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Ionic order and defect conductivity in the one-dimensional superionic conductor hollandite

J. B. Sokoloff
Department of Physics, Northeastern University, Boston, Massachusetts 02115

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The effects of impurities and stoichiometry on the ionic ordering proposed by Beyeler for hollandite ($K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$) are studied. Even relatively strong impurities are found to have little qualitative effect on the predicted x-ray diffraction peaks for the ground state of this model. Deviation of the potassium concentration from the perfect stoichiometric concentration of 0.75 ions per available site introduces new peaks in the x-ray scattering by enlarging the size of the unit cell from 4 to 13 lattice sites. The activation energy for the conductivity due to thermally activated defects in the ordered phase is an order of magnitude smaller than that observed in actual conductivity measurements.

I. INTRODUCTION

Recently Beyeler[1] proposed a model for the short-range order among the mobile potassium ions in the one-dimensional superionic conductor hollandite (with composition $K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$). In this material TiO_6 and MgO_6 octahedra form parallel channels which have 77% of their sites occupied by mobile potassium ions. The proposed ordering is based on an ordering for the ground state of stoichiometric hollandite ($K_{2x}Mg_xTi_{8-x}O_{16}$ for $x = 0.75$ which has 75% of the potassium sites occupied) in which a channel unit cell contains three potassium ions followed by a vacant site. Assuming Coulomb interactions between ions, Beyeler finds that in order to reproduce the observed displacements around a vacant site of 25% of a lattice constant, the near-neighbor Coulomb potential must be around 13 times the barrier height between neighboring lattice sites. At nonzero temperatures the potassium ions are never fully ordered either because of the one-dimensional nature of the system of potassium ions (which precludes long-range order[2]) or because this system is analogous to a charge-density-wave system, for which impurities destroy long-range order.[3,4] Beyeler *et al.* studied a lattice-gas model of this compound[5] in order to gain information about the nature of the screening of the interaction between mobile ions.

In the present article, the effect of impurities on the structure and scattering factors calculated from Beyeler's original model[1] is studied. The possibility of free-sliding electrical conduction of the ordered potassium lattice similar to that proposed for incommensurate charge-density waves[6-8] is ruled out by calculations like those used by the author in the charge-density-wave problem.[8] The activation energy to create current-carrying defects is found to be an order of magnitude smaller than the observed activation energy of the conductivity.

II. EFFECTS OF IMPURITIES AND STOICHIOMETRY ON THE STRUCTURE AND SCATTERING FACTORS

Random impurities (e.g., due to the random distribution of Mg and Ti ions) can modify the x-ray scattering factor by displacing the potassium ions from the equilibrium positions proposed by Beyeler.[1] In order to study such effects, we will find the equilibrium positions of the ions in the presence of impurities by a method similar to that used to study the modified Frenkel-Kontorova model.[8] The equation of motion for the jth potassium ion in the pure lattice is taken to be

$$m\frac{d^2x_j}{dt^2} = eE - \gamma\frac{dx_j}{dt} - \frac{2\pi}{a}V_0 \sin\frac{2\pi}{a}x_j + z\sum_l \frac{x_j - x_l}{|x_j - x_l|^3}, \tag{1}$$

where x_j is the location of the jth ion, m is the mass of an ion, a is the lattice constant of the channel, V_0 is the amplitude of the sinusoidal potential used for the channel potential seen by the potassium ions, γ is a damping constant, z is the square of the electronic charge divided by the dielectric constant in a channel, and eE is the force due to an external electric field. Here the potential of the channel is taken to be $V_0[1-\cos(2\pi/a)x_j]$. The application of such a one-dimensional model to superionic conductors was first made by Wang and Pickett.[9] The damping force (the first term on the right-hand side) is included for convenience. To find the equilibrium positions of the ions we solve the first-order differential equation which results if we neglect the inertial term on the left-hand side compared to the damping, which amounts to taking the extreme overdamped limit. The initial configuration of the ions is taken to be one in which either the ions are equally spaced or one in which each ion placed at the sinusoidal potential minimum nearest to the location it would have if the ions were equally spaced. If the site of the

