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Translated by Thomas Markvart

Phase transitions in superionic crystals induced by an electric field

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(Presented by Academician I. M. Lifshits, June 3, 1977)

(Submitted April 28, 1977)

Dokl. Akad. Nauk SSSR 236, 332-335 (September, 1977)

PACS numbers: 61.50.Ks, 61.70.Bv

1. Superionic crystals (solid electrolytes) are a special class of ionic crystals characterized by anomalously high ionic conductivity which develops abruptly at some temperature characteristic of a given crystal.^{1,2} This peculiarity is caused by a phase transition of the first kind, which causes an abrupt disordering of one of the ionic sublattices (usually the cation) while the other sublattice remains rigid. The theory of temperature phase transitions in superionic crystals, based on consideration of additional interactions occurring in the system because of disordering, has been considered in a number of studies (Refs. 3-7).

The application of an external electric field can have a significant effect on these phase transitions and leads to qualitatively new effects.

2. We will consider a crystal containing in a unit volume N lattice points and N' interstitial positions, over which cations are distributed. We denote the cation concentration at interstices by n_1 , and the vacancy concentration left by them at lattice points by n_2 , while in an electric field $n_1 \neq n_2$. For chemical potentials $\mu_{1,2}$ of cations at interstices and vacancies, within the framework of the mean-field approximation we have

$$\mu_1 = \mu_0 + w + e\varphi + kT \ln \frac{n_1}{N' - n_1} - kT \ln Z_1 - \lambda_1 \frac{n_1}{N} - \lambda_{12} \frac{n_2}{N}; \quad (1)$$

$$\mu_2 = -\mu_0 + e\varphi + kT \ln \frac{n_2}{N - n_2} + kT \ln Z_2 - \lambda_2 \frac{n_2}{N} - \lambda_{12} \frac{n_1}{N}; \quad (2)$$

Here μ_0 is the cation energy at a lattice point, and $\mu_0 + w$ is the cation energy at an interstice in the absence of interaction between defects; φ is the electric field potential; $Z_{1,2}$ are the vibrational partition functions for cations at interstices and lattice points. The last two terms in Eqs. (1), (2) correspond to the presence in the system of binary interactions; λ_1 , λ_2 , and λ_{12} are constants describing the interactions (possibly indirect) of cations among themselves, vacancies among themselves, and cations with vacancies.

Transforming in Eqs. (1) and (2) to dimensionless variables $x_{1,2} = n_{1,2}/N$ and denoting by x_0 the quantity $x = x_2$ for $\varphi = 0$, we obtain

$$-e\varphi = kT \ln \frac{x_1(N'/N - x_0)}{x_0(N'/N - x_1)} - \lambda_1(x_1 - x_0) - \lambda_{12}(x_2 - x_0); \quad (3)$$

$$e\varphi = kT \ln \frac{x_2(1 - x_0)}{x_0(1 - x_2)} - \lambda_2(x_2 - x_0) - \lambda_{12}(x_1 - x_0). \quad (4)$$

The quantity x_0 is determined from the condition $\mu_1 = \mu_2$:

$$w - \lambda_0 x_0 = kT \ln [(N'/N - x_0)(1 - x_0)/x_0^2], \quad (5)$$

where $\lambda_0 = \lambda_1 + \lambda_2 + 2\lambda_{12}$ and $\chi \equiv Z_1/Z_2$.

Equation (5) describes the thermodynamics of disordering in the absence of an electric field. If $\lambda_0 > 0$, upon change in system temperature phase transitions are possible, which are accompanied by discontinuous changes in x_0 . These temperature transitions were analyzed in detail in Ref. 6.

