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Abstract
We have studied by the first-principles total energy method the off-center instability of a substitutional Li impurity in KCl. We report here the results of super-cell calculations of the energy associated with displacing the Li along $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions relative to the K vacancy. To understand the influence of relaxations, we performed three levels of relaxations—only first nearest neighbors of the vacancy, first and second nearest neighbors, and full relaxation. Our calculations show that the relaxation significantly affects the energy surface and that the relaxation of the nearest neighbors to the vacancy accounts for most of the trend. The position of minimum energy for the Li was found to be along the $\langle 111 \rangle$ direction. The calculated well along $\langle 111 \rangle$ is 102 meV deep relative to the on-center energy and lies about 0.86 Å off-center. Minima along adjacent $\langle 111 \rangle$ directions are separated by a saddle-point barrier of 44 meV along the $\langle 110 \rangle$ direction. Our calculated results are in agreement with prior model calculations and we believe our calculated potential surfaces are the best theoretical result so far.

1. Introduction

The introduction of a 'rattler' to suppress lattice thermal conductivity remains a promising method for improving the utility of bulk thermoelectric materials [1]. By definition, rattlers are atoms or molecule groups whose translational or angular orientations are not exactly defined in a lattice. There may be two or more possible semi-stable positions for these rattlers and there is no long-range correlation between the positions or orientations of these loose or 'rattling' atoms or molecules. The rattlers can undergo reorientation, and tunneling or hopping among these semi-stable positions. One important feature of these motions in solids is that they are strongly coupled to phonons, i.e. they cause strong phonon resonance scattering and lead to a reduction in lattice thermal conductivity.

In fact, back in the 1960s, this concept had been widely investigated in impurity-doped alkali halide crystals. Among those, the KCl:Li was the most thoroughly investigated example. The substitutional Li impurity was revealed to have several equivalent minima off the center of the K vacancy. Measurements of electrocaloric [2] and dielectric [3] properties of KCl:Li established the existence of a dipole moment of the order of 1 Debye. Sound velocity and absorption measurements by Byer and Sack [4] showed that the Li$^+$ in KCl is displaced along a $\langle 111 \rangle$ axis. Bogardus and

Sack [5] observed a tunneling splitting of 0.15–0.81 cm^{-1}. The phonon resonance was first observed in KCl:Li through low temperature thermal conductivity measurements with Li concentrations varying from 2×10^{17} to 8×10^{18} cm^{-3} [6] and confirmed by specific heat measurements [7]. By assigning a 40 cm^{-1} infrared-active impurity mode to transitions in a tunneling model, Harrison *et al* [7] determined that the potential minima between which the Li ion can tunnel are displaced by 1.2 Å in the $\langle 111 \rangle$ directions from the center of the K vacancy, and adjacent wells lying in the $\langle 111 \rangle$ directions are separated by a potential barrier of about 8 meV crossing the $\langle 110 \rangle$ direction. To interpret better the above experimental results, Bowen *et al* [8] proposed a model potential with multiple harmonic wells arranged in an octahedral symmetry. By fitting the 40 cm^{-1} impurity mode to their potential model, Bowen *et al* obtained an appropriate potential barrier of about 16 meV and an off-center position of about 0.87 Å in order to have splitting of about 1 cm^{-1}. However, a later investigation carried out by Sangster *et al* [9] on the origin of this 40 cm^{-1} infrared absorption showed that this 40 cm^{-1} line was contributed by the neighboring Cl ions rather than the Li itself. Therefore, an accurate potential surface in the Li-doped KCl and investigation of the importance of relaxations in the Li-doped KCl are required.

