

Local field effects in ionic conductors

M. E. Lines

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 14 September 1978)

An analysis is carried out of the effects produced by the possibly strong electric dipolar coupling between intracell dielectric response and intercell hopping response in a simple model of thermally activated ionic conductivity. The results suggest the presence of two marked effects. The first is an enhancement of the low-frequency ionic conductivity over the noninteracting equivalent caused by the increase in effective local perturbing field (over the applied field) which is produced by the local vibrational dipoles. The second is the development of an inductive contribution to the real part of the dielectric constant which increases exponentially with increasing temperature and which can easily dominate this response component at moderate carrier concentrations. A diverging conductivity is predicted on approach to a second-order dielectric instability.

I. INTRODUCTION

Theoretical approaches to the problem of particle kinetics in ionic conductors have been vigorously pursued in recent years and have progressed along two distinct paths using a model of ionic motion in a periodic potential. One line of approach¹ has been to concentrate on the motion of noninteracting particles in a specific (say sinusoidal) potential (a problem that has yet to be exactly solved even in one dimension) to locate the high-frequency oscillatory and the low-frequency diffusive regions of dielectric response and to examine the relations between them. The high-frequency response corresponds to localized motion within a single "cell" while the low-frequency diffusive response describes the intercell motion. A second approach² has been to neglect high-frequency characteristics and to concentrate on a more detailed discussion of intercell hopping including hard-core interactions between the hopping ions (i.e., not allowing any two particles to simultaneously occupy the same site).

In real ionic and superionic conductors the itinerant particles are charged ions and must therefore interact strongly with each other through the long-range electric force field in addition to the short-range interactions which dictate the hard-core repulsion. Their in-cell high-frequency motion between "hops" therefore describes a strong optically active local vibrational mode. To date the only effort to discuss the importance of the strong long-range electrical interactions has been performed in a static (domain) context.³

In this paper we attempt to wed the two approaches discussed above and to include the important electric dipole interactions to boot. Obviously such an ambitious project can be initiated only at a comparatively low level of theoretical sophistication and we perform essentially a random-phase an-

alysis incorporating the electric dipole forces in the form of local fields that couple the oscillatory and hopping characteristics of the total dielectric response. The model, which is set out in detail below, has some relevance for the very active field of superionic conductivity but will be discussed here with an eye on potential dielectric instabilities that might result from the ordering effects of interacting lattice dipoles.

We address then the question of what interplay might be expected between in-cell dielectric characteristics and ionic conductivity in dielectrically soft ionic conductors via the strong electric dipole forces that couple them. The question is pertinent in the light of the recent preparation of dielectrically soft glasses⁴ and of the observation of significant ionic conductivity at and above room temperature in those containing alkali-metal cations.⁵ It is also a rather general question not necessarily restricted to crystalline or to amorphous materials and we shall attack it by utilizing a simple model that glosses over the details of structure and topology but which is sufficient for determining the fundamentals. Although we lay accent on systems for which the optically active mode associated with the conductivity is fairly soft (and possibly critically soft), since the local-field effects are most dramatic in this context, the results are applicable in a wider sphere of interest.

In order to demonstrate the typical relevance of the simple model to be studied, we first give a little thought to the relationship between the dominant polar mode and the microscopic conduction mechanism in a specific class of materials for which the model might be of some semiquantitative value. Consider, for example, an ABO_3 system made up of dielectrically soft oxygen-octahedral or quasioctahedral units, associated with the B cation, coupled to itinerant alkali-

metal A ions. The "hopping" A cation is, during its in-cell motion, strongly ionically bound to its associated B cation group to give the chemical characterization $A^+(BO_3)^-$ with each A ion carrying a unit positive charge e . The soft dielectric mode for such a system (e.g., the perovskite and pseudoperovskite ferroelectrics) consists of an in-phase motion of the cations against the oxygen framework.⁶ For systems where the A cation is very light and the B cation heavy the "soft-mode" amplitude of the A ion becomes large and that of the B ion small (e.g., in LiTaO_3 the relative Li to O to Ta soft-mode amplitudes are in the ratios⁷ 15:-6:1) so that the mode that dominates the dielectric response approximates that of the A cations vibrating against the anion framework. But this mode is of just the right character to contribute significantly to an attempt motion for A cation hopping in cases for which structural imperfections or lack of stoichiometry allow for such an event.

