we analyze data from quiescent periods in the experiment. These are times between magnetohydrodynamic bursts which are associated with irreproducible runaway electron dumps. (As noted above, these dumps change the plasma charge and consequently $u_\parallel$.) We only analyze discharges with a low-resistance anomaly permitting the protons to approach the banana regime.[14] The subthermal to thermal protons are always in the plateau regime, and are described by the shift piece of F_1, Eq. (11), which is proportional to r/R. The superthermal protons are in the banana regime and are described by the distortion piece of F_1, Eq. (10), which is proportional to $(r/R)^{1/2}$. The direction and magnitude of the experimental drift velocity agrees with that predicted from the distortion term in Eq. (10), and it changes sign when the plasma current is reversed, as it should.

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Dielectric Response of a Superionic Conductor

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A microscopic theory of ionic transport in superionic conductors is presented. Based on a liquidlike description of the ionic carriers, it describes the frequency and temperature dependences of the conductivity. A sum rule is obtained and the theory predicts the existence of a conductivity peak which scales with the inverse of the ionic carrier mass. The results are in good agreement with recent data on Na and Ag β-aluminas.

Superionic conductors, exemplified by systems like AgI, Na-β-Al_2O_3, and PbF_2, display a variety of properties that make them potentially useful for energy storage schemes.[1] With diffusion coefficients close to those of liquids, and ionic carrier concentrations of the order of 10^{23} ions/cm^3, they also pose interesting questions regarding the nature of the extremely high conductivities they display, which in some cases are connected with very well defined phase transitions.[2]

Recently there have been some theoretical attempts at incorporating detailed correlations into the usual random-walk theories in order to deal with diffusion in very dense systems.[3] Although the assumptions underlying these models seem reasonable and their limiting behavior in the absence of interactions yields the usual Arrhenius result, it is difficult to check their validity experimentally by using static probes. A more suitable approach would be to measure their dynamic properties, as superionic conductors are quite amenable to optical and microwave probes. This points to the need of obtaining expressions for the frequency dependence of the conductivity.[4]

In dealing with the dielectric response of superionic conductors, one must realize that at moderate temperatures the ionic carrier system lies between the usual region of a Debye solid and that of a Drude-like free-ion model. With hopping acactivation energies in the range of 0.2 to 0.01 eV, and diffusion coefficients of the order of 10^{-5} $\mathrm{cm}^2\ \mathrm{sec}^{-1}$, both the degrees of freedom of the ion in the potential well and those of its translational state must be taken into account.

Within this realm, we wish to present a microscopic ionic transport theory which relies on a quasicrystalline model of liquids originally proposed by Frenkel.[5] Besides describing the frequency and temperature dependences of the conductivity, it predicts the existence of a conductivity peak near the Debye frequency which scales with the inverse of the ionic carrier mass. As will be shown, the results of the theory are in good agreement with very recent data on Ag and Na β-aluminas.[6]

In our model, we assume the ionic carriers to have two basic degrees of freedom: (i) an oscillatory motion in the harmonic potential provided by the rigid lattice and (ii) a random-walk process through which they can diffuse throughout the crystal. At moderate temperatures the time spent in the free-ion-like state [$\tau_1 \simeq r_0 M^{1/2}\beta^{1/2}$, with r_0 the distance between potential minima, M the ionic mass, and $\beta=(k_BT)^{-1}$] is much shorter than the time between jumps ($\tau_0 = r_0^2/6D$ with D the diffusion coefficient), and so in that case we can think of the jump process as occurring "instantaneously" and being uncorrelated with the oscillatory motion.

It is clear that when probed within a time period τ that is short compared to the hopping time τ_0, the ions will respond as bound to a finite harmonic potential, but that for probing times longer than τ_0 the response will be essentially diffusive. We thus assume the ionic system to be described by a Debye spectrum above a temperature-dependent cutoff frequency ω_0, which is given by

$$\omega_0 = (12\pi/r_0^2)D_0 e^{-\beta U}, \tag{1}$$

with D_0 the diffusion coefficient and U the hopping activation energy. Moreover, we take care of the anharmonicity of the potential by assuming the ionic equation of motion to be that of a damped oscillator driven by a stochastic force,[7]

$$d^2u/dt^2 + 2\Gamma\omega\, du/dt + \omega^2 u = f(t), \tag{2}$$

with u the ionic coordinate, Γ a damping factor, and $f(t)$ a stochastic force with a Gaussian distribution such that

$$\langle f(t)\rangle = 0, \tag{3}$$

and

$$\langle f(0)f(t)\rangle = 2D\,\delta(t), \tag{4}$$

where the angular brackets denote a thermal average.

Below the cutoff frequency the equation of motion for the ion is the usual Langevin one,[8] i.e.,

$$d^2u/dt^2 + \gamma\, du/dt = f(t), \tag{5}$$

with γ to be determined by the $\omega = 0$ behavior, as will be shown below.

