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Thermal conductivities of Li, Na, K, and Ag β-alumina below 300 K†

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The thermal conductivities of single-crystal Li, Na, K, and Ag β-alumina have been measured in the temperature range of ≈ 0.1–300 K. The thermal conductivity is very sensitive to the cation present and is indicative of a broad band of excitations ($\lesssim 10^{-21}$ J, $\lesssim 10^{12}$ Hz) which scatter thermal phonons. The results are compared with a tunneling-states theory of disordered materials and with published data from specific-heat and light-scattering measurements.

I. INTRODUCTION

Sodium and silver β-alumina are layered crystals which exhibit very high ionic conductivity in two dimensions.[1,2] This property is of major technological importance and has focused research on these and other superionic conductors in the past few years.[3] Although the ionic conductivity is appreciable for β-alumina only above room temperature, efforts to understand the conduction mechanism have at times led to work at low temperatures. In particular, the specific heats of several β-alumina isomorphs have been measured[4] down to 1.3 K. At the lowest temperatures there appears to be an excess specific heat in addition to that attributable to the acoustic phonons.[5] This result implies the existence of a broad band of excitations having frequencies $\lesssim 2\times10^{11}$ Hz. Since the thermal conductivity also reflects the presence of excitations in this frequency range,[6-8] we were encouraged to perform thermal-conductivity measurements on a series of β-alumina isomorphs, namely, those containing Li, Na, K, and Ag as the diffusing ion. The experimental details are given in Sec. II, and the data and results are discussed in Sec. III. In brief, the thermal-conductivity data do provide evidence of a broad band of localized excitations associated with the cations and ranging in frequency from $\approx 10^{12}$ Hz down to at least 10^{10} Hz.

II. SAMPLES AND TECHNIQUE

The β-alumina structure has been extensively studied, although some important details have yet to be resolved.[3,9-12] The ideal composition is $M_2O\cdot 11Al_2O_3$, where M represents the cation of interest. These ions lie in mirror planes separating spinel-like blocks of alumina. The cations are actually between 15% and 30% in excess of the ideal composition.[13] Since additional oxygen ions or aluminum ion vacancies are required for charge compensation, the crystals have a highly defective structure.

Certain properties of the crystal depend on the method of crystal growth employed.[14] The single crystals of Na β-alumina used in the present work were grown from the melt.[15] As a test of crystal quality, the ionic conductivity was measured at a frequency of 10^4 Hz at 300 K. The result was $\approx 10^{-2}$ $\Omega^{-1}\mathrm{cm}^{-1}$ which is in rough agreement with other measurements on melt-grown crystals.[5] As a further check of crystal quality, samples cut from an optically more perfect melt-grown boule were obtained from the Argonne National Laboratory.

Samples having dimensions of approximately $2.0\times0.4\times0.06$ cm were cut from a boule using a diamond saw under kerosene. One sample was oriented with its long axis parallel to the c axis, i.e., perpendicular to the conducting planes. All other samples were cut with the long axis perpendicular to the c axis. In certain samples, the Na ions were replaced[13] by Li, K, or Ag by immersion in the appropriate nitrate salt at ≈ 350 °C. The fused salt left on the surface was removed with a brief water rinse and precipitated metallic silver was removed with dilute nitric acid. Density changes obtained with ion exchange, together with neutron activation analyses, indicated that there were close to 2.3 cations per unit cell. The samples provided by the Argonne National Laboratory appeared to have a somewhat higher cation density, about 2.5 per unit cell.

The mounting of the samples for thermal conductivity measurements in a dilution refrigerator at temperatures $\lesssim 10$ K is shown in Fig. 1. GE 7031 varnish was used for all thermal and mechanical bonds. The two pairs of carbon resistance thermometers were cut from 100- and 470-Ω Speer resistors.[16] The 100-Ω units were used at $T \lesssim 1$ K; the 470-Ω units were used at $T \gtrsim 1$ K to maintain sufficient temperature resolution. The lower pair of carbon-resistance thermometers was calibrated in each run against a cerous magnesium nitrate magnetic thermometer,[17] which, in turn, was cal-