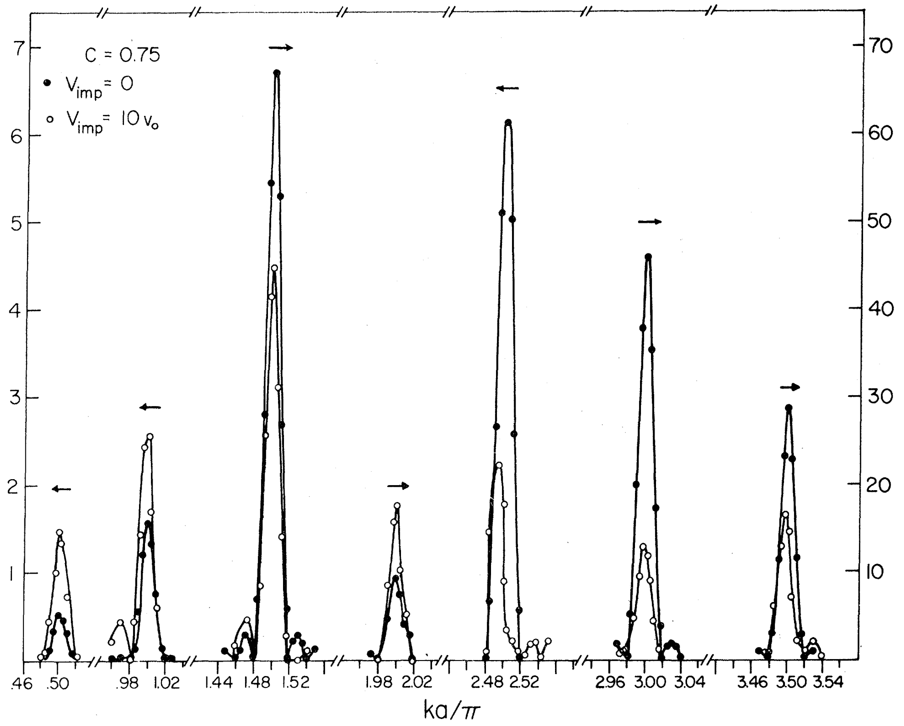

FIG. 1. Calculated x-ray scattering factor for the 75%-occupancy case. Dark circles signify no impurities present and light circles signify impurities of strength 10 V_0. The scattering factor is in arbitrary units. Arrows signify the scale that is being used.

nth sinusoidal potential well minimum has an impurity, the amplitude V_0 is changed to $V_0(1+\gamma)$ for $(n-\frac{1}{2})a \leq x_j \leq (n+\frac{1}{2})a$. The differential equations were then iterated with $E=0$ until steady state was reached. The ionic positions found in this way are equilibrium positions. The barrier height $2V_0$ was chosen to be $\frac{1}{13}$ of the near-neighbor Coulomb repulsion so as to have displacements of $0.25a$ for ions neighboring a vacant site as required by Beyeler's results.[1]

The method described in the previous paragraph was applied to a 100-atom chain with periodic boundary conditions, with the Coulomb potential cutoff after 100 ions. First of all, a stoichiometric case, in which the number of ions was equal to 75% of the number of channel potential minima, was studied. In Fig. 1 some of the peaks in the scattering factor, defined as

$$\left|\sum_j e^{ikx_j}\right|^2,$$

are plotted for this case with impurities of strength (defined as γV_0) equal to $10V_0$. (This strength was chosen so as to emphasize the effects of impurities; it is not meant to correspond to the actual strength of impurities in hollandite crystals.) The number of impurities is chosen to be half the number of potassium ions. This corresponds to the number of Mg ions. The scattering factor for the stoichiometric state proposed by Beyeler is listed in Table I.

There appears to be little if any increase of the peak widths over the widths for the pure lattice case (whose peak widths are due to the finite lattice size). Certainly, the peaks are not nearly as broad as the peaks observed through x-ray diffraction by Beyeler (i.e., a peak width of the order of $a\Delta k = 0.16\pi$). Thus, the impurities do not seem to

TABLE I. Beyeler's scattering factors for 75%-occupancy case.

ka (units of π)	Scattering factor (square of f_{sc} in Ref. 1)
0.5	0.0548
1.0	0.171
1.5	3.13
2.0	1.00
2.5	0.0548
3.0	5.81
3.5	3.13
4.0	1.00
4.5	3.13
5.0	5.81
5.5	0.0548
6.0	1.00
6.5	3.13
7.0	0.171
7.5	0.0548
8.0	1.000

