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Microwave and infrared conductivity of Na β-alumina; evidence for collective ionic effects

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Detailed measurements of the ionic conductivity in single-crystal Na β-alumina are reported for frequencies between 10^7 and 10^{13} Hz and for temperatures between 4.2 and 300 K. The quadratic temperature dependence of the conductivity at 10^{10} Hz and the large width (~ 23 cm^{-1}) of the 65-cm^{-1} phonon mode are consistent with a model in which there is a broad distribution of collective ion modes.

Solid electrolytes are presently the subject of intensive investigation which seeks to achieve an understanding of the low ionic activation energies and the anomalously high ionic conductivities which characterize these materials. The high density of mobile ions at room temperature in solids such as Na β-alumina gives rise to ionic conductivities which are comparable to those of liquid ionic conductors.

Recent efforts to understand ionic motion in β-alumina have focused on the question whether the ionic response to electromagnetic probes can be understood by considering the motion of ions to be essentially independent[1,2] or whether ion-ion correlation effects must be taken into account. Of special interest have been the intensive infrared (20–200 cm^{-1}) reflectivity peaks in Na and Ag β-alumina, which are found to scale with the mass of the Na$^+$ and Ag$^+$ ions, respectively.[1] It has been suggested that these results can be understood in terms of vibrations of essentially independent ions.[1,2]

In the present paper, we show that new and more extensive measurements of the microwave and far-infrared ionic conductivity of Na β-alumina are consistently interpreted in terms of a model which involves a rather broad spectrum of low-lying ionic modes. The spectrum of ionic modes exists because of ion-ion correlation effects. Recent theoretical and experimental work[3-7] indicates that such ionic correlation effects may play a fundamental role in determining the unique properties of solid electrolytes.

The measurements of the ionic conductivity of Na β-alumina presented here cover wider frequency and temperature ranges than heretofore (5×10^7 to 5×10^{12} Hz and 4.2 to 300 K). In the low-frequency region ($\omega \lesssim 10^{10}$ Hz) a quadratic dependence of the conductivity on temperature has been observed and is explained in terms of the proposed model which involves low-lying ionic modes and associated relaxation times. In contrast to earlier studies[1] in which conductivity was inferred from Kramers–Kronig analysis of reflectivity measurements, transmission measurements in the far infrared (10^{11}–10^{13} Hz) have been employed to provide a direct and accurate measure of the ionic conductivity as it varies over several orders of magnitude. In particular, the line shape of the broad 65 cm^{-1} phonon peak has been obtained between 4.2 and 300 K. We show that the unusually broad linewidth (~ 23 cm^{-1}) of this peak at $T = 4.2$ K (and negligible temperature dependence up to 300 K) is consistent with the predicted behavior of the proposed spectrum of ionic modes.

The conductivity measurements were made on high quality single-crystal specimens of Na β-alumina (obtained from the Carborundum Company). Samples for the far-infrared transmission measurements were in the form of thin platelets (thickness 75–1500 μm) cut parallel to the high-conductivity planes with a diamond wire saw from larger crystals. Thin rods cut from the platelets served as specimens for the microwave measurements. In the rf region large single crystals were inserted directly into a coil. The various experimental techniques that were employed are standard and have been described elsewhere.[8] We only note that the data at all frequencies over the 10^7–10^{13} Hz range were obtained without the use of contacting electrodes.

The ionic conductivity spectra measured at 300 and 4.2 K are shown in Fig. 1. In the high-frequency part of the spectrum there is a strong, temperature insensitive peak centered at 65 cm^{-1}. This peak position scales with the mass of the substituted cation in the β-aluminas[1] and can therefore be interpreted in terms of a phonon mode involving the substituted cation. The observed peak position is in agreement with previous data,[1] but the width is a factor of two narrower than previously reported. The line shape of the 65 cm^{-1} peak cannot be approximated by a Lorentzian response function as the conductivity on the low-frequency side falls off considerably faster than ω^2

The most striking feature of the lower-frequency data is the region below 3 cm^{-1}; here the magnitude of the conductivity at 300 K is comparable to that measured for the dc ionic conductivity σ_{dc} but exhibits a temperature dependence below 300 K