In fact, several theoretical investigations with various model calculations and *ab initio* calculations had been carried

out in order to clarify the configuration of the impurity Li ion and its surrounding ions. Using a point-ion model and adopting a Born–Mayer-type potential, Wilson *et al* [10] and Quigley *et al* [11] determined the minimum energy configurations for Li displacements in KCl along the ⟨111⟩, ⟨110⟩ and ⟨100⟩ crystal symmetry axes. Later, Catlow *et al* [12] and Sangster and Stoneham [13] studied this system with a shell model potential. Although these model calculations agreed with experimental observations, the calculated quantities—the off-center displacements and energy barriers between minima—are very much dependent on the potential models adopted in these calculations. In order to avoid the ambiguity which results from using model potentials, Yamada *et al* [14] studied the off-center instability in KCl:Li using an *ab initio* total energy calculation of a small ion cluster $LiCl_6^{5-}$. In the study by Yamada *et al*, the total energies of the cluster $LiCl_6^{5-}$ were calculated self-consistently for various positions of the Li nucleus with other nuclei fixed on their perfect lattice sites. That is, there was no relaxation included in this *ab initio* calculation. However, it had been pointed out in the prior model calculations that relaxations of surrounding ions were important in determining the off-center instability of the substitutional impurity. Therefore, to the best of our knowledge, even in this well-studied system, no *ab initio* calculations including relaxations have been published.

In this study, we report on *ab initio* calculations of super-cells of Li-doped KCl. First, we will focus on the detailed calculations of a $2 \times 2 \times 2$ super-cell. Then we will test the super-cell size effect on potential wells and off-center position by calculation on a $3 \times 3 \times 3$ super-cell. Our results confirm that the energy surface is sensitive to the relaxation of the lattice around the vacancy. We include relaxations of successive neighbor shells and find that the relaxation of the first neighbor shell accounts for most of the relaxation effect. We compare our calculated results to prior calculations and parameters extracted from experiment.

2. Computational details

The total energies for super-cells were performed in the framework of density functional theory (DFT) by using the Vienna *ab initio* simulation package (VASP) [15]. The projector augmented wave [16] potentials were used within the generalized gradient approximation (GGA) according to Perdew–Wang 1991 (PW91) [17] for exchange and correlation energies for all calculations. A cutoff energy of 280 eV was used for the plane wave basis set. The criterion for self-consistency in the electronic structure determination was that two consecutive total energies differed by less than 10^{-5} eV. The Brillouin zones of all super-cells were sampled using Monkhorst–Pack grids ($4 \times 4 \times 4$ grid for $2 \times 2 \times 2$ super-cell and $2 \times 2 \times 2$ grid for $3 \times 3 \times 3$ super-cell) within one primitive cell. In all of our calculations, lattice parameters were fixed at equilibrium GGA lattice constants when Li was on-site after substitution—6.3478 Å for $2 \times 2 \times 2$ super-cell and 6.3625 Å for $3 \times 3 \times 3$ super-cell.
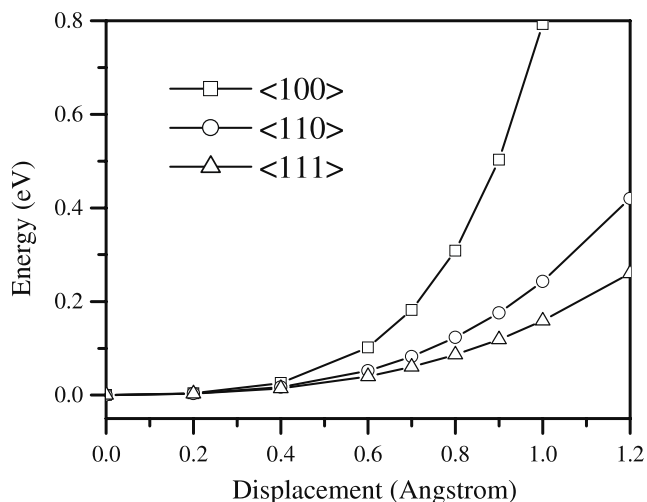
We use the super-cell method to attack the off-center instability in our calculations. We will focus on a $2 \times 2 \times 2$ super-cell (64 atoms per unit cell with Li concentration of 4.9×10^{20} cm^{-3}). We have chosen three displacement directions for examination, namely the ⟨111⟩, ⟨110⟩ and ⟨100⟩ axes of a perfect FCC lattice having the rock-salt structure. An off-center position along these axes has C_{3v}, C_{2v} and C_{4v} symmetry, and these symmetries remain unchanged in all our following calculations. In these directions the energy is studied as a function of the Li displacements. When we study the super-cell size effect on potential wells and off-center position by calculation on a $3 \times 3 \times 3$ super-cell (216 atoms per unit cell with Li concentration of 1.4×10^{20} cm^{-3}), only the minimum energies and their corresponding positions are calculated.