In the simple model to be examined in this paper, we assume that for an ionic conductor involving a hopping cation A , the A -ion motion between hops is dominated by a single optically active vibrational mode. The important consequence is that the electric field perturbation then experienced by the A ion on application of an external field $E_0(\omega)$ is not $E_0(\omega)$ itself but an internal effective field which is directly proportional to that $E(\omega)$ experienced by this mode. In general, the strong dipolar interactions involved in this motion make $E(\omega)$ larger than $E_0(\omega)$ and shift its phase. The effects are particularly pronounced for a dielectrically soft attempt motion and result in an enhanced ionic conductivity and a contribution to the permittivity which is negative (i.e., inductive) in sign from the hopping motion itself. The latter is proportional to the ionic conductivity and is therefore likely to dominate the in-phase response for systems with high conductivity. It would appear to have already been observed experimentally^{8,9} in some superionic conductors.

II. MODEL

As set out in Sec. I, we adopt a model for which both dielectric response and thermally activated hopping conductivity are describable in terms of a single potential function $V(x)$. The variable x is a configurational coordinate which, in the simplest physical situation, can be taken to be essentially that describing a soft-mode motion of the hopping cation against the anion framework. The in-cell dimension is $2x_M$ with potential barriers of height V_M peaking at $x = \pm x_M$. The precise form of the potential function within the cell "barriers" need not be specified in detail but might be any-

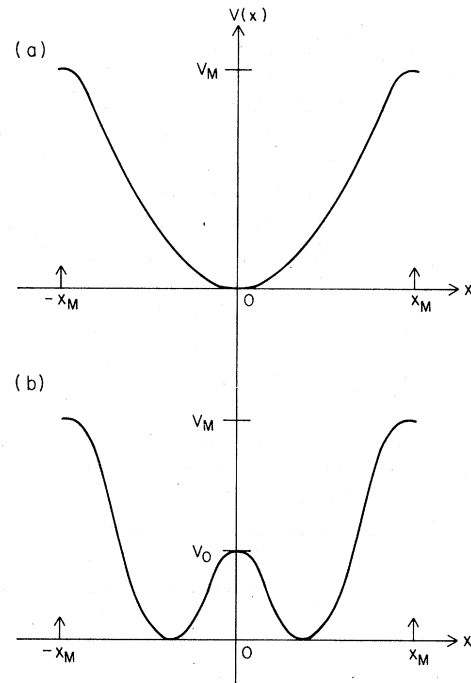


FIG. 1. Local potential function $V(x)$ for (a) a quasi-harmonic vibrational response and (b) a double-well oscillator. The potential amplitude V_M at the cell boundaries $\pm x_M$ denotes the barrier energy for thermally activated intercell hopping.

thing from quasiharmonic [Fig. 1(a)], through grossly anharmonic, to double well [Fig. 1(b)] in shape.

If the barrier height V_M is large compared to thermal energies kT , then the physical system represented by Fig. 1 has two characteristic frequency regions. One is associated with the intracell motion and we shall for definiteness term it "vibrational." The other is given by the inverse relaxation time associated with thermally activated hopping over the V_M barrier. Correspondingly, a contribution to the dielectric response function may be expected from each of these terms and, if the two frequency regions are well separated (which we shall assume), interference will be small and the two contributions can be treated independently and added in simple fashion.