3. To realize the transitions (described below) induced by an electric field at constant temperature, it is necessary that the condition $\lambda_1 > 0$ or $\lambda_2 > 0$ be fulfilled, which is more severe than $\lambda_0 > 0$. We will demonstrate the existence of phase transitions induced by an electric field for the case $\lambda_{12} = 0$ and $\lambda_1 > 0$, $\lambda_2 \leq 0$ or $\lambda_2 > 0$, $\lambda_1 \leq 0$. Moreover, we will limit ourselves to the case $N' = N$ (symmetric system), considering that these effects should appear for any relationship between N' and N . From Eqs. (3) and (4), with consideration of the above, we obtain

$$x_{1,2}(1 - x_0) = x_0(1 - x_{1,2}) \exp \{ [\lambda_{1,2}(x_{1,2} - x_0) - e\varphi] / kT \}. \quad (6)$$

Equation (6) describes the dependence of $x_{1,2}$ on φ . If the quantity λ_1 (or λ_2) is negative, then x_1 (or x_2) is a single-valued function of φ . If, however, $\lambda_1 > 0$ (or $\lambda_2 > 0$) it is not hard to see that the corresponding functions for the condition $\lambda_1 > 4kT$ (or $\lambda_2 > 4kT$) have S-shaped segments (Fig. 1). From this it follows immediately that at certain values of φ there must be discontinuities in x_1

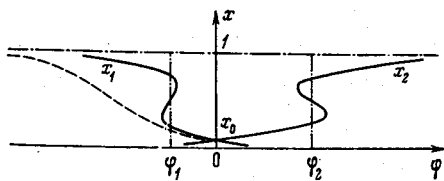


FIG. 1. Schematic representation of interstitial ion concentration (x_1) and vacancy concentration (x_2) versus potential $x_0 < 1$, $\lambda_{1,2} > 4kT$; the dashed line is for $\lambda_1 = 0$.

(if $\lambda_1 > 4kT$) and x_2 (if $\lambda_2 > 4kT$). From the condition of thermodynamic equilibrium in a system with a variable number of particles it follows that in the case considered the transition potentials φ_1 and φ_2 correspond to the centers of symmetry of the S-shaped sections of the curves $x_1(\varphi)$ and $x_2(\varphi)$; also the values $x_{1,2} = 1/2$ must satisfy Eq. (6) at $\varphi = \varphi_{1,2}$:

$$\varphi_{1,2} = \mp kT \ln [(1-x_0)/x_0] \pm \lambda_{1,2}(1/2 - x_0). \quad (7)$$

The function $x_1(\varphi)$ for $\varphi < \varphi_1$ is described (Fig. 1) by the upper branch of the curve, and for $\varphi > \varphi_1$, by the lower branch. The function $x_2(\varphi)$ for $\varphi < \varphi_2$ is described by the lower branch, and for $\varphi > \varphi_2$, by the upper. Denoting the solutions $x_{1,2}$ for $\varphi_{1,2}$ lying on the upper branch by $x_{1,2}^u$, and on the lower branch by $x_{1,2}^l$, we obtain from Eqs. (6) and (7) for the concentration jump $\Delta_{1,2} = x_{1,2}^u - x_{1,2}^l$ the equation

$$(1 + \Delta_{1,2}) / (1 - \Delta_{1,2}) = \exp\{\lambda_{1,2}\Delta_{1,2}/kT\}. \quad (8)$$

Field-induced phase transitions can be realized even at crystal parameter values for which temperature transitions are absent.¹⁾

4. The predicted transitions should lead to anomalous charge distributions in the surface regions.

Let the potential in the interior of a semiinfinite crystal be equal to zero, with potential φ_0 at the surface. Within the framework of the self-consistent field theory the potential distribution in the crystal volume is given by the equation

$$d^2\varphi/dz^2 = -4\pi N e \varepsilon^{-1} [x_1(\varphi) - x_2(\varphi)] \quad (9)$$

(here ε is the static dielectric permittivity of the crystal); the coordinate z is perpendicular to the surface, so that $\varphi = \varphi_0$ at $z=0$, $\varphi = 0$ at $z \rightarrow \infty$.

