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Percolation model for structural phase transitions in $Li_{1-x}H_xIO_3$ mixed crystals

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A percolation model is proposed to explain the structural phase transitions found in $Li_{1-x}H_xIO_3$ mixed crystals as a function of the concentration parameter x. The percolation thresholds are obtained from Monte Carlo simulations on the specific lattices occupied by lithium atoms and hydrogen bonds. The theoretical results strongly suggest that percolating lithium vacancies and hydrogen bonds are indeed responsible for the solid solution observed in the experimental range $0.22<x<0.36$.

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The lithium iodate (α-$LiIO_3$, hexagonal lattice) and the iodic acid (α-HIO_3, orthorhombic lattice) have been both intensively investigated, owing to their interesting properties and useful optical applications.[1–4] The lithium iodate is also interesting for fundamental reasons, specially those related to its structural phase transitions.[5] It is known that most of the properties of the α-$LiIO_3$ are strongly affected by its growth conditions, related to mainly three factors: the temperature, the evaporation rate, and the pH of the mother $LiIO_3$–H_2O–HIO_3 solution, which controls the quantity of impurities in the lattice. In this case, the impurities can be hydrogen atoms. Mixed crystals are easier grown using more acid solutions (with a greater HIO_3 concentration), but they have worse optical quality. $Li_{1-x}H_xIO_3$ mixed crystals are also important for technical applications, since they present a high piezoelectric coefficient.[6]

Although the structures of iodic acid and lithium iodate are known for more than 60 years, the structure of the mixed lithium iodate-iodic acid solid solution has been refined only in the last few years.[7–9] Regarding the lithium substitution, neutron-diffraction studies have shown that the hydrogen does not substitute the position of the lithium. Instead, when lithium goes out of the lattice, its site becomes empty, while the hydrogen forms hydrogen bonds between oxygens that belong to different iodate groups.[9]

Ricci and Amron[10] first mentioned the existence of the so-called solid solution of $Li_{1-x}H_xIO_3$ for x varying continuously over the range 0.22–0.36. Since then, much effort has been dedicated for studying these compounds, but the reason of these particular values is not yet well understood. In this work we propose a percolation model that explains the lower and upper limits experimentally observed for crystallizing the solid solution of these mixed crystals.

Let us first discuss the principal properties of pure lithium iodate. Structural phase transitions on this crystal have been largely studied.[5,11–13] At room temperature and low pressure, two forms are possible: α (hexagonal) and β (tetragonal). The α structure has been known since 1931 (Ref. 14) and is the more stable one at room temperature. There are two molecules per unit cell with the lithium atoms disposed on a simple hexagonal lattice. Lattice constants in angstrom, with errors in parentheses, are given by:[3] $a=5.48(1)$ and $c=5.18(1)$. The Li–O distance is approximately 2.12 Å. As the temperature increases, α-$LiIO_3$ exhibits two first-order phase transitions: $\alpha\rightarrow\gamma\rightarrow\beta$, where phases γ and β have orthorhombic and tetragonal symmetries, respectively.[5] Several works reveal discrepancies in the transition temperatures as well as in the temperature range where the γ phase exists. These differences are attributed to, among other reasons, the quantity of HIO_3 impurities in the lattice.[11–13] Thus, a good understanding of the alterations caused by the presence of hydrogen atoms is essential for studying these phase transitions.

