Surface properties of superionic crystals—relation to volume transition into an inhomogeneous state

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The singularity of a surface quantity (capacitance of a double layer near a surface) in the vicinity of the temperature of transition of a superionic conductor into a state with a charge density wave (CDW) is investigated phenomenologically. The equation that must be satisfied by the electric potential in the bulk of the crystal and the boundary conditions is found within the framework of the Landau theory. Accordingly, a regular procedure is proposed for finding the asymptotic form of the potential at the transition point. The procedure leads to a satisfactory approximate solution (confirmed by numerical calculations) for the case of "low" surface charge densities. An investigation of the first integrals of the principal equation shows that the second derivative of the surface capacitance at the point of the volume transition into the CDW state is discontinuous. The results are compared qualitatively with those of experiments on a crystal in which a CDW presumably exists.

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INTRODUCTION

The considerable attention paid at present to the investigation of the so-called superionic crystals (SC) or solid electrolytes is due not only the possibility of their extensive use,[1] but also to the variety of their properties that are of general physical interest.[1,2] A superionic conductor is an example of a system that is characterized, on the one hand, by an anomalously high ionic conductivity σ at temperatures far from the melting point (the record at room temperature is $\approx 0.44(\Omega\cdot\mathrm{cm})^{-1}$ of the crystal α-$RbCu_4Cl_3I_2$, Ref. 3; one usually speaks of melting of one of the sublattices, the cation one in the case of the SC AgI, Ag_2S, $RbAg_4I_5$, and others), and on the other by the presence of distinct attributes of a crystal structure defined by an ordered anion sublattice (Refs. 3 and 4).[1)]

Since the subsystem of disordered actions is highly "friable," the SC can be in a spatially inhomogeneous state under certain conditions. This phenomenon was observed several years ago,[6-8] namely, an x-ray structural investigation of ionic crystals of the β-aluminum type has made it possible to identify reflections corresponding to a two-dimensional superstructure ("microdomains" in the terminology of Refs. 6–8), with a characteristic period 40–50 Å, and the superstructure was found to be stable at $T \leq 400$ K. A two-dimensional modulated phase with a quasimacroscopic period was recently observed in the superionic crystal β-$LiAlSiO_4$ in the temperature interval $430\,^\circ\mathrm{C} \leq T \leq 490\,^\circ\mathrm{C}$ (Ref. 9). Finally, observation of an incommensurate (one-dimensional) superstructure in the superionic phase of the Ag_2S crystal at $T > 450$ K was reported in Ref. 10 (the experiments were performed up to a temperature $T \approx 570$ K).

Perrot and Fletcher[11] have experimentally demonstrated the existence of a heat-capacity anomaly at $T \approx 620$ K in the superionic crystal Ag_2S, but at that time it was impossible to confirm the phase transition by x-ray diffraction. On the basis of the experiments of Cava and McWhan,[10] it can be assumed that the temperature $T_c = 620$ K determines the phase-transition point below which the SC Ag_2S is in a spatially inhomogeneous state characterized by the presence of an incommensurate superstructure, whereas there is no periodic inhomogeneity above T_c.

The character of the transition into the highly conducting phase of SC was treated by the author in Refs. 12 and 13, where it was shown that under certain conditions the homogeneous state in the SC becomes unstable and a charge-density wave (CDW) is produced. The macroscopic description of such a transition is based on introducing, besides the strain tensor

$$u_{ik} = (\partial u_i/\partial x_k + \partial u_k/\partial x_i)/2,$$

where u is the displacement vector of the medium, a new variable, namely the local density ρ of the electric charge, with the homogeneous state corresponding to $\rho \equiv 0$ and $u_{ik} \equiv 0$. The use of the quantity ρ as an independent variable reflects a distinguishing feature of SC, namely the presence of an easily deformed system of mobile ions. In the isotropic-SC model, with which we shall deal hereafter, the free-energy density, with the principal terms taken into account, can be represented in the form

$$F = {}^1/_2\rho\varphi + {}^1/_2 K u_{ll}^2 + \mu(u_{ik} - {}^1/_3\delta_{ik}u_{ll})^2 + {}^1/_2\chi\rho^2 + {}^1/_2 g(\nabla\rho)^2 + {}^1/_4 D\rho^4 - \nu\rho u_{ll}, \quad (1)$$

where $K > 0$, $\mu > 0$ is the elastic modulus, and $g > 0$, $D > 0$, χ, ν are phenomenological parameters. The first term in (1) determines the Coulomb energy of the inhomogeneous SC, and the last describes the interaction of the strains with the charge fluctuations. Strictly speaking, the case considered admits of the appearance in F of an invariant cubic in F, and this could lead to a first-rather than second-order transition. We, however, shall use F in the form (1) as the first step in the description of the transition of the SC into an inhomogeneous state (the presently available data[9-11] do not identify the order of this transition precisely).