Our detailed model will now consist of an assembly of N such "cells," randomly occupied with a probability $1 - c$ (where $c \ll 1$) and interacting via electric dipolar interactions. Neglecting boundary effects (i.e., assuming the presence of Ohmic contacts or working at frequencies high enough to obscure electrode blocking effects¹⁰) the macroscopic concentration distribution of mobile ions is unaffected by the application of a perturbing field. Coupled with the long-range nature of the

electric dipole force field this assures that no significant dipole field is induced at a particular cell site by the hopping conductivity itself. Such, of course, would not necessarily be the case for a finite sample in the presence of a static field, for which a concentration gradient would develop in the presence of electrodes with blocking or partially blocking characteristics.¹¹ The induced dipole field will therefore result, in our approximation, entirely from the vibrational motion which is perturbed within each occupied cell by the field.

III. ISOLATED-CELL RESPONSE

Let us consider first the response of a representative j th cell to an "applied" field $E_0 e^{-i\omega t}$ in the absence of any intercell coupling. We shall refer to this as "isolated-cell" response and denote it by a subscript s . As discussed earlier, the response χ_s can be separated into vibrational and hopping components, $\chi_{s,v}$ and $\chi_{s,h}$, respectively, such that

$$\chi_s(\omega) = \chi_{s,v}(\omega) + \chi_{s,h}(\omega). \quad (1)$$

The vibrational contribution can be expressed in a damped harmonic oscillator formalism¹²

$$\chi_{s,v}(\omega) = \chi_{s,v}(0) \Omega_s^2 / (\Omega_s^2 - i\Gamma\omega - \omega^2), \quad (2)$$

for $V(x)$ of a quasi-harmonic form, where $\chi_{s,v}(0)$ is the corresponding static response, and Ω_s and Γ are, respectively, the frequency and the (positive) damping parameter of the relevant oscillator. On the other hand, if $V(x)$ is of the double-well form of Fig. 1(b), then a Debye representation is more appropriate,¹² viz.,

$$\chi_{s,v}(\omega) = \chi_{s,v}(0) / (1 - i\omega\tau_s), \quad (3)$$

in which τ_s is a relaxation time characterizing the *intracell* double-well hopping. For a grossly overdamped vibrational motion ($\Gamma \gg \Omega_s$), corresponding perhaps to a very anharmonic or shallow double-well intracell motion, the vibrational response (2) goes over to the Debye form (3) where $\tau_s = \Gamma / \Omega_s^2$.

The hopping response $\chi_{s,h}(\omega)$ can be calculated in a mean-field approximation by assuming that the dominant effect on conductivity of the existence of an occupational probability $1 - c$ per site on the potential hopping sites $j \pm 1$ is the reduction of the hopping probability W by a factor of $1 - (1 - c) = c$ from the value W_0 which would pertain if adjacent hopping sites were empty.¹³ In the absence of a perturbing field, W_0 is expressible as the product of an attempt frequency ν and a Boltzmann factor of $\exp(-V_M/kT)$, i.e.,

$$W = c\nu \exp(-V_M/kT). \quad (4)$$

For damped harmonic response the attempt frequency is of the order of $\Omega_s/2\pi$ and values $\sim 10^{12}$ are considered typical.

For isolated response, in the presence of a perturbing field $E_0 e^{-i\omega t}$, we must include the field energy in the potential function in the form $V(x) - V(x) - Sx E_0 e^{-i\omega t}$, where S is an effective-charge parameter. It follows that hopping probabilities W^+ and W^- parallel and contrary to the field direction respectively now differ such that

$$\begin{aligned} W^\pm &= c\nu \exp[-(1/kT)(V_M \mp Sx_M E_0 e^{-i\omega t})] \\ &= W [1 \pm (Sx_M/kT) E_0 e^{-i\omega t}]. \end{aligned} \quad (5)$$

Consider now the rate equation governing hopping into the cells $j \pm 1$. In the mean field approximation it is

$$\frac{d}{dt} \langle \eta_{j\pm 1} \rangle = W^\pm \langle \eta_j \rangle, \quad (6)$$

where $\langle \eta_j \rangle$ is the occupational probability of site j at time t . In particular,

$$\frac{d}{dt} \langle \eta_{j+1} - \eta_{j-1} \rangle = (2Wx_M \langle \eta_j \rangle S/kT) E_0 e^{-i\omega t}. \quad (7)$$

