Direct Measurement of the Attempt Frequency for Ion Diffusion in Ag and Na β -Alumina

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The attempt frequency for ion diffusion in the superionic conductors sodium and silver β -alumina is directly observed as a resonance in the far infrared dielectric response. Correlation of the measured attempt frequency with the observed diffusion coefficient suggests that the best conductors, Na and Ag β -alumina, can be described by a single ion hopping motion despite the relatively high density of diffusing species.

The potential use of superionic conductors as solid electrolytes in future battery systems has stimulated much experimental and theoretical interest in characterizing and understanding diffusion in these systems.¹ One of the more promising candidates for the sodium-sulfur battery, Na β -alumina,^{2,3} and its family of isomorphs have been extensively studied by NMR,⁴ tracer diffusion,^{2,3} ionic conductivity,^{5,6} dielectric loss,^{2,3} and x-ray diffraction.⁷ Stimulated by the meltlike conductivities observed in these systems, there have been a number of theoretical developments to explain the anomalously high diffusion coefficients observed in these systems, at relatively low temperatures. We draw particular attention to the theory of Rice and Roth⁸ which attempts to discuss the diffusion problem in terms of trapped and free particle states and theories preoccupied with collective behavior of the diffusing species such as the domain model of Van Gool⁹ and Van Gool and Bottelberghs¹⁰ and the extensive treatment of diffusion in an interacting system by Sato and Kikuchi.¹¹ At present it is not clear whether these theories, which represent substantial departures from models based on a random walk,¹² are necessary or indeed microscopically correct.

Here we measure the attempt frequency and assess the applicability of the random walk model by comparing the observed prefactor and exponential in the Arrhenius equation with that calculated from the directly measured attempt frequency. These preliminary results show that for the best conductors, Ag and Na β -alumina, the observed prefactor and activation energy can be obtained from the directly measured attempt frequency without substantial modification by interactions between diffusing ions. The theory of Rice and Roth appears inappropriate for Ag and Na β -alumina and the inclusion of cooperative effects for the long-wavelength current-carrying excitations is unnecessary. The attempt frequency was measured in Na and Ag β -alumina by far-infrared reflection¹³ spectroscopy from single-crystal platelets.¹⁴ An intense low-frequency resonant mode sensitive to substitution is identified with the attempt frequency and shown in Fig. 1 as a resonance in the frequency dependent conductivity.

There exists an approximate sum rule for the conductivity associated with a particular mobile ion:

$$\int_0^\infty \sigma(\omega) d\omega \approx \pi/2N(Ze)^2/M,\tag{1}$$

where N is the volume density of conducting species, M the mass, and Ze the charge carried by the ion. Thus sum rule is exact only if we can completely separate the mobile ion motion from the motion of the rest of the lattice and ignore local field effects.¹⁵ Subject to these uncertainties, we find the sum rule satisfied for $Z \approx 1$. It is interesting to point out here that the contribution to the sum rule from the dc ($\omega = 0$) conduc-



FIG. 1. Far-infrared conductivity versus frequency for Ag and Na β -alumina at 300°K.

tivity is extremely small at room temperature and that substantial perturbation of the integrated intensity is expected only at the highest temperatures $\geq 1000^{\circ}$ C. In this regard we note that results obtained at 77°K are unchanged from those shown in Fig. 1.

We identify the frequency at which the conductivity assumes a maximum as the attempt frequency. Although the mode is sensitive to substitution we cannot make this identification without some qualifications. We note that this is the collective, in-phase response of the ion and will be the same as the single-ion attempt frequency only in the absence of dispersion in this particular phonon branch and renormalization by local field effects. Considering the relatively stiff aluminum-oxide host lattice in which the Na⁺ ion moves and the low frequency of the mode in question, it seems reasonable to treat this as an Einstein-like oscillator with essentially no dispersion from near-neighbor interactions. The long-range Coulomb interaction will, however, renormalize this frequency via local field effects but these can be shown to shift the square of the local vibrational frequency down by no more than the square of the mobile-ion plasma frequency.¹⁶ This correction is expected to be $\lesssim 5 \text{ cm}^{-1}$ for Ag⁺, and ≤ 10 cm⁻¹ for Na⁺. We expect then that these resonances measure the attempt frequency for the diffusing species to within $\sim 20\%$. It is interesting here to compare these results with some recent far-infrared studies of α -AgI by Funke and Jost.¹⁶ It seems clear that in α -AgI the identification of such a mode, distinct from the whole system of phonon modes, is quite impossible.