Integrating Eq. (9) with the condition $d\varphi/dz = 0$ at $\varphi = 0$, we obtain

$$\frac{d\varphi}{dz} = -(\text{sgn } \varphi_0) \left[\frac{8\pi e N}{\varepsilon} \int_0^\varphi (x_2(\varphi) - x_1(\varphi)) d\varphi \right]^{1/2}. \quad (10)$$

For definiteness we will assume that $\lambda_1 > 4kT$ and $x_0 < \exp(-\lambda_1/2kT)$, so that $\varphi_1 < 0$. If $\varphi_1 < \varphi_0 < 0$, then $x_1(\varphi)$ and $x_2(\varphi)$ are continuous functions of φ (and the coordinate z) over the entire volume-charge region. If $\varphi_0 < \varphi_1$, then the volume-charge region proves to be divided into two subregions: normal and anomalous (Fig. 2), by the plane $z = z_*(\varphi)$, where $\varphi = \varphi_1$. In the normal region the distributions of interstitial cations and vacancies are close to the normal Boltzmann form. On the boundary of the regions the concentration of one type of charges changes discontinuously, so that the anomalous

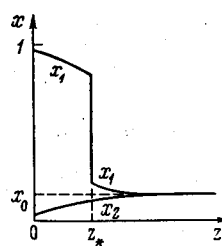


FIG. 2. Spatial distribution of interstitial ions (x_1) and vacancies (x_2) near surface; $\varphi_0 < \varphi_1 < 0$; z_* , boundary of anomalous region.

region is characterized by dominance of carriers of one sign (in the given case, interstitial cations). If $\lambda_1 \gg 4kT$, so that according to Eq. (8) $\Delta_1 \approx 1$ ("strong" transition), from Eq. (6) we obtain

$$x_2(\varphi) = x_0 \exp\{e\varphi/kT\} \text{ for } \text{всех } \varphi < 0, \\ x_1(\varphi) = \begin{cases} x_0 \exp\{-e\varphi/kT\} & \text{for } \varphi_1 < \varphi < 0, \\ 1 - x_0 \exp\{-2e\varphi_1/kT\} \exp\{e\varphi/kT\} & \text{for } \varphi < \varphi_1. \end{cases} \quad (11)$$

Integrating Eq. (10), we find for the thickness of the anomalous region

$$z_* = 4\kappa^{-1} x_0 \left[\sqrt{\frac{e|\varphi_1 - \varphi_0|}{4x_0 kT} + \text{sh}^2\left(\frac{e\varphi_1}{2kT}\right)} - \text{sh} \frac{e|\varphi_1|}{2kT} \right], \quad (12)$$

where $\kappa^{-1} \equiv (8\pi e^2 N x_0 / \varepsilon kT)^{-1/2}$ is the Debye length of the crystal. Thus the thickness of the anomalous region increases linearly for a small difference $\varphi_0 - \varphi_1$ and is proportional to the square root for sufficiently large values of $|\varphi_0|$.

We note that together with the anomalous region considered here, it is also possible for a narrow layer to exist near the surface⁸ with a structure differing from the bulk structure.

5. One of the simplest methods of detecting a field-induced transition is measurement of the differential capacitance C of the volume-charge region. Considering that the excess charge of a unit surface is

$$Q = eN \int_0^\infty [x_1(z) - x_2(z)] dz = -eN \int_0^\infty \frac{x_1(\varphi) - x_2(\varphi)}{d\varphi/dz} d\varphi,$$

for the capacitance $C = dQ/d\varphi$, with consideration of Eq.

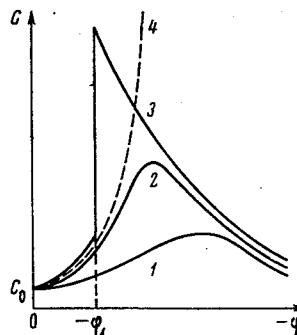


FIG. 3. Differential capacitance $C(\varphi_0)$ (schematic curves). 1) $\lambda_1 < 0$; 2) $\lambda_1 = 0$; 3) $\lambda_1 > 4kT$; 4) $\lambda_1 = 0$, no charge saturation.