Let us now turn to the α-HIO_3 crystal. The structure of α-iodic acid, though not as simple as that of the α-$LiIO_3$, has been known since 1941, by means of x-ray diffraction.[15] It is orthorhombic, with four molecules per unit cell and lattice constants in angstrom: $a=5.520(5)$; $b=5.855(5)$ and $c=7.715(5)$. The iodate group is pyramidal, although slightly distorted, and has the following interatomic distances in angstrom (with error of 0.04 Å or less): $I–O_I=1.81$; $I–O_{II}=1.89$; $I–O_{III}=1.80$; $O_I–O_{II}=2.75$; $O_I–O_{III}=2.78$ and $O_{II}–O_{III}=2.78$, where O_I, O_{II}, and O_{III} are the three oxygens of the iodate group. The hydrogen is bonded to the oxygen O_{II}, at a distance of 1.01 Å. This oxygen has two other neighbors: O_I' and O_{III}''. Here, prime and double primes denote different iodate groups. O_{II} forms two hydrogen bonds, $O_{II}–H–O_I'$ and $O_{II}–H–O_{III}''$, of equal intensities. The distances between the two oxygens indicate that the hydrogen bond is strong (there are here two bonds per iodate group each of which is about the strength of the single hydrogen bond in water and ice).[15] A better way to visualize this structure is to look at a projection onto the yz plane, as shown schematically in Fig. 1, where the whole IO_3 group has been represented by just one symbol (and no distinction is made among the three oxygens). There exists a kind of *bifurcated* hydrogen bond: a single proton is able to form two hydrogen bonds, i.e., the hydrogen closest to an iodate forms a bifurcated bond with two other iodates. Thus, there are two hydrogen bonds for each iodate group. These bifurcated bonds and the weak bonds between iodine and oxygens belonging to other iodate groups hold the iodates together.

The existence of bifurcated hydrogen bonds has been known since 1939, when the structure of glycine was

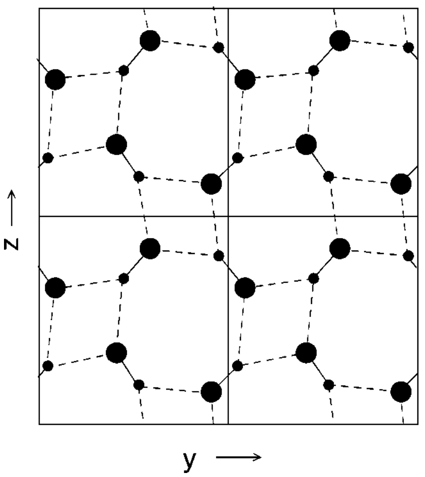

FIG. 1. Schematic representation of the HIO_3 structure onto the yz plane. Bigger circles represent IO_3 groups and the smaller ones hydrogen atoms. Bifurcated hydrogen bonds are represented by solid lines which bifurcate on dashed lines at the hydrogen atoms (after Ref. 15).

determined.[16] Nevertheless, with the exception of a few early studies,[17–19] this subject has not received much attention. The term *bifurcated* is used to denote two different kinds of bond. In a bifurcated *acceptor*, two different acceptor oxygens share the same donated proton. In the case of a bifurcated *donor* a single oxygen donates two protons to another single oxygen. The first case is what occurs in the structure of iodic acid, as determined in Ref. 15.

Several works have been devoted to the mixed crystal $Li_{1-x}H_xIO_3$.[7,10,20–23] Ricci and Amron[10] first reported the existence of the solid solution for hydrogen concentrations x in the range $0.22<x<0.36$. In 1990, Roy *et al.*[7] concluded that, for $x=0.33$, the mixed crystal possesses an average hexagonal symmetry, with an arrangement close to the hexagonal close packing. The structure at room temperature is shown in Fig. 2. Indeed, they observed that protons do not substitute the lithium atoms (2a in Wyckoff notation), but are randomly distributed through the lattice, occupying general positions (6c) between two oxygen atoms that belong to different iodates. Raman investigations[23] are consistent with this structure and show that the random presence of hydrogens changes the selection rules for the Raman scattering for x in the range $0.27<x<0.36$. The lattice constants are found to vary linearly with the concentration x, according to the relations:[7] $a=5.464+0.282x$ and $c=5.165-0.622x$, with a and c in angstrom. So, it is possible to obtain x via: $x=5.985-6.335c/a$, valid for $0.22<x<0.36$.