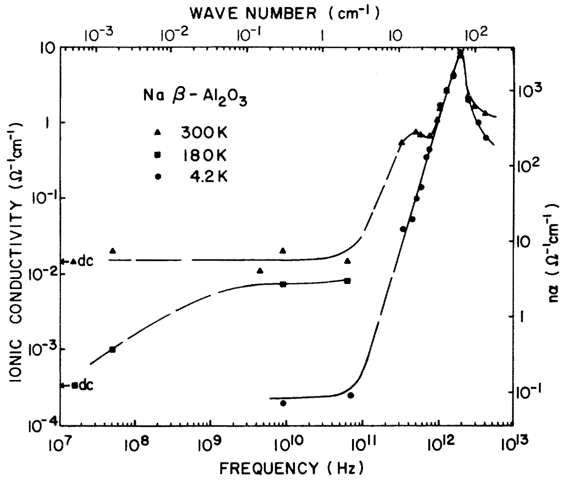

FIG. 1. In-plane ionic conductivity of single-crystal Na β-alumina. dc conductivity (Ref. 9) is shown for 300 and 180 K.

that is considerably weaker than that of σ_{dc}. The temperature dependence is shown in Fig. 2 where the dc thermally activated conductivity[6,9] is compared to the experimental observations at 9.1×10^9 Hz (0.3 cm^{-1}) and 64.4×10^9 Hz (2.15 cm^{-1}). Within experimental error (± 50%) the microwave conductivity is independent of frequency for all temperatures measured. The insert in Fig. 2 presents the data at 9.1×10^9 Hz replotted to demonstrate the power law ($\sim T^2$) dependence of the conductivity between 30 and 300 K. Below 30 K the conductivity rapidly becomes only weakly dependent on temperature.

A subsidiary peak in the conductivity is observed at 15 cm^{-1} and is strongly temperature dependent (in contrast to the main peak at 65 cm^{-1}), but because of the limited data available the nature of this structure cannot be identified at present.

The data at 5×10^7 Hz in Fig. 1 provide some information about the frequency dependence of the low-frequency conductivity. Measurements between 300 and 385 K (to be published elsewhere) show that the conductivity at 5×10^7 Hz is essentially equal to σ_{dc} (i.e., $\sigma_{dc}=\sigma_0 T^{-1}e^{-\Delta E/k_B T}$, where $\Delta E\simeq0.16$ eV and $\sigma_{dc}\simeq2\times10^{-2}\ \Omega^{-1}\ cm^{-1}$ at 300 K).[6,9] Below 300 K the conductivity becomes greater than σ_{dc} as the temperature is lowered. The results at 180 K (Fig. 1) represent the sensitivity limits of the inductive (contact free) rf technique employed. A comparison of the data at 5×10^7 Hz with those in the 10^{10}–10^{11} Hz region indicates that at 300 K between 10^8 and 10^{10} Hz the diffusive contribution to the conductivity decreases rapidly with increasing frequency, as has been predicted.[10] At temperatures below ~ 200 K the conductivity increases with frequency between 10^8 and 10^{10} Hz.

The quadratic temperature dependence observed in the microwave region, as well as the frequency dependence of the conductivity below 200 K between 10^8 and 10^{11} Hz, are difficult to account for on the basis of recently proposed models[2,11] which consider only single ion hopping and phononlike oscillatory modes in Na β-alumina. One particular aspect of such modes is multiphonon absorption, which involves higher-frequency single phonon modes of the diffusive ion. In the 0.1–1 cm^{-1} region, multiphonon absorption is generally in the form of phonon difference processes. Such processes exhibit a conductivity exponentially dependent on temperature at temperatures low compared to the energies of the participating phonon modes.[12] The strongest phonon modes observed in Na β-alumina fall in the 20–60 cm^{-1} range (or in equivalent temperatures between 20 and 60 K). The nearly temperature-independent conductivity observed in Fig. 1 below 30 K is therefore not consistent with absorption due to multiphonon processes.

These data can be understood by considering the effects of cooperative ionic motion in Na β-alumina, for which there is independent evidence. For example, it has been shown that the energy to move one Na^+ ion between available sites (Beevers–Ross to anti-Beevers–Ross)[3] is an order of magnitude larger than the observed thermal activation energy,[4,5] but that for several Na^+ ions moving to-

