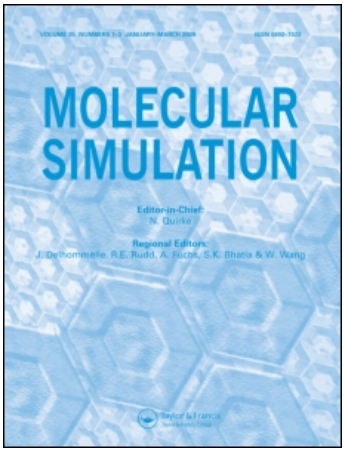
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK




**Molecular Simulation**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

# Molecular Dynamics Simulations of NaCl-type Solid Solution Crystals: The First Application of Molecular Dynamics to Solid Solutions

Tadashi Akamatsu[a]; Masaomi Fukuhama[a]; Hidemoto Nukui[a]; Katsuyuki Kawamura[b]
[a] Faculty of Education, Kochi University, Kochi, Japan [b] Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan

**To cite this Article** Akamatsu, Tadashi , Fukuhama, Masaomi , Nukui, Hidemoto and Kawamura, Katsuyuki(1994) 'Molecular Dynamics Simulations of NaCl-type Solid Solution Crystals: The First Application of Molecular Dynamics to Solid Solutions', Molecular Simulation, 12: 3, 431 — 434
**To link to this Article: DOI:** 10.1080/08927029408023050
**URL:** http://dx.doi.org/10.1080/08927029408023050

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

*Molecular Simulation*, 1994, Vol. 12(3–6), pp. 431–434
Reprints available directly from the publisher
Photocopying permitted by license only

© 1994 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

*Note*

# MOLECULAR DYNAMICS SIMULATIONS OF NaCl-TYPE SOLID SOLUTION CRYSTALS: THE FIRST APPLICATION OF MOLECULAR DYNAMICS TO SOLID SOLUTIONS

TADASHI AKAMATSU, MASAOMI FUKUHAMA and HIDEMOTO NUKUI

*Faculty of Education, Kochi University, Kochi 780, Japan*

KATSUYUKI KAWAMURA

*Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan*

*(Received January 1993, accepted May 1993)*

KEY WORDS: NaCl-KCl, MgO-CaO, excess enthalpy, excess volume, mixing property

Downloaded At: 19:32 14 January 2011

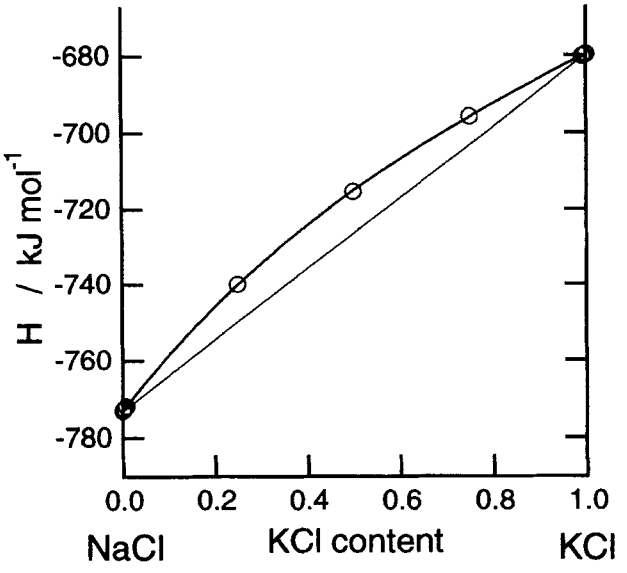
## INTRODUCTION

Solid solution crystals appear widely in the fields of earth sciences and inorganic material sciences. The physical properties of solid solutions may vary continuously with chemical composition. Sometimes, linear relationships of the properties with composition are assumed. However, this approximation is not always applicable (*e.g.*, [1], [2], [3]). In order to elucidate the properties of solid solutions, studies on the relation between the macroscopic properties and the atomic configurations (microscopic property) in the crystal are desirable. One of the most effective approaches to the subject is molecular dynamics (MD). However, as far as the authors are aware there have been no molecular dynamics studies on solid solution crystals.

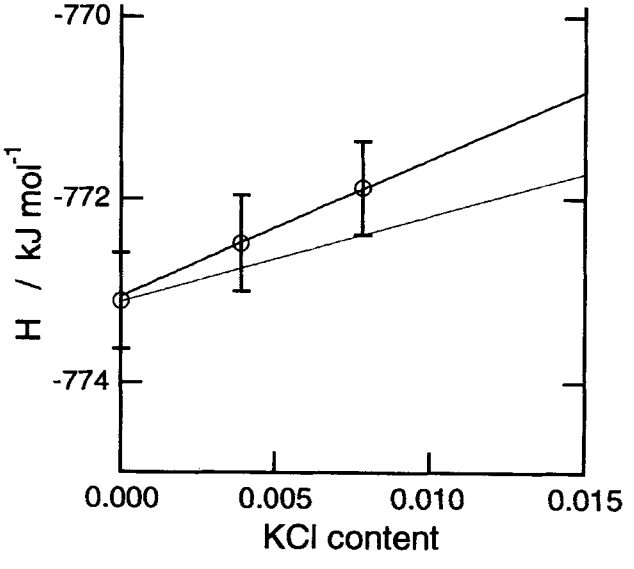
In this preliminary study, we have applied the MD technique to solid solution crystals for the first time, and investigated the variation of molar enthalpy and cell volume along with composition, assuming random mixing of cations.