In order to study the relaxation effects on the energy barrier, different levels of relaxations of the surrounding ions around Li were performed. Taking advantage of the constrained relaxations of internal coordinates executed in VASP, we did three levels of relaxations in the calculation of energy versus impurity displacement curves of the optimized $2 \times 2 \times 2$ super-cell. First, after Li is displaced, only its six first nearest Cl ions are allowed to relax. Second, we allow the six first nearest Cl and 12 second nearest K ions to relax. Here, the nearest neighbors are referred to the reference structures. The third, if the Li is displaced along the ⟨100⟩ direction, the Li (δ, 0, 0) and the K in the center of the ⟨100⟩ axis of a $2 \times 2 \times 2$ super-cell with fractional coordinate of (0.5, 0, 0) are fixed, all others are allowed to relax; if the Li is displaced along the ⟨110⟩ direction, except the Li (δ, δ, 0) and the K (0.5, 0.5, 0) in the face center of the (001) face of the $2 \times 2 \times 2$ super-cell to which Li moves toward, all other ions are allowed to relax; if the Li is displaced along the ⟨111⟩ direction, the Li (δ, δ, δ) and the K (0.5, 0.5, 0.5) in the body center of the $2 \times 2 \times 2$ super-cell are fixed, all other positions are optimized. Here, the K ions are fixed to prevent the origin drift without changing the symmetry of the systems. We refer to the third level of relaxation as 'full' relaxation later. In the $3 \times 3 \times 3$ super-cell calculations, the displaced Li was also allowed to relax in order to get the minimum energy configurations. The internal structure relaxations were considered to finish when all the forces on those relaxed ions were less than 10^{-2} eV Å^{-1}.

3. Results and discussions

In order to make the computation, we will focus on the $2 \times 2 \times 2$ super-cell first. The reference structure for the following calculations is taken to be a KCl super-cell with Li substituted for one K and then completely relaxed—holding the Li on-site and letting the volume change. Because of the Li substitution, the resulting volume shrinks following Vegard's law. With the Li at the center, the nearest neighbors move inwards significantly, especially the first six nearest Cl ions (0.264 Å from its perfect rock-salt structure position and resulting in an Li–Cl distance of 2.91 Å). In addition, the 12 second nearest neighbors—K ions—and the 24 fifth nearest neighbors—Cl ions—of Li have non-negligible inwards movements of 0.054 Å, and 0.025 Å, respectively. On the one hand, it is not surprising that the fifth neighbors have large inwards movements since they are the first nearest neighbors of the K ions. On the other hand, when we tested inwards movement
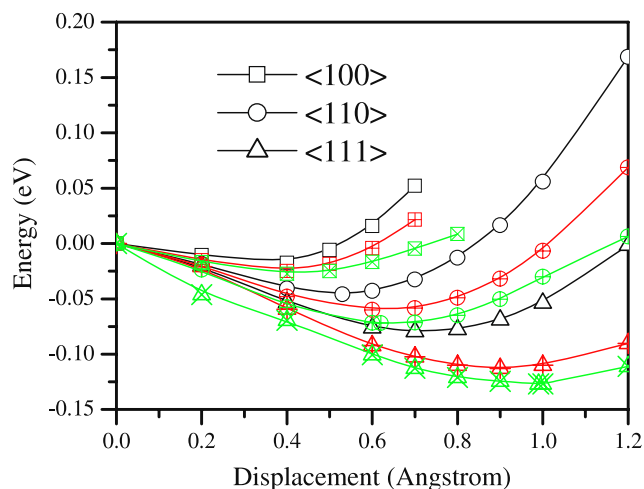
Figure 1. Potential curves for Li in a K vacancy, where now the host atoms around the vacancy are relaxed when the Li is on-center but then held fixed as the Li is displaced. The inward relaxation of the Cl towards the smaller Li has blocked the off-center minima.

Figure 2. Potential curves for Li in a K vacancy, where the host lattice is allowed to relax in response to the Li displacement. The open symbol corresponds to relaxation only of the Cl atoms nearest the vacancy. The symbol filled with '+' corresponds to relaxation of both the first and second nearest neighbors. The symbol filled with '×' corresponds to full relaxation. The relaxation of the host lattice in response to the Li displacement again allows the energy to be minimum when the Li is off-center.