Recognizing that the Coulomb potential φ satisfies the Poisson equation

$$\Delta\varphi = -4\pi\rho/\varepsilon, \quad (2)$$

where ε is the dielectric constant of the SC, and intro-

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ducing one-dimensional (along the z axis) fluctuations of $u_{zz}(z)$ and $\rho(z)$ in the form of Fourier expansions in the one-dimensional vector k, we obtain, after integrating F over the volume and excluding the strains, the following expression for the free energy per unit surface perpendicular to the z axis:

$$f=\frac{1}{2}\sum_k\left(\frac{4\pi}{\varepsilon k^2}+4\left(\frac{\pi g}{\varepsilon}\right)^{1/2}p+gk^2\right)|\rho_k|^2, \tag{3}$$

where

$$p\equiv(\varepsilon/16\pi g)^{1/2}[\chi-\nu^2/(K+4\mu/3)] \tag{4}$$

and account is taken of only terms of second order in F.

If the condition $p\leq -1$ can be realized in some temperature range, this corresponds to instability of the SC to fluctuations ρ_{k0} with wave vector $k_0\approx(4\pi/\varepsilon g)^{1/4}$ (Refs. 12, 13), i.e., to the appearance of a superstructure—a static CDW (and an associated strain wave). According to the results of Ref. 14, the dielectric constant of a crystal in the superionic state can be anomalously large, and accordingly the wave vector k_0 of the superstructure can be small enough, i.e., the resultant inhomogeneity can be macroscopic. We assume throughout that this is the case, and use a macroscopic approximation.

One of the important problems in the physics of SC is the study of the surface properties, particularly the surface capacitance. Naturally, the question arises of the character of the singularities of this and of other measured quantities in the vicinity of the temperature of the volume transition into the state with the CDW. The present paper is devoted to this question. It is shown within the framework of the Landau theory that the second derivative of the surface capacitance is discontinuous at the indicated transition point (i.e., it has a singularity of the bulk-heat-capacity type). This result agrees qualitatively with experiment[15] (see Sec. 5 below).

1. BASIC EQUATIONS AND BOUNDARY CONDITIONS

We consider a SC bounded by a free plane surface $z=0$ and assume that the inhomogeneous distributions of φ, ρ and u_{ik} are one-dimensional, i.e., they depend only on the coordinate z. In this case the total free energy of the crystal per unit surface can be represented in the form

$$\mathcal{F}=\int_0^\infty\left\{Z_0\rho+\rho\varphi-\frac{\varepsilon}{8\pi}\left(\frac{d\varphi}{dz}\right)^2+\frac{K}{2}u_{zz}^2+\mu\left(u_{ik}-\frac{1}{3}\delta_{ik}u_{zz}\right)^2+\frac{\chi}{2}\rho^2+\frac{g}{2}\left(\frac{d\rho}{dz}\right)^2+\frac{D}{4}\rho^4-\nu\rho u_{zz}\right\}dz+\rho_s\varphi(0)-q\rho_s\rho(0), \tag{5}$$

where the integrand is of volume origin, and the two last terms in (5) comprise the pure surface contribution and have respectively the meaning of the Coulomb energy of the charges ρ_s located on the surface proper (see Ref. 16) and the energy determined by the interaction of the pure surface charges with the bulk ones $\rho(0)$; Z_0 is the chemical potential of the charged "liquid" and q is a constant.

Varying $\mathcal{F}$ with respect to u_{zz} and taking into account the definition of the SC stress tensor $\sigma_{zz}=\delta\mathcal{F}/\delta u_{zz}$, as well as the fact that at equilibrium $d\sigma_{zz}/dz=0$, i.e., $\sigma_{zz}=0$ since there are no surface stresses, we obtain the first equation that relates u_{zz} with ρ and φ:

$$(K+4\mu/3)u_{zz}=\nu\rho. \tag{6}$$

It is necessary to vary with respect to φ and ρ independently. Equating the variation of $\mathcal{F}$ with respect to $\delta\varphi$ to zero, we obtain the Poisson equation

$$d^2\varphi/dz^2=-4\pi\rho/\varepsilon \tag{7}$$

and the first boundary conditions

$$d\varphi/dz|_0=-4\pi\rho_s/\varepsilon. \tag{8}$$

Varying the free energy (5) with respect to ρ, we arrive at the equation

$$Z_0+\varphi+\chi\rho-gd^2\rho/dz^2+D\rho^3-\nu u_{zz}=Z_\infty=\text{const}, \tag{9}$$

where we have used the fact that at equilibrium the electrochemical potential Z_∞ is constant and is in fact equal to Z_0. The terms of (5) outside the integral sign yield then the second boundary condition

$$(g\varepsilon/4\pi)d^3\varphi/dz^3|_0=q\rho_s. \tag{10}$$

This method of deriving the equations and the boundary conditions is analogous to that used by Kaganov and Omel'yanchuk.[17]

