Mass transport in ionic crystals induced by the ponderomotive action of a high-frequency electric field

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A possible explanation of the experimentally observed enhancement of mass transport processes in ionic crystalline solids under the action of high-frequency (HF) electromagnetic fields is suggested. It is based on the ponderomotive effects that occur due to the nonlinear interaction of the HF electric field with the space charge induced by it within the crystal near its surface. Due to the action of the tangential component of the field in the near-surface amorphized layer, where the vacancy mobility is greater than in the bulk, the ponderomotive effects are found to be of sufficient strength to manifest themselves in the experimental conditions.

Enhancement of mass transport processes in ionic crystalline solids under the action of high-frequency (HF) electromagnetic fields can be considered experimentally established to date. It has been observed in numerous experiments in such areas as atomic diffusion in single crystals,[1] solid-state reactions,[2] sintering of ceramics,[3] etc. In recent years, a number of attempts to find out a physical mechanism responsible for phenomena of that kind have been undertaken (see Ref. 4 for a brief review), however, no theory able to explain them quantitatively has been developed to date.

This paper is intended to show that the mass transport enhancement can be attributed to the ponderomotive action of the HF electric field on the mobile charge carriers in crystalline solids. The macroscopic (not oscillating in time) matter fluxes arise in this case due to the nonlinear interaction of the HF electric field with the space charge induced by it within the crystal near its free surface. The possibility of similar effects of rectification of HF vacancy drift currents was demonstrated by us earlier.[5] In fact, only the effect associated with the ponderomotive action of the normal (to the surface of the crystal) component of the HF electric field was considered in that paper. However, recent analysis has shown that if the mobility of charge carriers in the near-surface layer of the crystal is greater than in the bulk, then the action of the tangential component of the HF electric field can result in much more intense mass transport. This effect that seems to be of general physical interest is given most attention in this paper.

It should be noted that amorphized layers with greater vacancy diffusivity are known to actually exist near the surface of real crystals.[6] The estimates made with realistic values of parameters show that the effects obtained in this study are of sufficient strength to provide the basis for explanation of the above referred experiments.

The analysis that is the subject of this paper is carried out on the basis of the model that is basically similar to that used in Ref. 5. We consider an ionic crystal with the vacancy mechanism of diffusion predominating.[7] The flux of vacancies of each sort is determined by diffusion and drift:

$$\mathbf{J}_\alpha = -D_\alpha \nabla N_\alpha + D_\alpha N_\alpha \frac{e_\alpha}{kT}\mathbf{E}, \tag{1}$$

where the subscripts are introduced to distinguish vacancies of different sorts, $\mathbf{J}_\alpha$ is the flux density, D_α is diffusivity, e_α is the electric charge, N_α is dimensionless (normalized to the density of sites in the crystalline lattice) concentration of vacancies of sort α, $\mathbf{E}$ is the vector of electric field, and the vacancy mobility is expressed with the help of the Nernst-Einstein relation.

As a measure of mass transport, we will use the velocity $\mathbf{V}$ of deformation, i.e., of crystal surface displacement, which is connected with the total vacancy flux density, $\mathbf{J}$, on the surface:

$$\mathbf{V} = -\mathbf{n}\cdot(\mathbf{n}\cdot\mathbf{J}\big|_S). \tag{2}$$

Here $\mathbf{J}\big|_S$ is the value of $\mathbf{J}$ on the crystal surface and $\mathbf{n}$ is the outward unit normal to the surface.

In this Brief Report we will for simplicity restrict our consideration to a crystal having two sorts of vacancies with opposite charges $e_{1,2} = \pm e$ and equal diffusivities $D_{1,2} = D$.[8] As follows from the general results presented in Ref. 5, in this case the slowly varying (quasistationary) charge separation field is absent, and the quasistationary components of concentrations of vacancies of two sorts are equal. This allows us to formulate the problem of quasistationary vacancy flows for the total averaged vacancy concentration $N = \sum\langle N_\alpha\rangle$ and the total averaged vacancy flux

$$\mathbf{J} \equiv \sum \mathbf{J}_\alpha = -D\nabla N + \frac{\omega}{kT} D\langle\rho\mathbf{E}\rangle. \tag{3}$$

Here ω is the vacancy volume, $\rho = \sum e_\alpha N_\alpha/\omega$ is the density of electric charge (oscillating with the field frequency) associated with vacancies, and the angular brackets denote averaging over the period of the HF field. It should be noted that the second term on the right of Eq. (3) expresses vacancy drift under the action of the averaged ponderomotive force.[9] Our purpose is to calculate this force and the results of its action on vacancies.