The mean-field solution of (7) is obtained directly by putting $\langle \eta_j \rangle$ equal to its unperturbed equilibrium value $1 - c$ and integrating. We find

$$\langle \eta_{j+1} - \eta_{j-1} \rangle = \frac{-2W(1-c)Sx_M E_0 e^{-i\omega t}}{i\omega kT}. \quad (8)$$

Writing $\langle \eta_{j+1} - \eta_{j-1} \rangle = \Delta\eta e^{-i\omega t}$ we can define an electric dipole moment Δp associated with the A ion hopping in the form

$$\Delta p = 2ae\Delta\eta, \quad (9)$$

where we have taken the A ion charge to be $+e$ and the hopping distance to be $2a$ (i.e., a is the relative displacement of the A ion with respect to the anion framework when the collective displacement variable x has its maximum value x_M). Using Eqs. (8) and (9) we can now define the hopping response

$$\chi_{s,h}(\omega) = \Delta p / E_0 = i4W(1-c)ax_M Se / \omega kT \quad (10)$$

and writing $Sx_M = \lambda ae$ (where λ is a simple scalar quantity) and using Eq. (4) we obtain a final form

$$\chi_{s,h}(\omega) = \frac{i(2a)^2 \lambda e^2 c (1-c) \nu e^{-V_M/kT}}{\omega kT}. \quad (11)$$

Any dielectric response χ_i produces a contribution to dielectric constant $\epsilon = \epsilon' + i\epsilon''$ of the form $\epsilon_i \sim 4\pi\chi_i V$, where V is the volume of the relevant cell. It follows that $\chi_{s,h}(\omega)$ contributes only to the imaginary part of the dielectric constant (i.e., to the conductivity $\sigma = \omega\epsilon''/4\pi$).

IV. COLLECTIVE RESPONSE

Within mean-field theory the effect of intercell interactions is included as an effective field $E(\omega)$ at the particular reference cell site. As discussed earlier, for our case the induced component $E(\omega) - E_0(\omega)$ of effective field [where $E_0(\omega) = E_0^{-i\omega t}$] results solely from the vibrational component. The induced polarization $P(\omega)$ is therefore made up of the sum of vibrational and hopping components as follows

$$VP(\omega) = V[P_v(\omega) + P_h(\omega)] \\ = [\chi_{s,v}(\omega) + \chi_{s,h}(\omega)]E(\omega), \quad (12)$$

where

$$\chi_{s,v}(\omega)E(\omega) = \chi_v(\omega)E_0(\omega) \quad (13)$$

and $\chi_v(\omega)$ is the collective response of the ensemble of vibrational oscillators interacting via the electric dipole field.

In a random-phase approximation the collective response $\chi_v(\omega)$ can be formally calculated as a function of the isolated-cell response $\chi_{s,v}(\omega)$ and takes the form¹²

$$\chi_v(\omega) = \chi_{s,v}(\omega) / [1 - v(0)\chi_{s,v}(\omega)], \quad (14)$$

where $v(0) = \sum_k v_{jk}$, and $v_{jk} X_j X_k$ is the dipolar interaction operator between cells at sites j and k . Combining Eqs. (13) and (14) enables us to express the effective field $E(\omega)$ in terms of the applied field in the form

$$E(\omega) = E_0(\omega) / [1 - v(0)\chi_{s,v}(\omega)]. \quad (15)$$

$$P_h(\omega) = A_h \left(\frac{-(\Omega_s^2 - \Omega^2)\Gamma\omega + i[(\Omega_s^2 - \omega^2)(\Omega^2 - \omega^2) + \Gamma^2\omega^2]}{V\omega[(\Omega^2 - \omega^2)^2 + \Gamma^2\omega^2]} \right) E_0(\omega), \quad (20)$$

in which

$$A_h = [(2a)^2 \lambda e^2 c (1-c) v \exp(-V_M/kT)] / kT, \quad (21)$$

and we have used the fact (Eq. 18) that

$$\chi_{s,v}(0)\Omega_s^2 = \chi_v(0)\Omega^2. \quad (22)$$

The resulting dielectric constant follows from

$$\epsilon(\omega) = 1 + [4\pi/E_0(\omega)][P_v(\omega) + P_h(\omega)]. \quad (23)$$