Introducing the dimensionless coordinate and potential

$$\xi=(4\pi/\varepsilon g)^{1/4}z,\quad \Phi=D^{1/4}(\varepsilon/4\pi g)^{3/4}\varphi,$$

we rewrite Eq. (9) with allowance for (6) and (7) in the form

$$\Phi^{IV}-2p\Phi''+\Phi-\Phi'^3=0 \tag{11}$$

with boundary conditions

$$\Phi'(0)=-\sigma_s,\quad \Phi'''(0)=\lambda\sigma_s,\quad |\Phi(\infty)|<\infty, \tag{12}$$

where

$$\sigma_s\equiv(D/g)^{1/4}\rho_s,\quad \lambda\equiv q(\varepsilon/4\pi g)^{1/4}$$

and the primes denote everywhere derivatives with respect to ξ.

Within the framework of the Landau theory we must put

$$p=-1+\gamma(T-T_c),\quad \gamma>0, \tag{13}$$

where T_c is the temperature of the volume transition of the SC into the state with CDW. At $p>1$, the potential Φ_0, which is the solution of the linearized equation (11), decreases monotonically into the interior of the crystal. In the range $-1<p<1$ the linearized solution that satisfies the conditions (12) is of the form

$$\Phi_0(\xi)=\frac{\sigma_s}{2}e^{-\eta\xi}\left[\frac{\lambda-1+4\eta^2}{\eta}\cos s\xi+\frac{\lambda-3+4\eta^2}{s}\sin s\xi\right],\qquad \eta\equiv[(1+p)/2]^{1/2},\quad s\equiv[(1-p)/2]^{1/2}. \tag{14}$$

As the transition point is approached from above, we have $\eta\to 0$ and the linearized solution (14) diverges in the surface, namely, at any nonzero surface-charge density there is always a boundary region where the linearized equation for the potential is inapplicable. The depth of this region increases without limit as

$T \to T_c$ and becomes infinite at the transition point itself. At $T = T_c(\eta = 0)$ the decrease of Φ is not exponential as in (14), but follows a power law (see below).

As for the asymptotic behavior of the solution Φ as $\eta \to 0$, it is given by the linearized equation (11):

$$\Phi(\xi) \to A_> e^{-\eta\xi} \cos[s(\xi - \xi_\infty)], \quad \xi \to \infty, \tag{15}$$

but the constants $A_>$ and ξ_∞, naturally, do not coincide here with the corresponding constants in (14).

Defining the surface differential capacitance by the relation

$$c_s = [d\Phi(0)/d\sigma_s]^{-1}, \tag{16}$$

we obtain from (14)

$$c_{s0} = 2\eta/(\lambda - 1 + 4\eta^2).$$

We note that c_s turns out to be non-negative at $\lambda > 1$. Otherwise there should set in at the temperature $T_0 > T_c$ a surface instability corresponding to a restructuring of the crystal in the subsurface region when there is still no superstructure whatever in the volume. This possibility will not be discussed here and we assume hereafter $\lambda > 1$.

2. SOLUTION AT THE TRANSITION POINT

We describe now the method of finding the asymptotic solution of the nonlinear equation (11) at $T = T_c(p = -1)$. As $\xi \to \infty$ we represent the solution in the form of a series (a quantity with the subscript c pertains to the transition temperature T_c)

$$\Phi_c(\xi) = \frac{f_1(\xi)}{\xi} + \frac{f_2(\xi)}{\xi^2} + \frac{f_3(\xi)}{\xi^3} + \ldots, \tag{17}$$

where the sought functions $f_n(\xi)$ are assumed to oscillate and to contain no power-law parts. Substituting (17) in (11) and equating terms of like powers ξ^{-n}, we obtain the equations

$$f_1^{IV} + 2f_1'' + f_1 = 0, \tag{18}$$

$$f_2^{IV} + 2f_2'' + f_2 = 4(f_1' + f_1'''), \tag{19}$$

$$f_3^{IV} + 2f_3'' + f_3 = -4f_1 - 12f_1'' + (f_1'')^3 + 8(f_2' + f_2'''), \tag{20}$$