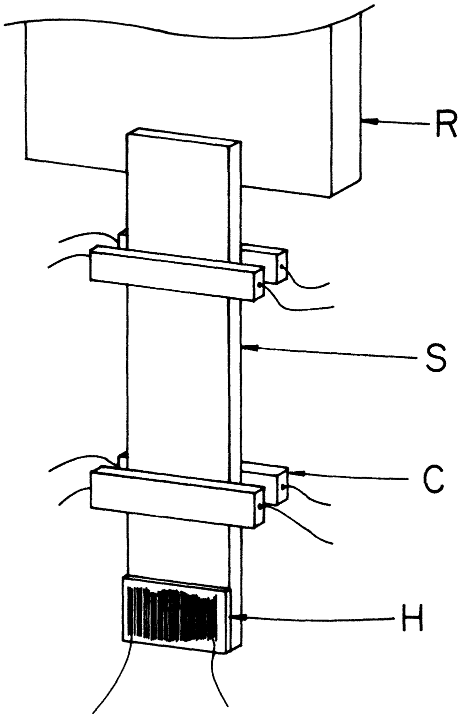

FIG. 1. Sample mounting arrangement. R, refrigerator; S, sample; C, carbon resistance thermometers; H, electrical heater on copper foil.

ibrated against the vapor pressure of pure ^{3}He. Above ≈4 K, a calibrated germanium-resistance thermometer[18] was used in place of the magnetic thermometer. In making a measurement of thermal conductivity κ, one of the top pair of uncalibrated thermometers was maintained at a constant resistance and hence constant temperature. The lower thermometer was read, electrical power $\dot{Q}$ applied to the heater, and the lower thermometer again read to give the temperature difference[16] ΔT between the two sets of thermometers separated by a distance L. Hence $\kappa = \dot{Q}L/A\Delta T$, where A was the cross-sectional area of the sample. The value of κ was independent of ΔT, and usually $\Delta T/T \approx 10\%$.

A simple ^{4}He cryostat was used for measurements in the range of roughly 10–100 K. Chromel-constantan thermocouples replaced the carbon resistance thermometers and were calibrated against a calibrated germanium-resistance thermometer.[18] Although any residual heat leaks to or from the sample should produce only second-order effects when thermometers are calibrated *in situ*,[19] the diameter and thermal grounding of the thermocouple wires were varied as a check. No change in the measured values of κ was noted. In addition, the known thermal conductivities of Cu and of high-purity fused SiO$_2$ were measured as a further check on the technique.

The major systematic error in the above measurements was the determination of L, which was uncertain by $\lesssim 5\%$. The largest random errors occurred for high conductivity samples near 10 K where the small ΔT and the limited temperature resolution of the thermocouples combined to give errors of about 15%.

One measurement at 300 K was made on Na β-alumina using a commercial thermal comparator.[20] This device was calibrated using a series of six materials of known thermal conductivity. The surface of the sample was polished, with 1-μm abrasive used in the final stage.

III. RESULTS AND DISCUSSION

The thermal conductivities of Li, Na, K, and Ag β-alumina are shown in Fig. 2, each measured parallel to the conducting planes, i.e., perpendicular to the c axis of the crystal. A sample of Na β-alumina having the long axis of the sample perpendicular to the conducting planes was measured at $T < 35$ K. It had a κ with a temperature dependence similar to the Na data of Fig. 2, but with a magnitude ≈40% larger. This larger magnitude partially reflects the 40% larger lateral dimensions of this sample (reducing the boundary scattering of phonons — see below), and hence κ is essentially isotropic. The κ of the optically more-

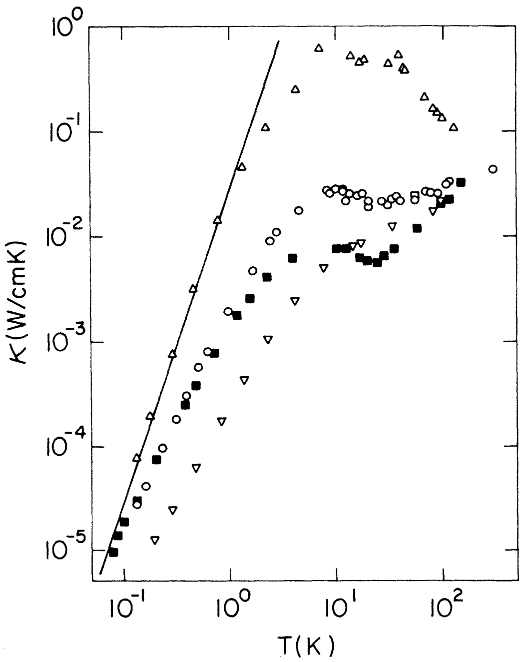

FIG. 2. Thermal conductivity κ vs temperature T for β-alumina isomorphs. Δ, K; ○, Na; ■, Ag; ∇, Li. The solid line represents the calculated phonon conductivity of the K sample as limited by phonon scattering from the surfaces of the crystal.