(This figure is in colour only in the electronic version)

to the center-sited Li in a $3 \times 3 \times 3$ super-cell, we found that this movement was much smaller in the $3 \times 3 \times 3$ super-cell (~0.01 Å). Actually, because of super-cell size effects and symmetry constraints on the super-cell, only certain coordinate components of these inwards movements are allowed. This is the case of the fifth nearest-neighbor relaxations, where one of their coordinates (fractional coordinate, 0.5) is constrained due to the finite super-cell size. The resulting super-cell size effects on our results will be discussed later.

In order to investigate the importance of the relaxation effects of surrounding ions, we first calculated the energy versus Li displacement along $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$ axes by keeping all ions fixed in the relaxed reference structure. The results are shown in figure 1. Clearly, there is no off-center instability. This behavior is understandable if we realize the short Li–Cl distance (2.91 Å) in the relaxed reference structure, in which there is no room for Li to move off-center. Therefore, the on-site position is the most energetically favorable site. This result is consistent with the *ab initio* cluster calculation by Yamada *et al* [14]. In their calculations, it showed that, when the Li–Cl distance was smaller than 3.05 Å, there was no off-center instability. These results imply the pressure effect on the off-center instability in these kinds of small-ion-substituted system—the pressure will favor the on-site position. On the other hand, the off-center instability can only possibly occur in systems where there is enough room, that is, atoms in large voids.

Second, we did the three levels of relaxations—first nearest-neighbor relaxation, both first and second nearest-neighbor relaxation, and 'full' relaxation—after Li was displaced along the $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$ directions. The potential surfaces are shown in figure 2. In contrast to figure 1, the off-center minimum appears by allowing even just the six first nearest neighbors to relax when the Li is displaced off-center. We can see clearly that the systems show strong off-center instabilities with surrounding ions'

relaxations. This result indicates significant coupling between the off-center Li and its host. Among all three directions' off-center displacements, the $\langle 111 \rangle$ axis has the deepest minimum, the $\langle 100 \rangle$ axis the shallowest. This ordering is consistent with the number of attractive Cl anions approached along each direction. They are 1, 2 and 3 attractive Cl anions along $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$, respectively. Our calculated well depths along $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ are in a ratio of about 1:2.5:4.5. In addition, the displacement of the minimum is largest along the $\langle 111 \rangle$ axis. From this, we infer that two $\langle 111 \rangle$ minima are separated by a saddle point which is the minimum along the $\langle 110 \rangle$ direction. This picture is consistent with the picture established in the literature [10–13, 18].

As shown in the figures, the relaxations of the six first nearest neighbors play the most important role, and relaxations of the second nearest neighbors are important, too. However, further nearest-neighbors' relaxations do not significantly influence the result, especially the barrier height and the off-center position. For example, when the Li is displaced along the $\langle 110 \rangle$ axis to 0.6 Å, the first nearest-neighbor relaxations make the total energy 0.095 eV lower compared to that of no relaxations, both first and second nearest-neighbors' relaxations make the total energy another 0.017 eV lower compared to that of the first nearest-neighbor relaxations only, and full relaxation make the total energy 0.012 eV lower compared to the second level relaxation. Along the $\langle 111 \rangle$ directions with displacement of 0.9 Å, the corresponding lowering of energies are 0.188, 0.044 and 0.012 eV, accordingly. With further nearest-neighbors' relaxations, the barrier height and off-center minimum position have no significant change. Our current results of different level relaxation effects on the off-center instability are

Table 1. Calculated energies and displacements for KCl containing substitutional Li ion in a $2 \times 2 \times 2$ super-cell (the corresponding results with a $3 \times 3 \times 3$ super-cell are shown in the brackets). ΔE is the off-center minima energy (in meV) along the $\langle 111 \rangle$ direction relative to the reference energy, that is, the energy when the impurity Li ion sits on-center. Energy barrier in units of meV is the energy difference between energy minima along the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions. The off-center equilibrium displacement in units of Å along $\langle 110 \rangle$ and $\langle 111 \rangle$ are shown in the last two columns. As a comparison, different model calculation results and experimentally extracted results are shown in this table, too.