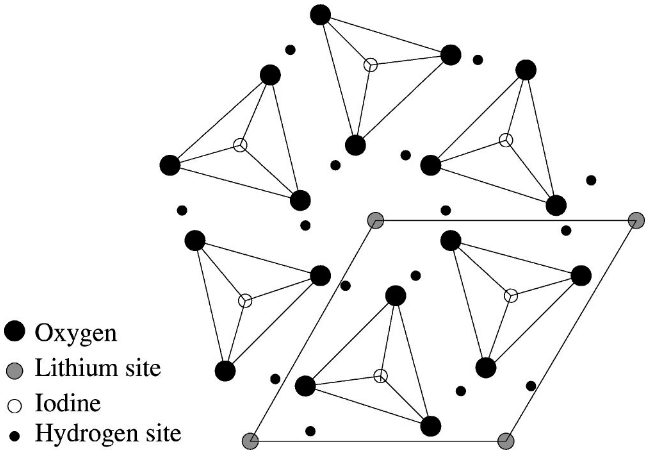

FIG. 2. The crystal structure of $Li_{1-x}H_xIO_3$ ($x\approx0.33$) projected onto the xy plane, according to Ref. 7. In this case, bifurcated bonds are not considered. The protons do not replace the lithium ions, but are randomly distributed in general positions between two oxygen atoms belonging to different iodate groups.

As mentioned before, only in the range $0.22<x<0.36$ the solid solution is constituted as a single phase. Out of this range, there is a mixture of solid solution and the pure compounds ($LiIO_3$ and HIO_3). Thus, these limits seem to be favorable for crystallizing the mixed crystal. Our purpose is identifying these values as the percolation thresholds on the corresponding lattices. In this manner, we expect that 0.22 corresponds to the critical point for site percolation on the $LiIO_3$ (simple hexagonal) lattice. Similarly, 0.36 might correspond to the percolation threshold for bond percolation on the HIO_3 (orthorhombic) lattice. This seems to be plausible since, as has been discussed above, it has been observed that the protons do not substitute the lithium atoms, but are randomly distributed through the lattice, occupying general positions between two oxygen atoms that belong to different iodates.[7,23] The proton positions should obey the arrangement depicted in Fig. 1. As the proton mediates the hydrogen bond, the net effect is a random dilution of hydrogen bonds on the crystal structure of Fig. 1. Thus, this system turns out to be a quite interesting problem involving site and bond dilution in the same crystalline structure.

It is known that, when lithium atoms are removed from their sites on the original hexagonal lattice, vacancies are left on their positions.[7] As more lithium atoms go out (which corresponds to an increasing x), clusters of neighboring vacancies are formed. There exists a given critical concentration x_c at which the lithium vacancies percolate through the lattice. In other words, for vacancies concentrations x such that $x\geqslant x_c$, there are an infinite cluster of neighboring vacancies. This fact should mean that, for $x\geqslant x_c$, the presence of vacancies causes an instability on the $LiIO_3$ hexagonal lattice and then propitiates the crystallization of the solid solution.

On the other hand, concomitantly to the removal of lithiums, hydrogen atoms are added in the lattice, originating H bonds. By an analogous argument, when the number of H-bonds is sufficiently large, there will be a cluster of neighboring bonds that percolates through the lattice, being possible to consolidate and stabilize the HIO_3 orthorhombic lattice.

We performed Monte Carlo simulations in order to obtain the percolation thresholds on the corresponding lattices. The algorithm we have used is that due to Newman and Ziff,[24] applied to three-dimensional lattices.[25] Despite to the fact that the percolation threshold for the hexagonal lattice need not be recomputed, since its value is quite well known from the literature [for instance, $p_c=0.2625(2)$,[25] $p_c=0.2623(2)$ (Ref. 26)], we have done just one simple simulation on a large lattice to see the performance of the method in order to apply it to the less studied case of the present bond dilution. In the site dilution problem, for a given system size, we start with an empty lattice. So, we fill the lattice, choosing sites to be occupied, at random. When a new site is added, it can originate an isolated cluster (if all its neighbors are empty), or it joins together two or more clusters. After a complete filling of the lattice (which corresponds to one Monte Carlo step), we can evaluate quantities of interest, such as the percolation threshold. Repeating this procedure several times, we get more accurate results. Using periodic boundary conditions, the percolation threshold is the concentration of occupied sites at which a cluster of neighboring occupied sites wraps around the system. The bond problem is treated in an analogous way.

For simulating the removal of the Li atoms, we can think that it is necessary to begin with a full lattice and then take out sites at random. In this sense, percolation means that there exists an infinite cluster of vacancies. If we replace Li *atoms* by *empty sites* and *vacancies* by *occupied sites*, we restore the standard percolation problem.