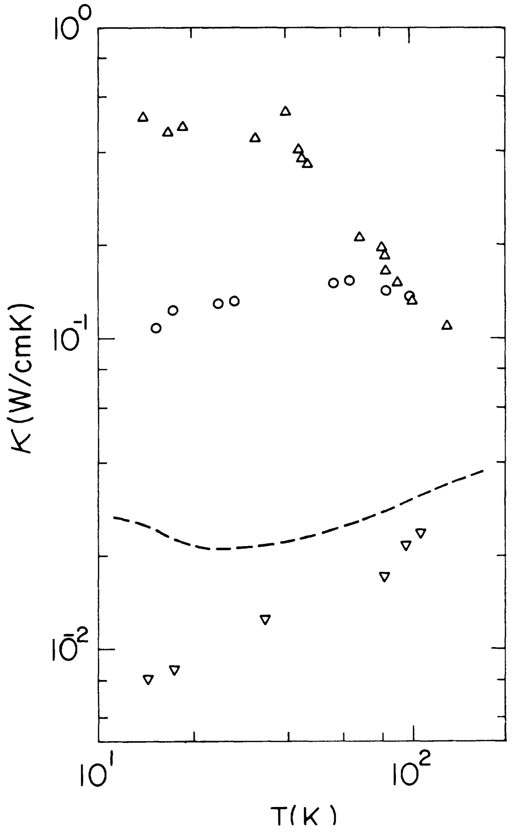

FIG. 3. Thermal conductivity versus temperature of β-alumina after two successive ion exchanges in the same crystal, starting from Na β-alumina. Dashed line, original Na β-alumina; ▽, first exchange, Li; ○, second exchange, K; △, K β-alumina for comparison.

perfect samples from the Argonne National Laboratory agreed with the Na and Ag data of Fig. 2 to within the experimental uncertainty of ≈ 5%, thus demonstrating an apparent insensitivity to the number of excess cations.

The substitution of K for Na increased κ near 10 K by a factor of ≈ 40 (Fig. 2), while ion exchange with Li lowered κ. To determine if the substitution of Li into the lattice introduced permanent defects, thereby reducing κ, K was substituted into a Li β-alumina sample. The result is shown in Fig. 3. The measured conductivity after a double-ion exchange (Na → Li → K) is larger than in the original material. Assuming a linear variation between the Li content and the inverse phonon mean free path l^{-1} associated with this ion, the data of Fig. 3 suggest that ≈ 5% of the Li remained after an incomplete substitution of K. This is consistent with density measurements which suggest that ≤ 10% of the Li remained in the sample. In brief, it is concluded that substitution of Li in β-alumina does not disrupt the lattice significantly and that ion exchange is a reversible process. Of greater importance is the conclusion that the variation of κ between isomorphs shown in Fig. 2 is to be associated with the particular cation present.

Two qualitative comments can be made concerning the results shown in Fig. 2. Although the κ of the four isomorphs differ by as much as 100 near 10 K, the data appear to converge near 300 K and below 0.1 K. The minima in κ near 20 K for Na and Ag β-alumina are real reproducible characteristics.

Quantitative comments concerning the data require a computation of κ using the expression

$$\kappa = (6\pi^2)^{-1} \sum_i \int C(\omega) l_i(\omega) v_i^{-2} \omega^2 \, d\omega, \tag{1}$$

where $C(\omega)$ is the contribution to the heat capacity by phonons having frequency ω, v is the phonon velocity, and the sum is over the three phonon modes. An isotropic material is assumed for the calculations. Assuming the Debye approximation (v_i constant[21]) and scattering of phonons only by the boundaries,[22] the κ of the K β-alumina was calculated using no adjustable parameters and is shown as the solid line in Fig. 2. The agreement with the experimental data implies that boundary scattering dominates κ below 1 K for the K sample. It is likely that boundary scattering also influences the κ of the other samples at somewhat lower temperatures. The data of Fig. 2 can be corrected for boundary scattering by assuming that $l(\omega)$ of Eq. (1) may be approximated by

$$l(\omega)^{-1} = l_B^{-1} + l_{\text{ion}}^{-1}, \tag{2}$$

where l_B is the phonon mean free path due to boundary scattering only[22] and l_{ion} is that related to the cations. The corrected κ as limited by the cations varies as $T^{1.8}$, $T^{2.0}$, and $T^{1.6}$ for the Li, Na, and Ag β-alumina samples, respectively, below ≈ 5 K.

