Derivation of Interatomic Potentials from *Ab-initio* Calculations for Molecular Dynamics Simulations of Na$_x$CoO$_2$

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A parameter set for Buckingham-type potentials to describe interatomic bonding between Na$^+$-O$^-$, Co$^{2+}$-O$^-$, and O$^2$-O$^-$ in Na$_x$CoO$_2$ thermoelectric materials having a high figure of merit was determined by *ab-initio* calculations. Parameters for pairs other than O$^2$-O$^-$ were chosen so that they reproduce the lattice constants and elastic constants of NaCoO$_2$ obtained by *ab-initio* calculations. Fitting was also performed using the corresponding binary oxides as well as Na$_x$CoO$_2$ in order to improve transferability and accuracy. Lattice constants calculated using the potential were in good agreement those of the binary oxides and the reproducibility of elastic constants was also satisfactory. The potential is robust enough to simulate atomic vibrations in molecular dynamics even at elevated temperatures. In-plane phonon thermal conductivities calculated by perturbed molecular dynamics with the potential are in good agreement with experimental values and the reduction of the thermal conductivity with increasing temperature due to phonon-phonon scattering is also reproduced well. Molecular dynamics simulations with this potential set enable features unobservable by experiment to be revealed, such as Co valence distribution at elevated temperature.

Key words: thermoelectric materials, *ab-initio*, molecular dynamics, interatomic potential, force field

1. INTRODUCTION

Thermal conductivity is one of the most important basic properties of a material, which determines its performance in various applications. The thermal conductivity is governed by nanoscale interactions between electrons and phonons, which cannot be observed on the macro-scale. Thus, theoretical approaches and calculations of thermal conductivity are necessary for analysing detailed mechanisms. There are generally two approaches for calculating thermal conductivity. One is to use *ab-initio* calculations on the quantum level. The other is to use molecular dynamics (MD) simulations based on the classical laws of motion. Each of these methods has advantages as well as disadvantages. Recent improvements in computational power has decreased the cost of performing *ab-initio* calculations. *Ab-initio* calculations enable various properties of materials, such as the most stable atomic structure, to be analyzed accurately without any experimental parameters. Also, one of important factor in analyzing thermal conduction is the density of states of phonons, which can be obtained at 0 K by *ab-initio* methods. However, the harmonic approximation, employed in combination with *ab-initio* calculations in many cases, cannot describe phonon-phonon interactions without including a number of assumptions. At room temperature or higher, the magnitude of phonon-phonon interactions becomes dominant; except at very low temperatures, phonon thermal conductivity is mainly governed by phonon-phonon scattering. Thus, since *ab-initio* calculations cannot evaluate phonon-phonon scattering themselves, thermal conductivity cannot be evaluated unambiguously without introducing any assumptions. Instead, an interatomic potential, or force field, describing atomic interactions has proven effective, i.e., phonon thermal conductivity can be obtained quantitatively by MD calculations using such an interatomic potential.

MD calculations require information about the nature of the interatomic bonding and atomic configuration but do not require any other materials properties prior to the calculation, unlike in other methods such as finite element methods (FEM). In addition to direct methods and equilibrium methods, a perturbed MD method has been developed by Yoshiya *et al.* which enables calculation of phonon thermal conductivity of oxides.

Thermoelectric (TE) materials have attracted attention since they represent an alternative method for energy generation using waste heat. The figure of merit measures the efficiency of heat-to-electricity conversion; a high figure of merit requires low thermal conductivity with high Seebeck coefficient and high electronic conductivity. Thermal conduction can be classified into two types: that due to electrons and that due to phonons. A decrease in the electronic thermal conductivity inevitably results in a decrease in electronic conductivity, which needs to be high for a high figure of merit. Thus, it is important to decrease the phonon thermal conductivity of TE materials through analyzing the detailed mechanisms of thermal conductivity.