Writing $\epsilon(\omega) = 1 + \epsilon_v(\omega) + \epsilon_h(\omega)$ to define the vibrational and hopping contributions to dielectric constant, and separating each into real and imaginary parts according to $\epsilon_i = \epsilon'_i + i\epsilon''_i$ ($i = v, h$), we obtain the final explicit forms for vibrational and hopping contributions to the real and imaginary parts of the dielectric constant as follows:

$$\epsilon'_h(\omega) = -4\pi A_h \Gamma (\Omega_s^2 - \Omega^2) / VD(\omega), \quad (24)$$

Using the damped harmonic oscillator form of Eq. (2) for the isolated-cell vibrational response, Eq. (15) transforms to

$$E(\omega) = E_0(\omega)(\Omega_s^2 - \omega^2 - i\Gamma\omega) / (\Omega^2 - \omega^2 - i\Gamma\omega), \quad (16)$$

in which

$$\Omega^2 = \Omega_s^2 [1 - v(0)\chi_{s,v}(0)]. \quad (17)$$

The collective response $\chi_v(\omega)$ also follows as

$$\chi_v(\omega) = \frac{\chi_{s,v}(0)\Omega_s^2}{\Omega^2 - \omega^2 - i\Gamma\omega} = \frac{\chi_v(0)\Omega^2}{\Omega^2 - \omega^2 - i\Gamma\omega}, \quad (18)$$

indicating that the frequency Ω is just the re-normalized frequency of the collective vibrational oscillators.

We note that $E(\omega)$ is in general not in phase with $E_0(\omega)$. This has the important consequence that the hopping response can now contribute to the real and imaginary parts of the dielectric constant. Also, since Ω_s^2/Ω^2 is in general larger than unity, the low-frequency response is possibly considerably enhanced by the presence of the dipolar interactions. This implies an enhanced ionic conductivity as well as a perturbed permittivity.

Substituting (16) in (12) and using the isolated response forms of Eqs. (2) and (11) we can now write explicit forms for the vibrational and hopping contributions to the collective frequency-dependent polarization. They are

$$P_v(\omega) = \left(\frac{\chi_v(0)\Omega^2(\Omega^2 - \omega^2 + i\Gamma\omega)}{V[(\Omega^2 - \omega^2)^2 + \Gamma^2\omega^2]} \right) E_0(\omega), \quad (19)$$

and

$$\epsilon''_h(\omega) = 4\pi A_h [(\Omega_s^2 - \omega^2)(\Omega^2 - \omega^2) + \Gamma^2\omega^2] / V\omega D(\omega) \quad (25)$$

$$\epsilon'_v(\omega) = 4\pi \chi_v(0)\Omega^2(\Omega^2 - \omega^2) / VD(\omega), \quad (26)$$

$$\epsilon''_v(\omega) = 4\pi \chi_v(0)\Omega^2\Gamma\omega / VD(\omega), \quad (27)$$

in which

$$D(\omega) = (\Omega^2 - \omega^2)^2 + \Gamma^2\omega^2. \quad (28)$$

The equivalent calculation for the order disorder situation expressed by the isolated response of Eq. (3) follows in an analogous fashion from Eqs. (14) and (15). We find in particular the effective field

$$E(\omega) = E_0(\omega)\tau(1 - i\omega\tau_s) / \tau_s(1 - i\omega\tau), \quad (29)$$

where

$$\tau = \tau_s / [1 - v(0)\chi_{s,v}(0)], \quad (30)$$

is the relaxation time for the collective diffusive motion within the cells. Thus, for example,

$$\chi_v(\omega) = \chi_v(0)/(1 - i\omega\tau), \quad (31)$$

where

$$\chi_v(0)/\chi_{s,v}(0) = \tau/\tau_s. \quad (32)$$

The explicit order-disorder forms for "vibrational" and hopping contributions to dielectric constant follow from Eq. (12) as