Above ≈ 50 K, the κ of the K β-alumina is probably limited by phonon-phonon scattering. Indeed, the measured magnitude and temperature dependence is in qualitative agreement with thermal conductivities limited by phonon-phonon scattering as observed for other spinel structures.[23] The empirical magnitude of the mean free path associated with this process for the K isomorph is

$$l_{pp}^{-1} \approx 2(\hbar/vk)\omega T^3 \ (\text{cm}^{-1}), \tag{3}$$

where $\hbar$ is the Planck constant divided by 2π, and k is the Boltzmann constant. Presumably this process occurs also in the other isomorphs but is overwhelmed by the magnitude of l_{ion}^{-1}.

It is reasonable to expect that l_{ion} would depict some of the same characteristics observed in photon scattering. Raman scattering exhibits re-

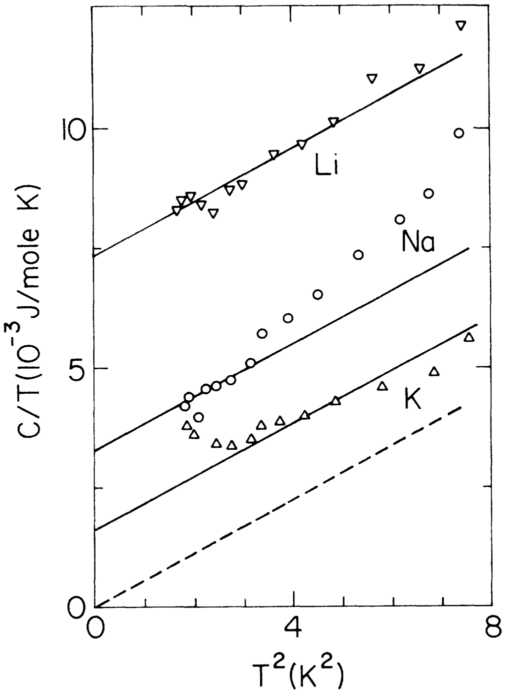

FIG. 4. Specific heat C of β-alumina isomorphs divided by temperature T vs T^2. The data were obtained from Ref. 4. ∇, Li; ○, Na; △, K. The dashed line represents the acoustic phonon contribution as calculated from the phonon velocities, Ref. 21.

sonances at roughly 25, 60, and 80 cm^{-1} for Ag, Na, and K β-alumina, respectively, although the method of crystal growth may influence the scattering.[24] (No lines are observed for Li.) Since the integrand of Eq. (1) is maximum near $\hbar\omega = 3.8kT$, the foregoing resonances would effect κ near 10, 25, and 30 K, respectively. In Fig. 2, there are indeed minima for Ag and Na near the appropriate temperatures. (There is no minimum in the K data near 30 K, but this might reflect a weaker coupling of phonons to the cation motion in this isomorph.) A *strong* resonant phonon scattering process that is not temperature dependent, however, would not prevent κ from monotonically increasing with temperature and thus no minima would be possible. But if the width of the resonance broadened with temperature, phonons having a frequency below the resonant frequency would have their mean free paths reduced as the temperature increased and κ could pass through a minimum. Using in Eqs. (1) and (2) various forms of $l_{\rm ion}$ which might be appropriate for a resonance, such as

$$l_{\rm ion}^{-1}(\omega) \propto \omega^4 \gamma \left[(\omega^2 - \omega_r^2)^2 + \gamma^2 \omega^2 \right]^{-1} \tag{4}$$

[where ω_r is the resonant frequency, $\gamma = \gamma_0(1 + BT)$ is the resonance width, and B is the strength of the temperature-dependent broadening] gives good fits to the Na and Ag data near the minima. However, the temperature-dependent broadening of the resonance widths [parameter B in Eq. (4)] must be a factor of 10^2 stronger than is observed in Raman scattering.[25] In addition, resonant scattering does *not* explain the strong scattering associated with $l_{\rm ion}$ below ≈ 5 K. Consequently, using the resonances observed in light scattering cannot explain the data below ≈ 5 K, nor does this process provide a convincing explanation of κ above ≈ 5 K.