For a small-sized crystal (whose dimensions are much less than the electromagnetic wavelength inside it) the

problem of finding ρ and $\mathbf{E}$ can be reduced to solving equations of quasielectrostatics

$$\begin{aligned} \text{rot } \mathbf{E} &= 0; \\ \text{div } \mathbf{E} &= 4\pi\rho \end{aligned} \tag{4}$$

(here the lattice dielectric constant is assumed equal to unity for simplicity) together with the continuity equation

$$\partial\rho/\partial t + \text{div } \mathbf{j} = 0. \tag{5}$$

The density of the ionic electric current $\mathbf{j} \equiv \sum e_\alpha \mathbf{J}_\alpha/\omega$ in the case being considered ($e_{1,2} = \pm e$, $D_{1,2} = D$) obeys the equation

$$\mathbf{j} = -D\nabla\rho + G\mathbf{E}, \tag{6}$$

where $G = 2N_0e^2D/\omega kT$ is the ionic conductivity of the crystal (we assume that the HF electric field perturbs the vacancy concentration only slightly). The boundary conditions for Eqs. (6)–(8) at the surface of the crystal should correspond to continuity of the normal and tangential component of electric field, and to absence of the normal component of electric current.

The quasistationary flux of vacancies in a single crystal with no other defects than vacancies and without vacancy sources and sinks in the bulk obeys Fick's equation

$$\text{div } \mathbf{J} = 0. \tag{7}$$

For known ρ and $\mathbf{E}$, the quasistationary picture of vacancy flows is completely determined by Eqs. (3) and (7) with the standard boundary condition at the surface of crystal:[10]

$$N\big|_S = N_0 \exp(\sigma\omega/kT) \approx N_0(1 + \sigma\omega/kT), \tag{8}$$

where N_0 is temperature-dependent bulk equilibrium concentration of vacancies, $\sigma \equiv \sigma_{ik}n_in_k$, and σ_{ik} is the stress tensor on the crystal surface.

The quasistationary problem (7) and (8), as well as the HF problem (4)–(6), can be solved up to the end only for certain simple geometries (e.g., for a spheric body in the uniform external HF field). However, some features of solutions can be revealed for rather general cases. In particular, it can be shown[5] that in a homogeneous crystal the HF ionic charge is localized in a thin near-surface layer, the thickness of which is determined by the smaller of the Debye-Huckel radius $\lambda = \sqrt{\omega kT/8\pi e^2N_0}$ and the characteristic diffusion length $l = \sqrt{D/\Omega}$ (Ω is the frequency of the applied electric field).

In real crystals, due to the inhomogeneity of ionic conductivity, the applied electric field induces electric charge within the whole amorphized layer (if its thickness, a, is greater than λ and l). Nevertheless, the thickness of the charge layer remains small compared with the dimensions of the crystal. This simplifies the analysis of the quasistationary problem significantly.

For better understanding of the main result of this paper it is convenient to consider separately the ponderomotive actions produced on the near-surface charge layer by the normal and tangential components of the HF electric field. Since the thickness of the charge layer is small, the normal component of the field can be excluded from the quasistationary equations with the help of the substitution

$$\tilde{\mathbf{J}} = -D\nabla\tilde{N};$$
$$\tilde{N} = \begin{cases} N & \text{in the bulk;} \\ N - \frac{\omega}{kT}\int\langle\rho\,\mathbf{n}\cdot\mathbf{E}\rangle dx & \text{in the charge layer,} \end{cases} \tag{9}$$

where x is the coordinate counted along the outward normal to the surface, and the integration starts from the inner boundary of the charge layer. Note that the normal component of $\tilde{\mathbf{J}}$ is the same as of the vacancy flux $\mathbf{J}$. Therefore Eq. (2) can be rewritten in the following form:

$$\mathbf{V} = -\mathbf{n}\cdot(\mathbf{n}\cdot\tilde{\mathbf{J}}\big|_S). \tag{10}$$

With the substitution (9), if only the normal component of the HF field is considered, the problem of plastic deformation of the crystal under its ponderomotive action coincides formally with the problem of crystal deformation under external uniaxial mechanical stresses:

$$\begin{aligned} \text{div } \tilde{\mathbf{J}} &= 0; \\ \tilde{N}\big|_S &= N_0(1 + \sigma_E\omega/kT), \end{aligned} \tag{11}$$

where the role of the mechanical stresses is played by the equivalent stress

$$\sigma_E = -\frac{1}{N_0}\int\limits_{\rho\neq 0}\langle\rho\,\mathbf{n}\cdot\mathbf{E}\rangle dx \tag{12}$$

(the integration is over the whole thickness of the charge layer). Respectively, the velocity of plastic deformation can be estimated in the same way as it is usually done for mechanical stresses:[10]

$$V_{(En)} \simeq \left(D_b + D_a\frac{a}{\Lambda}\right)\frac{N_0}{\Lambda}\frac{\sigma_E\omega}{kT}, \tag{13}$$

where Λ is the scale of nonuniformity of the (equivalent) stress (in a single crystal it is of the order of its dimensions), D_b is the vacancy diffusivity in the bulk (the subscript b will further denote the bulk values), and $D_a \equiv \int\limits_a D dx/a$ is the characteristic value of the diffusivity in the amorphized layer (the integration is over its thickness).