etc. Taking the statements made above in account we choose as the solution

$$f_1(\xi) = A_1 \cos(\xi - \xi_1), \quad f_2(\xi) = A_2 \cos(\xi - \xi_2), \tag{21}$$

where A_1, A_2, ξ_1, ξ_2 are constants (we point out that the right-hand side of (19) vanishes identically). With allowance for the solutions obtained, Eq. (20) takes the form

$$f_3^{IV} + 2f_3'' + f_3 = 8A_1 \cos(\xi - \xi_1) - A_1^3 \cos^3(\xi - \xi_1),$$

where we obtain in the right-hand side, after trigonometric transformations,

$$(8 - {}^3/_4 A_1^2) A_1 \cos(\xi - \xi_1) - {}^1/_4 A_1^3 \cos[3(\xi - \xi_1)]. \tag{22}$$

It is easily seen that retention of the first term in (22), which is the solution of a homogeneous equation of the type (18), would lead to the appearance in f_3 of terms of the form $\xi \cos(\xi - \xi_1)$, which should not be there (otherwise this would mean simple a redefinition of the function $f_2(\xi)$). It follows from this directly that the coefficient of $\cos(\xi - \xi_1)$ in the right-hand side of (22) should vanish, i.e.,

$$A_1^2 = {}^{32}/_3, \tag{23}$$

and the constant A_1 itself is defined only accurate to the sign.

The function f_3 is now easy to determine and equals

$$f_3(\xi) = -{}^1/_{24} A_1 \cos[3(\xi - \xi_1)] + A_3 \cos(\xi - \xi_3), \tag{24}$$

A_3 and ξ_3 are constants. Writing also the equation for f_4:

$$f_4^{IV} + 2f_4'' + f_4 = -24A_1 \sin(\xi - \xi_1) + 24A_2 \cos(\xi - \xi_2)$$
$$+ 3A_1^2 \cos^2(\xi - \xi_1)[-A_2 \cos(\xi - \xi_2) + 2A_1 \sin(\xi - \xi_1)] + 12(f_3' + f_3''')$$

and making the necessary transformations in the right-hand side, we represent this equation in the form

$$-8[A_1 + 2A_2 \sin(\xi_1 - \xi_2)] \sin(\xi - \xi_1)$$
$$-8A_2 \cos(3\xi - 2\xi_1 - \xi_2) + 4A_1 \sin[3(\xi - \xi_1)], \tag{25}$$

from which it follows that a solution of the type of interest to us is possible if

$$A_2 = -A_1/2 \sin(\xi_1 - \xi_2). \tag{26}$$

The equations for the functions that follow turn out to be more cumbersome, and their main feature is that trigonometric transformations carried out in the right-hand sides always single out independent terms of the type $\cos(\xi - \xi_1)$ as well as $\sin(\xi - \xi_1)$ (we note that terms of one of this type vanished identically in (22) and (25)). As a result, for the power-law terms to vanish we must stipulate simultaneous vanishing of the coefficients of both $\cos(\xi - \xi_1)$ and $\sin(\xi - \xi_1)$. This yields each time two equations for the determination of the constants A_n and ξ_n at the specified $n \geq 3$, i.e., all the constants are found to be expressed in terms of two, ξ_1 and ξ_2.

The described method serves as the basis for the construction of an approximate solution of Eq. (11) at $p = -1$ in the entire range of variation of ξ. We represent the sought solution in the form

$$\Phi_c(\xi) = A_1 \frac{\cos(\xi - \xi_1)}{\xi + \xi_0}, \quad 0 \leqslant \xi \leqslant \infty, \tag{27}$$

where ξ_1 and ξ_0 are unknown constants that must be determined from the boundary conditions (12). Substituting (27) in (12) and carrying out simple transformations we obtain

$$\sin\xi_1 = \frac{\sigma_s \xi_0}{2A_1}\left(\frac{6}{\xi_0^2} + \lambda - 3\right), \quad \cos\xi_1 = \frac{\sigma_s \xi_0^2}{2A_1}\left(\frac{6}{\xi_0^2} + \lambda - 1\right),$$

after which we arrive at the equation

$$[6 + (\lambda - 3)\xi_0^2]^2/\xi_0^2 + [6 + (\lambda - 1)\xi_0^2]^2 = 4A_1^2/\sigma_s^2. \tag{28}$$