An explanation of the data for $T \lesssim 5$ K requires a broad band of excitations of frequency $\approx 10^{10}$–10^{12} Hz, the former value related merely to the lowest temperatures for which κ was measured. As mentioned in Sec. I, specific-heat measurements provide evidence for low-frequency excitations in β-alumina. The excess specific heat was said to deviate toward a linear temperature dependence.[4] This, together with the disordered state of the cations in the mirror plane, suggested[26] that the tunneling model of localized states[27] might be applicable. This model was originally developed to account for a similar excess specific heat in glassy materials. Since the model also predicts a T^2 dependence of κ at low T, it is tempting to explain κ of the β-alumina in terms of this model.[28]

In Fig. 4, we have replotted the specific heat (C) data of Ref. 4 as C/T vs T^2 to emphasize any linear temperature dependence. The phonon contribution to C/T is represented by the dashed line; all lines

TABLE I. Densities of states calculated from measured specific heats (n_C) and thermal conductivities (n_κ), and parameters l_B, A, ω_0 used in calculating the thermal conductivities depicted in Fig. 5.

	n_C (10^{39} J^{-1}cm^{-3})	n_κ (10^{39} J^{-1}cm^{-3})	l_B (cm)	A (cm^{-1} K^{-1})	ω_0 (cm^{-1})$^{\rm a}$
Li	60	2	0.13	300	11
Na	30	0.2	0.12	19	5
K	10	$\lesssim$0.01	0.14	0.9	9
Ag	...	0.2	0.14	23	3

[a] 1cm^{-1} = 3×10^{10} Hz = 2×10^{-23} J.

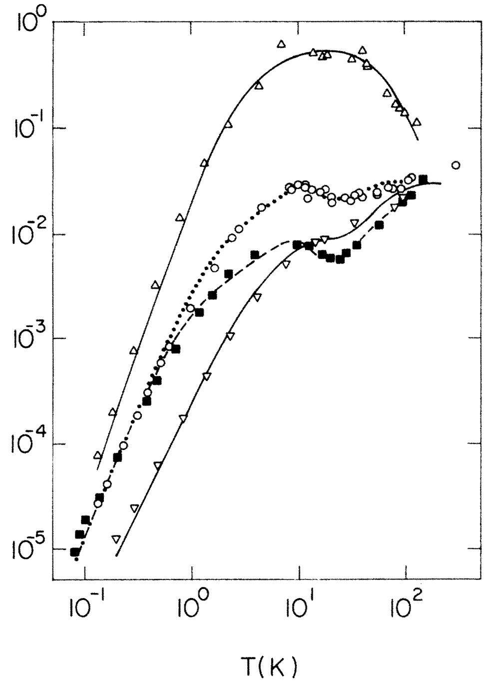

FIG. 5. Thermal conductivity vs temperature of β-alumina showing the same data as Fig. 2. The curves were computed using a model developed for amorphous materials as described in the text. Only two parameters in the computation were varied to fit the four sets of data.

through the data are drawn with the same slope. At higher temperatures for Ag, Na, and K β-alumina there is an additional contribution to C from the resonances mentioned previously.[4] Indeed, the resonance contribution from the low-frequency Ag resonance is so large that neither a T nor a T^3 term can be distinguished and the Ag data have been omitted from Fig. 4.

The linear behavior of the data in Fig. 4 is less than convincing, but if the lines are taken as drawn, a constant density of excitations per unit energy interval n_C can be calculated. The results are given in Table I. Likewise, a density n_κ can be deduced from the $\approx T^2$ portion of the thermal-conductivity data[29] by assuming a deformation potential of 0.5 eV, a value consistent with measurements in glass.[30] The resulting values of n_κ are given in Table I and are considerably smaller than the corresponding values of n_C. This is not an encouraging result, but on the other hand a similar problem has been encountered in applying the tunneling-states model to glassy materials.[31]

