separated by $y=2\pi/k_\perp$.[12,13] Substituting the measured values of $\nu_c(k)\simeq 0.1\omega_{pi}$, $\sum_k \tilde{E}_k{}^2/4\pi n_0 T_{i0} \simeq 0.04$, $\omega_{\text{peak}} \simeq \frac{2}{3}\omega_{pi}$, we obtain $(1/T_{i0})(dT/dt) = 0.009\omega_{pi}$, corresponding to $\tau_{\text{heating}} \simeq 20$ μsec, in agreement with Fig. 3.

To check the quasilinear heating rate, Fig. 4(a) presents the $T_{i_\perp}$ increase versus time for various saturated wave energies. As seen in Fig. 4(b), the ion-heating rate is proportional to the saturated wave energy, quantitatively confirming the quasilinear relation with $\nu_c \simeq$ constant. Furthermore, since we have observed a linear relation between the saturated wave energy and the radial voltage drop (pumping energy), the ion heating rate is proportional to the power input through the $\vec{E}\times\vec{B}$ motion of the electrons. A similar result is obtained for the electron heating rate in parametrically driven instabilities.[14]

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Correlation and Effective Interionic Potential in a One-Dimensional Ionic Conductor

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A new method that includes long-range interactions is described and used to compute the site-occupancy correlation in a one-dimensional ionic conductor. The method is applied to hollandite, for which the ions move within independent channels. Through this analysis, we deduce specific information about the interionic potential from experimental data on cationic order. Because of the peculiar screening provided by this material, the potential between mobile ions decays quickly for the first few lattice sites and has only a weak Coulomb tail.

One dimensionality often plays a special role in physical systems. This is the case for ions moving within channels and occupying a fraction ρ of the available sites. The self-diffusion coefficient is zero (for an infinite system) but not the dc conductivity. Furthermore, in one dimension the correlation is very sensitive to details of the interionic potential.[1]

In this Letter, we investigate the general relationship between long-range interionic potentials and the site-occupancy correlation and show to what extent information about the effective interionic potential may be extracted from experimental data about the state of order. As an application we will consider the ionic conductor $K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$ (hollandite)[2] in which the mobile K^+ ions move within channels and occupy 77% of the available sites. A recent analysis of diffuse x-ray scattering shows a strong correlation between mobile ions.[3]

The problem we study is the following: Given a channel consisting of N sites with ρN ions ($\rho < 1$), what is the probability to find n consecutive occupied sites? We assume that the ion-ion interaction is given by a two-body electrostatic potential

$$V(z_{ij}) = q^2/\epsilon z_{ij}, \tag{1}$$

where q is the charge and ϵ the dielectric constant. No short-range repulsion is included because in a conducting channel the distance between sites a_0 is larger than the ionic diameter (in hollandite, $a_0 = 2.9$ Å and $2R_{K^+} = 2.66$ Å). Since generally $\rho > \frac{1}{2}$ and we assume a uniformly charged background to ensure charge neutrality, it is convenient to look at the vacancies as interacting particles. We then define an array A_n (with associated probability P_n) as a set of sites that starting from a vacancy includes all the ions up to the next vacancy (excluded). (See Fig. 1.)

For an infinite system there is no analytical solution if the interaction is long ranged. In order to test possible approximations, we have studied systems of finite size and periodic boundary conditions on a computer (including all possible configurations with their associated Boltzmann factor).[4] As a result, it became evident that the exactly solvable case of interaction between nearest-neighbor sites[5] only yields, in most cases, an extremely poor approximation to the true state of order.

When we use the concept of arrays, the simplest approximation consists in allowing each vacancy to interact only with the preceding and the following vacancy. We thus associate to each array the energy corresponding to the interaction between the vacancy at the head of the array and that one immediately following the array. We call this approximation—which includes the V_1 and V_2 in Fig. 2, but not such terms as V_{12}—the independent-array approximation. Because it does not include any interaction between different arrays, the succession of the arrays within a channel is irrelevant. Contrary to the nearest-neighboring-sites approximation, the independent-array approximation already provides good results compared with exact numerical studies for finite systems.[4] We can then directly write the probability for an array A_n to occur as

$$P_n = \exp[(n-1)\beta\mu] \exp[-\beta V(n)], \tag{2}$$

where μ is the chemical potential corresponding to an occupied site [we remember that an array of length n has $n-1$ occupied sites (see Fig. 1)], $V(n)$ is the interaction between two vacancies at a distance of n sites, and $\beta = 1/kT$. The normalization of P_n will be achieved through a condition for the chemical potential μ [see Eq. (4)]. The average number of ions per array is given by

$$\bar{n} = \sum_{n=1}^{n^*} (n-1) P_n, \tag{3}$$

where n^* is the longest array considered. If the density of ions ρ is fixed, as in our case, the chemical potential μ is determined by the relation

$$\bar{n}/(\bar{n}+1) = \rho. \tag{4}$$

One can improve on this approximation by including the interactions between nearest arrays (V_{12} in Fig. 2). This is done by introducing a transfer matrix between the ith and $(i+1)$th array:

$$Q(n_i, n_{i+1}) = \exp[(n_i - 1)\beta\mu] \times \exp\{-\beta[V(n_i) + V(n_i + n_{i+1})]\}. \tag{5}$$

The partion function for a system of N sites as N

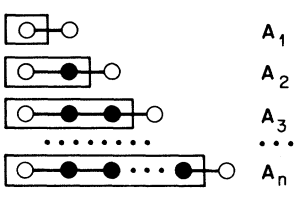

FIG. 1. Definition of an array A_n as an empty site followed by $(n-1)$ occupied sites before the next vacancy occurs.