Having identified the resonant frequency with the attempt frequency we now attempt to calculate the diffusion coefficient with the aid of the theory of Sato and Kikuchi¹¹ (S-K). Although it is our intention to demonstrate that the diffusion coefficient is very nearly given by a single-ion hopping model and the S-K model was developed to treat an interacting system, the S-K theory is most useful from our point of view for one can recover both the conventional random-walk result and the effects of interactions by considering the appropriate limits of the interaction parameters.

According to $S-K^{11}$ we write the diffusion coefficient as

$$D = D_0 e^{-U/kT}, \tag{2}$$

where

$$D_0 = a^2 \nu W V f; \tag{3}$$

 ν is the measured attempt frequency and *a* is the separation between lattice lines, ¹¹ ~ 2.8 Å. *U* is the barrier for hopping from the normal site to the interstitial site (Beevers-Ross and anti-Beevers-Ross sites, respectively), and can be related to the attempt frequency by assuming a particular model for the potential variation be-tween these sites. If the barrier is sinusoidal, we have

$$U \approx \frac{8}{3} M \nu^2 a^2. \tag{4}$$

All of the above parameters may be described as single-ion parameters in that they do not depend on interactions between ions or the density of diffusing species.

W, V, and f are parameters derived by S-K,¹¹ which depend on the interaction between mobile ions and differences in energy for occupation of the different sites. W is the effective jump frequency factor, V is the vacancy availability factor, and f is the correlation factor in the random walk¹² sense. The essence of the theory is contained in the dependence of the product VWf on temperature, the interaction energy between ions, and the occupancy energy. A strong temperature dependence of this product would indicate the importance of interactions or site availability in these systems. By directly measuring ν in Eq. (3) and inferring an approximate value of U from (4) we can experimentally decompose the measured diffusion coefficient into its singleion terms, $a^2 \nu e^{-U/kT}$, and the many-body terms in *VWf* and thus expose the essential result of S-K unencumbered by the single-ion parameters.

In Table I we compare the measured prefactor and activation energy with those obtained from the far-infrared data with the aid of (3) and (4). In the third column the ratio of tracer to far-infrared diffusion coefficient is calculated to give *VWf* and should be compared with the results of S-K which are approximated by $VWf \approx 0.28$ $\times \exp(-E/KT)$ for $\rho = 0.6$. The close agreement between the observed activation energy and that derived from the attempt frequency imply little activation energy for the product VWf. However, one must admit errors as large as 100% for the estimates of the barrier height from the far-infrared results, giving an upper bound for the energy *E* used to parametrize the S-K result of 0.15 eV. In the theory, *E* is controlled by the larger of two energies: ϵ , the interaction energy,

	D_0 (cm ² /sec)		U (e V)			
					VWf	
Ion	Tracer ^a	Far IR	Tracer ^a	Far IR	Tracer/far IR	Sato-Kikuchi ^b
Na ⁺	2.4×10 ⁻⁴	$13.5 \times 10^{-4} VWf$	0.17	0.15	0.18	$0.28 \exp(-E/KT)$
Ag+	1.65×10^{-4}	$6.6 \times 10^{-4} VWf$	0.18	0.17	0.25	$0.28 \exp(-E/KT)$
^a Refs. 2 and 3.			^b Ref. 11.			

TABLE I. Comparison of measured parameters with those deduced from far-in-frared data.

or w, the site occupancy energy. We conclude that in β -alumina both ϵ and w are less than 0.15 eV and do not substantially alter the diffusion coefficient derived from single-ion models.

This is not expected. Estimates of the Coulomb contribution to ϵ are in excess of 1 eV.^{10,17} Further, recent diffuse x-ray studies¹⁸ of Ag β -alumina suggest that the temperature dependence of the conductivity is related to the short-range order of the ions which implies that ion-ion interactions control the diffusion process. Other x-ray studies⁷ indicate that w is sufficiently large to strongly bias occupation of the Beevers-Ross site. On the other hand, detailed analysis of the configurational contribution to the specific heat in RbAg₄I₅ by Wiedersich and Geller¹⁹ gives site occupancy and interaction energies substantially less than 0.1 eV. Thus, although it is clear that ion-ion interactions and site occupation energy must play a role in determining the state of the system, they do not have an overriding influence on the diffusion coefficient in β -alumina.