Attention has been directed at a few layered cobalt oxides since they exhibit a higher figure of merit. These materials cost less than conventional Bi-Te, which has been widely used as a TE material so far. Na$_x$CoO$_2$...
is one such layered cobalt oxide, and exhibits a high figure of merit at high temperatures\(^8\). It is reported that the high Seebeck coefficient and high electronic conductivity in this material are due to strongly-correlated 3d electrons and their corresponding density in Co-O layers\(^7,8\). However, understanding the origin of the modest thermal conductivity is still limited. In general, oxides possess much more complicated crystal structures than the metals or metalloids on which theories of thermal conduction have been based, which hinders the application of such theories to oxides. Consequently, theoretical analysis of phonon thermal conductivity in oxide materials is still needed. Unfortunately, no consistent interatomic potential parameter set for reproducing the crystal structures, even at 0 K, of Na\(_x\)CoO\(_2\) have been reported, making it difficult to quantitatively analyze phonon scattering. Therefore, in this study, we aimed at determining a potential parameter set that describes atomic interactions in Na\(_x\)CoO\(_2\) particularly for use in MD calculations at high temperatures to analyze phonon thermal conduction. To do so, ab-initio calculations have been carried out, not to directly calculate thermal conductivity itself, but to obtain theoretical values of physical properties from which interatomic potential parameters could be derived. Next, static calculations were carried out to explore the interatomic potential parameters, followed by MD calculations to see if the dynamic motion of the atoms is realistic. From these simulations preliminary data regarding the thermal conductivity of Na\(_x\)CoO\(_2\) were obtained.

2. METHODS

In the Born-Mayer-Huggins potential function (eq. (1)), ion-ion interactions are partitioned into Coulomb interactions and short-range interactions. A Buckingham-type potential function was used for the short-range interactions, as is commonly used for ionically bonded oxides. Here, \(q_i\) is the formal charge of ion \(i\), and \(r_{ij}\) is the distance between ions \(i\) and \(j\). In the Buckingham potential, parameters, \(A_{ij}\), \(\rho_{ij}\), and \(C_{ij}\) are fitted to quantitatively reproduce physical properties of the system. \(O^2-O^2\) interactions are the dominant interactions in oxides and we considered that transferability of these parameters is more important than highly accurate reproduction of Na\(_x\)CoO\(_2\). We thus employed general potential parameters reported by Cherry et al.\(^9\) without modification for the \(O^2-O^2\) interactions. Fitting of the other potential parameters was performed to reproduce the properties of Na\(_x\)CoO\(_2\). In the case of metal-metal interactions, only Coulomb interactions were considered, since the ionic radii of metals are much smaller than those of oxygen. Consequently, short-range potential parameters for Na\(^+\)-O\(^2\), Co\(^{3+}\)-O\(^2\), and Co\(^{3+}\)-O\(^2\) pairs only were determined.

Transferable potential parameters for Na\(^+\)-O\(^2\) and Co\(^{3+}\)-O\(^2\) have been reported by Grimes et al.\(^10\) and Cherry et al.\(^9\) respectively. However, as mentioned in the previous section, these potential parameters do not reproduce the structure of Na\(_x\)CoO\(_2\) well. Thus, these potential parameters needed to be modified and improved to reproduce Na\(_x\)CoO\(_2\) crystal structure and its atomic motions. To our knowledge, no potential parameters for Co\(^{3+}\)-O\(^2\) have been reported, and thus these parameters were modified by commencing with parameters for Co\(^{3+}\)-O\(^2\) and changing the charge of the cobalt ion.

To obtain appropriate potential parameters for Na\(_x\)CoO\(_2\), lattice constants for the most stable structure and its elastic constants were used in the fitting procedure. Lattice constants provide information about the equilibrium interatomic distances, and elastic constants represent curvatures around the equilibrium bond length. The most stable atomic positions were determined by minimizing the total energy of the ab-initio calculations from initial structure found in experiment\(^11,12\) with respect to the atomic positions as well as lattice constants. The ab-initio calculations were carried out using the PAW pseudo-potential method\(^13\). The exchange-correlation term parameterized by Perdew, Burke, and Ernzerhof\(^14\) was used. Elastic constants were determined using Muraghan's equation of state for the above stable structure by imposing a uniaxial strain to unit cells:

\[
E(\epsilon) = \frac{BY}{2(B-1)}[\epsilon_0 (1 - \frac{\epsilon'}{\epsilon_0})^{\frac{3}{2}} - 1] + E(\epsilon_0)
\]

where \(B\) is the elastic constant, \(B\) is the pressure derivative of the elastic constant, \(V\) is volume, \(V_0\) is the equilibrium volume and \(E\) is the total energy at each \(V\). Finally, the potential parameters were determined so that lattice constants and elastic constants calculated by classical static lattice energy minimization calculations using the potential parameters reproduce those obtained by ab-initio calculations. These tests were performed not only from Na\(_x\)CoO\(_2\) and Na\(_x\)CoO\(_2\) but also for binary oxides Na\(_2\)O and Co\(_2\)O\(_3\), in order to confirm the transferability and accuracy of the potential parameters.

3. RESULTS AND DISCUSSION

3.1 Determination of potential parameters

It has been reported that Na\(_x\)CoO\(_2\) exhibits three phases, depending on \(x\), which differ in layer stacking sequence. NaCoO\(_2\) and Na\(_{0.5}\)CoO\(_2\) exist in the stable \(\gamma\) phase with space group \(Rm-3m\) and \(\alpha\) phase with space group \(Pmnn\), respectively\(^11,12\). At first, in order to confirm which phase is the most stable for a given \(x\), formation energies of NaCoO\(_2\) and Na\(_{0.5}\)CoO\(_2\) for each phase were obtained by ab-initio calculations (Table I). It was confirmed that NaCoO\(_2\) and Na\(_{0.5}\)CoO\(_2\) are most stable in the \(\alpha\) and \(\gamma\) phases, respectively. These structures were thus used during fitting of interatomic potential parameters.

Table II shows lattice constants and elastic constants of the most stable structure of each composition obtained by ab-initio calculations. The crystal structure of Na\(_{0.5}\)CoO\(_2\) is shown in a hexagonal form converted from orthorhombic form for ease of comparison. Due to the symmetry of the crystal structures, lattice constants \(a\) and \(b\), and elastic constants along \(a\), \(C_{11}\), and \(b\), \(C_{22}\), were the same, for the whole composition range; in Na\(_x\)O (space group \(Pm-3m\)) and CoO\(_2\) (space group \(Fd-3m\)) lattice constants and elastic constants were the same. The lattice constants obtained by ab-initio
TABLE I. Formation energies [kJ/mol] for each phase at 0 K obtained by ab-initio calculations.

<table>
<thead>
<tr>
<th></th>
<th>NaCoO_3</th>
<th>Na_0.5CoO_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>-2261.86</td>
<td>-2130.15</td>
</tr>
<tr>
<td>β</td>
<td>-2211.37</td>
<td>-2130.16</td>
</tr>
<tr>
<td>γ</td>
<td>-1921.92</td>
<td>-2137.01</td>
</tr>
</tbody>
</table>

TABLE II. Lattice constants a [Å] and c [Å], and elastic constants C_11 [GPa] and C_12 [GPa], obtained by ab-initio calculations, employed during fitting of the potential parameters set. Values in parentheses are relative to experimental values^{11, 12, 15, 16}.

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>C_11</th>
<th>C_12</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCoO_3</td>
<td>2.94</td>
<td>15.6</td>
<td>-0.269</td>
<td>337</td>
</tr>
<tr>
<td>Na_0.5CoO_2</td>
<td>11.3 (0.79%)</td>
<td>11.2 (0.87%)</td>
<td>354 (-)</td>
<td>105 (-)</td>
</tr>
<tr>
<td>NaO</td>
<td>5.42</td>
<td>(2.4%)</td>
<td>97.9</td>
<td>(23%)</td>
</tr>
<tr>
<td>CO_3O_4</td>
<td>8.06</td>
<td>(0.24%)</td>
<td>483 (-)</td>
<td>(-)</td>
</tr>
</tbody>
</table>


FIG. 1. Murnaghan’s equation of state fitted to the total energy curve along the uniaxial strain direction obtained by ab-initio calculations.

calculations agree well with those reported in the literature^{11, 12, 15} with errors below 1.6%. Figure 1 shows a nearly-parabolic curve of Murnaghan’s equation of state fitted to total energies calculated by ab-initio under uniaxial strain in order to determine these elastic constants. The potential parameters were fitted to reproduce these values.