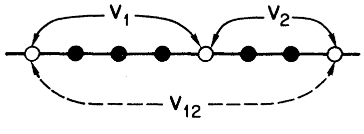

FIG. 2. The independent-array approximation includes V_1 and V_2 but neglects V_{12} (since $\rho > \frac{1}{2}$ it is more practical to think at the vacancies as interacting).

$\to\infty$ is[6]

$$Z = \sum_{\{n_1, n_2, \dots, n_N\}} Q(n_1, n_2) Q(n_2, n_3) \cdots Q(n_N n_1) = \mathrm{Tr}\, Q^N = \lambda_M{}^N. \tag{6}$$

We then have

$$\bar{n} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu} = \frac{1}{\beta} \frac{1}{\lambda_M} \frac{\partial \lambda_M}{\partial \mu}, \tag{7}$$

and

$$P_n = \sum_{n'=1}^{n^*} Q(n, n'). \tag{8}$$

For Coulomb-type interactions the inclusion of the terms of type V_{12} (Fig. 2) modifies the distribution P_n by only a few percent with respect to the independent-array approximation. In the following analysis of the correlation in hollandite, we shall therefore neglect the V_{ij} terms.

In the composition $K_{2x}Mg_xTi_{8-x}O_{16}$, hollandite consists of a framework of (Ti, Mg)O_6 octahedra forming independent parallel channels.[2,3] Within each channel there is a string of equivalent sites whose fractional occupancy is equal to x. The potassium ions are highly mobile within the channels, although long-range motion appears to be inhibited by lattice defects and impurities.

As shown in Ref. 3, the diffuse x-ray scattering exhibits the existence of two types of short-range order: (a) a displacement of the ions adjacent to a vacancy and (b) a nonrandom distribution of the vacancies. Whereas (a) mainly governs the intensities of the diffuse planes, (b) primarily determines the width of those planes.

The analysis of the experimental data in terms of our model consists of computing the diffuse scattering corresponding to a given distribution of probabilities P_n including the displacements of ions neighboring a vacancy as determined in Ref. 3, and a comparison of this scattering with the experimental data.[7] Different strengths of effective interionic interaction mainly result in different widths of the diffuse structure so that the actual fitting reduces to a comparison of the widths of the two most prominent diffuse planes.

For Coulomb interaction between the mobile ions, the experimental widths of the diffuse planes can be reproduced with an effective dielectric constant $\epsilon_{\mathrm{eff}} \sim 6$. The corresponding P_n distribution is shown in Fig. 3. This dielectric constant has to be compared to that given by the framework polarizability, i.e., the total polarizability of hollandite minus the displacive contribution of the mobile ions. There are two experimental values of the dielectric constant of hollandite available: Singer *et al.*[8] investigated the dielectric response of polycrystalline hollandite. At frequencies above the dispersion caused by the mobility of the cations, they find an ϵ of about 100; from the far-ir reflectivity[9] of single-crystal hollandite (below the reststrahlen resonances) one may deduce values of 126 and 36, respectively, for the dielectric constants parallel and perpendicular to the channel axis. The experimental values of ϵ are thus in severe disagreement with our ϵ_{eff} of 6. Furthermore by assuming a sinusoidal host-lattice potential of total amplitude $2V_0$, our effective Coulomb potential requires $2V_0 = 0.06$ eV in order to produce the observed displacements of 24% for an ion near a vacancy.[3] This is an unreasonably low value for a barrier height along a diffusion path.[10,11]

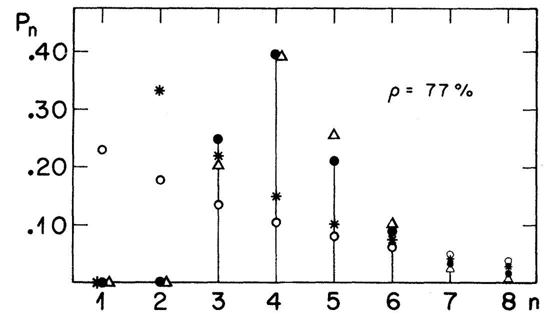

FIG. 3. Probability distributions P_n for arrays of length n as given by independent-array approximation [Eqs. (2)–(4)]; ○, no interactions; *, interaction only between nearest sites; △, Coulomb interaction with $\epsilon_{\mathrm{eff}} = 6$; ●, interaction given by Eq. (9) with $\epsilon_i = 2$, $\epsilon_a = 100$, and $R = 4.3$ Å. Note that with the interaction only between nearest sites (*) it is not possible to obtain even the qualitative behavior (● or △) corresponding to the x-ray data.

