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Configurational excitations and low-temperature specific heat of the Frenkel-Kontorova model

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We study the specific heat due to configurational changes in a Frenkel-Kontorova model with a finite density of defects. This model provides an example of *intermediate disorder* related only to the diffusing ions. The results show that it is possible to obtain excitations with very low energy due to quasidegenerate configurations, but it is not possible to obtain a smooth distribution for these energies. The present model applied to the one-dimensional ionic conductor hollandite can very well describe the peak structure recently observed in the low-temperature specific heat.

I. INTRODUCTION

The long-standing problem of the low-temperature extra specific heat of glasses and amorphous materials[1-3] receives further interest from the measurements of analogous effects in the ionic conductor β-alumina[4] and very recently in hollandite[5] where a peaked contribution is observed instead of the usual pseudolinear behavior. The phenomenological model that seems to be the most consistent with various observations (specific heat, sound absorption, etc.) is based on the assumption that two-level systems exist in disordered systems and that the occurrence probability of various energy gaps between the two levels is nonzero and smooth for small gaps.[6,7] This smooth distribution is necessary to reproduce the pseudolinear behavior of the specific heat as a function of temperature.[1-3]

In order to say something about the microscopic origin of these excitations one has to consider specific models of disordered systems. In this respect the observation in ionic conductors of anomalies similar to those of other amorphous systems is of particular interest because these materials are rather well characterized microscopically. The basic model is that of a periodic potential (due to the host lattice) whose pots are partly filled by the interacting diffusing ions. In particular, in hollandite[8] ionic diffusion is along channels so that the corresponding model is one-dimensional and it is essentially the Frenkel-Kontorova model with a finite density of defects.[8-10] We have therefore a precise formulation for a problem of *intermediate disorder*, the disorder being only that due to the diffusing ions while the cage ions are assumed to give rise to the periodic potential.

The questions of interest are the following: (i) Does this model give rise to low-energy (~ 1 K) configurational excitations (two-level systems with low gap)? (ii) Do these excitations have a distribution that can give rise to a pseudolinear specific heat? As we will see the answer is *yes* to the first question and *no* to the second one. In fact it is possible to have very low excitations because of quasidegenerate configurations but the spectrum of these excitations is discrete and we conjecture this discreteness not to be removed by going to two or three dimensions. The present model applied to hollandite is in very good agreement with observations. On the other hand, from this model we see that the disorder due to the diffusing ions in a periodic potential *does not* give rise to a *linear* extra specific heat. From this we conclude that in those ionic conductors where the linear part is actually observed there must be additional sources of disorder. In β-alumina[4] this additional disorder could be due, for example, to the field of the randomly placed " compensating ions."

In Sec. II we define the model and recall the transformation to a spin system defined in Refs. 8 and 10. In Sec. III we give simple arguments for the characteristic energies of the configurational excitations. In Sec. IV we study the partition function and derive analytical expressions for the specific heat. In Sec. V we discuss the application of the present model to the case of hollandite. In Sec. VI the main results are summarized.

II. THE MODEL AND A USEFUL TRANSFORMATION

The model we consider is that of Frenkel-Kontorova[9] generalized to an arbitrary density of defects,[8,10] see Fig. 1. We also adopt the condition of *fixed average density* of particles that is the appropriate one for ionic systems where the ionic density is fixed by stoichiometry. This condition is different from that of the fixed chemical potential adopted by various authors[11] and applicable to the case of neutral overlayers. As in Ref. 8 our starting Hamiltonian is

$$H = \sum_{l=1}^{N} \tfrac{1}{2} m \dot{x}_l^2 + \sum_{l=1}^{N} V(x_l) + \tfrac{1}{2} A \sum_{l=1}^{N} (x_{l+1} - x_l - b)^2 , \qquad (2.1)$$

where x_l denotes the position of the lth ion. The substrate potential V has periodicity a. In general this periodicity is different from b, the periodicity that the interaction between particles would produce in the absence of a substrate potential. With respect to the unit cell of length a the density of ions is

$$\rho = a/b = N/N_s , \qquad (2.2)$$

where N_s is the number of pots defined by the substrate potential (one pot per unit cell) and N is the number of atoms. For the substrate we use a piecewise parabolic potential

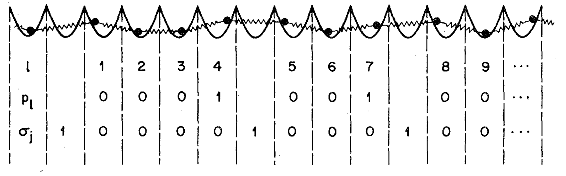
$$V(x) = \begin{cases} V(x+a), \\ \tfrac{1}{2} m \omega_0^2 x^2, & |x| < \tfrac{1}{2} a . \end{cases} \qquad (2.3)$$

This is convenient for the calculations and we know from numerical calculations[8] that the specific shape of the potential is not crucial for the properties we consider here.

In general in ionic systems the same pot can only be occupied by one ion. We use this restriction and introduce the variable

$$p_l = 0,1,2,... \qquad (2.4)$$

which denotes the number of empty pots which follow the lth ion. Since



l		1	2	3	4		5	6	7		8	9	···
p_l		0	0	0	1		0	0	1		0	0	···
σ_j	1	0	0	0	0	1	0	0	0	1	0	0	···

FIG. 1 Example of a portion of our system with the various symbols l, p_l, σ_j used in the text. The final equation (2.14) consists of a sum over all pairs of holes and the interaction depends on the number of ions (n^*) between the two holes.

$$N_s = \sum_{l=1}^{N} (1 + p_l) = N(1 + \langle p \rangle) , \qquad (2.5)$$

we have

$$\langle p \rangle = (1/\rho) - 1 . \qquad (2.6)$$

A particular configuration is then specified by the set of values $\alpha \equiv \{ p_l \}$.

It has been shown in Ref. 8 that the total static energy U of a given configuration α, including the relaxation of particles in their pots, can be written in terms of a spin Hamiltonian with exponential (long-range) interaction:

$$U = \tfrac{1}{2} \sum_{l,l',l \neq l'} C'(l - l') p_l p_{l'} = J \sum_{l < l'} C'(l - l') p_l p_{l'} , \qquad (2.7)$$

where

$$J = 8 J_0 \frac{\alpha}{(1 - \alpha^2)} = A a^2 \left[1 + \frac{4A}{m \omega_0^2} \right]^{-1/2} , \qquad (2.8)$$

$$J_0 = \tfrac{1}{2} m \omega_0^2 (\tfrac{1}{2} a)^2 , \qquad (2.9)$$

$$\alpha = \frac{(1 + 2g)^{1/2} - 1}{(1 + 2g)^{1/2} + 1}, \quad g = \frac{2A}{m \omega_0^2} , \qquad (2.10)$$

and

$$C'(l - l') = \alpha^{|l - l'|} = e^{|l - l'|/\lambda} \qquad (2.11)$$

with

$$\lambda - [ln(1/\alpha)]^{-1} . \qquad (2.12)$$

Note that since $g \geq 0$ we have

$$0 \leq \alpha < 1 \qquad (2.13)$$

and therefore $\lambda \geq 0$. Some configurations α can be unstable (i.e., evolve into α'). These configurations should be neglected. For a discussion see Ref. 8.

If the system is rather dense $\rho \gtrsim 0.75$ and the interaction appreciable (this is certainly the case for $1d$ ionic conductors) we can neglect the probability of having two (or more) empty pots nearest to each other. In this case p_l can only be either 0 or 1 and we can think of Eq. (2.7) as arising from an effective interaction between holes. Defining in fact $\sigma_j = 0$ or 1 if the jth pot is filled or empty we can rewrite Eq. (2.7) as

$$V = J \sum_{j < j'} C'(n^*) \sigma_j \sigma_{j'}, \quad C'(n) = \alpha^{|n|} , \qquad (2.14)$$

where n^* is the total number of particles between the pots j and j'. The index l was in fact only defined for particles while now we use j that refer to pots. A configuration is then also defined by the set of n_j where n_j is the number of *consecutive occupied pots* following the jth empty pot. For example, the configuration (as in Fig. 1)

$$\alpha \leftrightarrow \{ n_j \}: 4; 3; 3; \cdots \tag{2.15}$$

means that there is a vacancy, then *four* occupied pots, a vacancy, *three* occupied pots, a vacancy, *three* occupied pots, etc.

III. CONFIGURATIONAL EXCITATIONS

In the previous section, using the results of Ref. 8 we have seen how to reduce the problem of finding the energy of a configuration α from the original continuous Hamiltonian [Eq. (2.1)] to the discrete (spin-type) one [Eq. (2.13)]. In view of this discreteness and since the interaction $C'(n)$ (even if it extends to all the holes) decays exponentially we can expect a *discrete spectrum for* the energies of various configurations. In this section we show with a simple example how to obtain the characteristic energies of the spectrum. In the next section we consider in a more formal way the partition function and the calculation of the specific heat.

In order to be specific we consider the case used to study the one-dimensional ionic conductor hollandite.[8] The density of occupied pots in this material is $\rho = 77\%$ and defining $\langle n \rangle$ as the average n_j we have

$$\rho = \langle n \rangle / (\langle n \rangle + 1) = 0.77 \tag{3.1}$$

and

$$\langle n \rangle = \rho/(1-\rho) = 3.35 \; . \tag{3.2}$$

From an analysis of the structure factor $S(k)$ (at $T = 300$ K) the two parameters of the model were determined. They are (see Table I in Ref. 8), in units of eV,

$$J_0 \simeq 0.23 \tag{3.3}$$

and

$$C_I = \tfrac{1}{2} A a^2 \simeq 0.74 \; . \tag{3.4}$$

We have then

$$g = \frac{2A}{m\omega_0^2} = \frac{C_I}{2J_0} \simeq 1.61 \tag{3.5}$$

so that

$$\alpha \simeq 0.34 \tag{3.6}$$

and

$$\lambda \simeq 0.94 \; . \tag{3.7}$$

From the value of $\langle n \rangle = 3.35$ we see that at low temperature the system has mainly $n = 3$ or 4. A change of configuration due to the hop of an ion changes, for example, $\cdots$; 4; 4; $\cdots$ into $\cdots$; 3; 5; $\cdots$ or $\cdots$; 3; 4; $\cdots$ into $\cdots$; 4; 3; $\cdots$, etc. Because of the exponential decay of $C'(n)$ in Eq. (2.13) the energy gap Δ_1 between the configurations $\cdots$; 4; 4; $\cdots$ and $\cdots$; 3; 5; $\cdots$ is essentially

$$\begin{aligned} \Delta_1 &\simeq J[C'(3) + C'(5) - 2C'(4)] \\ &= J\alpha^4(\alpha + 1/\alpha - 2) \; . \end{aligned} \tag{3.8}$$

In Eq. (3.8) we have only included the interaction between nearest holes. With the above parameters we obtain $\Delta_1 \simeq 150$ K. Assuming this subsystem to give rise to a two-level system (with gap Δ) independent of the rest of the system we have for the corresponding specific heat

$$C^*(T) = \frac{\Delta^2}{T^2} \frac{e^{\Delta/T}}{(1+e^{\Delta/T})^2} \quad (k_B = 1) \; . \tag{3.9}$$

Equation (3.9) produces a peak at $T \sim 0.4\Delta$. For $\Delta_1 \simeq 150$ K we obtain a peak at $T \sim 60$ K (Ref. 10). The configuration change from $\cdots$; 3; 4; $\cdots$ to $\cdots$; 4; 3; $\cdots$ is instead *degenerate* with respect to the nearest-neighbor interaction. We then have to specify the configuration more precisely including other neighbors. For example, $\cdots$; 3; 4; 3; 4; $\cdots$ changes into $\cdots$; 3; 3; 4; 4; $\cdots$. The main interaction is now that with the second neighbors and the gap can be estimated as

$$\begin{aligned} \Delta_2 &= J[C'(6) + C'(8) - 2C'(7)] \\ &= J\alpha^7(\alpha + 1/\alpha - 2) \simeq 5.9\,\text{K} \; , \end{aligned} \tag{3.10}$$

which gives rise to a peak in specific heat at $T \sim 2.3$ K. This value compares nicely with the recently observed peak at $T \sim 1$ K (Ref. 5) especially if one notices that Δ_2 is very sensitive to the value of $\alpha (\Delta_2 \propto \alpha^7)$. The value of α used here corresponds in fact to parameters determined by analyzing $S(k)$ at room temperature and a change of 20% in the value of g produces a change of a factor of 2 in Δ_2. The peak predicted at $T \sim 60$ K cannot be observed because at this temperature the phonon contribution is already dominant but the gap Δ_1 could be determined by looking, for example, at ultrasound absorption.

In analogy to the previous argument we can go on and find transitions that are degenerate with respect to both nearest and second-nearest interactions. This is the case, for example, for the transition between the two configurations: $\cdots$ 4; 3; 3; 4; 3; 3; $\cdots$ and $\cdots$; 4; 3; 4; 3; 3; 3; $\cdots$. In such a case we have to include the interaction between third-neighboring holes. The corresponding gap is then

$$\begin{aligned}\Delta_3 &\simeq J[C'(9)+C'(11)-2C'(10)]\\ &= J\alpha^{10}(\alpha+1/\alpha-2)\simeq 0.23\ \mathrm{K}\ , \qquad (3.11)\end{aligned}$$

which produces a specific-heat peak at $T \sim 0.09$ K. Looking at more degenerate configurations we can define $\Delta_4 \sim 0.009$ K; $\Delta_5 \sim 0.000\,36$ K, etc. In general we can write

$$\Delta_n \simeq \alpha^{3(n-1)}\Delta_1\ . \qquad (3.12)$$

With respect to the physical meaning of these low gaps it should be pointed out that the present model is incomplete for discussing energies $<< 1$ K because quantum-mechanical effects (tunneling) then become important even for atoms.

The simple example discussed here has allowed us to obtain an intuitive understanding of the discrete nature of the spectrum and of the origin of the low-energy gaps. We have completely neglected in the hand-waving arguments presented in this section the combinatorial aspects related to the intensity of the specific heat contributed by a given gap. In order to study these effects we have to be more formal and start from the partition function of the total system. This will be the subject of the next section.

IV. THERMODYNAMICS AND SPECIFIC HEAT

In this section we start from the expression (2.13) and compute the partition function. Even if the problem is one dimensional a complete solution cannot be obtained because the interaction extends to all distances. Nevertheless, since the interaction is exponentially decaying with distance we will see that it is possible to simplify the problem and obtain analytical solutions that are essentially exact in a given range of temperature. For example, from the discussion of the previous section we can expect that around $T \sim 60$ K the specific heat is dominated by the interaction between nearest neighbors and only at temperatures below 10 K the other terms (second nearest, etc.) become relevant. In this case we can adopt the following simplification.

A. Interaction only between nearest holes

This implies that we only include the interaction between one hole and the *next one* no matter how far they are. Introducing a chemical potential μ for the particles the statistical weight of an "array" of n filled pots (preceded and followed by empty pots) is

$$z_n = \exp\{(\mu n - J\alpha^n)/T\}\ . \qquad (4.1)$$

The partition function is then simply

$$\begin{aligned}Z &= \sum_{\{n_1,n_2,\ldots,n_{N'}\},n_i=1}^{\infty} z_{n_1}z_{n_2}\cdots z_{n_{N'}}\ ,\\ &= \left[\sum_{n=1}^{\infty} z_n\right]^{N'} \equiv \exp(-\Omega/T)\ , \qquad (4.2)\end{aligned}$$

where N' is the number of holes (empty pots) and Ω is the grand potential. The summation over n (size of an array) extends in principle to infinity but it is actually converging very rapidly.[12] The grand potential "per hole" is then

$$\Omega_h = \Omega/N' = -T\ln f_0 \qquad (4.3)$$

having introduced

$$f_0 = \sum_{n=1}^{\infty} z_n\ . \qquad (4.4)$$

The total free energy is

$$F = \Omega + \mu N_p\ , \qquad (4.5)$$

where N_p is the total number of particles. Other relations are

$$\frac{N_p}{N'} = \langle n\rangle = -\frac{1}{N'}\frac{\partial\Omega}{\partial\mu} = -\frac{\partial\Omega_h}{\partial\mu} = \frac{1}{f_0}\sum_{n=1}^{\infty} n z_n \qquad (4.6)$$

and the specific heat per hole is

$$\begin{aligned}C^* &= T\frac{dS}{dT} = -T\frac{d}{dT}\left[\frac{\partial\Omega_h}{\partial T}\right]\\ &= -T\left[\frac{\partial^2\Omega_h}{\partial T^2} + \frac{\partial^2\Omega_h}{\partial\mu\,\partial T}\frac{d\mu}{dT}\right]\ , \qquad (4.7)\end{aligned}$$

where S is the entropy per hole. In order to compute the second term of Eq. (4.7) we have to take into account that the total number of particles N_p and therefore $\langle n\rangle$ are constant in our model. This implies

$$d(\langle n \rangle) = -\frac{\partial^2\Omega_h}{\partial T\,\partial\mu}dT - \frac{\partial^2\Omega_h}{\partial\mu^2}d\mu = 0 \tag{4.8}$$

and therefore

$$\frac{d\mu}{dT} = -\frac{\partial^2\Omega_h}{\partial T\,\partial\mu}\left[\frac{\partial^2\Omega_h}{\partial\mu^2}\right]^{-1} . \tag{4.9}$$

We can then rewrite Eq. (4.7) as

$$C^* = -T\left[\frac{\partial^2\Omega_h}{\partial T^2} - \left[\frac{\partial^2\Omega_h}{\partial T\,\partial\mu}\right]^2\left[\frac{\partial^2\Omega_h}{\partial\mu^2}\right]^{-1}\right] . \tag{4.10}$$

If $\langle n \rangle$ is assigned Eq. (4.6) fixes the value of the chemical potential μ at each temperature. The specific heat is then given directly by Eq. (4.10). All the sums of type $\sum_{n=1}^{\infty}$ appearing in the various expressions are exponentially converging and their explicit evaluation is straightforward. The resulting specific heat consists of one or more peaks in the temperature region $T \sim \Delta_1$ as discussed in the previous section and in Ref. 10.

Of much more interest is the eventual structure at "lower" temperature ($T << \Delta_1$). In order to say something about this part of the energy spectrum we have to include additional terms in the interaction as discussed in Sec. III.

B. Interaction up to second-nearest holes

We study here the effect of the next-neighbor interaction between holes. This implies that for each array of length n we also include the interaction with the previous and following array. This problem can be treated with the method of the transfer matrix. The size of the matrix is given by the number of different values that the array size n can take. In practice, if we are interested in a temperature range $T << \Delta_1$ the system is "frozen" with respect to the energies of order Δ_1 and only very few values of n have an appreciable statistical weight. For example, in hollandite $\langle n \rangle = 3.35$ and, as we have seen in Sec. III $\Delta_1 \sim 150$ K. At temperatures of the order of a few degrees ($T \lesssim 3$ K) the system is in the ground state with respect to excitations involving energies of the order of Δ_1 so that only arrays with $n = 3$ or 4 can be present. The statistical weight of arrays with $n < 3$ or $n > 4$ can be estimated to be of order $p \sim \exp(-\Delta_1/T)$ that is $p \lesssim \exp(-50)$ for our value of Δ_1 and $T \lesssim 3$ K. Generalizing this result we can conclude that for $T << \Delta_1$ there are only two values to be considered for n. These are $n = m$ and $n = m + 1$, m being the integer value of $\langle n \rangle$. This is a pleasant consideration because it reduces the size of the transfer matrix to 2 and we can obtain analytical expressions for the thermodynamic quantities. There can be situations in which this reduction is not possible, for example, if we want to know the effect of the interaction with second-neighboring holes at $T \sim \Delta_1$ or if the characteristic energies $(\Delta_1, \Delta_2, \ldots)$ are not well separated. In such cases one has to resort either to numerical methods or to different types of approximations.

Allowing for only two values of n and including the interactions up to the second-nearest holes we can write the partition function as

$$Z = \sum_{\{n\}} B(n_1,n_2)B(n_2,n_3)\cdots B(n_{N'},n_1) , \tag{4.11}$$

where

$$\{ n \} = \{ n_1, n_2, \cdots, n_{N'} \} \tag{4.12}$$

and each $n_i (i = 1, \ldots, N')$ can take the values m and $m + 1$. The matrix elements of B are

$$B_{11} = B(m,m) = \exp[(\mu m/J - \alpha^m - \alpha^{2m})/t] , \tag{4.13}$$

$$B_{22} = B(m+1,m+1)$$
$$= \exp\{[\mu(m+1)/J - \alpha^{(m+1)} - \alpha^{2(m+1)}]/t\} , \tag{4.14}$$

$$B_{12} = B_{21} = B(m,m+1)$$
$$= \exp[\tfrac{1}{2}\mu(2m+1)/Jt]$$
$$\times \exp\{[-\tfrac{1}{2}(\alpha^m + \alpha^{(m+1)}) - \alpha^{(2m+1)}]/t\} , \tag{4.15}$$

where we have introduced for convenience

$$t = T/J . \tag{4.16}$$

The transfer matrix method[12] then gives

$$Z = \lambda_M^{N'} , \tag{4.17}$$

where λ_M is the maximum eigenvalue of the transfer matrix B. The grand potential "per hole" is now given by

$$\Omega_h = -T\ln\lambda_M \tag{4.18}$$

and in analogy to Eqs. (4.6)–(4.10) we have

$$\langle n\rangle = -\frac{\partial\Omega_h}{\partial\mu} \tag{4.19}$$

and

$$C^* = C_1 + C_2\,, \tag{4.20}$$

$$C_1 = -T\frac{\partial^2\Omega_h}{\partial T^2} = t\frac{\partial^2}{\partial t^2}(t\ln\lambda_M)\,,$$

$$C_2 = T\left(\frac{\partial^2\Omega_h}{\partial\mu\,\partial T}\right)^2\left(\frac{\partial^2\Omega_h}{\partial\mu^2}\right)^{-1}. \tag{4.21}$$

The explicit evaluation of these quantities is rather lengthy but straightforward. We obtain

$$\lambda_M = \tfrac{1}{2}\eta_m(1+S)[1+(1+\xi)^{1/2}] \tag{4.22}$$

and

$$\langle n\rangle = m + \frac{S}{1+S} - \frac{1}{2}\frac{S-1}{S+1}\frac{\xi}{(1+\xi)^{1/2}[1+(1+\xi)^{1/2}]}, \tag{4.23}$$

where

$$\eta_m + \exp[(\mu m/J - \alpha^m - \alpha^{2m})/t]\,, \tag{4.24}$$

$$S = \exp[(\mu/J + f_m)/t]\,, \tag{4.25}$$

$$f_m = \alpha^m(1-\alpha) + \alpha^{2m}(1-\alpha^2)\,, \tag{4.26}$$

$$\xi = \frac{4S}{(1+S)^2}[\exp(u_m/t) - 1]\,, \tag{4.27}$$

$$u_m = \alpha^{2m}(1-\alpha)^2\,. \tag{4.28}$$

Equation (4.23) fixes the relation between $\langle n\rangle$ and μ. This relation has to be considered with caution because different values of μ can give rise to the same value of $\langle n\rangle$ but of course only one is the "physical" value.

For the first term of the specific heat we obtain

$$C_1 = \frac{t^2}{\lambda_M}\frac{\partial^2\lambda_M}{\partial t^2} - \frac{t^2}{\lambda_M^2}\left(\frac{\partial\lambda_M}{\partial t}\right)^2 + \frac{2t}{\lambda_M}\frac{\partial\lambda_M}{\partial t}\,, \tag{4.29}$$

where

$$\frac{1}{\lambda_M}\frac{\partial\lambda_M}{\partial t} = A + \frac{BS}{(1+S)} + \tfrac{1}{2}D\xi\{[1+(1+\xi)^{1/2}](1+\xi)^{1/2}\}^{-1} \tag{4.30}$$

and

$$A = (-\mu m/J + \alpha^m + \alpha^{2m})/t^2\,, \tag{4.31}$$

$$B = -(\mu/J + f_m)/t^2\,, \tag{4.32}$$

$$D = \left(\frac{(\mu/J + f_m)}{t^2}\right)\left(\frac{S-1}{S+1}\right) - \left(\frac{u_m}{t^2}\right)\left[1 - \exp\left(\frac{-u_m}{t}\right)\right]^{-1}. \tag{4.33}$$

For the term containing the second derivative of λ_M we obtain

$$\frac{1}{\lambda_M}\frac{\partial^2\lambda_M}{\partial t^2} = \frac{2ABS}{1+S} + \frac{AD\xi}{[1+(1+\xi)^{1/2}](1+\xi)^{1/2}} + \frac{BDS\xi}{(1+S)[1+(1+\xi)^{1/2}](1+\xi)^{1/2}} + A\left(\frac{-2}{t} + A\right) + \frac{BS[(-2/t)+B]}{1+S} + \frac{-\frac{1}{2}(1+\xi)^{-1}(D\xi)^2 + \xi(\partial D/\partial t + D^2)}{2[1+(1+\xi)^{1/2}(1+\xi)^{1/2}]}\,, \tag{4.34}$$

where

$$\frac{\partial D}{\partial t} = -2\left(\frac{(\mu/J + f_m)}{t^3}\right)\left(\frac{S-1}{S+1}\right) + \left(\frac{(\mu/J + f_m)}{t^2}\right)\frac{2BS}{(S+1)^2} + \frac{2u_m}{t^3}\left[1 - \exp\left(\frac{-u_m}{t}\right)\right]^{-1} - \frac{u_m^2}{t^4}\left[1 - \exp\left(-\frac{u_m}{t}\right)\right]^{-2}\exp\left(\frac{-u_m}{t}\right). \tag{4.35}$$

For the second term of the specific heat we have

$$C_2 = \frac{t}{J} \frac{[(\Omega_h)_{\mu t}]^2}{(\Omega_h)_{\mu\mu}} , \tag{4.36}$$

where the subindices μ and t indicate partial derivation. From Eqs. (4.19) and (4.23) we then obtain

$$\begin{aligned}(\Omega_h)_{\mu x} = &- \frac{S_x}{(1+S)^2} + \frac{S_x}{(1+S)^2} \frac{\xi}{(1+\xi)^{1/2}[1+(1+\xi)^{1/2}]} \\ &+ \frac{1}{2} \frac{S-1}{S+1} \xi_x \frac{(1+\xi)^{1/2}[1+(1+\xi)^{1/2}] - \xi[2+(1+\xi)^{-1/2}]}{(1+\xi)[1+(1+\xi)^{1/2}]^2} , \quad (x=\mu,t)\end{aligned} \tag{4.37}$$

where

$$S_\mu = \frac{\partial S}{\partial \mu} + \frac{1}{Jt} S , \tag{4.38}$$

$$S_t = \frac{\partial S}{\partial t} = - \frac{(\mu/J + f_m)}{t^2} S , \tag{4.39}$$

$$\xi_\mu = \frac{\partial \xi}{\partial \mu} = \frac{1}{Jt} \left[\frac{1-S}{1+S} \right] \xi , \tag{4.40}$$

$$\begin{aligned}\xi_t = \frac{\partial \xi}{\partial t} = &- \frac{(\mu/J + f_m)}{t^2} \frac{1-S}{1+S} \xi \\ &- \frac{u_m}{t^2} \frac{4S}{(1+S)^2} \exp \left[\frac{u_m}{t} \right] .\end{aligned} \tag{4.41}$$

The specific heat is now given explicitly by these formulas. A particular application will be discussed in the next section.