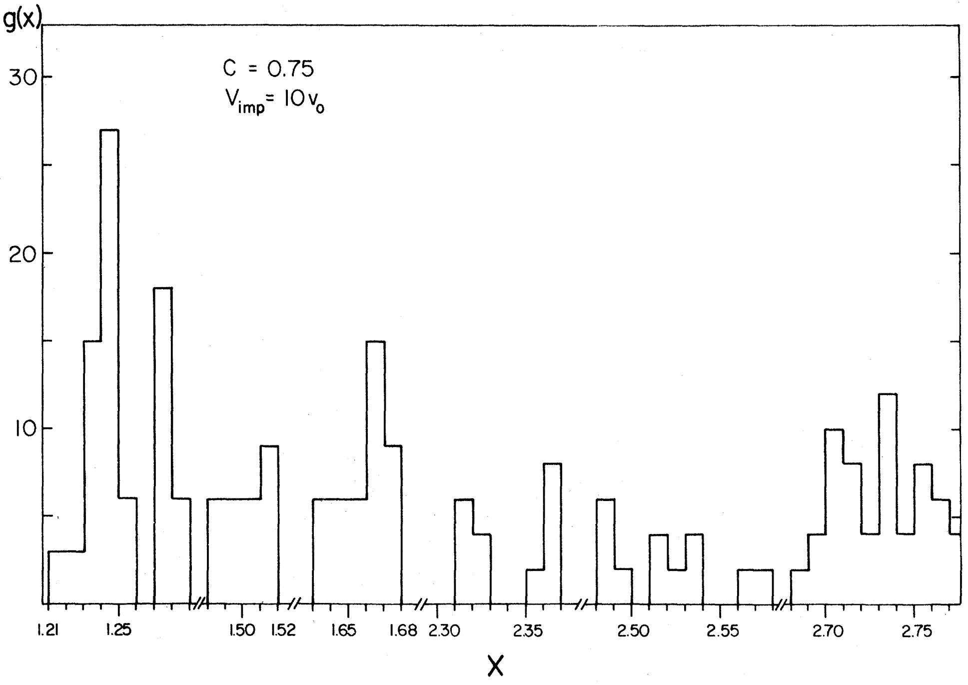

FIG. 2. Calculated structure factor $g(x)$ for the 75%-occupancy case with impurities of strength $10\,V_0$. The spacing between a pair of ions is in units of the channel side lattice spacing a and $g(x)$ is in arbitrary units.

produce a correlation length in the ground state like the one observed by Beyeler at higher temperatures, which implies that the scattering peaks observed by Beyeler should narrow at very low temperatures. As for peak intensities, we generally find that those peaks which reflect the host lattice translational symmetry (such as peaks at k = multiples of $2\pi/a$) are increased in intensity by the substitutional impurities whereas other peaks are reduced in intensity. Different distributions of random impurities produce different peak heights, but the location of most of the peaks for the pure lattice are unchanged by the presence of impurities. A few peaks (such as the one at $ka = 2.5$) are broadened and shifted. Many other weak peaks are produced by the impurities, but these change locations and intensities when a new random-impurity configuration is generated, indicating that in a real sample, which has many channels with many different impurity configurations, they will only appear as structureless background. In order to study change in the distribution of ions caused by the impurities, the structure factor, defined as $g(x)$ = number of atoms between x and $x+\Delta x$ with $\Delta x = 0.01a$, where x is the distance between a pair of atoms, was calculated for the impure lattice. It is illustrated in Fig. 2. We see that the effect of the impurities is primarily to broaden the δ-function peaks in $g(x)$, which occur for the pure lattice. The detailed shapes of the peaks depend on impurity configuration, and thus an average over impurity configurations should wipe out most of the structure leaving smooth peaks. Such peak broadening often leads to a reduction of scattering intensity with increasing wave vector, with accompanying increase of background scattering, but not to a broadening of the scattering peaks (for example, molecular vibrations only reduce the intensity through the Debye-Waller factor but do not broaden the peaks[10]). This is precisely what we had found.