In an improved model, we take into account that the exceptionally high dielectric constant of the framework (originating from the high polarizability of the TiO_6 octahedra) is only effective outwards from the first Ti shell around a channel. Within the channel, the effective dielectric constant is very much lower and determined by the electronic polarizability of potassium and oxygen ions. We approximate this situation by a dielectric cylinder of radius R, an outside dielectric constant ϵ_a, and an inside value of ϵ_i. The potential $\varphi(z)$ on the z axis of the cylinder corre-

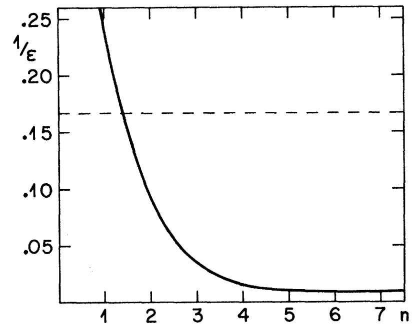

FIG. 4. Screening function $1/\epsilon(z)$ vs distance (expressed in units of intersite distance a_0) as given by Eq. (9) with $\epsilon_i = 2$, $\epsilon_a = 100$, and $R = 4.3$ Å. This is the screening for the interaction between K^+ ions in hollandite. The dashed line corresponds to Coulomb interaction with $\epsilon_{\text{eff}} = 6$.

sponding to a charge q in $z = 0$ is

$$\varphi(z) = \frac{q}{\epsilon_i z}\left[1 - G\left(\frac{\epsilon_a}{\epsilon_i}, \frac{z}{R}\right)\right] \equiv \frac{q}{\epsilon(z) z}. \tag{9}$$

The second equation in (9) is to be understood as a definition of the z-dependent ϵ shown in Fig. 4. G describes the influence of the framework on the potential and is given by the Fourier integral

$$G(a, \zeta) = (2/\pi) \int_0^\infty dx \sin(\zeta x) x^{-1} g(\alpha, x), \tag{10}$$

with

$$g(\alpha, x) = (\alpha - 1) x^2 [K_0{}^2(x) + K_1{}^2(x)] \times [1 + (\alpha - 1) I_0(x) x K_1(x)]^{-2}, \tag{11}$$

where I_n and K_n are the modified Bessel functions of order n. The asymptotic behavior of $\varphi(z)$ for large z is determined by $g(\alpha, 0) = 1 - \alpha^{-1}$ and leads to $\epsilon(\infty) = \epsilon_a$.

To obtain (9)–(11), we start with a finite charge density $\rho(z)$ inside a cylinder of Radius $R' < R$. The Poisson equation is solved by Fourier transformation with respect to z so that

$$(\partial_r{}^2 + r^{-1}\partial_r - k^2)\tilde{\varphi}(r, k) = -(4\pi/\epsilon_i)\tilde{\rho}(k)\theta(R' - r). \tag{12}$$

The solution is

$$\tilde{\varphi}(r, k) = a(k) I_0(kr) + b(k) K_0(kr) + (4/\epsilon_i k^2)\tilde{\rho}(k)\theta(R' - r), \tag{13}$$

with constants of integration a and b which are different in each of the regions $r < R'$, $R' < r < R$, and $r > R$. They are determined by the regularity conditions of φ in $r = 0$, R', R, and ∞. Retransforming (13) for $r = 0$ and evaluating the point-charge limit lead to (9).

With use of the interaction potential given by Eq. (9) with the values $\epsilon_i = 2$ (typical value for ionic crystals[12] due to the electronic polarizability of potassium and oxygen ions) and $\epsilon_a = 100$ (polarizability of the TiO_6 octaedra), the experimental widths of the diffuse planes can be reproduced with $R = 4.3$ Å. This value corresponds to slightly more than the distance to the nearest Ti ions. (The fit is rather insensitive to ± 20% variations in ϵ_i and ϵ_a.) For this potential the independent-array approximation is even better than for the Coulomb case. The inclusion of the terms V_{12} (Fig. 2) modifies the P_n values by only 1–2%. The function $1/\epsilon(z)$ given by these parameters is shown in Fig. 4, and the corresponding array distribution P_n in Fig. 3. The displacement of 24% of an ion near a vacancy corresponds, with this new interaction potential, to a sinusoidal host-lattice potential of amplitude $2V_0 = 0.2$ eV. This is a typical value for barrier heights in superionic conductors.[10,11]

We conclude, therefore, that the space-dependent dielectric function given in Fig. 4 characterizes quantitatively the potential acting between the K^+ ions in hollandite.

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