In the long-wavelength limit, where the photon wave vector is much smaller than the Debye-Hückel inverse screening length [typically of the order of $(10\ \text{Å})^{-1}$], we can neglect the effects of ion-ion correlations, which will become important at very short wavelengths and high energies. The real part of the frequency-dependent conductivity is given in terms of the current-current correlation function $\langle J(0)J(t)\rangle$ by[9]

$$\sigma(\omega) = \frac{1-e^{-\beta\hbar\omega}}{2\hbar\omega}\int_{-\infty}^{\infty}\langle J(0)J(t)\rangle\, e^{-i\omega t}\,dt. \tag{6}$$

Neglecting ion-ion correlations we can write Eq. (6) in terms of single-particle contributions as

$$\sigma(\omega) = [\pi n (Ze)^2/2\hbar\omega]\,(1-e^{-\beta\hbar\omega})z(\omega), \tag{7}$$

where $z(\omega)$ denotes the Fourier transform of the velocity autocorrelation function $\langle v(0)v(\tau)\rangle$, n is the ionic concentration, and Ze is the ionic charge.

The velocity autocorrelation function for the stochastically driven damped harmonic oscillator of Eq. (2) has been calculated in detail by Chandrasekhar[10] and by Rahman, Singwi, and Sjölander[11] for a Debye spectrum. It is given by

$$\langle v(0)v(t)\rangle = \frac{3kT}{M}\left[\left(\frac{\omega_0}{\omega_D}\right)^3 e^{-\gamma t} + \frac{3}{\omega_D{}^3} I\right], \tag{8}$$

with I determined by

$$I = \int_{\omega_0}^{\omega_D} d\omega\,\omega^2 e^{-\omega\Gamma t}\{\cos[\omega(1-\Gamma^2)^{1/2}t] - \tfrac{1}{2}\Gamma(1-\Gamma^2)^{-1/2}\sin[\omega(1-\Gamma^2)^{1/2}t]\}, \tag{9}$$

where ω_D denotes the Debye frequency of the ionic system and ω_0 is given by Eq. (1).

Using the fact that in the limit $\omega = 0$, the diffusion coefficient is given by

$$D = \tfrac{1}{3}\,\mathrm{Re}\int_0^\infty \langle v(0)v(t)\rangle\, dt, \tag{10}$$

and using Eq. (1), we obtain for γ the following expression:

$$\gamma = (12\pi)^3 (r_0^2\omega_\mathrm{D})^{-3} D_0^2 e^{-2\beta U} k_\mathrm{B} T/M, \tag{11}$$

with $D_0 = De^{\beta U}$, given in terms of the phonon frequency ω_D by[12] (neglecting correlations)

$$D_0 = r_0^2 \omega_\mathrm{D}. \tag{12}$$

So a measurement of ω_D gives in principle D_0.

Taking the Fourier transform of Eq. (8) and taking the classical limit we finally obtain for the ionic conductivity

$$\sigma(\omega) = \frac{n(Ze)^2}{M}\left[\left(\frac{\omega_0}{\omega_\mathrm{D}}\right)^3 \frac{\gamma}{\gamma^2+\omega^2} + \frac{3\Gamma\omega^2}{\omega_\mathrm{D}^3} F(\omega,\Gamma)\right], \tag{13}$$

with $F(\omega,\Gamma)$ given by

$$F(\omega,\Gamma) = \int_{\omega_0^2}^{\omega_\mathrm{D}^2} x\,dx/[(x-\omega^2)^2 + 4\Gamma^2\omega^2 x], \tag{14}$$

which can be calculated by standard methods and gives rise to lengthy algebraic expressions depending on the value of Γ.

Equation (13) is shown in Fig. 1, curve *a*, as a function of frequency for parameter values typical of the β-aluminas, i.e., $U = 0.15$ eV, $n = 2\times10^{21}$ carriers/cm^3, $D_0 = 2\times10^{-4}$ cm^2 sec^{-1}, $\omega_\mathrm{D} = 2.3\times10^{12}$ sec^{-1}, and $M_i = M_{\mathrm{Na}^+}$. As can be seen $\sigma(\omega)$ has a broad maximum close to ω_D (its magnitude determined by Γ). Since $\omega_\mathrm{D} \propto M_i^{-1/2}$, this implies that the location of the conductivity peak will scale with $M_i^{-1/2}$ in agreement with what is observed in Na and Ag β-aluminas (Ref. 6).

Before embarking on a discussion of the experimental situation, we should comment on several points concerning Eq. (13). (1) In the limit $\omega \to 0$ the conductivity becomes

$$\sigma(\omega = 0) = [n(Ze)^2/kT] D_0 e^{-\beta U}, \tag{15}$$

which is the well known Nernst-Einstein relation. In other words, the dc transport properties of a superionic conductor become purely diffusive (i.e., Arrhenius behavior). (2) For $\omega \to \infty$ the conductivity goes to zero as ω^{-2}. (3) In the $T = 0$ limit, Eq. (13) predicts a true Debye spectrum, with the low-temperature specific heat behaving as T^3. (4) As the temperature increases the cutoff frequency ω_0 moves towards the Debye frequency, and for temperatures close to the hopping activation energy [for $\omega_0 \to \omega_\mathrm{D}$, $F(\omega,\Gamma) \to 0$] the conductivity becomes Drude-like, as shown by curve *b* in Fig. 1. In other words, the response of the