Lack of perfect stoichiometry in the sample studied by Beyeler will also affect the scattering cross-section. Since 77% instead of 75% of the channel sites are occupied, the perfectly ordered structure with a four-site unit cell cannot occur. We find instead that the ground state of the lattice containing no impurities has approximately a 13-site unit cell. The fourth, ninth, and thirteenth sites contain vacancies. This ground state was found by iterating Eq. (1) for a 100-site chain with periodic boundary conditions. The scattering factor, defined as

$$\left|\sum_{\vec{b}} e^{i\vec{k}\cdot\vec{b}}\right|^2,$$

where $\vec{b}$ runs over all atoms in the 13-site unit

TABLE II. Scattering factor for the 13-atom unit cell for the 77%-occupancy case.

ka (units of π)	Scattering factor (arbitrary units)	ka (units of π)	Scattering factor (arbitrary units)
0.153 85	0.023 77	7.692 31	2.172 76
0.307 69	0.007 87	7.846 15	1.245 33
0.461 54	0.444 20	8.000 00	14.100 08
0.615 38	0.055 36	8.153 85	58.589 91
0.769 23	0.020 30	8.307 69	15.369 20
0.923 08	0.211 03	8.461 54	0.185 43
1.076 92	1.706 04	8.615 38	0.156 55
1.230 77	0.197 87	8.769 23	1.399 44
1.384 62	1.906 22	8.923 08	1.906 17
1.538 46	85.587 22	9.076 92	0.415 75
1.692 31	2.407 61	9.230 77	10.139 71
1.846 15	0.089 52	9.384 62	0.016 74
2.000 00	10.010 36	9.538 46	25.345 57
2.153 85	0.189 35	9.692 31	32.698 39
2.307 69	0.137 76	9.846 15	23.548 57
2.461 54	1.679 80	10.000 00	0.679 92
2.615 38	5.931 71	10.153 85	4.271 52
2.769 23	1.101 55	10.307 69	1.468 85
2.923 08	6.933 73	10.461 54	1.190 62
3.076 92	51.573 68	10.615 38	0.756 97
3.230 77	6.004 68	10.769 23	14.236 71
3.384 62	0.000 11	10.923 08	1.650 83
3.538 46	31.963 62	11.076 92	32.498 34
3.692 31	0.001 21	11.230 77	8.272 74
3.846 15	0.214 99	11.384 62	25.641 89
4.000 00	3.458 12	11.538 46	2.677 22
4.153 85	7.219 01	11.692 31	12.152 19
4.307 69	2.272 44	11.846 15	3.375 51
4.461 54	10.558 21	12.000 00	0.725 49
4.615 38	18.234 39	12.153 85	4.124 90
4.769 23	7.005 67	12.307 69	11.328 92
4.923 08	0.809 17	12.461 54	4.487 87
5.076 92	56.693 96	12.615 38	30.229 39
5.230 77	1.248 46	12.769 23	0.058 93
5.384 62	0.179 83	12.923 08	20.010 80
5.538 46	3.287 44	13.076 92	7.982 20
5.692 31	5.247 78	13.230 77	17.275 37
5.846 15	2.888 01	13.384 62	8.565 81
6.000 00	9.301 89	13.538 46	0.457 68
6.153 85	1.366 79	13.692 31	6.454 99
6.307 69	4.581 52	13.846 15	5.466 95
6.461 54	5.042 51	14.000 00	6.417 23
6.615 38	68.608 76	14.153 85	19.219 88
6.769 23	6.470 11	14.307 69	8.685 33
6.923 08	0.126 43	14.461 54	10.322 40
7.076 92	1.039 86	14.615 38	17.580 80
7.230 77	2.713 07	14.769 23	14.058 15
7.384 62	2.643 54	14.923 08	17.344 04
7.538 46	4.366 65	15.076 92	0.241 45
		15.230 77	5.413 40
		15.384 62	1.404 88

cell, was calculated for the wave vectors $k = 2\pi n/13a$ (where n is an integer), the reciprocal lattice vectors for this lattice. The displacements of the atoms, taken from our solution of Eq. (1), are given in Fig. 3 and the resulting scattering factor is given in Table II. As can be seen, several new peaks of low intensity appear. The main peaks found for the 75% occupancy case still appear (slightly shifted, of course).

Besides those effects of impurities on the dif-

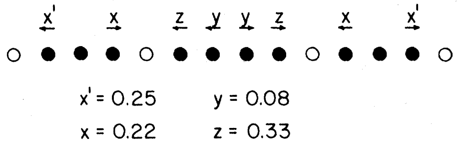

FIG. 3. Displacements of the ions for the 77%-occupancy case. The displacements are in units of the channel lattice constant a.

fraction described for the 75% occupied case, impurities can pin the vacancies in the 77% case destroying the periodic ionic order described in the previous paragraph. The scattering factor was calculated for the 77% case for a 100-site chain containing impurities. The equilibrium atomic positions were found by iterating Eq. (1) with the atoms initially evenly spaced. The resulting atomic configuration does not have the periodic pattern found for the pure case, i.e., the ordering with the 13-atom unit cell). The changes in the intensities and widths of the peaks in the scattering factor are qualitatively like the 75% case, and hence are not shown. It was found that if the iterations of Eq. (1) are started with the ordering with the 13-atom unit cell of the last paragraph, the equilibrium state found still has this regular atomic arrangement, and this state has lower energy than the irregular configuration discussed above. Apparently the interionic interaction, which favors periodic ordering of the ions, wins over the channel potential, for the impurity potential equal to ten times the periodic channel potential chosen for these calculations.

