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N.M.Plakida

CHARGE DENSITY WAVES IN SUPERIONIC CONDUCTORS

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As has been pointed out in recent experiments (see, e.g., refs. [1-3]), static charge density waves (CDW) may exist in superionic conductors (SC) as a result of a nonuniform distribution of moving ions in the crystal. A phenomenological description of CDW in SC was proposed in [4], and a microscopic model for the development of CDW due to the interaction of moving-ion density fluctuations with optic lattice vibrations was considered in [5].

In the present paper the stability condition for lattice of SC based on the model [5] is analysed. It is shown that CDW can develop only due to interaction of moving-ion density fluctuations with acoustic phonons as proposed in [4] and CDW can exist for a sufficiently strong coupling in the temperature range $T_1 < T < T_2$, where $T_1 \leq D \leq T_2$, D being the activation energy for moving ions.

2. Let us consider a model for SC described by the Hamiltonian analogous to [5]:

$$H = \sum_k E_k a_k^+ a_k + \frac{1}{2} \sum_{\vec{q} \neq 0} V(q) \rho_{\vec{q}} \rho_{-\vec{q}} + \frac{1}{\sqrt{N}} \sum_{\vec{q} j} g(\vec{q}, j) \rho_{-\vec{q}} Q_{\vec{q} j} + \frac{1}{2} \sum_{\vec{q} j} \{ |P_{\vec{q} j}|^2 + \omega^2_{\vec{q} j} |Q_{\vec{q} j}|^2 \} + \frac{1}{4!} \sum_{q_1 \dots q_4} V(q_1 q_2 q_3 q_4) Q_1 Q_2 Q_3 Q_4 , \qquad (1)$$

where a_k^+, a_k are Fermi creation and annihilation operators for a moving ion with the momentum $\vec{k}$ and energy $E_k = D + k^2/2M$, where D is the activation energy and M is its effective mass; $\rho_{\vec{q}} = \sum_{\vec{k}} a^+_{\vec{k}} a_{\vec{k}+\vec{q}}$. In what follows we consider only the classical limit and the type of statistics (Fermi or Bose) is irrelevant. $V(q) = (1/N) [4\pi (Ze)^2 / q^2 \epsilon v + \beta(q)]$ is the Coulomb and short-range, $\beta(q)$, interaction between moving ions with charge Ze in a crystal with the dielectric constant ϵ. The number of unit cells in the crystal of volume V is $N = V/v$. Interaction of moving ions with lattice vibrations for branch j is given by the function $g(q, j)$ which in the long-wave limit, $q \to 0$, is equal to: $g(q, 0) \approx i\lambda_0 / q$ for the optic (O) phonons, $\omega_{q0} \approx \omega_0$, and $g(q, A) \approx i\lambda_A q$ for the acoustic (A) phonons, $\omega_{qA} \approx cq$. Lattice vibrations are described by the operators $P_{\vec{q}j} = P^+_{-\vec{q}j}$, $Q_{\vec{q}j} = Q_{-\vec{q}j}$, $\omega_{\vec{q}j}$ are phonon frequencies and the last term in (1) takes into account the anharmonic interaction of phonons: $1 \equiv q_1 \equiv (\vec{q}_1 j_1)$, etc.

3. Equilibrium conditions for a crystal lattice in the model (1) can be obtained if one equates to zero an average force canonically conjugated to the normal coordinate Q_q:

$$-\langle \frac{d}{dt} P_q(t) \rangle = -\frac{i}{h} \langle [P_q, H] \rangle = \omega_q^2 \langle Q_{-q} \rangle + \frac{1}{\sqrt{N}} g(q) \langle \rho_{-q} \rangle + \frac{1}{8} \sum_{q_1 q_2 q_3} V(q, q_1, q_2, q_3) \langle Q_1 Q_2 Q_3 \rangle = 0, \quad (2)$$

where the statistical average $\langle ... \rangle$ is taken with the Hamiltonian (1). When CDW exists, $\langle \rho_q \rangle \neq 0$, it produces the corresponding lattice deformation, $\langle Q_q \rangle \neq 0$, for the definite wave vector $\vec{q} = \pm \vec{q}_o \neq 0$ and branch $j = j_o : \pm q_o = (\pm \vec{q}_o, j_o)$. In order to obtain the necessary condition for existing of a nonzero solution of eq. (2) for the order parameter $y(q_o) = y^*(-q_o) = \langle Q_{q_o} \rangle / \sqrt{N}$ one should calculate the density fluctuations $\langle \rho_q \rangle$ in the presence of arbitrary deformation $\langle Q_q \rangle$. To this end we employ the equation-of-motion method for the thermodynamic Green function. In the lowest order in $g(q)$ we get as in[5] for the nondiagonal Green function

$$\langle\langle a_{k+q} | a_k^+ \rangle\rangle_\omega = \frac{\lambda(q)}{[\omega - \epsilon_1(k)][\omega - \epsilon_2(k)]} \quad (3)$$

with the usual notation for the Fourier-transform of the two-time Green functions. Here we introduced

$$\epsilon_{1,2}(k) \approx \epsilon_{1,2} = D \pm \phi(q), \quad \phi(q) = 2\sqrt{|\lambda/q)|^2}, \quad \lambda(q) = V(q) \langle \rho_q \rangle + g(q)\, y(q). \quad (4)$$