Methods		ΔE	Energy barrier	Displacement $\langle 110 \rangle$	Displacement $\langle 111 \rangle$
DFT (three levels of relaxation)	1st NN	79 (54)	34 (23)	0.53 (0.45)	0.70 (0.67)
	1st and 2nd NN	113 (85)	53 (42)	0.60 (0.50)	0.90 (0.87)
	Full	127 (102)	55 (44)	0.62 (0.61)	0.99 (0.86)
Exp. [7]			8.0		1.20
Point-Ion model [10]		269.4	7.3	1.16	1.16
Point-Ion model [11]		30	8.0	0.50	0.60
Shell model [12]	Pot. I	50	17.0	0.49	0.63
	Pot. II	8	3.0	0.30	0.39
Shell model [13]		190	70.0	0.66	0.92
Ab initio cluster [14]		51.57	16[a]	0.75[a]	1.02[a]

[a] These figures were not obtained directly from *ab initio* cluster calculations; instead from a model with parameters obtained in *ab initio* calculations.

essentially in agreement with prior model calculations and our previous ion movement analysis when Li is on-center. Wilson *et al* [10] did find that further relaxations from the first up to the third nearest-neighbor ions lowered the minimum energy. Catlow *et al* [12] found that the relative energies of the different off-center minima were unchanged by the increase in size of the relaxed region in the shell model and the calculated displacements of the substitutional ion agreed to within 0.01 times the cation–anion separation. However, the relaxed regions in Catlow *et al*'s work were already up to sixth and eighth nearest neighbors. None of them investigated the relaxation effects up to different nearest neighbors systematically.

The resultant barrier heights and off-center positions are listed in table 1 in comparison with prior model calculations and experimentally extracted results. It is noted that, in the point-ion model calculation, the results listed in table 1 were obtained by relaxation of only first nearest-neighbor ions, and in the shell model calculation, up to sixth nearest-neighbor ions were allowed to relax. Our calculated off-center displacement and barrier height with relaxations are within the range of prior model calculations [10–14] and experimental observations, but the barrier height is about an order of magnitude larger than that deduced from experimental measurement [7]. As seen above in the relaxation process of the reference structure, the super-cell size may have a significant effect on the calculated results. It is worthwhile to see how super-cell size will affect our calculated results. Therefore, we optimized the minimum energy configurations of a $3 \times 3 \times 3$ super-cell with the same three levels' relaxations done for a $2 \times 2 \times 2$ super-cell. The resultant barrier height and off-center position for a $3 \times 3 \times 3$ super-cell are also shown in table 1. It indicates that increasing the size of the super-cell will significantly reduce the barrier height and make it agree better with the experimental result.

We should point out here that the size effect on the barrier height is not contributed by dipole–dipole (consisting of the positive lithium ion and the effective negative charge centered in the potassium cavity) interactions in our super-cell calculations. The total contribution from dipole–dipole

interactions is zero because of the cubic symmetry—the dipoles are sitting in the corner of primitive cubes—in our super-cells, as can be seen from the form of the dipole–dipole interaction energy, $W_{12} = \frac{\vec{p}_1 \cdot \vec{p}_2 - 3(\vec{n} \cdot \vec{p}_1)(\vec{n} \cdot \vec{p}_2)}{|\vec{r}_1 - \vec{r}_2|^3}$, where $\vec{p}_1$ and $\vec{p}_2$ are dipole moments, and $\vec{n}$ is a unit vector in the direction of $(\vec{r}_1 - \vec{r}_2)$. Therefore, the well depth difference in different super-cells is not due to the dipole–dipole interaction. We believe that the reduction in the barrier height is related to the artificial forces due to the super-cell size constraint, as seen above.

4. Summary

Through the *ab initio* total energy calculation, we have confirmed the off-center instability of substitutional Li in KCl. Our systematic calculations with different levels of relaxations show the importance of surrounding ions' relaxations in determining the off-center instability. The calculated equilibrium Li displacement is 0.86 Å from the centro-symmetric site, in agreement with experimental measurement. Our calculated barrier height is 44 meV, which is consistent with prior model calculations but is much higher than the values obtained by fitting experimental results to model potentials.

Acknowledgments

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