PHYSICAL REVIEW B VOLUME 18, NUMBER 6 15 SEPTEMBER 1978

Theory of one-dimensional ionic and solitary-wave conduction in potassium hollandite

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(Received 11 April 1978)

It is argued that ions moving in hollandite crystals should not be significantly scattered by impurities. This could lead to large conductivities for low ionic concentrations. Ionic conduction for high concentration of ions occurs by motion of solitary-wave-like defects whose motion is damped by phonon radiation. An expression for the electrical conductivity is found using models for the motion of such solitary waves which were previously applied to the study of dislocation motion under an applied stress. Comparison is made with experiments on hollandite with the aid of an interrupted-strand model.

I. INTRODUCTION

Recently there has been a good deal of interest in one-dimensional electrical conductors.[1] Because of their one-dimensional nature, they can exhibit unusual, often striking behavior in their electrical conduction. There is also much interest today in superionic conductors because of their potential use as solid electrolytes in solid-state batteries.[2] Hollandites are superionic conductors which exhibit one-dimensional character in the sense that the mobile ions move in one-dimensional channels provided by the other ions.[3] Thus, we would expect oriented single-crystal samples of these materials to exhibit one-dimensional electrical conduction. As will be discussed in the next section, impurities do not significantly scatter the potassium ions, essentially because the ions behave as classical particles, and thus, once they are thermally activated above the potentials due to the impurities, they are not backscattered in the channel.

In a previous publication, it was shown that electrical conduction in potassium hollandite is due to the motion of defects in the periodic ordering of potassium ions in the channel.[4] For the case of a nearly completely filled channel, the conduction is caused by the motion of vacancies. Since a vacancy and certain solitary waves or dislocations are identical in one dimension, we may apply the one-dimensional Frenkel-Kontorova model, proposed for the study of dislocations in solids, directly to this problem. This model consists of a chain of atoms connected by springs, situated in a sinusoidal potential well. The primary mechanism for dissipation of the motion of a vacancy in the potassium-ion system, once it is set in motion, is the creation of lattice vibrations among the potassium ions.[5] This will be discussed in Sec. III.

II. INTERACTION OF THE MOBILE IONS IN HOLLANDITE WITH IMPURITIES

There is a theorem which states that the conductivity of a one-dimensional conductor should be zero if there are random impurities in it.[6] The reason for this can be roughly understood on the basis of the following simple picture: Let us represent the distribution of impurities by a row of n potential barriers, each with a reflection coefficient R_1. Consider a particle incident on this distribution of impurities from one side. The transmission coefficient for the impurities is, when we consider all multiple reflections from the barriers, given by

$$\mathcal{T} = (1 - R_1)/(1 - R_1 + nR_1) . \tag{1}$$

We have neglected all coherence effects between barriers, which is reasonable if their spatial distribution is truly random. Since n approaches infinity in the thermodynamic limit, $\mathcal{T}$ approaches zero.[6] If classical instead of quantum mechanics had been used, we would find that $\mathcal{T}$ is zero for a particle whose energy is less than, and 1 for a particle whose energy is greater than the energy of the highest potential barrier because a classical particle is not reflected by an impurity if the height of the impurity's potential barrier is less than the particle's energy. This does not, of course, predict infinite conductivity for a classical particle in two and three dimensions because the particle can always be deflected no matter how high its energy. In reality, a particle whose energy is higher than all potential barrier heights will suffer some scattering at each impurity (because $\hbar \neq 0$), and hence, in the thermodynamic limit Eq. (1) will give $\mathcal{T} = 0$.[6]

If the particle is classical enough, however (i.e., if its de Broglie wavelength is short enough), its mean free path (i.e., the distance over which it can travel through a distribution of random impurities before its wave function decays to zero) could be of macroscopic dimensions. The conductivity could be, in such a case, for all purposes infinite for any normal size sample. To estimate the mean free path, consider Eq. (1) with $n = cx$, where c is the impurity concentration and x is the length of sample which the particle has passed through. Equation (1) can only deviate significantly from 1 when $nR_1 \approx 1$ from which we see that the mean free path can be taken to be

$$(CR_1)^{-1} . \tag{2}$$

In order to estimate R_1, we consider scattering of a particle of energy E from a potential barrier of the form

$$V_0(1+e^{x/b})^{-1} , \tag{3}$$

where V_0 is the barrier height and b represents the distance over which the potential varies. This problem has an exact solution.[7] [Equation (3) could represent the potential barrier on one side of an impurity.] For $E > V_0$, the reflection coefficient is given by

$$R_1 = \left(\frac{\sinh \pi (k_1 - k_2) b}{\sinh \pi (k_1 + k_2) b}\right)^2 , \tag{4}$$

where

$$k_1 = (2mE)^{1/2}/\hbar , \tag{5a}$$

$$k_2 = [2m(E - V_0)]^{1/2}/\hbar . \tag{5b}$$

Equation (4) is the same for the potential given by Eq. (3) with x replaced by $-x$ (i.e., it also gives the reflection coefficient for the other side of the impurity potential barrier). In the semiclassical limit (i.e., $k_1 b$, $k_2 b \gg 1$),

$$R_1 \approx e^{-4\pi k_2 b} . \tag{6}$$

Let us apply these arguments to potassium hollandite.[3] Consider a single potassium ion in an otherwise empty channel. For $E - V_0 = 10^{-4}$ eV, the wavelength is already equal to 10^{-8} cm (i.e., a typical order of magnitude for b) and is smaller for larger $E - V_0$. For such a wavelength and for $c = 10\%$ the mean free path found from Eqs. (2) and (6) is already of the order of 0.1 mm.

Because the potassium ions are in fact quite classical they cannot tunnel through the potential barriers in the channel potential, and hence, they must be thermally activated to an energy above the top of these barriers in order for them to conduct. Once raised to such energies by thermal excitation and set in motion by an electric field, the ions will not be significantly scattered by impurities, as we have seen. Ion-ion interaction, however, can dissipate the motion of a given ion by distributing its energy among the various ions. Because of the channel potential, the total momentum of the ions is not conserved, and thus when the energy of all ions drops below the height of the barriers because of collisions with other ions, the current stops flowing (since the ions cannot tunnel through the barriers). Such mechanisms of damping of the current will be discussed in Sec. III. By growing crystals with very low concentrations of mobile ions in the channels, however, this process can be minimized.

This leaves only phonon umklapp scattering as a source of resistance. Nonumklapp scattering will not dissipate current because of the phenomenon of phonon drag.[8] Because of the high polarizability of the ions which comprise the channel, the mobil-ion–phonon interaction should be weak, and therefore, ordinary one-phonon processes should dominate. Phonon umklapp scatterings require the existence of phonons near the zone boundary. The probability for the existence of such phonons is $\sim e^{-\Theta/T}$, where T is the temperature and Θ is the Debye temperature which should be of the order of 500 °K or higher in a covalent compound like hollandite.[8] Thus, at temperatures below Θ, there will be little resistance to the flow of such ions, if the activation energy for the motion of the ions over potential barriers is smaller then $k\Theta$ (because $\sigma \propto e^{-\Delta E/kT} e^{\Theta/T}$, where ΔE is the barrier height). Although the activation energy for the conductivity of potassium hollandite measured on polycrystalline samples is 0.2 eV,[9] this need not be equal to the barrier height. Because the samples are highly imperfect, the channels could have finite lengths. Then, the only way that an ion could traverse the length of the crystal would be to move into a neighboring channel or over a break in the channel. Thus, the measured activation energy might be the activation energy for getting into a neighboring channel as will be discussed in more detail in Sec. IV. Beyeler, Pietronero, Strässler, and Wiesmann[3] find that a dielectric constant of 6 is required in order to obtain the observed x-ray diffraction peak widths (if the dielectric constant is not position dependent). With this dielectric screening of the interionic Coulomb interaction, they found that in order to obtain the observed displacements of the ions around a vacant site,[3] the channel potential barrier must be about 0.06 eV, which is comparable to $k\Theta$. This energy could be reduced still further by substituting more polarizable ions in the synthesis of the crystal. If we assume with Beyeler, Pietrenero *et al.* that the high polarizability of the ions which make up the channel is only effective inside the channel, we might still expect high ionic mobility because the inelastic phonon umklapp scattering should be relatively weak (because the electron-phonon interaction is weak).

Such phenomena can only occur in crystals with a very low concentration of potassium ions. Samples grown to data have much higher ionic concentrations, and thus, for these samples, the primary mechanism for dissipation of the ionic current is the creation of phonons among the potassium ions, which will be discussed in more detail in Sec. III. In the high-ionic-concentration regime, it is more appropriate to speak of vacancy rather than ionic motion. As we shall see the vacancy's motion is usually strongly damped because it radiates phonon excitations among the potassium ions as it moves.

III. DAMPING OF VACANCY MOTION IN HOLLANDITE BY PHONON RADIATION

As was pointed out in Ref. 4, the electrical conduction in the samples of potassium hollandite that have been grown to data, which have the channels between 75% and 100% filled with potassium ions, must be due to the motion of defects. For example, for a channel that is nearly full, the principal current carriers are vacancies. For potassium vacancies in hollandite, there are very large displacements of the ions on neighboring sites.[3] In one dimension, such a vacancy is identical to a dislocation or solitary wave in which $N-1$ ions are shared among N lattice sites.

Let us now consider the damping of the motion of these defects by phonon radiation.

These vacancies undergo steady-state motion above a certain speed under an applied field[5] (the electric field in our case is equivalent to a shear stress in previous work on dislocations). It has been shown by Earmme and Weiner in a modified Frankel-Kontorova model that such dislocations can move without any phonon radiation damping if they move at certain speeds[5] (about $\frac{1}{4}$ of the speed of sound in this model). Unfortunately, in order to set the vacancies into such motion it is necessary to apply a stress (in the dislocation problem) above the Peierls stress, which corresponds to an electric field, in the application of this model to hollandite, comparable to typical electric breakdown fields [i.e., of the order of 10^6 V/cm—which is obtained by dividing the activation energy for defect hopping found in Ref. 4 by a lattice constant]. Furthermore, vacancy velocities comparable to a quarter of the sound velocity are equivalent to enormous current densities. For example, if the vacancy concentration were 10^{20} cm^{-3}, the current density would be of the order of 10^6 A/cm^2. Clearly, in accelerating the vacancies up to such high velocities in an electric field, the sample would almost certainly be destroyed by such high currents long before we reached the lossless regime.

At much lower velocities, defect motion proceeds by thermally activated hopping as shown by Weiner and Sanders.[5] Let us apply their method to study the thermally activated motion of vacancies in hollandite. Weiner and Sanders replace the sinusoidal potential in the Frenkel-Kontorova model by the piecewise continuous potential

$$V(x) = \begin{array}{ll} \frac{1}{2}\alpha_2 x^2 \ \text{ for } |x| \le \phi & \text{(7a)} \\ \frac{1}{4}\alpha_2\phi a - \dfrac{\alpha_2\phi}{a-2\phi}\left(\frac{1}{2}a - x\right)^2 \ \text{ for } \phi \le |x| \le \frac{1}{2}a & \text{(7b)} \end{array}$$

where α_2 is the force constant and x is the displacement of an ion from the bottom of the well. That is, they replace the sinusoidal potential by parabolic and inverted parabolic potentials. We will arbitrarily take $\phi = \frac{1}{4}a$ in our calculations (i.e., we will take the potential to be symmetric, like the sinusoidal potential). As in the Frenkel-Kantorova model the atoms interact with each other by a harmonic potential

$$\frac{\alpha_1}{2}\sum_j (x_{j+1} - x_j)^2 , \tag{8}$$

where x_j is the displacement of the jth ion from the bottom of the jth potential well. The lattice will be taken to have only one vacancy, which is a good model for the case in which most potassium sites are filled. Far from the vacancy, the ions will be assumed to lie at the bottom of the nearest minimum in the periodic channel potential, which is correct if the spring constant α_1 is not too strong compared to α_2 (i.e., if the chain is not too stiff). The displacements of the ions surrounding a vacancy are illustrated in Fig. 1, where the u's signify displacements of the various ions from the bottom of the nearest potential minimum, when they are in equilibrium. Assuming that all the u's are less than $\frac{1}{4}a$, the equilibrium equations in this model become

$$(\alpha_1 + \alpha_2)u_0 + \alpha_1 u_1 = \alpha_1 a , \tag{9a}$$

$$\alpha_1 u_0 - (2\alpha_1 + \alpha_2)u_1 + \alpha_1 u_2 = 0 , \tag{9b}$$

$$\alpha_1 u_1 - (2\alpha_1 + \alpha_2)u_2 + \alpha_1 u_3 = 0 , \tag{9c}$$

with the symmetry relations $u_0 = -u_{N-1}$, $u_1 = -u_{N-2}$, etc. Assuming u_3 to be negligible and solving the resulting simultaneous equation for u_0, u_1, and u_2, we obtain

$$u_0 = a\{\alpha_1[(2\alpha_1 + \alpha_2)^2 - \alpha_1^2]/D\} , \tag{10a}$$

$$u_1 = a[\alpha_1^2(2\alpha_1 + \alpha_2)/D] , \tag{10b}$$

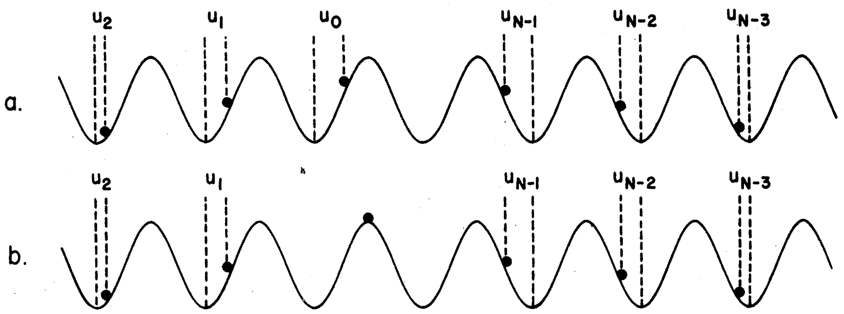

FIG. 1. (a) Equilibrum configuration of the ions around a vacancy. (b) The unstable equilibrium configuration of the ions when one neighboring ion has moved to the top of the barrier separating it from the vacant site in the configuration of (a).

$$u_2 = a(\alpha_1^3/D)\,, \qquad (10c)$$

where

$$D = (\alpha_1 + \alpha_2)[(2\alpha_1 + \alpha_2)^2 - \alpha_1^2] + \alpha_1^2(2\alpha_1 + \alpha_2)\,.$$

If we instead solved Eqs. (9a) and (9b) simultaneously, neglecting u_2, our results for u_0 and u_1 differ by less than 1%. Thus, our truncation procedure appears to be reasonable. Calculations of the equilibrium ionic positions for the Frenkel-Kontorova-like model with Coulomb interactions studied in Ref. 4 for the single-vacancy case give displacements of the ions neighboring a vacancy equal to about 35% of a lattice constant. It was found by solving the equilibrium equations that in the present modified Frenkel-Kontorova model, it is impossible to have stable equilibrium solutions with near-neighbor displacements greater than $0.25a$. Let us take $\alpha_1 = \frac{1}{3}\alpha_2$, which gives us

$$u_0 = \tfrac{24}{105}a\,, \quad u_1 = \tfrac{5}{105}a, \quad u_2 = \tfrac{1}{105}a\,.$$

In the model with Coulomb interactions studied in Ref. 4, although the near-neighbor Coulomb interaction of ions was chosen to be about 13 times the sinusoidal potential well depth, the interionic force constant and the force constant of the sinusoical potential near the bottom of the well were of the same order of magnitude. Thus, the present model calculations should give semiquantitatively correct results. It is expected, however, that the calculations may underestimate the conductivity due to defect motion and overestimate the activation energy because the chain of ions should be stiffer than we have taken it to be.

Defect hopping occurs by u_0 in Fig. 1(a) increasing until it is equal to $1.5a$ (i.e., the ion rests on a peak in the potential). The resulting equilibrium configuration [shown in Fig. 1(b)] is unstable, as we will see later in this section. The equilibrium equations are

$$\alpha_2 u_1 + \alpha_1 u_2 = \tfrac{1}{2}\alpha_1 a\,, \qquad (11a)$$

$$\alpha_1 u_1 - (2\alpha_1 + \alpha_2)u_2 + \alpha_1 u_3 = 0\,, \qquad (11b)$$

$$\alpha_1 u_2 - (2\alpha_1 + \alpha_2)u_3 + \alpha_1 u_4 = 0\,, \qquad (11c)$$

with

$$u_0 = 0, \quad u_{N-1} = -u_1, \quad u_{N-2} = -u_2, \text{ etc.}$$

Here we are measuring u_0 from the top of the peak in the potential. The solution if we assume $u_4 = 0$, is

$$u_1 = \tfrac{1}{2}a\alpha_1\{[(2\alpha_1 + \alpha_2)^2 - \alpha_1^2]/D'\}\,, \qquad (12a)$$

$$u_2 = \tfrac{1}{2}\alpha_1 a[\alpha_1(2\alpha_1 + \alpha_2)/D']\,, \qquad (12b)$$

$$u_3 = \tfrac{1}{2}\alpha_1 a(\alpha_1^2/D')\,, \qquad (12c)$$

where

$$D' = \alpha_2(2\alpha_1 + \alpha_1)^2 + 2\alpha_1^3\,.$$

For $\alpha_1 = \frac{1}{3}\alpha_2$,

$$u_1 = \tfrac{12}{17}a \qquad (13a)$$

$$u_2 = \tfrac{5}{154}a \qquad (13b)$$

$$u_3 = \tfrac{1}{154}a\quad. \qquad (13c)$$

The activation energy, the difference in potential energy between the stable and unstable configurations, calculated by substituting these calculated equilibrium displacements in the expressions for the potential energy of the lattice, is found to be

$$\Delta E_a = 0.243\,\Delta V_0\,, \qquad (14)$$

where ΔV_0 is the barrier height of the channel potential, equal to $\frac{1}{16}\alpha_2 a^2$ in the present model.

The hopping rate of the defect found by Weiner and Sanders[6] is given by

$$f_\pm = \frac{1}{2\pi}\left(\frac{\alpha_2}{m}\right)^{1/2}\nu \exp\left(-\frac{\Delta E_a \pm \frac{1}{2}eaE}{kT}\right)\,, \qquad (15)$$

for small applied field, where ν is a dimensionless quantity, E is the applied electric field (which plays the role of the stress $\bar{\sigma}$ in Weiner and Sander's notation), m is the ionic mass, f_+ is the rate of hopping along, and f_- is the rate of hopping against the field. The electric current density due to defect motion is given in the weak-field limit (for which it is reasonable to assume that thermal equilibrium is reestablished between hops) by

$$J = nea(f_+ - f_-) , \tag{16}$$

from which we obtain the conductivity

$$\sigma = \frac{ne^2b^2}{kT}\frac{1}{2\pi}\left(\frac{\alpha_2}{m}\right)^{1/2}\nu e^{-\Delta E_a/kT}, \tag{17}$$

where n is the number of defects per unit volume. The dimensionless parameter ν can be found from the decay rate (i.e., imaginary frequency) of the unstable mode in the unstable configuration [i.e., Fig. 1(b)]. The equation of motion for the lattice vibrations for the unstable configuration is

$$m\ddot{q}_j = -\alpha_1(2q_j - q_{j-1} - q_{j+1}) - \alpha_2 q_j + 2\alpha_a q_j \delta_{j,0} , \tag{18}$$

where m is the mass of a potassium ion,

$$q_j = x_j - u_j$$

and

$$q_N = q_0 .$$

This equation has a bound-phonon mode of frequency given by

$$1 - (2\alpha_2/m)G(\omega) ,$$

where

$$G(\omega) = \frac{b}{2\pi}\int_{-\pi/b}^{\pi/b} dk\left[\frac{\alpha_2}{m} + \frac{\alpha_1}{m}(1 - \cos ka) - \omega^2\right]^{-1} . \tag{19}$$

This integral can be done exactly to give

$$G(\omega) = \left[\left(\frac{\alpha_2}{m} + \frac{\alpha_2}{m} - \omega^2\right)^2 - \frac{\alpha_1^2}{m^2}\right]^{1/2} . \tag{20}$$

The resulting bound-state frequency is given by

$$\omega^2 = \frac{\alpha_2}{m} + \frac{\alpha_1}{m} - \left(4\frac{\alpha_2^2}{m^2} + \frac{\alpha_1^2}{m^2}\right)^{1/2} . \tag{21}$$

We find that ω^2 is negative if

$$\alpha_1 < \tfrac{3}{2}\alpha_2$$

which it is in our case. Thus, the bound-state phonon is unstable. Following Weiner and Sanders[5] methods using this expression for the frequency of the unstable mode, we obtain

$$\nu = 1.5656$$

for $\alpha_1 = \frac{1}{3}\alpha_2$. The resulting expression for the conductivity in $(\Omega\,\mathrm{cm})^{-1}$ for a 1% concentration of defects is

$$\sigma = (0.11725/kT)e^{-\Delta E_a/kT} \tag{22}$$

with kT in eV. To obtain this expression, we have taken

$$\alpha_2 = \left(\frac{2\pi}{a}\right)^2 V_0 ,$$

where V_0 is the amplitude of the sinusoidal potential in Refs. 3 and 5, and we have taken $V_0 = 0.4$ eV. This is the value obtained for V_0 by assuming that the barrier height $2V_0$ is $\frac{1}{13}$ of the bare near-neighbor Coulomb repulsion of the ions. The activation energy ΔE_a was taken to be $\frac{1}{4}$ of $2V_0$, implied by Eq. (14). Since the Coulomb potential is actually screened, V_0 is probably smaller than this and hence σ should be larger than the value that we have found. Also, since there are thermally activated defects at room temperature, σ should be still higher. Nevertheless, using the values for the parameters that we have quoted, we find a room-temperature conductivity of 0.086 $(\Omega\,\mathrm{cm})^{-1}$. What we have found is the ideal conductivity for a single-crystal sample with channels that run across the sample and without any complications caused by the attachment of electrodes. The effects of having breaks in the channels will be discussed in Sec. IV.

Of course our estimates for the conductivity are based on a single-vacancy model which assumes that the vacancies do not interact. Thus, our results are only numerically applicable to hollandite samples with very dilute vacancy concentrations. Our method should only give rough order-of-magnitude results for the conductivity away from the low-vacancy-concentration limit.

IV. BROKEN-STRAND MODEL APPLIED TO HOLLANDITE

The dc conductivity in a sample with one-dimensional conducting properties such as hollandite should depend critically on both the degree of orientation and degree of perfection of the crystals because the conductivity is high only along the length of an unbroken channel. If there is a break in a channel, the ions will have to either hop into a neighboring channel or hop over the potential barrier of the blockage of the channel in order to conduct electricity.[10] Thus, we would expect the activation energy of the dc and low frequency ac conductivity to be determined by these potential barriers, and not the much lower energy activation processed discussed in Sec. III and in Ref. 4.

To calculate the conductivity for a system with breaks in the chain, we may estimate the frequency with which a defect striked the barrier at the end of a channel (i.e., the mean speed of a defect divided by the distance from the barrier) by

$$f_\pm a/L_0 , \tag{23}$$

where L_0 is the average distance of a defect in a channel from the barrier for defects incident in a direction along the field [for the (+) sign] and opposite the field [the (−) sign]. The probability of scaling the barrier by a defect is $e^{-\Delta E_b/kT}$, where ΔE_b is the height of the barrier which must be scaled in order to get around the blockage. Then, the current density is given by

$$J = neL_0[(f_+ - f_-)b/L_0]e^{-E_b/kT} \tag{24}$$

which is just ne multiplied by $e^{-\Delta E_b/kT}$ and by the velocity, which is $(f_+ - f_-)b/L_0$ multiplied by L_0. Thus, the effect of a break in the channel is simply to increase the activation energy by ΔE_b. We expect that the activation energies measured in dc and low-frequency ac-conductivity experiments are probably determined mainly by blockages in the channels which provide large barrier heights and not by the processes discussed in Sec. III and in Ref. 5. Replacing ΔE_a in Eq. (17) by ΔE_b, assumed to be the experimental activation energy, σ is found to be two orders of magnitude smaller than the value found in Sec. III, in agreement with Réau *et al.*[9]

Although imperfections in the crystals which produce breaks in the channels will severely limit the dc conductivity, we would still expect higher ac conductivity at sufficiently high frequency.[10] To estimate the frequency at which the ac conductivity falls off because of interruptions in the channels, let us apply a classical free-particle model to the motion of potassium-ion vacancies:

$$m\frac{dv}{dt} = e\left(E - \frac{n_1 e}{\epsilon L_0^2}\int v\,dt\right) - \frac{m}{\tau}v\,, \tag{25}$$

where m and v are the vacancy effective mass and drift velocity, E is the electric field, n_1 is the number of vacancies per unit length, τ is a phenomenological damping time, and ϵ is the dielectric constant. The second term in the large parentheses represents the reverse Coulomb electric field produced by the buildup of charge at a break in the channel. For a harmonically oscillating electric field, we solve for the strand conduction defined as

$$\sigma_1 = \mathrm{Re}\,n_1 ev = \frac{n_1 e^2\tau}{m}\,\frac{\omega^2}{2}\left[\left(\omega^2 - m_1 e^2/mL_0^2\right)^2 + \omega^2/\tau^2\right]^{-1} \tag{26}$$

which for $\omega^2 \gg n_1 e^2/mL_0^2$ reduces to the usual Drude form

$$\sigma_1 = \frac{n_1 e^2}{m}\,\frac{1/\tau}{\omega^2 + 1/\tau^2}\,. \tag{27}$$

Assuming a 1% concentration of ions, m equal to the potassium-ion mass, L_0 equal to 100 lattice sites, and taking the lattice constant from Ref. 2, we estimate that ideal carrier conductivity that we have predicted in Sec. III should occur for ω greater than a frequency $(m_1 e^2/mL_0^2)^{1/2}$ of the order of 10–100 sec^{-1}. For about 100 times the ionic concentration and for L_0 equal to only 10 lattice sites (as might occur in highly imperfect crystals), we obtain values of $(n_1 e^2/mL_0^2)^{1/2}$ comparable to the frequencies used in the measurements made in Ref. 9. This is consistent with the speculation that we made previously that the measured low-frequency conductivity for polycrystalline samples be primarily thermally activated with activation energy equal to the energy to make an ion hop into a neighboring channel.

The ideas expressed in this section can be tested by doing ac-conductivity measurements on good single-crystal samples of hollandite as a function of frequency.

V. CONCLUSIONS

We have shown that the motion of a dilute concentration of mobile ions in hollandite should not be damped by the presence of impurities in the sample, as long as the ions have been thermally excited to an energy greater than all potential barriers in the crystal. Since single crystals with such dilute concentrations of ions have not been grown to date, this idea has not been confirmed experimentally. At larger ionic concentrations, ionic conduction occurs by motion of defects among the ordered potassium ions. The motion of such defects is damped by phonon radiation, just as the motion of dislocations in one-dimensional models is damped. At slow speeds, defect motion occurs entirely by thermally activated hopping, as does dislocation motion.[5] The one modified dimensional Frenkel-Kontorova model frequently used to discuss dislocation motion has been applied to the calculation of the conductivity of potassium hollandite. The conductivities found were generally higher and the activation energies lower than those found in experiments on polycrystalline samples.[10] Breaks in the channels were shown to have the effect of raising the activation energy and lowering the dc and low-frequency ac conductivity, but at sufficiently high frequencies, the conductivity and activation energy should become the ideal values predicted in Sec. III of this paper.

ACKNOWLEDGMENTS

We would like to thank Robert Boughton for stimulating discussions. We would like to thank the Department of Energy (Contract No. EG-77-5-02-4432) and the National Science Foundation (Grant No. DMR 75-06789) for their financial support.

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