As $|\sigma_s| \to 0$ and at $\lambda > 1$ we have approximately

$$\xi_0 = [2|A_1|/(\lambda - 1)|\sigma_s|]^{1/3}.$$

The value of $\Phi_c(0)$ is given in this case by

$$\Phi_c(0) = [2({}^2/_3)^{1/3}(\lambda - 1)|\sigma_s|]^{1/3} \operatorname{sgn}\sigma_s, \tag{29}$$

from which we obtain for the surface capacitance at the transition point ($p = -1$) the expression

$$c_{sc} = [d\Phi_c(0)/d\sigma_s]^{-1} = 6^{1/3}(\lambda - 1)^{-1/3}|\sigma_s|^{1/3}. \tag{30}$$

A simple analysis of (28) shows that at $\lambda \sim 1$ real solutions for ξ_0 exist in the region $|\sigma_s| \leq 1$; at $\lambda \gg 1$ this region becomes narrower: $|\sigma_s| \leq \lambda^{-1/2}$. To find the capacitance at $|\sigma_s| \gg 1$ a more complicated approximation of $\Phi_c(\xi)$ must be used. We, however, will not deal with this and confine ourselves to low surface-charge densities.

3. SOLUTION IN THE REGION OF THE TRANSITION POINT

Before we proceed to report the results of the solution of Eq. (11) at $T \neq T_c$, we determine the important first integral. Multiplying (11) by and integrating, we obtain

$$\Phi'^2+2p\Phi''^2-2\Phi\Phi''-\Phi'''^2+\Phi''''/2=G, \tag{31}$$

where G is a constant. At $p>-1 (T>T_c)$ the potential Φ and its derivative tend asymptotically to zero, whence $G \equiv 0$. As for the value of G at $T<T_c (p<-1)$, it can be obtained in the following manner. At $p<-1$, in view of the presence of a periodic superstructure in the volume of the SC, we represent the solution far from the boundary in the form of the expansion

$$\Phi_\infty(\xi)=\sum_{n=0}^{\infty} a_{2n+1}\cos[(2n+1)\xi], \quad T\to T_c-0, \tag{32}$$

where the constant phases are left out for brevity. Substituting (32) in (11) and using trigonometric transformation formulas, we obtain, equating the coefficients of cosines of like argument, accurate to the principal terms:

$$a_1^2=-8(p+1)/3, \quad a_3=-a_1^3/256 \tag{33}$$

etc. Substutution of (32) in (31) with allowance for (33) yields now

$$G=-4(p+1)^2/3\sim-(T_c-T)^2, \quad T<T_c, \tag{34}$$

where we have again restricted outselves to the principal terms in $T-T_c$.

Thus, at $T<T_c$ there is a periodic solution (32) far from the boundary. It is useful to indicate the additional terms that decrease at large distances and are due to the presence of the boundary. We seek the solution of (11) in the form

$$\Phi(\xi)=\Phi_\infty(\xi)+\Phi_<(\xi)$$

(here and elsewhere the symbol $<$ indicates that the solution pertains to the temperature region $T<T_c$). Linearizing the equation with respect to $\Phi_<(\xi)$, we arrive at the equation

$$\Phi_<^{IV}-2p\Phi_<''+\Phi_<-3(\Phi_\infty'')^2\Phi_<=0. \tag{35}$$

We note now that at $p<-1$ the principal asymptotic terms of $\Phi_<(\xi)$ can be represented in the form

$$\Phi_<(\xi)=\Phi_{0<}(\xi)+f_{1<}(\xi)/\xi,$$

where $\Phi_{0<}(\xi)$ and $f_{1<}(\xi)$ contain no power-law parts and satisfy Eq. (35), with $f_{1<}(\xi)\to f_1(\xi)$ (see (17)) at the transition point. Solving Eq. (35) (see the Appendix), we obtain at $T<T_c$:

$$\Phi(\xi)=a_1\cos\xi+(A_<+A_1/\xi)\exp[-(|p|-1)^{1/2}\xi]\cos\xi, \tag{36}$$

where we have again left out the phase constants, and $A_<\to 0$ as $T\to T_c-0$.

We consider now the case $T>T_c$. Equation (11) has the asymptotic form (15). There is, however, also another type of solution that goes over into (17) at $T=T_c (p=-1)$: the function $f_{1<}(\xi)$ (the symbol $>$ indicates the case $T>T_c$) is again a solution of a linear equation that coincides formally with the linearized equation (11). Again comparing with the case $p=-1$, we have at $T>T_c$:

$$\Phi(\xi)=(A_>+A_1/\xi)\exp\{-[(1-|p|)/2]^{1/2}\xi\}\cos\xi, \tag{37}$$

where the first term is defined by (15) and $A_>\to 0$ as $T\to T_c+0$. Of course, it is impossible to determine the temperature dependence of $A_\lessgtr$ from the asymptotic behavior, the dependence is determined essentially by the behavior of the solution in the subsurface region (cf. the solution (14) corresponding to the linearized boundary-value problem). We call attention also to the fact that the correlation length ξ_k, the distance at which the influence of the surface is "felt," is equal to $\xi_{k<}=(|p|-1)^{-1/2}$ at $T<T_c$ (see (36)); at $T>T_c$, as follows from (37), we have $\xi_{k>}=[(1-|p|)/2]^{-1/2}$.

