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Journal of Solid State Chemistry 176 (2003) 203–205
JOURNAL OF SOLID STATE CHEMISTRY
http://elsevier.com/locate/jssc

Investigation of energy and structural changes of Li_n ($n = 3, 4$) microclusters based on temperature

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Received 16 January 2003; received in revised form 26 June 2003; accepted 10 July 2003

Abstract

The energy and structural changes of lithium microclusters based on temperature has been investigated by using Molecular-Dynamic simulation Method. Two and three-body interacted semi-empiric potential energy formula that characterized the interaction has been used. It has been calculated that the dissociation of atoms from cluster has started after 1300 K for Li_3 and 1350 K for Li_4, respectively. