

theory, but the agreement is only qualitative. Nonetheless, from the shape of the curves and from the presence of the isotope effect, it can be concluded that tunneling of methyl groups is indeed involved in viscoelastic relaxation. This, incidentally, is the first observation of an isotope effect in the field of viscoelastic properties of polymers.

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Ion-Ion Correlations and Diffusion in β -Alumina

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A comparison of the correlation length for short-range order (30, 40, 70, and 110 Å), the attempt frequency for diffusion (56, 28, 80, and 85 cm⁻¹), and the previously reported values of tracer diffusion coefficient for Na, Ag, K, and Rb, respectively, suggests that ion-ion correlations inhibit diffusion in the β -aluminas.

The high ionic conductivity of solid electrolytes requires the simultaneous occurrence of large ion mobilities and large concentrations of mobile ions. In these materials the ionic mobility results from the existence of interconnecting channels for the mobile ions.¹ However, the persistence of large ion mobilities in the channels when they are filled with a large concentration of diffusing ions is one of the key problems in our understanding of solid electrolytes. Disorder

among the mobile ions is essential. How much disorder is required or the relationship between disorder and conductivity is at present not quantitatively understood.² This communication reports measurements of the correlation length for the short-range order (SRO) from x-ray diffuse scattering from Na, Ag, K, and Rb β -alumina. The correlation length is found to be almost temperature independent but to increase with the radius of the diffusing ion. The increase in correla-

tion length inhibits the conductivity and results in a breakdown of the single-ion random-hopping behavior. This is inferred from a comparison of far-infrared and tracer diffusion measurements.³

Crystals of sodium β -alumina in the form of hexagonal plates were grown from a flux at 1300 C, in contrast to earlier work where crystals were obtained by direct fusion at a higher temperature. β -alumina containing Li, K, Rb, Ag, or Eu in place of Na was obtained by ion exchange in the appropriate molten halide or nitrate as described in the literature.⁴ The weight change on exchange gives a nominal composition of $(1.26 \pm 0.05)\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$; i.e. there are 26% excess sodium ions over the stoichiometric composition. Long-exposure Gandolfi and precession photographs showed single-phase material with the β -alumina structure.

The diffusing plane in β -alumina is shown schematically in the top of Fig. 1. The diffusing ions

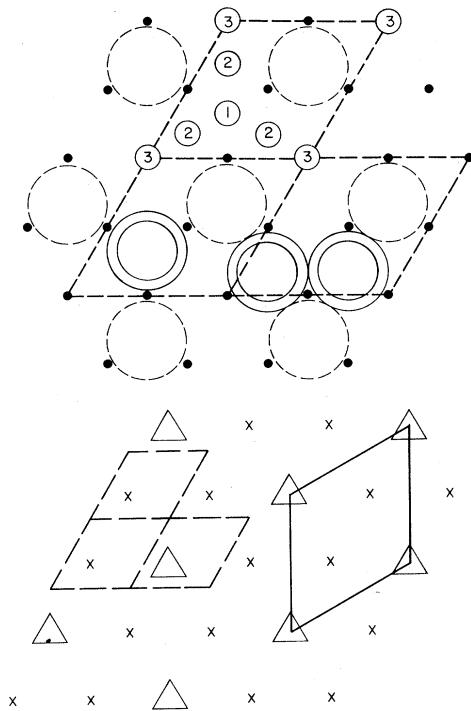


FIG. 1. (Top) Diffusing plane in β -alumina showing oxygen atoms in the plane (large dashed circles) and those above and below the plane (small closed circles); possible sites for the diffusing ions are numbered 1, 2, and 3. The double circles show relative packing of Na (inner circles) and K (outer circles) in singly (lower left) or doubly (lower right) occupied cells. (Bottom) Possible $\sqrt{3}a \times \sqrt{3}a$ superlattice for doubly occupied cells with two of three site-2 positions occupied (triangles) and singly occupied site-1 cells (crosses).

are distributed over three crystallographically independent sites numbered 1, 2, and 3, and these are referred to in the literature as the Beevers-Ross, mid-oxygen, and anti-Beevers-Ross sites, respectively. The average occupancy of each site is different in Na β -alumina⁵ and Ag β -alumina,⁶ but it is the same in Na and K β -alumina.⁷ Sites 1, 2, and 3 contain two, six, and two symmetry-equivalent positions per unit cell, respectively, whereas the numbers of Na, Ag, and K atoms are respectively $n(1) = 1.50(7)$, $1.34(1)$, $1.42(2)$; $n(2) = 1.04(9)$, $0.34(1)$, $1.22(4)$; $n(3) = 0$, $0.871(1)$, 0 .

Although the average crystal structures of Na and K β -alumina are quite similar, the local distribution of the diffusing ions as reflected in the diffuse x-ray scattering is markedly different. The diffuse scattering was surveyed using the fixed-crystal, fixed-film technique and monochromatic Mo $K\alpha$ radiation from either graphite or LiF monochromators. Our patterns for Na and Ag β -alumina are similar to those observed by LeCars *et al.*⁸ In K, Rb, and Eu β -alumina the patterns show clearly defined rods of diffuse scattering parallel with the c axis at the positions $h + \frac{1}{3}, k + \frac{1}{3}$ and $h + \frac{2}{3}, k + \frac{2}{3}$, where h and k are Bragg positions as shown in the upper right of Fig. 2. A similar distribution of rods but with different relative intensities was reported for Ag at 77 K.⁸ As a result of the excess sodium or other ions, in each diffusing plane approximately one third of the unit cells are doubly occupied and the rods of diffuse scattering result from correlations among the singly and doubly occupied cells. A possible ordered structure for the cells in K β -alumina is the $\sqrt{3}a \times \sqrt{3}a$ superlattice shown at the bottom of Fig. 1. Absolute measurements of the diffuse scattering which will be published elsewhere are consistent with this model, but the magnitude of the scattering and the oscillations in the intensity of the diffuse rods along the c axis show that some of the diffuse scattering results from displacements of the oxygen and aluminum ions around the diffusing ions. A different superlattice has been suggested for Ag β -alumina in which sites 1 and 3 are occupied.⁹

The correlation length was determined from the scan shown in Fig. 2 using a paper-tape-controlled General Electric XRD-5 diffractometer equipped with a scintillation counter and decade scaler. Mo $K\alpha$ radiation was obtained using Zr-Y balanced filters with the diffractometer set at a 2° take-off angle.¹⁰ The resolution was determined by scanning a nearby Bragg peak both in the $(h,$

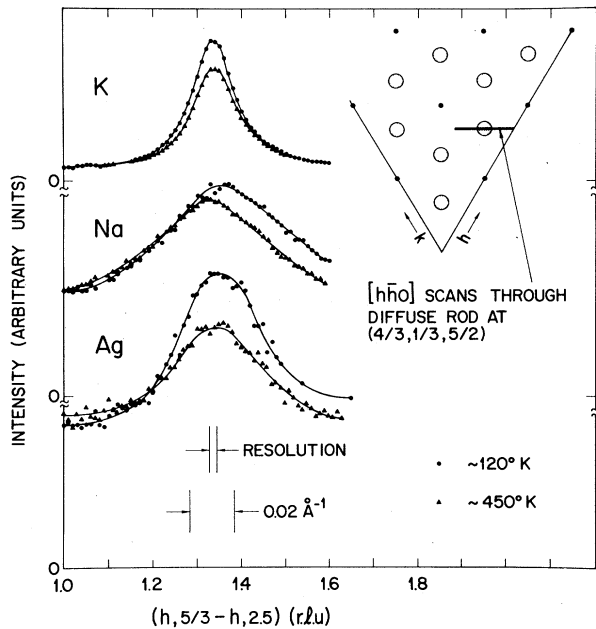


FIG. 2. Measurement of the correlation length for different ions in β -alumina at 120 K (circles) and 450 K (triangles). The direction of the scan through the diffuse rod in reciprocal space is shown in the inset. The correlation length increases with increasing size of the diffusing ion but is almost independent of temperature.

$-h, 0)$ direction and in a θ - 2θ scan. Measurements were made at 120, 298, and 450 K for K, Na, and Ag (Fig. 2), and at 298 for Rb. It is evident that the correlation length (as determined from the full width at half-maximum) hardly varies with temperature,⁹ but increases by a factor of 3.6 on going from the smaller Na ion to the larger Rb ion.

The far-infrared measurements reported for Na and Ag were extended to Li, K, and Rb β -alumina.³ In Na and Ag a broad resonance in the dielectric response was associated with the attempt frequency for ion diffusion. Similar resonances with somewhat reduced intensities were observed in K and Rb and a lower limit was set for the resonance in Li. The measured attempt frequencies are >160 (Li), 56 (Na), 28 (Ag), 80 (K), and 85 cm^{-1} (Rb). From the change in reflectivity, the corresponding changes in the dielectric constant $\epsilon(0) - \epsilon(\infty)$ are <3 , ~ 8 , ~ 8 , ~ 2 , and ~ 1 .

In order to discuss the microscopic mechanism for diffusion in β -alumina, the x-ray and far-infrared results are compared with the prefactor and activation energy for tracer diffusion in Fig.

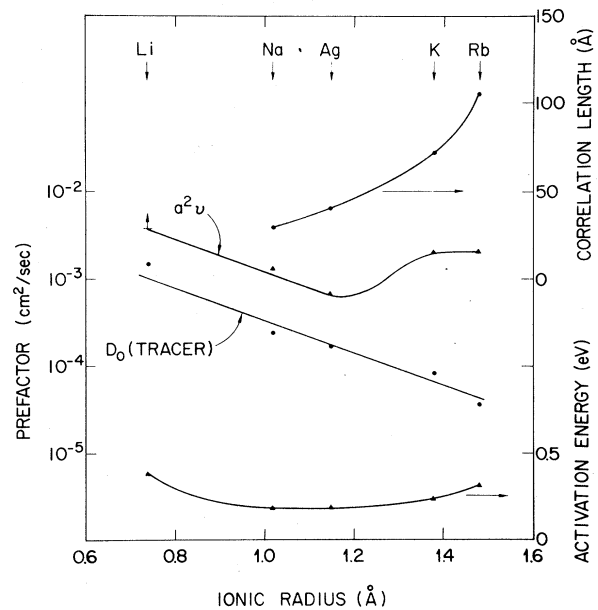


FIG. 3. Comparison of the variation with ionic radius of the correlation length and $a^2\nu$ with the prefactor and activation energy for tracer diffusion from Ref. 4. The data for Na and Ag are compatible with the single-ion random-hopping model, but with increasing correlation length the points for K and Rb deviate markedly from this model.

3.⁴ It has been suggested that the dependence of the activation energy on ionic radius can be understood in terms of polarization forces and hard-core repulsion. Quantitative comparisons can be made by assuming that diffusion occurs on a honeycomb lattice (sites 1 and 3 in Fig. 1). Although this model is rigorously applicable to Ag only, it can still provide a useful framework for the following comparisons. The prefactor D_0 is given by $D_0 = a^2\nu$, where a is one half the lattice parameter a_0 , and ν is the attempt frequency. If the barrier is sinusoidal, then the activation energy is given by $U = \frac{2}{3}M\nu a^2$, where M is the mass. The quantitative relations between the attempt frequency, the prefactor, and the activation energy will depend on the basic jump mechanism and entropy factors. Ignoring the latter and assuming a random hopping inhibited only by site occupancy, Sato and Kikuchi find the prefactor to be reduced to $D_0 = 0.26a^2\nu$ for the 26% deviation from stoichiometry found in β -alumina.¹¹ If the resonance in the far-infrared dielectric response is taken as the average attempt frequency then from the above formulas both the prefactor and the ac-

tivation energy should exhibit a minimum for Na and Ag. There is quantitative agreement for both D_0 and U in Li, Na, and Ag (the straight-line portions of the curves for $a^2\nu$ and D_0 through Li, Na, and Ag are displaced by 0.26). The measured attempt frequency for K and Rb would predict much larger activation energies (0.5 eV for K and 1.2 for Rb) than are observed, and a prefactor for K and Rb larger than for Na and Ag, in marked contrast to the experimental prefactors which decrease smoothly with increasing ionic radius. One concludes that the deviation of D_0 and U from the random-hopping values is related to the increase in correlation length and caused by a decrease in site availability.

The repulsive interactions among the diffusing ions would normally result in an order-disorder transition at some critical temperature. However, the excess diffusing ions require either excess oxygens or aluminum vacancies for charge neutrality, and the attractive interactions between the ions and their randomly distributed, compensating defects tend to inhibit the onset of long-range order. The degree of order is determined by the difference between these two competing interactions, and, therefore, the temperature dependence of the correlation length might be fairly small as is observed—whereas the competition may be a sensitive function of the size of the ion because the ion-ion interactions will depend on both strain fields and the screening of the Coulomb interaction.

The conductivity or diffusion is related to the degree of order. Following O'Keeffe, the conductivity prefactor should increase relative to the random-hopping value in the presence of a cooperative mechanism of diffusion but decrease if there are large ordered regions.¹² More detailed calculations based on path probability,¹¹ lattice-gas models,¹³ or computer simulation¹⁴ show that with increasing ion-ion interactions the number of ions available for diffusion is reduced. Physically ions jump to sites only if the jump does not substantially change the overall energy of the system, and the availability of such jumps varies with the amount of disorder. These models only include the ion-ion interaction, and it would be of

interest to have calculations based on models which include the competition between the ion-ion and ion-compensating-defect interactions. This competition would seem to allow the large conductivity to persist to low temperatures without encountering the transition to an ordered state which is found in many other solid electrolytes, e.g., AgI, RbAg₄I₅, or BaF₂.

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