## MOLECULAR DYNAMIC CALCULATIONS

We have adopted binary solid solutions $(Na_{1-x}, K_x)Cl$ and $(Mg_{1-x}, Ca_x)O$ with the NaCl-type structure because of the simplicity of the composition and structure. The total number of particles in the MD basic cell was 512 (= 256 cations + 256 anions).




(a)




(b)

Downloaded At: 19:32 14 January 2011

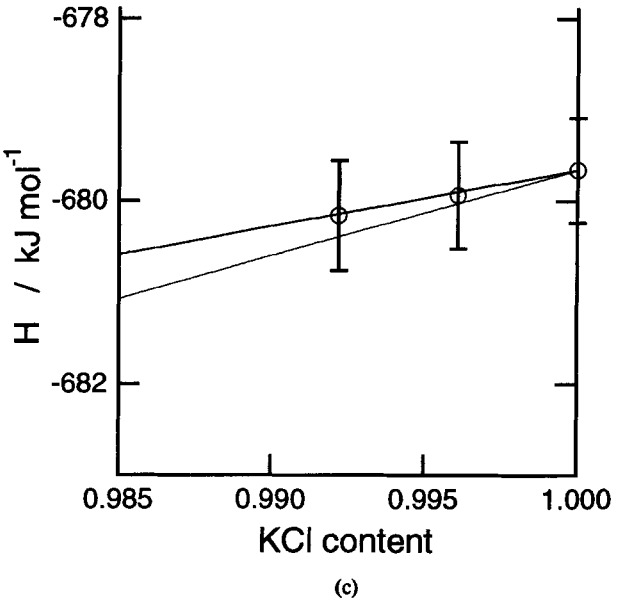



**Figure 1** Relation between calculated molar enthalpy and the composition for $(Na_{1-x}, K_x)Cl$ solid solution crystals under 0.1 MPa at 900 K. **a**: $x = 0 \sim 1$, **b**: $x = 0.000 \sim 0.015$, **c**: $x = 0.985 \sim 1.000$. The 'error bars' in **b** and **c** show the magnitude of fluctuation in the MD runs of 8000 steps.

The composition of the solid solutions was varied by substituting some cations of an end member crystal with those of the opposite end member. The compositions adopted are as follows;

*Dilute Solutions:*

$x = 0.0000$ (no substitution), 0.0039 (1/256 substitution), 0.0078 (2/256 substitution) for the compositions near the end member NaCl or MgO, and 1.0000 (no substitution), 0.9961 (1/256 substitution), 0.9922 (2/256 substitution) for the compositions near the opposite end member KCl or CaO. In the case of 2/256 substitution, two substituted cations were placed so as to be mostly isolated each other.

*Intermediate Compositions:*

$x = 0.2500$ (64/256 substitution), 0.5000 (128/256 substitution), 0.7500 (64/256 substitution). It is noted that there are so many cases of configurations of smaller ($Na^+$ or $Mg^{2+}$) and larger ($K^+$ or $Ca^{2+}$) cations in the crystals. In this preliminary study, random mixing of smaller and larger cations was assumed, and such structures were generated by using random number.

Calculations were carried out with the full ionic pair potentials [4] and MD program MXDORTO [5] under constant pressure and temperature [$P = 0.1$ MPa, $T = 900$ K for (Na, K)Cl and 2500 K for (Mg, Ca)O]. The step time was 2 fs throughout the calculations. The initial structures were first equilibrated for 5000 steps, and then the data were collected for the subsequent 8000 steps.

Downloaded At: 19:32 14 January 2011

## RESULTS AND DISCUSSION

The relation between calculated molar enthalpy and composition for (Na, K)Cl under 0.1 MPa at 900 K is shown as an example in Figure 1.

(1) Enthalpy varies smoothly along with composition.
(2) The data points of solid solution crystals ($0 < x < 1$) are above the line passing through the points of end members ($x = 0$ and $x = 1$), indicating the positive excess enthalpy of mixing. This is qualitatively consistent with the experimental results (see *e.g.*, [6]).

The relations like (1) and (2) are also applicapble to the cell volume of (Na, K)Cl, enthalpy and volume of (Mg, Ca)O.

The positive excess enthalpy suggests that some cationic clustering occurs in the real crystals of (Na, K)Cl and (Mg, Ca)O, rather than random mixing of cations. The calculations on the crystals with cationic clustering are in progress.

### *References*

[1] S. Akimoto, Y. Matsui, and Y. Syono, "High-pressure crystal chemistry of orthosilicates and the formation of the mantle transition zone", in *The Physics and Chemisry of Minerals and Rocks*, R.J.G. Strens, ed, John Wiley and Sons, New York, 1976, pp. 327–363.
[2] T.S. Duffy and M.T. Vaughan, "Elasticity of enstatite and its relationship to crystal structure", *J. Geophys. Res.*, **93**, 383–391 (1988).
[3] B. O'Neill, J.R. Smyth, and M.T. Vaughan, "Elasticity of a grossular-pyrope-almandine garnet", *J. Geophys. Res.*, **94**, 17819–17824 (1989).
[4] K. Kawamura, "Interatomic potential models for molecular dynamics simulatins of multicomponent oxides", in *Molecular Dynamics Simulations*, F. Yonezawa, ed, Springer Series in Solid-State Sciences 103, Springer-Verlag, Berlin, Heidelberg, 1992, pp. 88–97.
[5] K. Kawamura, "MXDORTO", *JCPE Newsletter*, **4**, No. 3, 48 (1992).
[6] P.K. Davies and A. Navrotsky, "Quantitative correlations of deviations from ideality in binary and pseudobinary solid solutions", *J. Solid State Chem.*, **46**, 1–22 (1983).

Downloaded At: 19:32 14 January 2011