(10), we obtain

$$C = eN |x_2(\varphi_0) - x_1(\varphi_0)| \left[\frac{8\pi eN}{\varepsilon} \int_0^{\infty} (x_2(\varphi) - x_1(\varphi)) d\varphi \right]^{-1/2}. \quad (13)$$

A detailed analysis of the function $C(\varphi_0)$ in ionic crystals in the absence of the transitions considered here was presented in Ref. 9.

As follows from Eq. (13), in the general case induced transitions at $\varphi_0 = \varphi_1$ and $\varphi_0 = \varphi_2$ should lead to discontinuities in $C(\varphi_0)$. In particular, from Eqs. (11) and (13) we obtain

$$C = C_0 \begin{cases} \text{ch}(e\varphi_0/2kT); & \varphi_1 < \varphi_0 < 0, \\ \left[4x_0 \left(\frac{e|\varphi_0 - \varphi_1|}{kT} + 4x_0 \text{sh}^2 \left(\frac{e\varphi_1}{2kT} \right) \right) \right]^{-1/2}, & \varphi_0 < \varphi_1 \end{cases} \quad (14)$$

Here $C_0 \equiv \varepsilon/(4\pi\kappa^{-1})$. From Eq. (14) it follows (Fig. 3) that the transition from the standard potential dependence of capacitance, i.e., $C = C_0 \cosh(e\varphi_0/2kT)$ to the function $C \propto (|\varphi_0| + \text{const})^{-1/2}$, caused by the effect of charge saturation⁹ (i.e., by the fact that $x_{1,2} \leq 1$ for any φ_0), must occur discontinuously.

Since the high ionic conductivity is caused by high mobility of interstitial cations, the development of an anomalous surface region in the case considered here of $\varphi_0 < 0$ and a discontinuity in x_1 should be accompanied by a sharp increase in the ionic conductivity. If $\varphi_0 > 0$ so that the discontinuity (at potential φ_2) occurs in x_2 , then despite the discontinuity in capacitance, no sharp growth in surface conductivity should be observed.

In Eqs. (11), (12), and (14) the variant $x_0 \ll 1$ was analyzed. For $1 - x_0 \ll 1$ development of an anomalous surface region is also possible. The general form of the function $C(\varphi_0)$ is of the same character as for $x_0 \ll 1$, i.e., the function $C(\varphi_0)$ can have discontinuities. The difference reduces essentially to a change in the value of the parameter C_0 . The value of the ionic conductivity of the anomalous region developing at a potential $\varphi_0 = \varphi_1(x_0)$ (with $\varphi_1 > 1$) is now sharply reduced in comparison to the volume value.

6. The predicted effect of development of a surface layer with anomalous properties, whose dimensions may be controlled by the applied potential, should appear in a number of physicochemical processes sensitive to charge distribution near the boundary.

¹⁾In particular, this implies that such transitions are possible in ionic crystals in which temperature anomalies in ionic conductivity have not been observed.

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Translated by Joseph F. Caffrey

Gasdynamic equations and one-dimensional collisionless motion of a degenerate plasma consisting of heavy neutral particles

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(Submitted October 6, 1976)

Dokl. Akad. Nauk SSSR **236**, 336-338 (September 1977)

PACS numbers: 47.10.+g

It is well known that hydrodynamic equations can be used approximately under certain conditions in the one-dimensional collisionless motion of a plasma. In this case the local pressure is obviously

$$p(x) = m \int n(u, x) (u - \bar{u})^2 du.$$

Comparing it with the expression for the density

$$\rho(x) = m \int n(u, x) du,$$

we find

$$p = \rho(\overline{u^2} - \bar{u}^2) = \rho[\overline{u^2} - (\bar{u})^2].$$

The concept of the pressure is not connected with the interaction (by collisions) of the particles. It is known that the one-dimensional motion of a collisionless plasma leads to an effective adiabatic index equal to 3, i.e., $p \sim \rho^3$. This result follows from the Liouville theorem: In one-dimensional motion along the x axis the role of the pressure is played by the component T_{xx} of the strain tensor (the tensor is not reduced to a scalar and isotropy of the pressure, i.e., Pascal's law, is violated). T_{xx} is expressed in terms of integrals containing u_x , and the width