4. CALCULATION OF THE SINGULAR PART OF THE SURFACE CAPACITANCE

To obtain the answer we must find the value of the potential Φ on the SC surface as a function of the surface-charge density σ_s and of the degree of proximity to the transition point. It is, however, a very complicated matter to obtain as $T\to T_c$ a solution $\Phi(\xi)$ valid over the entire interval $0<\xi<\infty$, and the temperature dependence of $\Phi(0)$, as will be shown below, differs even qualitatively from that given by the asymptotic formulas (36) and (37).

Yet the dependence of $\Phi(0)$ on σ_s can be determined if two independent first integrals of Eq. (11) are known:

$$F_1(\Phi, \Phi', \Phi'', \Phi''')=G, \quad F_2(\Phi, \Phi', \Phi'', \Phi''')=H,$$

where G and H are constant determined by the asymptotics of the arguments F_1 and F_2. Indeed, referring F_1 and F_2 to the value $\xi=0$ and using the boundary conditions (12), we obtain the sought function $\Phi(0;\sigma_s)$ (as well as $\Phi''(0;\sigma_s)$).

Unfortunately, it is impossible to obtain one more exact first integral of (11) (other than (31)). At small $|\sigma_s|$ we can, however find an approximate first integral by the following procedure. We multiply (11) by Φ' and integrate term by term. The only difficulty encountered here is in the integration of the last term. By integrating in it several times by parts and using (11), we have

$$\int \Phi'''\Phi' d\xi=\frac{1}{2}\Phi'^2\Phi''^2-\frac{1}{3}\Phi'^3\Phi'''+\frac{p}{6}\Phi'^4-\frac{1}{6}\Phi^2\Phi'^2$$
$$+\frac{1}{9}\left(\Phi^3\Phi''-\int\Phi^3\Phi'''d\xi\right)+\frac{1}{3}\int\Phi'^3\Phi'''^3 d\xi. \tag{38}$$

The last integral in (38) can be neglected because of the smallness of $|\sigma_s|$ and of the proximity to the transition point. In the next to the last, however, we can put approximately $\Phi \simeq -\Phi''$ (it is easily seen from (12), (29) and (31) that for $|\sigma_s| \ll 1$ this is indeed satisfied at $\xi=0$, and that as $\xi\to\infty$ this relation is more accurate the

closer the transition point, see (32) and (33)). We then obtain

$$\int \Phi^3\Phi'''d\xi \approx -\Phi''^4/4.$$

Thus, at $|\sigma_s| \ll 1$ the second independent first integral can be represented, accurate to the principal terms, in the form

$$\Phi'\Phi''' - \frac{1}{2}\Phi''^2 - p\Phi'^2 + \frac{1}{2}\Phi^2 - \frac{1}{2}\Phi'^2\Phi''^2 + \frac{1}{3}\Phi'^3\Phi''' - \frac{p}{6}\Phi'^4 + \frac{1}{6}\Phi^2\Phi'^2 - \frac{1}{9}\Phi^3\Phi'' - \frac{1}{36}\Phi''^4 = H, \quad (39)$$

where the value of the integration constant H, determined from the asymptotic solution, turns out to be (accurate to $(|p|-1)^2$):

$$H = 2(|p|-1)^2, \quad p < -1; \quad H \equiv 0, \quad p > -1. \quad (40)$$

Choosing now $\xi = 0$ as the argument of the first integrals (31) and (39), using the boundary conditions (12), and eliminating $\Phi(0)$ from the equalities obtained, we find

$$Q^2\left\{\left(1+\frac{1}{3}\sigma_s^2\right)\left[|p| + \frac{(\lambda^2-1)\sigma_s^2+G}{2Q^2} - \frac{Q^2}{4}\right]^2 + \frac{2}{9}Q^2\left[|p| + \frac{(\lambda^2-1)\sigma_s^2+G}{2Q^2} - \frac{Q^2}{4}\right]^3 - 1 - \sigma_s^2 - \frac{Q^2}{18}\right\} = 2\left[H + (\lambda - |p|)\sigma_s^2 + \frac{\lambda}{3}\sigma_s^4\right\}, \quad Q \equiv \Phi''(0). \quad (41)$$

At $p = -1$ and at small $|\sigma_s|$ we obtain from this

$$\Phi_c(0) \approx -Q_c \approx [3^{1/2}(\lambda-1)|\sigma_s|]^{1/2}\,\mathrm{sgn}\,\sigma_s, \quad (42)$$

where the difference of the coefficient at $|\sigma_s|^{1/2}$ from that given by (29) is ~3%.