As follows from Eqs. (12) and (13), the ponderomotive action of the normal component of the electric field appears to be N_0^{-1} times more effective than would be the action of the mechanical stress equal to the field pressure $\int\limits_{\rho\neq 0}\langle\rho\,\mathbf{n}\cdot\mathbf{E}\rangle dx$. This result (obtained in our previous paper[5]) can be understood easily if we realize that the electric field acts on the charged vacancies, i.e., directly on the atoms neighboring an empty site of the lattice—the only atoms that are able to move—whereas the mechanical stresses are applied to the whole crystal in which most of the atoms are fixed.

As for the tangential component $\mathbf{E}_\tau$ of the HF field, it

cannot be excluded from the quasistationary equations (7) and (8), therefore its action cannot be expressed explicitly in terms of equivalent stresses appearing in the boundary conditions only. With the same substitution (9) maintained, the term with $\langle \rho \mathbf{E}_\tau \rangle$ plays the role of the source of particles (here "particles" should be understood as "effective particles" whose concentration is $\tilde{N}$):

$$\operatorname{div} \tilde{\mathbf{J}} = -\operatorname{div} \left(\frac{\omega}{kT} D \langle \rho \mathbf{E}_\tau \rangle \right). \tag{14}$$

Since this source is localized in the thin near-surface charge layer, in the frame of the quasistationary problem virtually all "particles" originating from it go to the surface. Therefore, the contribution into the velocity of crystal deformation (in other words and with the opposite sign, into the normal component of the vacancy flux on the surface) made by the ponderomotive action of the tangential component of the field is

$$\mathbf{V}_{(E\tau)} = \mathbf{n} \frac{\omega}{kT} \int\limits_{\rho \neq 0} \operatorname{div} \left(D \langle \rho \mathbf{E}_\tau \rangle \right) dx. \tag{15}$$

Comparing this contribution with that made by the normal component of the HF field, we should remember that the area of localization of the space charge basically coincides with the amorphized layer (if the latter is not too thin). Hence the value of the integral in Eq. (15) is basically determined by the diffusivity in the amorphized layer, i.e.,

$$V_{(E\tau)} \simeq \frac{D_a}{\Lambda} \frac{\omega}{kT} \int\limits_{\rho \neq 0} \langle \rho \mathbf{E}_\tau \rangle dx. \tag{16}$$

It can be seen from Eqs. (13) and (16) that for equal values of $\left| \int\limits_{\rho \neq 0} \langle \rho \, \mathbf{n} \cdot \mathbf{E} \rangle dx \right|$ and $\left| \int\limits_{\rho \neq 0} \langle \rho \mathbf{E}_\tau \rangle dx \right|$ the velocity of the deformation caused by the ponderomotive action of the tangential component appears approximately $(D_b/D_a + a/\Lambda)^{-1}$ times greater than the velocity of the deformation caused by the action of the normal component. On the whole, the ponderomotive action turns out to be equivalent to the action of mechanical stresses that are

$$[N_0 (D_b/D_a + a/\Lambda)]^{-1} \tag{17}$$

times greater than the pressure of the field. The efficiency of the ponderomotive action is thus substantially greater than it was predicted in Ref. 5.

The actual distribution of ρ and $\mathbf{E}$ can be obtained by solving the electrodynamic problem (4)–(6) in a concrete geometry using standard methods. The complex dielectric permittivity ϵ of the ionic crystal can be introduced in our approximation as

$$\epsilon = 1 + i 4\pi G/\Omega. \tag{18}$$

For example, inside a spheric crystal with homogeneous vacancy diffusivity the electric field is uniform, and the charge density in the frame of ϵ description equals zero everywhere except the crystal surface $r = R$:

$$E_r = \frac{3E_0 \cos\theta}{\epsilon + 2}; \quad E_\theta = -\frac{3E_0 \sin\theta}{\epsilon + 2}; \qquad \rho = \frac{1}{4\pi} \frac{3E_0(\epsilon - 1)\cos\theta}{\epsilon + 2} \delta(r - R), \tag{19}$$

where E_0 is the intensity of the external electric field. It can be seen from Eqs. (19) that $\langle \rho E_\theta \rangle = \operatorname{Re}(\rho E_\theta^*)/2 = 0$ (i.e., ρ and E_θ have the phase shift $\pi/2$). Therefore, within this approach the tangential component of the HF field does not contribute into the deformation velocity.