While there is no ambiguity in charge state of Na and O in ionic oxides, the valence of Co can vary. Even in this series of materials, the valence of Co varies with Na content, x, to maintain charge neutrality. In NaCoO_2, Co has a valency of 3+, but as the Na content decreases, the valence of some of the Co ions changes from 3+ to 4+, to give an average valence of 3.5+ in Na_0.5CoO_2. Ab-initio calculations do not require the valence of each Co to be specified prior to calculation; they are obtained as a result of self-consistent calculation of charge distribution. However, when interatomic potentials of the Buckingham type are used, they must be specified (and fixed) prior to running the simulation. To do so, we assumed that some of the Co ions close to O have valence 4+ and those further from O have valence 3+, based on the concept of ionic radii, which is one of simplest approaches to estimate Co valence distributions. As a result, Co^{3+} and Co^{4+} were ordered in rows down both a and b axes as shown in Fig. 2. The difference in thermal conductivity based on the Co valence ordering will be discussed later.

The fitted potential parameters are summarized in Table III, and Table IV shows lattice constants and using these parameters. Errors in lattice constants are below 3.1 %, in spite of the fact that crystal structures of all the materials shown have quite different atomic configurations. On the other hand, agreement between elastic constants was less satisfactory with errors of about 40% even in NaCoO_2. However, the error in the atomic vibration is proportional to the square root of the error in the elastic constant, e.g., an error of 40% results in only 1.18 times larger amplitude of vibration. Furthermore, these results were calculated using simple formal charge instead of the more realistic spatially distributed charges. Also, ab-initio calculations are not considered to be good at reproducing experimental elastic constants as they are lattice constants, as can be seen in Table II. Taking these into account, the accuracy of the potential set is satisfactory.

3.2 Molecular Dynamics Simulations

The potential parameter set determined in the previous section was used in MD simulations of NaCoO_2 and Na_0.5CoO_2. Trajectories and mean square displacements (MSD) of each atom in both structures are shown in Fig. 3. Judging from the trajectories and the MSD, vibrations of atoms are stable and the appropriate crystal structures are maintained. The MSD shows a larger amplitude of vibration for Na in Na_0.5CoO_2 due to the looser bonding to neighboring atoms. The MSD of Na in Na_0.5CoO_2 is remarkably high because some Na in Na_0.5CoO_2 can jump into the Na vacancies, as can also be seen in the trajectory plot, while in NaCoO_2 Na atoms simply vibrate around their lattice positions. Using the perturbed MD method\(^1\), in-plane phonon thermal conductivities at 300 K and 800 K were
4. CONCLUSION

A potential parameter set for describing atomic interactions in Na$_x$CoO$_2$ was determined that can reproduce lattice constants and elastic constants obtained from ab-initio calculations. The potential parameters reproduce lattice constants better than elastic constants, but are robust enough to simulate atomic vibrations in MD simulations even at high temperatures with reasonable accuracy. In-plane phonon thermal conductivities measured using the perturbed MD method with these potentials were in good agreement with experiment, and reduction of thermal conductivity with increasing temperature due to more pronounced phonon-phonon interactions at elevated temperature was also reproduced well. The potential parameters thus provide an important step in revealing mechanisms of phonon thermal conduction in layered cobalt oxides.

ACKNOWLEDGEMENTS

This study was in part supported by a Grant-In-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. M. T and H. Y. are supported by Priority Assistance for the Formation of Worldwide Renowned Centers of Research - The Global COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design) from MEXT.

REFERENCES


(Received December 9, 2009; Accepted February 24, 2010)