It is therefore tempting to pursue the tunneling-states model further by applying it in a calculation of κ for the entire temperature range as has been done for glassy materials.[8] In Eq. (2), we use $l_{\text{ion}} = l_A$ for $\omega < \omega_0$; otherwise, $l_{\text{ion}} = l_{\text{min}}$. Here l_{min} is the minimum conceivable acoustic-phonon mean free path (roughly the size of a unit cell) as suggested by Kittel[32] and, from the tunneling-states model,[29]

$$l_A^{-1} = A(\hbar\omega/k)\tanh(\hbar\omega/kT) + (\tfrac{1}{4}A)\beta T^3 \qquad (5)$$

for $\hbar\omega/k > \beta T^3$, or

$$l_A^{-1} = A(\hbar\omega/k)\tanh(\hbar\omega/kT) + (\tfrac{1}{4}A)(\hbar\omega/k) \qquad (6)$$

for $\hbar\omega/k < \beta T^3$. Further details have been given in Ref. 8 and will not be repeated here. Substitution of $l(\omega)$ into Eq. (1) produced the curves shown in Fig. 5. The $l(\omega)$ at 0.1 K for Na β-alumina is shown in Fig. 6. Equation (3) has been included in the calculations for completeness, but κ is not very sensitive to the magnitude of l_{pp} or l_{min} below 100 K. Also the abrupt drop at ω_0 in Fig. 6 could vary as ω^{-4} and not affect the calculated results in Fig. 5. Only two of the adjustable parameters, A and ω_0, were varied in fitting the four isomorphs (see Table I); l_{pp}, l_{min} (=25 Å), and β (=6×10^{-4} K^{-2}) were held constant. From the values of the parameters A and β used in the fits, densities of localized excitations n_κ could again be calculated. These values, which are now independent of any assumption concerning the magnitude of the deformation potential, are the same as calculated

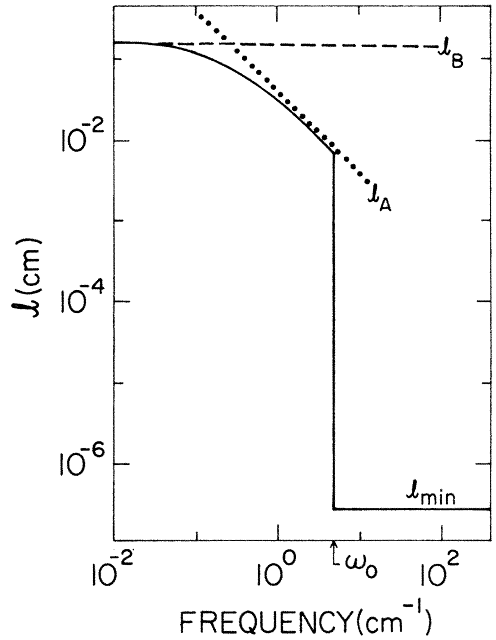

FIG. 6. Phonon mean free path l vs frequency ω corresponding to the fit to the Na β-alumina data shown in Fig. 5. l_B, contribution due to boundary scattering; l_A, contribution due to localized excitations; l_{min}, Kittel limit; ω_0, frequency near which l decreases rapidly with increasing ω.

previously and listed in Table I.

Although the above calculation is a gross approximation for temperatures above ≈ 20 K (as usual, dispersion has been ignored), it does provide for the minima in the Na and Ag data while still fitting reasonably well the κ of Li and K β-alumina. Thus the calculation suggests that the κ of β-alumina between 10 and 100 K might be determined by a scattering mechanism different from that detected in light-scattering experiments.

It is appropriate to ask if tunneling motion in the mirror planes is a reasonable expectation. There is some evidence for "glassy behavior" in other slightly disordered systems, i.e., in polycrystalline materials.[33-35] In β-alumina it has been suggested[4] that the cations tunnel between sites, a distance of ≈ 4 Å. Alternatively, the ions might tunnel within the different cation sites, distances of ≈ 0.4 Å. Another possibility is that of the bridging O atoms in the mirror plane, since the two Al-O bonds are probably not collinear. This would allow the O atoms to tunnel about this axis, with energy levels determined by the neighboring ions. For all tunneling possibilities, the range of excitation energies observed might be produced by the disorder in ion site potentials due to the random occurrence of excess ions and charge compensating defects. Only one cation (or bridging O) in 10^2–10^4 need be involved in tunneling motion over the frequencies probed in order to explain the excess specific heat and the low-temperature thermal conductivity.

In summary, the thermal conductivity of single-crystal β-alumina between 0.1 and 300 K has been shown to depend strongly on the cation (Li, Na, K, Ag) placed in the conducting plane. The data indicate that a broad band of excitations ($\lesssim 10^{-21}$ J) are present and associated with the cations. The data may be explained in terms of a tunneling-states theory which was originally developed to explain a similar band of excitations in amorphous materials. From available data, it can not be determined conclusively that this is the appropriate explanation, nor indeed that β-alumina behaves the same as a glassy material.

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