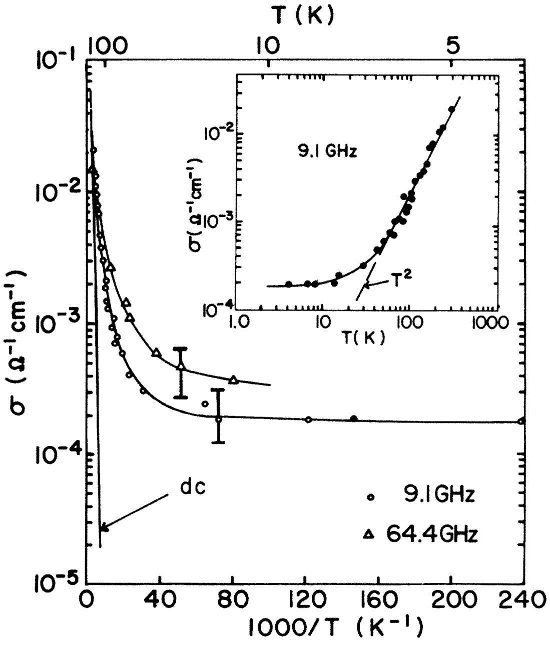

FIG. 2. Temperature dependence of the ionic conductivity of single-crystal Na β-alumina at 9.1×10^9 Hz and 64.4×10^9 Hz. The 9.1×10^9 Hz data, replotted in the insert, exhibit an approximate T^2 dependence between 40 and 300 K.

gether, the energy decreases.[4,5] In addition, the x-ray data of Peters *et al.*[3] suggest that the Na^+ ions form "clusters" which are stabilized by the Coulomb interactions between ions and the polarization of surrounding atoms. We therefore expect that ionic motions involve cooperative changes in position and energy of varying numbers of ions and atoms in clusters of different geometry, and that these cooperative effects can give rise to a spectrum of excitation energies.

For the spectrum of excitations discussed above, the low-frequency conductivity ($<10^{11}$ Hz) is given by transitions between the ionic configurations due to coupling to their dipole moments. The temperature dependence of the conductivity gives information about the density in energy of the modes: specifically, a power law dependence of the conductivity on temperature over a wide range of temperatures, such as is observed $[\mathrm{Re}\sigma(\omega) \sim T^2]$ for $T > 30$ K (Fig. 2) implies a smooth, power law density of modes for such energies. As discussed above, we suggest that the distribution in energy of these modes arises from ion-ion interactions.

To see more specifically the origin of the temperature dependence of $\sigma(\omega)$ for low frequencies, consider a simple model of the system in which the conductivity arises from transitions between ionic configurations $(i, j, \ldots)$. Then [13,14]

$$\mathrm{Re}\sigma(\omega) \cong \sum_{i,j} d_{ij} \left(\frac{1}{4k_B T \cosh^2(E_{ij}/2k_B T)} \right) \times \left(\frac{1}{\omega\tau_{ij} + (\omega\tau_{ij})^{-1}} \right) \rho(E_{ij}, \tau_{ij}), \qquad (1)$$

where E_{ij} is the energy difference between i, j, and τ_{ij} is the lifetime for the process, ρ is the density of states with energy E_{ij} and lifetime τ_{ij}, and d_{ij} is an effective dipole moment difference. Suppose ρ is negligible for $E_{ij} < E_{\mathrm{min}}$ and $\rho \propto E_{ij}^q$ for $E_{ij} > E_{\mathrm{min}}$; then $\mathrm{Re}\sigma(\omega)$ is exponentially small for $k_B T \ll E_{\mathrm{min}}$ and $\mathrm{Re}\sigma(\omega) \propto T^{1+q}$ for $k_B T \gg E_{\mathrm{min}}$. The T^2 dependence of $\sigma(\omega)$ shown in Fig. 2 corresponds to this behavior and indicates a relatively smooth distribution of excitation energies above 3 meV and a negligible density below that.[15]

Consider now the phonon peak at 65 cm^{-1}. Two especially notable features are that the line is very wide at all temperatures and that the width is temperature independent. The origin of this width has not been treated in detail. Possible contributions to the phonon width include (i) scattering by other phonons and (ii) coupling of the phonon to the distribution of collective ionic modes. Because the energy of this optically active phonon lies within the energy distribution of the proposed collective ionic modes, the coupling between them will be strong. This coupling is therefore expected to give a substantial contribution to the phonon linewidth at all temperatures. Furthermore, the temperature dependence of the linewidth contribution, by coupling to the collective ionic modes, has an interesting consistency with experiment. Using the model of the ionic mode spectrum introduced above, the lowest-order contribution to the phonon linewidth Γ from phonon decay by excitation of an ionic mode has the form[14]