Of course, samples with other concentrations of potassium ions will have different structure in the x-ray scattering from the ground state from the structure than we have found for the 77% case. These ideas can be tested by doing x-ray diffraction near $T = 0$ on several samples of hollandite of different composition.

III. ELECTRICAL CONDUCTION BASED ON BEYELER'S MODEL

Previous studies of the Frenkel-Kontorova model[8] showed that for sufficiently weak sinusoidal potential compared to the interatomic interactions the sliding chain of atoms is not pinned in place, but it can slide freely if the periodicity of the chain of atoms is incommensurate with that of the sinusoidal potential. Since the model studied in this article is a generalization of the Frenkel-Kontorova model which takes the interatomic interaction to be a Coulomb rather than a harmonic potential and the ionic lattice is incommensurate with the sinusoidal potential for the 77% occupancy case, we must consider the possibility of such free sliding occurring for this model. Because of the long-range nature of the interatomic interaction, however, it is not possible simply to carry over the results found in Ref. 8 for the Frenkel-Kontorova model. In order to examine the possibility of free sliding, the methods of Ref. 8 were used. That is, Eq. (1) was iterated to obtain equilibrium atomic positions. E was then given a small, nonzero value [we chose $eE = 0.1(2\pi/a)V_0$ in our calculations], and Eq. (1) was iterated again. The maximum fluctuation per atom in the potential energy of the chain of ions as it slid through the lattice was plotted as a function of the reciprocal of the square root of the length of the chain in Fig. 4. As we see, these fluctuations per lattice site do not extrapolate to zero in the thermodynamic limit, indicating that the lattice is pinned.

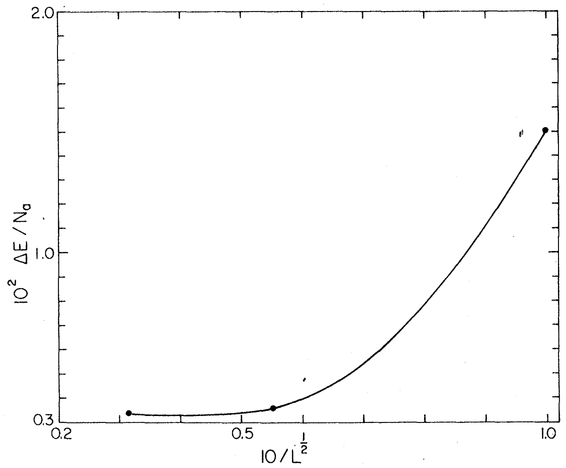

FIG. 4. Maximum fluctuation in the ionic potential energy per ion $\Delta E/N_a$ as a function of $L^{-1/2}$, where L, the length of the ionic chain, is in units of the channel lattice constant a and ΔE is in units of V_0.

Conductivity can proceed, however, by hopping of defects thermally activated from the ordered ground state. The lowest energy defect that can be created in the ground state for the 75% occupancy case is one in which an atom is displaced to a previously vacant site, illustrated in Fig. 5. The result of this displacement is the creation of defect pairs consisting of two vacancies separated by only two atoms and two vacancies separated by four atoms. We will refer to each of these as a two-atom and four-atom defect, respectively. Under an applied electric field, these defects move in opposite directions by thermally activated hopping of atoms onto vacant sites, as illustrated in Fig. 5. Thus, a two-atom defect could be considered negative and a four-atom defect could be considered positive. To calculate the energy of

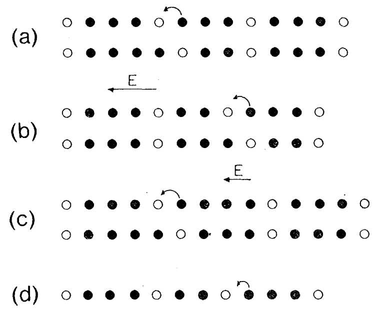

FIG. 5. Illustrations of how defects can be created and can hop in an electric field. (a) Creation of a two-ion–four-ion defect pair. (b) Motion of a two-ion defect in an electric field E. (c) Motion of a four-ion defect in an electric field. (d) Thermally activated step in the hopping of a two-ion defect. Dark circles are sites occupied by ions and open circles are vacant sites.

such a defect, each ion is initially placed at the channel potential minimum nearest the location it would have if the ions were evenly spaced. One ion neighboring a vacancy is then displaced onto the vacant site. Equation (1) is then iterated (for $E = 0$). The energy to create a two-atom–four-atom defect pair is the difference between the energy that we find and that of the ground state. Following this procedure we find an energy of $0.38V_0$. To consider well-separated defects, we start each ion at its nearest potential minimum as previously. At one point we place the next atom in what should be a vacant site, and then start the procedure again, from now on placing each atom in the potential minimum nearest to where it would be if the atoms were evenly spaced. This procedure generates two well-separated defects. The resulting energy for a well-separated two-ion–four-ion defect pair is $0.45V_0$. If an atom on a site next to one of the vacancies neighboring a two-atom defect is moved half the distance that it would have to move in order to occupy the vacant site [the process is illustrated in Fig. 5], the energy of the system increases by $0.07V_0$. This can be taken as an estimate of the defect hopping activation energy. Thus, the effect of the interatomic interaction in overriding the channel potential barriers is to considerably reduce the activation energies for the conductivity, an effect noted by Wang and Pickett.[9] If we take $2V_0$ to be 1/13 of the bare near-neighbor Coulomb potential between ions, $V_0 = 0.38$ eV, with smaller values if the Coulomb potential is screened. Our calculations give activation energies for defect hopping which are smaller than the observed 0.2 eV for activation energies of the conductivity of hollandite[11] by a factor of about 10. Since the studied sample of hollandite[1] has defects present in the ground state because the ground-state ionic ordering is incommensurate with the channel potential, this should be the activation energy of the conductivity. One possible way to explain this discrepancy is to say that the observed activation energy for the conductivity is due to the three-dimensional nature of the crystal. For example, in real crystals, the channels will never have infinite length; there will always be breaks in each channel. When an ion comes to such a break in a channel, it must jump into a neighboring channel in order to continue moving through the crystal. Then, the observed activation energy for the conductivity could be the activation energy for a jump into a neighboring channel. This will be true for the dc conductivity. For the ac conductivity, however, if the frequency is sufficiently high so that a defect cannot travel the length of a typical channel in a period, the activation energy should revert to the activation energy that has been calculated in this article.

Another possibility is that the samples studied in Ref. 10 were commensurate ones (with 80% of the sites occupied), and hence, we would not expect them to have defects in the ground state. Therefore, we expect the conductivity activation energy to be the activation energy for defect creation, which is closer to the experimentally observed value.

Both of these two effects might be present in the samples studied. To study them further additional ac and dc conductivity measurements should be made on good single-crystal samples of hollandite with both commensurate and incommensurate potassium-ion distributions.

IV. CONCLUSIONS

We have shown that ground-state ordering of the potassium ions in the model proposed by Beyeler to interpret his x-ray data on hollandite ($K_{1.59}Mg_{0.77}Ti_{7.23}O_{16}$) is not significantly affected by impurities. The major effect of the impurities is to change some of the intensities of the diffraction peaks found for the ground state of the model, but not to broaden the peaks. The widths of the peaks predicted for the ground state should be much narrower than those found by Beyeler at higher temperatures. Imperfect stoichiometry leads to several new peaks in the x-ray spectrum of the ground state.

The thermal activation of the conductivity found in this model is much smaller than that observed,[11] which could imply a one-dimensional model with infinitely long channels is not adequate for calculating the conductivity of the samples whose conductivity has been studied to date.

This dramatic reduction of the activation energy for thermally activated hopping of ions caused by interionic interaction (from $2V_0$ to about $0.07V_0$) should also occur in other superionic conductors to some extent. The reason for this reduction is that the interactions push the ions out of their lattice potential minima.

The present work presents predictions of the ordering of hollandite near absolute zero, a temperature regime that has not been studied to date. It also presents some predictions about the conductivity of hollandite, which must be tested on good single-crystal samples. Such experiments are needed to test the correctness of Beyeler's proposed ordering scheme.

ACKNOWLEDGMENT

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