$$\epsilon'_h(\omega) = -4\pi A_h(\tau - \tau_s)\tau/V(1 + \omega^2\tau^2)\tau_s, \quad (33)$$

$$\epsilon''_h(\omega) = 4\pi A_h(1 + \omega^2\tau\tau_s)\tau/V\omega(1 + \omega^2\tau^2)\tau_s, \quad (34)$$

$$\epsilon'_v(\omega) = 4\pi \chi_v(0)/V(1 + \omega^2\tau^2), \quad (35)$$

$$\epsilon''_v(\omega) = 4\pi \chi_v(0)\omega\tau/V(1 + \omega^2\tau^2). \quad (36)$$

V. ANALYSIS

Let us consider first the static limit for the damped oscillator case. From Eqs. (24)–(28) we find

$$\epsilon'_h(0) = -4\pi A_h \Gamma \Omega_s^2/V\Omega^4, \quad \sigma_h(0) = A_h \Omega_s^2/V\Omega^2, \quad (37)$$

$$\epsilon'_v(0) = 4\pi \chi_v(0)/V, \quad \sigma_v(0) = 0, \quad (38)$$

where we have assumed $\Omega_s^2/\Omega^2 \gg 1$ (which is essentially the definition of a dielectrically soft material) and have transformed the imaginary contributions to conductivities using $\sigma = \omega\epsilon''/4\pi$. The vibrational contributions of Eq. (38) are just those expected for a soft dielectric in the absence of ionic conductivity. On the other hand, the hopping contributions to conductivity and permittivity are both very different from what one would calculate in the absence of coupling to a vibrational mode. In the latter case we would have $\epsilon'_h(0) = 0$ and $\sigma_h(0) = A_h/V$. The ionic conductivity in the static limit is therefore enhanced by a factor of $(\Omega_s/\Omega)^2$. In the limit of approaching a second-order dielectric instability at say T_c , the ionic conductivity of Eq. (37) actually diverges as $|T - T_c|^{-1}$ in the mean-field approximation since

$$\frac{\Omega_s^2}{\Omega^2} = \frac{\chi_v(0)}{\chi_{s,v}(0)} = \frac{1}{|T - T_c|}, \quad (39)$$

as $T \rightarrow T_c$. In this same limit $\epsilon'_h(0) \propto |T - T_c|^{-2}$ and $\epsilon'_v(0) \propto |T - T_c|^{-1}$ so that hopping activity dominates the permittivity also, and is negative (i.e., inductive).

At finite frequencies and in the overdamped limit $\Gamma^2 \gg \Omega_s^2 \gg \Omega^2$, where the latter inequality defines a soft dielectric, we can make contact with the double well format. If we write

$$\tau = \Gamma/\Omega^2, \quad (40)$$

the equations (24) to (28) appear as

$$\epsilon'_h(\omega) = -4\pi A_h \tau (\Omega_s^2/\Omega^2)/V(1 + \omega^2\tau^2) \quad (41)$$

$$\sigma_h(\omega) = A_h [(\Omega_s^2/\Omega^2) + \omega^2\tau^2]/V(1 + \omega^2\tau^2), \quad (42)$$

$$\epsilon'_v(\omega) = 4\pi \chi_v(0)/V(1 + \omega^2\tau^2), \quad (43)$$

$$\sigma_v(\omega) = \chi_v(0)\omega/V(1 + \omega^2\tau^2). \quad (44)$$

These equations, as may be seen by inspection, are just those which follow from the double-well response of Eqs. (33)–(36) if we associate τ_s with Γ/Ω_s^2 and take $\tau \gg \tau_s$ to define a soft dielectric. The only difference is the fact that for the double well format the characteristic times τ and τ_s both contain an exponential temperature factor $\exp(V_0/kT)$ where V_0 [Fig. 1(b)] is the height of the intracell energy barrier at $x = 0$.