$$\Gamma(\omega) \simeq D^2 \sum_{E_{ij}} \rho(E_{ij}) \tanh(E_{ij}/2k_B T)\, \delta(\omega - E_{ij}), \qquad (2)$$

where D is a coupling parameter. Note that Γ is a decreasing function of T: for $k_B T \ll E_{\mathrm{min}}$ all modes E_{ij} contribute to Γ, whereas for $k_B T > E_{\mathrm{min}}$ only modes $E_{ij} \gtrsim k_B T$ contribute. Contributions of anharmonicity and multiphonon processes, on the other hand, are expected to be important in the temperature range investigated and are increasing functions of temperature. The approximate temperature independence of the linewidth observed experimentally is, therefore, consistent with the suggestion that decay into the ionic modes [Eq. (2)] makes a significant contribution to Γ which tends to cancel the temperature increase of anharmonicity and multiphonon effects.

While the above discussion suggests that phonon coupling to the ionic collective modes makes a significant contribution to the phonon linewidth, a detailed treatment of this contribution is not possible until a fuller knowledge of these modes and their coupling to the phonon is available.

In summary, we have measured the ionic conductivity of Na β-alumina over extensive frequency and temperature ranges. We have shown that a model of collective Na^+ ionic excitations is consistent with the experimental observations. Extension of these measurements to β-alumina substituted with other cations (Ag, K, Rb) would be useful in testing the validity of the model. The three-dimensional solid electrolytes such as AgI which exhibit three-dimensional ionic transport are physically different from Na β-alumina in which the cations move in planes. It will be interesting to determine whether microwave and far-infrared measurements in such materials[16] can be interpreted in terms of a collective dynamic response of the mobile ions.

Note added in proof: We have also calculated the contribution to the phonon width $\Gamma(\omega)$ owing to the coupling of phonons to the distribution of collective ionic modes to order D^4. The contribution to order D^2 is given in Eq. (2). The contribution to order D^4 turns out to be temperature independent and is expected to be appreciable in magnitude compared to the order D^2 contribution. Details of this calculation will be published elsewhere by two of the authors (T. L. R. and K. L. N.).

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[1] S. J. Allen, Jr. and J. P. Remeika, Phys. Rev. Lett. **33**, 1478 (1974).

[2] B. A. Huberman and P. N. Sen, Phys. Rev. Lett. **33**, 1379 (1974).

[3] C. R. Peters, M. Bettman, J. W. Moore, and M. D. Glick, Acta Crystallogr. B **27**, 1828 (1971).

[4] W. van Gool and P. H. Bottleberghs, J. Solid State Chem. **7**, 59 (1973).

[5] J. C. Wang, M. Gaffari, and Sang-il Choi, J. Chem. Phys. **63**, 772 (1975).

[6] J. T. Kummer, Progr. Solid. State Chem. **7**, 141 (1972).

[7] W. L. Roth, Trans. Am. Crystallogr. Soc. **11**, 51 (1975).

[8] U. Strom, J. R. Hendrickson, R. J. Wagner, and P. C. Taylor, Solid State Commun. **15**, 1871 (1974).

[9] M. S. Whittingham and R. A. Huggins, J. Chem. Phys. **54**, 414 (1971).

[10] P. N. Sen and B. A. Huberman, Phys. Rev. Lett. **34**, 1059 (1975).

[11] P. Bruesch, S. Strassler, and H. R. Zeller (unpublished).

[12] R. Stolen and K. Dransfeld, Phys. Rev. **139**, 1295 (1965).

[13] An expression formally similar to Eq. (1) has been discussed by Pollack and Pike [Phys. Rev. Lett. **28**, 1449 (1972)] for the physically somewhat different case of ac conductivity in glasses.

[14] In the range of frequencies discussed here, the thermal factors have been chosen to correspond to a spectrum of two-level excitations; a more general representation gives a thermal factor (which arises from detailed balance) with the same temperature dependences discussed in the text. Further, the usual form of the dc conductivity can be obtained from Eq. (1) by a modification of this representation appropriate to very low frequencies to give percolation; this point is discussed in detail by P. N. Butcher [Linear and Non-Linear Electronic Transport in Solids, edited J. T. by Devreese (to be published).

[15] A quantitative measure of the energy dependence of ρ from these data is not justified because of the possible energy dependence of the sum over τ_{ij}.

[16] K. Funke and A. Jost, Ber. Bunsenges. Phys. Chem. **75**, 436 (1971).