V. DISCUSSION

We specify now the results of the previous section to the one-dimensional ionic conductor hollandite. A description of this system together with a discussion of the applicability of the present model to it can be found in Ref. 8. Figure 2 shows the low-temperature configurational specific heat as computed from Eq. (4.29) with the parameters given by Eqs. (3.3) and (3.4) and for different concentrations of diffusing ions. As expected from the discussion in Sec. III we have a peak at $T \sim 0.4\Delta_2$. In addition there is a strong dependence of the peak intensity on the ionic concentration ρ (or $\langle n \rangle$). In order to understand the origin of this dependence we have to go back and analyze the excitations that give rise to the gap Δ_2. In Sec. III we have seen that a typical case is a transition from a configuration $\{n\}$: $\cdots$ 3; 4; 3; 4; $\cdots$ to a new configuration $\{n'\}$: $\cdots$ 3; 3; 4; 4; $\cdots$. It is easy to see that the probability of having in the ground state a series of values like the above one is maximum if the values 3 and 4 have equal probability and decreases when one of the two is much more probable. According to this simple argument the maximum peak height corresponds then to $\langle n \rangle = 3.5 (\rho = 0.7\bar{7})$ while the peak vanishes for $\langle n \rangle = 3$ or $\langle n \rangle = 4$. In fact, for $\langle n \rangle = 3$ we can only have

$$\begin{aligned}&\{n\}: \cdots ; 3; 3; 3; 3; \cdots \\ &\quad \to \{n'\}: \cdots 3; 2; 4; 3; \cdots ,\end{aligned} \tag{5.1}$$

which involves always energies of the order of Δ_1. This behavior is qualitatively in agreement with that of Fig. 3 where we have plotted the peak height of the specific heat (per hole[13]) as a function of the ionic concentration. For a random sequence of arrays with $n = 3$ and $n = 4$ we would have

$$C^*_{\max} \simeq p^2(1-p)^2 , \tag{5.2}$$

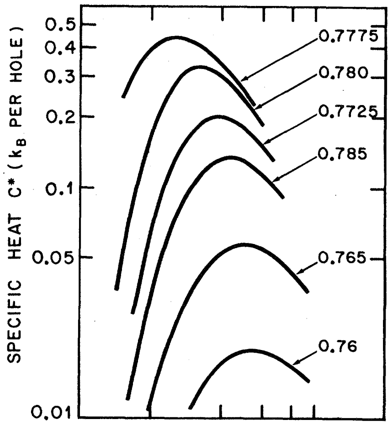


FIG. 2. Low-temperature specific heat as computed from Eq. (4.27) using the hollandite parameters (see text) for different values of the ionic density ρ. The units are in k_B per hole (Ref. 13).

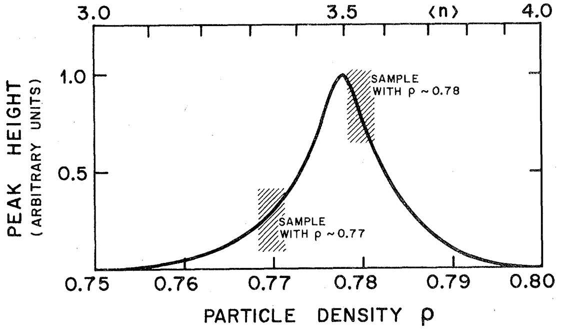


FIG. 3. Dependence of the low-temperature specific-heat peak intensity ($C^*_{\max}$) on the ionic concentration ρ. As expected from the discussion in Sec. III the maximum is at $\langle n \rangle = 3.5[\rho = \langle n \rangle/(1+\langle n \rangle) = 0.7\overline{7}]$ and the intensity goes to zero for the two "commensurate" cases $\langle n \rangle = 3(\rho = 0.75)$ and $\langle n \rangle = 4(\rho = 0.80)$. The sharpness of the peak around $\langle n \rangle = 3.5$ indicates that the positions of the various arrays (holes) are quasiordered.

where p is the probability for $n = 3$ and $(1-p)$ for $n = 4$. The ion density ρ is linked to p through the relation $\langle n \rangle = 3p + 4(1-p)$. The fact that the curve in Fig. 3 is much sharper than predicted by Eq. (5.2) implies that the positions of the arrays are actually not random but quasiordered.