In the classical limit of the Boltzmann statistics one obtains from (3):

$$\frac{1}{N} \langle \rho_q \rangle = -\frac{\lambda(q)}{\phi(q)} \operatorname{sh} \frac{\phi(q)}{T} e^{-\frac{D}{T}} = -\lambda(q)\, f(T), \quad (5)$$

where $f(T) \approx (1/T) \exp(-D/T)$ for $\phi(q) \ll T$. Now substituting (5) after taking into account definition (4), one gets the equilibrium condition (2) in the form:

$$y(-q) \{ \omega_q^2 - \frac{|g(q)|^2 f(T)}{1 + NV(q)\, f(T)} + \sum_{q'} B(q, q') \langle |Q_{q'}|^2 \rangle + B(q)\, |y(q)|^2 \} = 0, \quad (6)$$

where we have introduced the anharmonic coupling constant: $B(q) = NB(q, q)$, $B(q, q') = 2V(q, -q, q', -q')$. We point out that this equation has the same form as the equation for the order parameter in the vibronic model of ferroelectric[6].

4. Nonzero solutions of eq.(6) $y(q) = y(q_o) \neq 0$ can exist only if the screened ion-phonon interaction is sufficiently strong:

$$r(q) = \frac{|g(q)|^2 f(T)}{1 + NV(q)\, f(T)} > 1. \quad (7)$$

The latter condition can be fulfilled in the definite temperature range $T_1 < T < T_2$, where T_1 and T_2 are solutions of the equation

$$\gamma_{ph} - \gamma_c = 1/Df(T) = (T/D)\, e^{D/T}. \quad (8)$$

Here we introduced $\gamma_{ph} = |g(q)|^2 / D\omega_q^2$, $\gamma_c = NV(q)/D$. Eq.(8) has two real solutions $T_1 \leq D \leq T_2$, when $\gamma_{ph} - \gamma_c > e$. An estimation of the anharmonic term in (6) shows that in the case of a sufficiently small coupling constant $TB(q, q')/\omega_q^2 \omega_{q'}^2 \leq 10^{-2}$, the temperature range, where nonzero solutions of eq.(6) exist, is given to a high degree of accuracy by the same condition (7) (contrary to the model of vibronic ferroelectric in[6]). Therefore one can estimate the temperature range of the CDW formation as $T_1 < T < T_2$, where T_1 and T_2 are the solutions of eq.(8).

The value of the modulation wave vector $\vec{q}_o$ of CDW depends on the maximum of interaction (7):

$$(dr(q)/dq)_{q = q_o} = 0. \quad (9)$$

For optic phonons $|g(\vec{q}O)|^2/\omega_{qo}^2 \approx \lambda_o^2/\omega_o^2 q^2$ and $r(q)$ has its maximum at $q = 0$, therefore CDW of $q \neq 0$ does not exist. For acoustic phonons $|g(\vec{q}A)|^2/\omega_{qA}^2 \approx \lambda_A^2/c^2$ and the maximum value of $r(q)$ is given by $dV(q)/dq = 0$. Putting $\beta(q) = \beta(0) + sq^2$ one gets in accordance with[4]: $q_o = (4\pi(Ze)^2/\epsilon v s)^{1/4}$. Since the dielectric constant ϵ in SC can be large enough, q_o may be sufficiently small, and CDW with a macroscopic period can develop.

For strong coupling $\gamma_{ph} - \gamma_c \gg 1$ one finds from eq.(8) $T_1 \ll D$, and CDW can develop in SC just after the phase transition to the superionic state at temperature $T_o > T_1$. This type of situation is probably observed in Ag_2S[2] and AgI[3]. In β-$LiAlSiO_4$[1] the incommensurate phase with a small q_o value exist in the temperature range 703 < T < 763 K that can be obtained as solutions T_1 and T_2 of eq.(8) for the model parameters $D = 0.063$ eV and $\gamma_{ph} - \gamma_c = 2.720 > e$, that seems to be physically reasonable.

In conclusion we point out that calculation of the phonon Green function $\langle\langle Q_q | Q_q^+ \rangle\rangle_\omega$ for the model (1) shows that the frequencies of lattice vibration become unstable in the same temperature range, where eq.(6) has nonzero solutions.

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Плакида Н.М. E17-84-425

Волны зарядовой плотности в суперионных проводниках

Для модели суперионного проводника исследована возможность образования волны зарядовой плотности /ВЗП/ при учете взаимодействия подвижных ионов с фононами. На основе условия равновесия для решетки показано, что ВЗП может существовать в области температур $T_1 < T < T_2$, где $T_1 \leq D \leq T_2$, D – энергия активации подвижных ионов.

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Plakida N.M. E17-84-425

Charge Density Waves in Superionic Conductors

For the model of superionic conductor the possibility of the CDW formation due to the interaction between fast ions and phonons is considered. On the basis of the equilibrium condition for the lattice it is shown that the CDW can exist in the temperature range $T_1 < T < T_2$, where $T_1 \leq D \leq T_2$. D is the activation energy for fast ions.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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