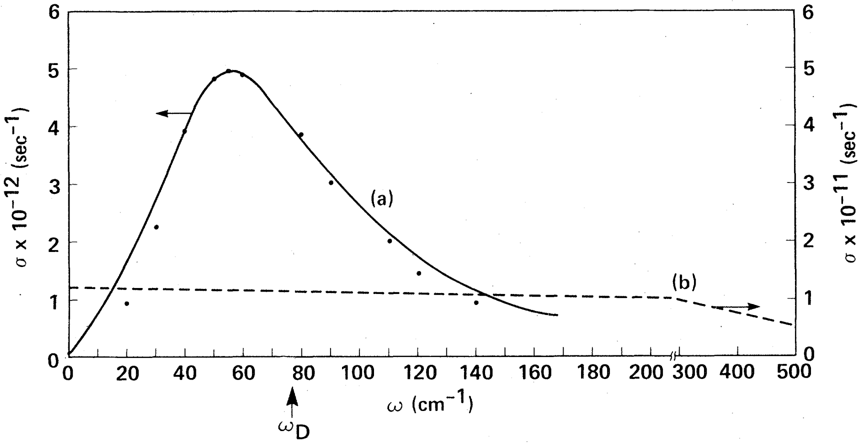

FIG. 1. The frequency dependence of the ionic conductivity. Curve *a* corresponds to $T = 300$°K with $D_0 = 2\times10^{-4}$ cm^2 sec^{-1}, $n = 2\times10^{21}$ carriers cm^{-3}, $\omega_\mathrm{D} = 2.3\times10^{12}$ sec^{-1}, $U = 0.5$ eV, $M = M_{\mathrm{Na}^+}$, and $\Gamma = 0.5$. The integrated value between $\omega = 0$ and $7\omega_\mathrm{D}$ is $0.9\pi n(Ze)^2/2M$. The circles denote the experimental values from Ref. 6. Curve *b* corresponds to $T = 2000$°K with the same parameter values. In both cases the zero-frequency intercept is given by Eq. (15).

system shifts from solidlike at low temperatures to liquidlike at moderate temperatures (characterized by a hopping diffusion) to a classical gas response as the cutoff frequency approaches the Debye frequency.

It is possible on general grounds to obtain a sum rule obeyed by Eq. (6). Integrating Eq. (7) and remembering that

$$\int z(\omega)\,d\omega = kT/M\,, \tag{16}$$

we obtain in the classical limit

$$\int \sigma(\omega)\,d\omega = \pi n(Ze)^2/2M\,. \tag{17}$$

Integrating Eq. (13) between 0 and $7\omega_{\rm D}$, we find that the sum rule is almost exhausted by these processes, and therefore other contributions at higher energies will have vanishingly small transition probabilities.

The frequency dependence of the conductivity in Ag-β-Al_2O_3 and Na-β-Al_2O_3 has been measured recently by far-infrared techniques by Allen and Remeika.[6] These layered systems are quite suitable for a check of our theory since they display molten-salt-like conductivities, the parameters are well known, and most important, it is easy to substitute the ionic carrier species. From their data, they concluded that correlation effects are unimportant and that a single-ion picture was all that was needed to obtain the value of the diffusion coefficient. Moreover, the conductivity peak scaled with the inverse of the ionic mass, and the frequency dependence of the conductivity contained all the general features of Eq. (13). The lack of any noticeable changes in the conductivity in going from 77 to 300°K is also in agreement with Eq. (13), as it predicts a very slow crossover into a Drude-like response at these temperatures. It should be mentioned that in the light of our results the identification of the conductivity peak with the attempt frequency should be made with care as the maximum in $\sigma(\omega)$ occurs at slightly lower frequencies than $\omega_{\rm D}$, regardless of the value of Γ.[13] Moreover, since the conductivity maximum does not depend as strongly on Γ as it does on the ionic plasma frequency, we were able to calculate the number of Na^+ carriers by choosing the ionic plasma frequency so as to obtain a good fit to the observed conductivity maximum. We thus obtained $n \simeq 2\times10^{21}$ carriers cm^{-3} for $\Gamma = 0.5$ which gives an order-of-magnitude estimate. From their data we can predict that the conductivity peaks for K β-alumina and Li β-alumina will be located at 5.76×10^{-3} eV and 1.36×10^{-2} eV, respectively.

In conclusion, we have presented a model of ionic transport which describes well the properties of superionic conductors. Regardless of the parameter values, it describes three different regimes of conductivity that are likely to be encountered in many of these systems: (a) a Debye-like spectrum at low temperatures, (b) a liquidlike behavior when hopping diffusion becomes important, and (c) a Drude response for temperatures close to the hopping activation energy. Although for simplicity we have limited ourselves to a single type of defect and a simple cutoff frequency for all modes, the main predictions of the model will not change by incorporating more complicated situations. Besides providing a needed conceptual framework within which these systems can be studied, the theory can easily be adapted to describe short-wavelength effects or Raman processes, which are likely to be present if allowed by the local site symmetry.

We wish to thank S. J. Allen for kindly sending us his data prior to publication and for his enlightening comments.

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