

## Thermally Activated Microwave Conductivity in the Superionic Conductor Hollandite ( $\text{K}_{1.54}\text{Mg}_{0.77}\text{Ti}_{7.23}\text{O}_{16}$ )

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We report the microwave conductivity of a single crystal of the superionic conductor hollandite ( $\text{K}_{1.54}\text{Mg}_{0.77}\text{Ti}_{7.23}\text{O}_{16}$ ). The charge carriers are potassium ions which propagate along channels. Transport is determined by thermally activated hopping of the potassium collective coordinate over an effective potential barrier. The conductivity effective barrier height agrees with a model which accounts for the structural parameters of hollandite. This represents the first detailed agreement between transport and structural data for a superionic conductor.

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Coulomb interactions between ions are expected to lead to significant effects in ionic conductors when only a fraction of the available sites are occupied. In the superionic conductor hollandite ( $\text{K}_{1.54}\text{Mg}_{0.77}\text{Ti}_{7.23}\text{O}_{16}$ ), the potassium ions move in channels provided by the ionic framework, the fractional occupancy of the available sites in the channels  $p = 0.77$ . Recent diffuse x-ray structural studies<sup>1</sup> have been interpreted<sup>2</sup> in terms of a model which assumes comparability of the potassium ion Coulomb-Coulomb repulsion and the (bare) lattice potential experienced by the potassium ions. This results in a collective-coordinate description of the ionic motion, and an off-center ionic position in equilibrium configurations. The model was used<sup>2</sup> to calculate the off-center positions of the potassium ions, and to correlate these values with the diffuse x-ray scattering data. A concomitant outcome of the model is the reduction of the observed potential barrier height for ionic motion along the channels in which the potassium ion moves. At low frequencies (millihertz and below), impurity-induced defects dominate transport,<sup>3</sup> and the effective potential barrier heights in the unperturbed portion of the channels are not relevant to the charge transport. We have performed microwave conductivity experiments on hollandite at X band (9 GHz) from 77 K to room temperature. At this frequency and temperature range, diffusion lengths are much shorter than the separation of impurity-induced defects. Hence the intrinsic or pure charge trans-

port dominates, and one can observe the effects of the effective barriers directly. We find that the conductivity exhibits a simple activated behavior, with activation energy 0.034 eV. This value correlates well with the predicted<sup>2</sup> reduction in the effective barrier height from the bare value, and represents the first example where structural and transport data are adequately explained by the same model.

The microwave conductivity and dielectric constant were measured on long, needle-shaped crystals with use of a cavity perturbation technique described in Refs. 3 and 4. This method has been used for similar measurements on organic conductors and is especially advantageous for measurement of small single crystals. A sample inserted into a microwave cavity leads to a shift  $\delta$  and change of half-width  $\Delta$  of the absorption. The conductivity and dielectric constant at frequency  $f$  are then given by

$$\sigma = (f\alpha/2\eta^2) \left( \frac{\Delta/2}{(\Delta/2)^2 + [(\alpha/\eta) - \delta]^2} \right), \quad (1)$$

$$\epsilon_1 = 1 + (1/\eta) \left( \frac{\delta[(\alpha/\eta) - \delta] - (\Delta/2)^2}{(\Delta/2)^2 + [(\alpha/\eta) - \delta]^2} \right), \quad (2)$$

where  $\alpha = 2V_s/V_c$  (with  $V_s$  and  $V_c$  the volume of the sample and of the cavity, respectively) is the filling factor, and  $\eta$  the depolarization factor.

For a rectangular parallelepiped,

$$\eta = (bc/a^2) \{ \ln[4a/(b+c)] - 1 \}, \quad (3)$$

where  $a$  is the length,  $b$  the width, and  $c$  the thickness of the sample.