We would like to touch briefly on the applicability of the Rice-Roth⁸ model for diffusion to the β -aluminas. Although it is amply clear that one can easily go from the Rice-Roth model to the conventional hopping model by the suitable identification of parameters,²⁰ it is apparent from these results that the Rice-Roth model has no microscopic basis in this system. Taken at face value, their density of states, g(E), is zero for E less than U, the activation energy. At low temperatures $(kT \ll U)$, apart from a weak Drude tail, $\sigma(\omega)$ should be near zero for $\omega < U/\hbar$, and nearly all of the weight in the sum rule (1) should appear above U/\hbar . This is clearly not the case. Further, the key identification in going from the Roth-Rice model to the hopping model is the equating of $1/\tau_0$, a lifetime, to ν , a resonant attempt frequency. Microscopically, one clearly sees a well-defined resonance well below activation energy carrying almost all the weight in the sum rule. One concludes that there is a real

physical basis for parametrizing the system by an attempt frequency as distinct from a scattering process.

The experimental results are less decisive with regard to collective effects such as the domain model of Van Gool and Bottelberghs.¹⁰ The domain model is invoked to remove the influence of the Coulomb interaction between ions. However, both the dc and far-infrared response sense the long-wavelength excitations and hence may be mutually consistent without the inclusion of the short-range Coulomb interaction.

Despite the fact that we have raised many questions, it is apparent from these preliminary results that valuable information concerning the microscopic parameters controlling diffusion in the β -aluminas can be had by studying the dielectric response of these systems in the far-infrared as well as the microwave regime. The β -aluminas are particularly suitable for it appears that the vibrations of the mobile ions are distinct from the host lattice. The study of the resonant modes of other mobile ions, as a function of chemical composition and temperature. will be pursued to confirm or deny the above speculations and shed further light on the microscopic interactions controlling diffusion in these systems.

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Note added.—Recently similar resonances have been reported on β -alumina powders dispersed in polyethylene.²¹

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Observation of a Coupled Phonon–Damped-Plasmon Mode in n-GaAs by Raman Scattering

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We have observed a coupled mode of a phonon with a plasmon in the Landau damping region for the first time by Raman scattering from heavily doped *n*-GaAs specimens at 100 K with the use of Ar-ion laser lines. The line shape as well as the dispersion relation was calculated by taking into account the nonlocal effect caused by the motion of free carriers, giving good agreement with the observed spectra.

After theoretical predictions that plasmons are coupled to the longitudinal optical phonons in polar crystals with free carriers,¹ Raman scattering from coupled LO-phonon-plasmon modes at wave number $q \sim 0$ was observed by Mooradian and Wright² in *n*-GaAs at 90° with the use of a $1.06-\mu m$ yttrium-aluminum-garnet laser. The polarization properties and relative intensities of the scattered light were thoroughly investigated both experimentally and theoretically.³ In this Letter we report the observation of a coupled mode which appeared in heavily doped specimens in the Landau damping region where the wave number q times the Fermi velocity $v_{\rm F}$ is larger than the mode frequency ω . Only little is known about this mode, which we would like to call "the coupled phonon-damped-plasmon mode."

By using Ar-ion laser lines (5145, 4880, 4765 Å, and other lines) with a backscattering configuration.⁴ we probed elementary excitations having q about a factor of 4 larger than that of the case of 90° scattering with an yttrium-aluminumgarnet laser. The (100) faces of *n*-GaAs samples less than a millimeter in thickness were polished and etched by standard procedures. The typical incident angle of the light was chosen as 80° . The direction of the wave vector inside the crystal was at 13° with the normal axis according to Snell's law.⁵ The polarization of the laser light inside the crystal was chosen to be nearly along a $\langle 010 \rangle$ axis. Raman-scattered light was collected from $\langle 100 \rangle$ directions. In this configuration, one can observe an intense allowed LO line together with a TO line weakly allowed as a result of a 13° tilt of the incident beam from a $\langle 100 \rangle$