Except for temperatures pathologically close to a sharp second order dielectric instability, the applied frequency $\omega \ll \Omega$ if ω is less than $\sim 10^8$ Hz. It follows that at these frequencies the underdamped vibrational equations reduce to their static counterparts. For overdamped vibrational modes or double-well situations, however, crossover from low-frequency ($\omega\tau \ll 1$) to high-frequency ($\omega\tau \gg 1$) regimes can occur at frequencies $\omega \ll \Omega$. In the high-frequency region (assuming a frequency-independent damping factor or relaxation time) both contributions to permittivity decrease in magnitude with frequency as $1/\omega^2$ while both contributions to conductivity attain frequency-independent values. In particular, the high-frequency hopping conductivity is simply A_h/V , which is the value expected in the absence of any coupling to the vibrational mode.

Away from any dielectric instability ϵ'_v and σ_v are not markedly temperature dependent. On the other hand ϵ'_h and σ_h both possess an exponential temperature factor of $\exp(-V_M/kT)$ coming from the factor of A_h of Eq. (21) which will dominate the hopping response. The exponent is slightly modified for the case of double-well vibrational motion by the exponents also appearing in τ and τ_s . Using Eqs. (33) and (34) we find for the low and high-frequency regions, respectively,

$$-\epsilon'_h \propto \sigma_h \exp(V_0/kT) \propto \exp[(V_0 - V_M)/kT], \quad \omega\tau \ll 1, \quad (45)$$

$$-\epsilon'_h \propto \sigma_h \exp(-V_0/kT) \propto \exp[-(V_0 + V_M)/kT], \quad \omega\tau \gg 1. \quad (46)$$

The major conclusion is that the interaction between hopping response and localized vibrational response produces two marked effects. The first is an enhanced ionic conductivity at low frequencies due to the increase in effective local

field (over the applied field) produced by the interacting vibrational dipoles. The second is the development of a contribution to permittivity which is negative in sign and proportional to the con-

centration of carriers. This inductive response may easily dominate the real component of dielectric constant particularly at high temperatures.

-
- ¹A. K. Das and P. Schwendimann, *Physica (Utr.) A* **89**, 605 (1977); P. Brüesch, S. Strässler and H. R. Zeller, *Phys. Status Solidi A* **31**, 217 (1975); B. A. Huberman and P. N. Sen, *Phys. Rev. Lett.* **33**, 1379 (1974); **34**, 1059 (1975); P. Fulde, L. Pietronero, W. R. Schneider and S. Strässler, *ibid.* **35**, 1776 (1975).
- ²P. A. Fedders, *Phys. Rev. B* **17**, 40 (1978); D. L. Huber, *ibid.* **15**, 533 (1977); P. M. Richards *ibid.* **16**, 1393 (1977).
- ³W. Van Gool and P. H. Bottelberghs, *J. Solid State Chem.* **7**, 59 (1973).
- ⁴A. M. Glass, M. E. Lines, K. Nassau, and J. W. Shiever, *Appl. Phys. Lett.* **31**, 249 (1977).
- ⁵A. M. Glass, K. Nassau, and T. J. Negran, *J. Appl. Phys.* **49**, 4808 (1978).
- ⁶See, for example, M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Oxford University, Oxford, 1977), Chap. 8.
- ⁷M. E. Lines, *Solid State Commun.* **10**, 793 (1972).
- ⁸R. D. Armstrong and K. Taylor, *J. Electroanal. Chem.* **63**, 9 (1975).
- ⁹I. M. Hodge, M. D. Ingram, and A. R. West, *J. Am. Ceram. Soc.* **59**, 360 (1976).
- ¹⁰J. R. MacDonald, *J. Chem. Phys.* **61**, 10 (1974).
- ¹¹J. R. MacDonald, *Phys. Rev.* **91**, 412 (1953); **92**, 4 (1953).
- ¹²M. E. Lines and A. M. Glass, in Ref. 6, Chap. 2.
- ¹³The mean-field approximation is quite good in the equivalent cell scheme of the present paper but can be misleading in a more general context; see Ref. 2.