The recently measured low-temperature specific heat of hollandite[5] (for two samples with $\rho \sim 0.77$ and $\rho \sim 0.78$) shows a peak around 1 K with a larger intensity for the system with $\rho \sim 0.78$. This behavior corresponds rather well to our results of Figs. 2 and 3. The only discrepancy between the present model and the experiments is that the absolute value of the measured specific heat is much lower than predicted. This probably has to do with the many impurities that are present in this material. For a more detailed discussion see Ref. 5.

An interesting question is what happens in two or three dimensions. This problem is of direct relevance for β-alumina that is usually described by the two-dimensional version of the present model. Contrary to hollandite the low-temperature specific heat of β-alumina shows a pseudolinear behavior[4] like many amorphous materials. In Ref. 14 this has been explained as due to two-level systems (sites for the position of an ion) in which the energy difference arises from the Coulomb field induced by a random distribution of ions (in two or three dimensions). The crucial point to obtain a linear term in the specific heat is to have an appreciable *continuous* probability distribution for small energy gaps. This is the case for a random distribution of ions in two and three dimensions[14] and in the Appendix we show that it also happens in one dimension. A random distribution of ions in any dimension gives rise therefore to a smooth distribution of small gaps and to a linear specific heat.

On the other hand, we have seen in the previous sections that diffusing interacting ions in a periodic potential produce a *discrete* distribution of gaps. The model studied is one dimensional but since the origin of the discrete spectrum is not directly related to the dimensionality (it arises from the periodicity of the potential plus the interaction between ions) we conjecture that the discrete nature of the spectrum will remain in two or three dimensions. This implies that interacting ions in a periodic potential *cannot* be described as randomly distributed and therefore the linear specific heat observed in β-alumina has to be linked to a different "random field" like for example that of the compensating ions.[14]

VI. SUMMARY

The configurational excitations of the Frenkel-Kontorova model are shown to have a discrete distribution of energy gaps. This behavior is in good agreement with the peak observed in the low-temperature specific heat of the one-dimensional ionic conductor hollandite.

This model also shows that the disorder due to diffusing interacting ions in a periodic potential does not give rise to a linear specific heat. This is probably due to additional random fields like for example that of the compensating ions in β-alumina.

APPENDIX: PROBABILITY DISTRIBUTION OF THE SITE ENERGIES FOR A ONE-DIMENSIONAL RANDOM DISTRIBUTION OF IONS

Given an ion that can occupy two sites at distance a from each other we compute now the distribution of energy difference $P(E)$ between these two positions under the influence of other ions randomly placed on a line. The same problem for two- and three-dimensional cases has been studied in Ref. 14 using the method of Markov[15] that we also adopt here. Our result here will be qualitatively similar to the two- and three-dimensional cases.[14] The function $P(E)$ starts from a nonzero value $P(0)$ and decreases with increasing E. This is completely different than what we have obtained for the model discussed in the rest of the paper and shows that interacting ions in a periodic potential *cannot* be described as being randomly distributed.

The energy difference between two sites at distance a (small) under the influence of N ions is

$$E = \sum_{i=1}^{N} \phi_i \ , \tag{A1}$$

$$\phi_i = \frac{\alpha}{r_i^2}\operatorname{sgn}(r_i) \ , \tag{A2}$$

$$\alpha = \frac{e e_i a}{\epsilon} \ , \tag{A3}$$

where ϕ_i is the field due to the ith ion at distance r_i with charge e_i and ϵ is the dielectric constant. The probability distribution $P(E)$ is given by

$$P(E) = \int_{-L/2}^{L/2} dr_1 \cdots \int_{-L/2}^{L/2} dr_N \delta\left[\sum_{i=1}^{N}\phi_i - E\right] \times \tau(r_1, \ldots, r_N) \ , \tag{A4}$$

where τ is the probability distribution of the various ions. For a random distribution we have $\tau(r_1, \ldots, r_N) = (1/L)^N$ where L is the length of the chain. With the method of Ref. 15 we obtain (in the limit of large N)

$$P(E) = \frac{1}{\pi}\int_0^\infty d\rho \cos(\rho E) \exp[-n(2\pi\alpha\rho)^{1/2}] \ , \tag{A5}$$

where $n = N/L$ is the ionic density. From Eq. (A5) we obtain

$$P(0) = \frac{1}{\pi^2} n^2 \alpha \tag{A6}$$

and

$$\tilde{P}(E) = \frac{P(E)}{P(0)} = \pi^2 \epsilon^{-3/2} g(\epsilon^{-1/2}) \ , \tag{A7}$$

where $\epsilon = E/n^2\alpha$ and the function g is defined and tabulated in Ref. 16. The function (A7) decreases montonically from the value one to zero. This behavior is qualitatively similar to the case of ions distributed in two and three dimensions as discussed in Ref. 14.

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