Things go quite different if there is the amorphized layer near the crystal surface. If the layer is thin, i.e., $a \ll R$, then using the fact that the tangential component of the field almost does not change in it we can obtain the following approximate solution of the electrodynamic problem in the layer:

$$E_r = \frac{3E_0 \cos\theta}{\tilde{\epsilon}(R) + 2} \frac{\tilde{\epsilon}(r)}{\epsilon(r)}; \quad E_\theta = -\frac{3E_0 \sin\theta}{\tilde{\epsilon}(R) + 2};$$
$$\rho = \frac{1}{4\pi} \frac{3E_0 \cos\theta}{\tilde{\epsilon}(R) + 2} \left\{ \tilde{\epsilon}(r) \frac{\partial}{\partial r} \left[\frac{1}{\epsilon(r)} \right] + \tilde{\epsilon}(R) \left[1 - \frac{1}{\epsilon(R)} \right] \times \delta(r - R) \right\}, \tag{20}$$

where $\tilde{\epsilon}(r) = \epsilon_b + (2/R) \int_{R-a}^{r} (\epsilon - \epsilon_b) dr$, and the integration starts from the inner boundary of the amorphized layer. The contribution of the tangential component E_θ into the deformation velocity is now nonzero and can be obtained from Eq. (15). Performing the integration, we obtain

$$V_{(E\tau)} = \frac{D_R}{R} \frac{\omega}{kT} \frac{E_0^2}{8\pi} \frac{9(3\cos^2\theta - 1)}{|\tilde{\epsilon}(R) + 2|^2} \left[\frac{\arctan \epsilon_R''}{\epsilon_R''} - 1 - \frac{\arctan \epsilon_b''}{\epsilon_R''} + \frac{\epsilon_b''}{\epsilon_R''} \left(1 + \frac{1}{2} \ln \frac{1 + \epsilon_R''^2}{1 + \epsilon_b''^2} \right) \right], \tag{21}$$

where $\epsilon_b'' = \operatorname{Im} \epsilon_b$, $\epsilon_R'' = \operatorname{Im} \epsilon(R)$, and the subscript R here and further denotes values at the outer boundary of the amorphized layer (at $r = R$). This result allows us to reveal the frequency dependence of the effect. As follows from Eq. (21), the effect vanishes at high frequencies, when Ω becomes much greater than $4\pi G_R$. At such high frequencies the HF field is not perturbed by the crystal, including its amorphized layer, and no electric charge is induced. In the low-frequency limit the effect disappears when $\Omega \ll \max(4\pi G_b, 4\pi G_R a/R)$ because of the decrease in the tangential component of the electric field. In the range between these limits the effect reaches its maximum,

$$V_{(E\tau)\,\max} = -\frac{D_R}{R} \frac{\omega}{kT} \frac{E_0^2}{8\pi} (3\cos^2\theta - 1) \tag{22}$$

[which is consistent with our preliminary estimate (17)], and practically does not depend upon the frequency. It should be noted that the fact that the ponderomotive effect in the optimal frequency range does not depend upon the equilibrium vacancy concentration which (along with the diffusivity) is a thermally-activated quantity can

be a possible explanation of the observed reduction of apparent activation energies for mass transport processes under microwave action.[1]

The quantitative estimates of the described ponderomotive effects require knowledge of the thickness of the amorphized layer and of the vacancy diffusivity in it. The available data on these quantities vary greatly from one experiment to another; however, for ionic crystals with dimensions in the micrometer range and higher it may be taken with sufficient reliability that $D_b/D_a + a/\Lambda \leq 10^{-3}$.[6] The equilibrium vacancy concentration N_0 at temperatures still far enough from the melting point can be as high as 10^{-5}.[10] Hence, if the frequency is within the above specified limits, the action of the electric field $E_0 \simeq 1$ kV/cm [that can be considered a typical value for technological systems of rf and microwave processing (see, e.g., Ref. 3)] whose pressure $p = E_0^2/8\pi$ is of order of 0.1 Pa can become equivalent to the action of mechanical stresses of 10^7 Pa. Stresses of similar magnitude are known to be responsible for the mass transport in such technologies as hot isostatic pressing or sintering of ceramics.[10] This comparison shows that the ponderomotive action may provide an explanation of the experimentally observed enhancement of mass transport in solids under the action of HF fields.

A direct experimental test for the proposed ponderomotive effect may consist in comparative measurements of mass transport properties in a given crystalline material at fixed temperature performed for different frequencies or for different intensities of the applied field. Another idea which was suggested and implemented in Ref. 4 is to measure dc electric currents that should occur in the material due to the ponderomotive action (if the diffusivities of positive and negative vacancies are not equal). The microwave-induced currents observed in these experiments proved to be proportional to the microwave power ($\propto E_0^2$), which is consistent with our model.

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