We applied the cited algorithm on the simple hexagonal lattices with up to 8000 sites, which corresponds to a linear dimension $L=20$. As we are interested only in the lithium positions, each site represents a lithium atom (the iodates localization are not relevant in this case). Performing 2.0×10^5 Monte Carlo steps, one obtains $x_c=0.26$ for the percolation threshold on this lattice. It is clear from the above result that for the purpose of the present study just this lattice gives a value which is quite comparable to those listed above from a more accurate finite size scaling approach, namely, $p_c=0.2625(2)$ (Ref. 25) and $p_c=0.2623(2)$.[26] Within our conjecture, this value might correspond to the lower limit for crystallizing the solid solution of $\mathrm{Li}_{1-x}\mathrm{H}_x\mathrm{IO}_3$.

Due to the complex structure of HIO_3, some modifications on the algorithm concerning the bond dilution are needed, in comparison with the usual percolation model. Since hydrogen bonds are formed between different iodate groups, we can represent, in our simulations, each iodate by a single site in the lattice. One has the restriction that bonds can exist only between sites that are located on different planes in order to reflect the fact that, in the real iodic acid, the distance between neighboring iodates on the same plane is greater than the maximum value for existing hydrogen bonds. The presence of bifurcated bonds leads to the additional constraint that one has always to choose a couple of bonds together. Since we know *a priori* the bonds that share the same hydrogen, we can choose a site (iodate) and then fill the two corresponding bonds. Using lattices with a total number of sites up to 6912 (which corresponds to a linear size $L=12$, since there are four molecules per unit cell), and 5.0×10^5 Monte Carlo steps for each system size, simulations yield $x_c=0.33$ for the critical hydrogen concentration on the specified crystal structure. Assuming the same accuracy as the previous site diluted model we believe that the number above is quite fine to be compared with the experimental one. A finite-size scaling estimate, providing a critical concentration with more digits of precision, would be irrelevant for the present purpose.

Before achieving these results, other similar hypotheses were tested, although all of them sharing the same fundamental concepts. The first attempts did not include bifurcated bonds. Bonds were chosen randomly one by one. Besides results were unsatisfactory, there is an incompatibility between the concentration of lithium vacancies and the corresponding concentration of hydrogen bonds. This can be explained as follows. For $x=0$ (pure LiIO_3) there is one lithium for each iodate. Imagine a lattice with a total of N lithium atoms. So, there are also N iodates. Since each iodate has four neighbors there are $2N$ possible bonds. Removing one lithium, we need to introduce one hydrogen. If each hydrogen forms a single bond, when all N lithium atoms will be removed $(x=1)$, there will be N hydrogen bonds, which corresponds to a fraction $N/2N=0.5$ of the total number of bonds. This fact precludes the equivalence between the hydrogen concentration x and the related percolation thresholds. Bifurcated bonds avoid this problem, since N hydrogens form $2N$ bonds. Thus, the fraction of vacancies is equal to the fraction of bonds.

According to our results, the solid solution should exist as a single phase for x in the range $0.26<x<0.33$. In this sense, when x rises from 0 to 0.26, lithium atoms are removed from the lattice but the α-LiIO_3 structure remains stable. For $x>0.26$, the number of vacancies is so great that the α-LiIO_3 lattice does not support itself. Concomitantly, while $x<0.33$, the hydrogen bonds are insufficient for supporting the HIO_3 orthorhombic structure. Thus, in the range $0.26<x<0.33$ the system is disordered and we find the so-called solid solution. For $x>0.33$ the percolating cluster of bonds maintains the HIO_3 lattice stable.

We conclude that our results are in good agreement with the experimental values and, although not stated in the experimental works, within the experimental errors. [For instance, the smaller concentration varies from 0.22 (Ref. 10) to 0.27 (Ref. 23)]. Thus, our results evidence the percolating character on these mixed compounds and clearly indicate that the crystal stability is, in fact, related to the percolation thresholds supported by the corresponding crystal structures. Further experimental studies regarding the structural transition of this material would be very welcome, mainly concerning its second-order character.

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