To obtain reliable information on the dependence of Q on p in the vicinity of $p = -1$ we solved Eq. (11) with the boundary conditions (12) with a computer. The parameters chosen were $\sigma_s = 0, 2; \lambda = \sqrt{2}$. The calculation results are shown in Fig. 1 (points). The figure shows also plots calculated from the approximate expression (41), which differ from the "exact" (computer) results by not more than 5% in the indicated p interval. It can thus be assumed that the appropriate formula (41) yields in the case $|\sigma_s| \ll 1$ a satisfactory solution of the problem of the temperature dependence of the surface capacitance near the transition point.

It follows from (41) that Q (as well as $\Phi(0)$) is a nonanalytic function of $T - T_c$, and has a discontinuous

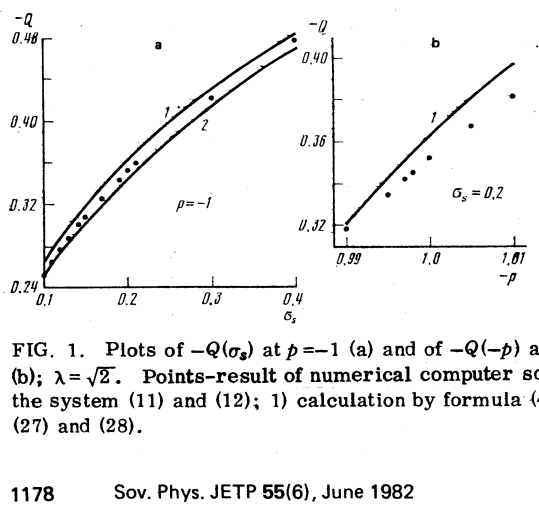

FIG. 1. Plots of $-Q(\sigma_s)$ at $p = -1$ (a) and of $-Q(-p)$ at $\sigma_s = 0.2$ (b); $\lambda = \sqrt{2}$. Points-result of numerical computer solution of the system (11) and (12); 1) calculation by formula (41), 2) by (27) and (28).

second derivative. The same holds for the capacitance, the singularity δc_s of which is determined near the transition point by the expression

$$\delta c_s = 3^{1/4}(2H-G)/(\lambda-1)^{3/4}|\sigma_s|^{1/2}, \quad |\sigma_s| \ll 1. \quad (43)$$

Calculating the derivatives with respect to temperature and taking (34), (40), and (13) into account we have

$$\left.\frac{d^2\delta c_s}{dT^2}\right|_{T_c-0} = \frac{32\gamma^2}{3^{1/2}(\lambda-1)^{5/2}|\sigma_s|^{1/2}}, \quad \left.\frac{d^2\delta c_s}{dT^2}\right|_{T_c+0} = 0. \quad (44)$$

A propos these results, the following remarks are in order. The surface charge density σ was regarded everywhere above as an external given parameter. Yet it is clear that under conditions of thermodynamic equilibrium the quantity σ_s (and ρ_s) must itself be determined by the minimum condition that the free energy (5) be a minimum with respect to variation of $\delta\sigma_s$. Taking this into account and using the equilibrium conditions (6), (7), and (9) we arrive at the sought equation

$$\Phi(0) + \lambda Q = Z_0 D^{1/2}(\varepsilon/4\pi g)^{3/4},$$

which, together with (31) and (41), allows us to express the equilibrium density charge located on the surface proper in terms of the system parameters. In this case, since both the volume and surface (q, which enters in λ) parameters are within the framework of the Landau theory regular functions of $T - T_c$, the only singularity of the capacitance is contained as before in $2H-G$, although the coefficient of $2H-G$ in δc_s will now differ from (43).

5. DISCUSSION OF RESULTS

We have analyzed above, on the basis of the Landau model, the character of the singularity that determines the temperature dependence of the surface capacitance in the vicinity of the point of the volume transition of a SC into a spatially inhomogeneous state. The discontinuity of the second derivative of the surface quantity is evidence of the appearance, in the capacitance c_s, of singularities that are typical of the second-order phase transition that takes place in the bulk of the crystal. It can therefore be stated that the singular part of d^2c_s/dT^2 in the vicinity of T_c will coincide (apart from a numerical factor) with the singular part of the bulk heat capacity.

