1 rather well.

## §4. Discussions

In the previous section we have calculated the commensurability in the case of the one-dimensional quarter-filled Fröhlich model. The analytic expression of the commensurability energy derived in the weak coupling case consists of two parts, one coming from the contribution of the fundamental ($2k_F$) order parameter only and the other due to the appearance of the higher harmonic ($4k_F$) order parameter $\Delta_2$. Even without the contribution of $\Delta_2$, however, the expression (10) is different from that given by Lee, Rice and Anderson,[10] which can be read in the quarter-filled case as

$$E_{com}^{LRA}(\phi) = \frac{e^2}{16\sqrt{2}}(\Delta_1^{(0)})^4(1-\cos 4\phi) \quad . \tag{11}$$

The presence of $K_1$ in eq. (10) is due to the logarithmic singularity of the integral $I_1(\Delta_1^{(0)})$ for $\Delta_1^{(0)} \to 0$. In the expression $E_{com}^{LRA}(\phi)$, this logarithmic singularity seems not to be taken into account properly. Furthermore, as has been already pointed out in the introduction, Lee, Rice and Anderson did not take care of the effect of the higher harmonic order parameter.

Here it would be worth while to discuss about the soliton in

the present system. The soliton connects two of the four-fold degenerate ground states, by locally changing the phase $\phi$ of the fundamental order parameter. Thereby the change of $\Delta_2$ with $\phi$ is not negligible as has been discussed in the previous section. In Fig. 3, the equipotential lines on the $\phi$-$\Delta_2$ plane are depicted

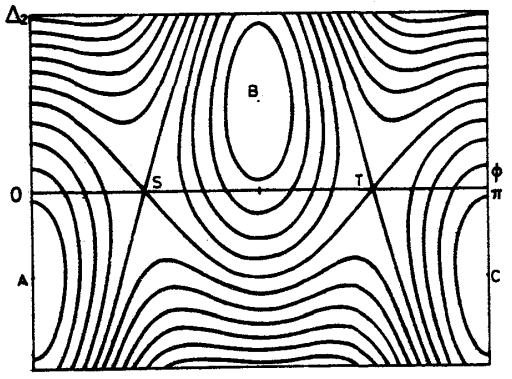


Fig.3; Equipotential lines on the $\phi$-$\Delta_2$ plane (schematic). $\Delta_1$ is taken to be its ground state value.

schematically when $\Delta_1$ is fixed at $\Delta_1^{(0)}$. The soliton pass on this plane will be such that starting from one of the energy minimum point (e.g. A in Fig. 3) and going to the nearest minimum point (B) through the saddle point (S). The real pass may deviate from this minimal pass because of the excess energy due to the spacial change of $\phi$ and $\Delta_2$. It is, however, possible to give a very rough estimation of the soliton creation energy in the form,

$$E_{sol} \sim 2\xi\alpha E_{com}(\pi/4) \quad , \tag{12}$$

where $2\xi$ is the soliton width in the unit of the lattice constant a, $E_{com}(\pi/4)$ the height of the saddle point measured from the minimum point, and $\alpha$ a factor of the order of unity. If we note that $E_{sol}$ is the sum of the energies due to the commensurability energy and the spacial derivatives of $\phi$ and $\Delta_2$, then $\alpha$ is expected to be larger than 1. If we apply the similar formula as eq. (12) for the one-third-filled Su-Schrieffer-Heeger model, which was numerically investigated by Su and Schieffer,[7] $\alpha$ should take the value about 4.

Let us apply the present theory to $TaS_3$, for which the experimentally obtained value of $\Delta_1$ is equal to 0.25.[12] This value of $\Delta_1$ corresponds to $K_1 = 1.418$ and $K_2 = 2/836$ and the $\phi$-dependent part of the total energy for this case is given in Fig. 4, where the curves 1 to 3 have the same meaning as in Fig. 1. From the

curve 1 in Fig. 4, we can estimate the soliton creation energy using eq. (12). Assuming $\xi \sim 10$ and $\alpha \sim 4$ we have $E_{sol} \sim 190K$ which is near the experimentally observed value 250K.[12] In Fig. 4, the change of $\Delta_1$ with $\phi$ seems to give non-negligible contribution to the commensurability energy. This will be because the values of coupling constants are out of range of the weak coupling approximation. The present theory may not be applied directly to the strong coupling case, but it will be plausible to conclude that the changes of $\Delta_1$ and $\Delta_2$ with $\phi$ become more and more important as the coupling between electrons and phonons is getting stronger.

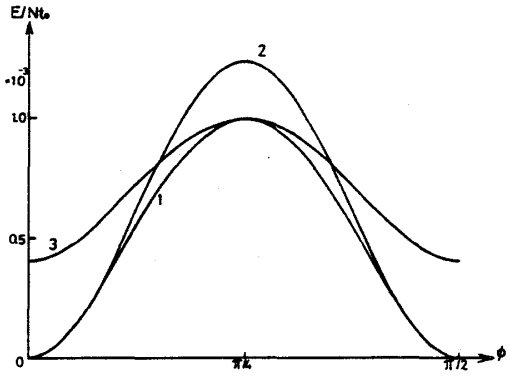


Fig.4; Dependence of the total energy E on $\phi$ when $K_1 = 1.418$ and $K_2 = 2.836$. Three curves have the same meaning as in Fig. 1.

In a recent paper,[11] we have discussed the similar problem as investigated in the present paper, for the case of the quarter-filled Su-Schrieffer-Heeger model where the coupling between electrons and phonons is derived from the dependence of the transfer integral on the lattice spacing. In that case, the higher harmonic order parameter $\Delta_2$ is equal to zero in the ground state but becomes finite to lower the commensurability energy when the phase $\phi$ changes e.g. from 0 to $\pi/4$. On the contrary, $\Delta_2$ in the present Fröhlich model is finite in the ground state to lower the ground state energy and changes its sign as $\phi$ goes e.g. from 0 to $\pi/4$. The commensurability energy in this case is enhanced by the appearance of $\Delta_2$. The role of $\Delta_2$ in determining the commensurability energy looks very different in the two models. This difference seems to originate from the fact that the Fröhlich model does not have the electron-hole symmetry which the Su-Schrieffer-Heeger model has.

Acknowledgment

The authors are grateful to Professor Y. Wada for stimulating discussions and constant encouragements.

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