Figures 1(a) and 1(b) exhibit the temperature dependence of the absorption half-width and frequency shift of the two samples measured. The sample dimensions,  $3.85 \times 2.2 \times 2.2 \text{ mm}^3$  and  $3.49 \times 2.4 \times 2.4 \text{ mm}^3$ , lead to a theoretical  $\alpha/\eta$  of  $4.65 \times 10^{-3}$  and  $3.75 \times 10^{-3}$ , respectively, for samples  $A$  and  $B$ . The dielectric constant is found to be large, and independent of the temperature at low temperatures where the conductivity is small. The room-temperature value ( $\epsilon_1 \sim 80$ ) is in rough agreement with values deduced from infrared experiments at room temperature<sup>1</sup>:  $\epsilon_1 \sim 126$  parallel to the channels, and 36 perpendicular to the channels. The temperature dependence of the conductivity is shown in Fig. 2, in the form  $\sigma T$  vs  $T^{-1}$ . It is evident from Fig. 2 that the behavior of  $\sigma(T)$  can be described by the relation

$$\sigma = (ne^2 a_0^2 \nu_i / k_B T) \exp(\Delta k_B T) (\Omega \text{ cm})^{-1}, \quad (4)$$

where  $a_0$  is the lattice constant,  $\nu_i$  is the attempt frequency, and  $n$  is the number of charges involved in the conduction process. The activation energy appearing in (4) is the effective barrier height, which, from Fig. 2, is found to equal

$$\Delta_{\text{eff}} = 0.034 \text{ eV}. \quad (5)$$

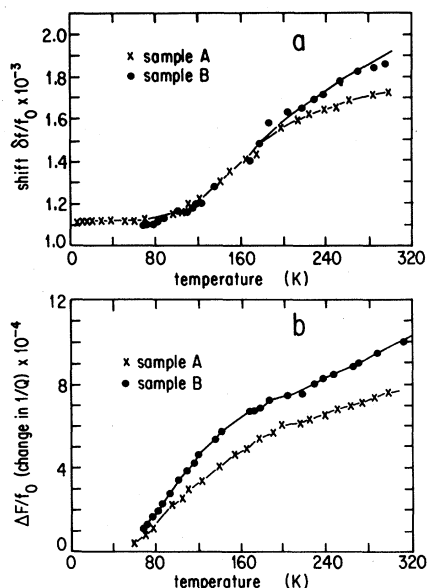


FIG. 1. (a) Temperature dependence of the cavity frequency shift  $\delta f/f_0$  with  $E$  field along the crystal needle axis. (b) Temperature dependence of the change in cavity full width at half maximum  $\Delta f/f_0$  with  $E$  field along the crystal needle axis.

We note that the measured room-temperature conductivity equals  $0.22 \Omega^{-1} \text{ cm}^{-1}$  and  $0.24 \Omega^{-1} \text{ cm}^{-1}$ , for samples  $A$  and  $B$ , respectively.

The diffuse x-ray scattering was accounted for in Ref. 2 by taking the potassium ions to lie at off-center equilibrium configurations. The number and character of the configurations were a consequence of the precise form used for the lattice potential experienced by the potassium ion. For example, the diffuse x-ray scattering could be accounted for by a particular ratio of short-range Coulomb to parabolic lattice potential interaction coefficients. This ratio was found to lead to a reduction factor of  $\sim 0.4$  for the effective barrier height from the bare value. A sinusoidal lattice potential would have led to a reduction factor of 0.1. Long-range Coulomb interactions yielded reduction factors of 0.45 and 0.08 for the two forms of bare lattice potentials, respectively. The fit of the diffuse x-ray data for long-range Coulomb and a parabolic lattice potential resulted in a bare lattice potential barrier of 0.144 eV.<sup>2</sup> The calculated reduction factor, 0.45, leads to an effective barrier height of 0.065 eV. Our measured value, Eq. (5), of 0.034 eV is in good agreement with this value. We also note that, although the effective barrier height was not calculated with use of a sinusoidal potential, the larger reduction of the barrier height implies a smaller effective barrier than for the parabolic case.

The model also accounts for the magnitude of the conductivity. The number of holes  $n_h = n_r(1-p) = 1.52 \times 10^{21} \text{ cm}^{-3}$ , and  $a_0 = 2.97 \text{ \AA}$ . The attempt frequency is determined with use of a para-

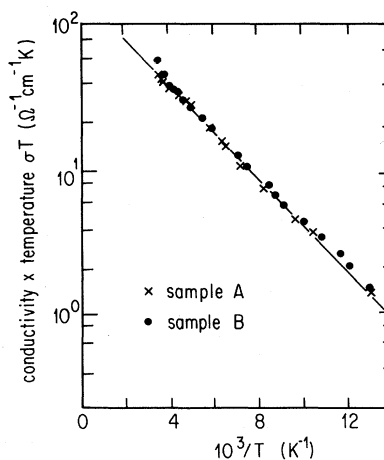


FIG. 2. Plot of  $\sigma(T) \times T$  vs  $10^3/T$ .

bolic potential  $V(x) = m\omega_0^2 x/2$ . The activation energy  $\Delta = V(a_0/2)$ . Thus  $\omega_0 = (4\Delta/ma_0^2)^{1/2} = 4 \times 10^{12} \text{ sec}^{-1}$ . With this value for  $\omega_0$ , Eq. (4) then leads to  $\sigma(T = 300 \text{ K}) = 2 \Omega^{-1} \text{ cm}^{-1}$ , in adequate agreement with the measured values of  $\sim 0.2 \Omega^{-1} \text{ cm}^{-1}$ .

In summary, the model of Beyeler, Pietronero, and Strässler<sup>2</sup> utilized the Coulomb interaction to produce collective behavior of the potassium ion motion in the presence of the underlying lattice potential. The collective coordinate which also describes charge transport generated off-center (incommensurate) equilibrium potassium ion positions. These were fitted to the observed diffuse x-ray scattering data. The same model predicts a significant reduction from the bare lattice potential for the effective barrier height for collective-coordinate motion. These reduced barrier heights are masked at low frequencies by impurity-induced defects in the potassium ion channels. Measurements at X-band frequencies lead to observation of intrinsic behavior because the root-mean-square distance for collective coordinate motion is much less than the distance between defects. We find simple activation behavior with the lowest barrier height ever found for a superionic conductor. As an example, the archetypal superionic conductor,  $\alpha$ -AgI, has a barrier height of  $\sim 0.07 \text{ eV}$ , while we find [Eq. (5)]  $\sim 0.034$

eV for hollandite. We interpret this as evidence that the configurational model of Beyeler, Pietronero, and Strässler<sup>2</sup> yields an essentially correct picture of the microscopic processes underlying charge transport in hollandite. The result appears to provide conclusive experimental evidence for strong barrier height reduction caused by many-particle interaction effects.

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## Corrections to Scaling and Universality: Experimental Evidences

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Large corrections to scaling have been discovered in the susceptibility  $\chi$  and in the order parameter  $m$  of the binary mixture triethylamine-water, allowing accurate determinations of the universal exponent  $\Delta = 0.52 \pm 0.03$  and of the correction amplitudes  $a_\chi^+$  and  $a_m^-$ . Together with our previous determination of the specific-heat correction amplitude  $a_c^+$ , this allows the calculation of three different universal ratios, in particular  $a_c^+/a_\chi^+ = 7.9 \pm 1.2$ , which agrees well with the theoretical prediction  $8.5 \pm 0.9$  obtained by field theories.

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Near a second-order phase transition the expression of a thermodynamic quantity  $\pi$  which exhibits a critical behavior governed by the exponent  $\tilde{\omega}$  should include "corrections-to-scaling" or "nonanalytical correction" terms<sup>1</sup> which correct the behavior when the temperature  $T$  is not very close to the critical temperature  $T_c$ ; then  $\pi$  can generally be written as  $\pi^{+,-} = Pt^{-\tilde{\omega}} [1 + a_\pi^{+,-} \times t^\Delta + \dots] + \pi_B^{+,-}$ .  $t = |(T - T_c)/T_c|$  is the re-

duced temperature,  $\Delta$  is close to 0.5, and the amplitude  $a_\pi$  determines the first-order correction-to-scaling term.  $\pi_B$  is an eventual background (regular) contribution. Superscript + (-) denotes the homogeneous (inhomogeneous) region. The exponents  $\tilde{\omega}$  and  $\Delta$  are universal and their value depends only on the universality class of the system.<sup>2</sup> The amplitudes  $P$  and  $a_\pi$  depend on the system, but there exist universal combina-