Zekunde and Bukun[15] reported the results of measurements of the surface capacitance of the SC $[C_5H_5NH]Ag_5I_6$, in which an anomalous behavior of c_s is observed near ≈35 °C. A characteristic heat-capacity peak was noted earlier[18] near this very same temperature, but x-ray methods did not reveal a transition in this temperature region. It can be suggested that these anomalies are due to the transition of the superionic crystal $[C_5H_5NH]Ag_5I_6$ into a spatially inhomogeneous phase corresponding to the appearance of the CDW considered above. The qualitative behavior of the temperature dependence of the surface capacity on the vicinity of the transition point[15] does not contradict the possibility of the type of heat capacity as a result of the existence of a singularity of d^2c_s/dT^2. More precise experiments are needed for a clear-cut answer

to this question.

To my knowledge, in none of the investigations listed in the Introduction, in which a spatially inhomogeneous state of SC was observed, were the surface properties studied. In light of the statements made above concerning the experiments in Refs. 9 and 10 it is of interest to study the correlation of the singularities of the surface and bulk properties of SC.

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APPENDIX

Equation (35), written in the form

$$y^{IV}+2\{(2-|p|)-2(|p|-1)\cos 2\xi\}\,y''+y=0, \tag{A1}$$

has periodic coefficients, and its solution can be obtained in the following manner. We represent the solution of (A1) in series form:

$$y=\sum_{n=-\infty}^{\infty}C_n\exp[(\omega+2ni)\xi], \tag{A2}$$

where ω is the so-called characteristic exponent.[19] Substituting (A2) in (A1) and equating coefficients of like exponentials, we obtain the recurrence formula

$$C_n+\{\gamma_n^{(-)}(\omega)C_{n-1}+\gamma_n^{(+)}(\omega)C_{n+1}\}=0, \tag{A3}$$

where

$$\gamma_n^{(\pm)}(\omega)=[2(n\pm1)-\omega i]^2\theta_0/[(2n-\omega i)^4-2h(2n-\omega i)^2+1]$$

and we put

$$\theta_0\equiv 2(|p|-1)>0,\quad h\equiv 2-|p|<1.$$

It follows from (A3) that

$$\frac{C_n}{C_{n-1}}=-\cfrac{[2(n-1)-\omega i]^2\theta_0}{(2n-\omega i)^4-2h(2n-\omega i)^2+1+[2(n+1)-\omega i]^2\theta_0 C_{n+1}/C_n}\equiv R_n(\omega). \tag{A4}$$

Applying this relation in succession, we obtain a converging infinite continued fraction $R_n(\omega)$. On the other hand, from (A3) we have also

$$\frac{C_n}{C_{n+1}}=-\cfrac{[2(n+1)-\omega i]^2\theta_0}{(2n-\omega i)^4-2h(2n-\omega i)^2+1+[2(n-1)-\omega i]^2\theta_0 C_{n-1}/C_n}\equiv L_n(\omega), \tag{A5}$$

where $L_n(\omega)$ is again an infinite continued fraction. To determine ω, we have the equation

$$L_0(\omega)R_1(\omega)=1. \tag{A6}$$

As $\theta_0\to 0$, Eq. (A6) has a solution $\omega=-i+\delta$, $|\delta|\ll 1$. We obtain the value of δ, assuming it to be real. Taking the principal terms into account, we have from (A.6)

$$1=(1-i\delta)^2(1+i\delta)^2\theta_0^2/[(1-i\delta)^4-2h(1-i\delta)^2+1-9\theta_0^2/64]\,[(1+i\delta)^4-2h(1+i\delta)^2+1-9\theta_0^2/64].$$

The root δ with the minimum value of $|\delta|$, i.e., corresponding to the solution that decreases most slowly at infinity, turns out to be

$$\delta=-(\theta_0/2)^{1/h}=-(|p|-1)^{1/h}.$$

It follows from (A4) and (A5) that in this case $C_1=C_0$, $C_{-1}/C_0\sim\theta_0$ etc. Taking this into account we obtain Eq. (36) of the text.

[1)] A special case of systems in which intrinsic defects can exhibit liquid properties are quantum crystals.[5] In SC, just as in quantum crystals, the number of sites of one of the sublattices is larger than the corresponding objects. Although the analogy is incomplete (an SC is a system with Coulomb interactions, and furthermore quantum effects are of no importance for it), we shall sometimes use it.

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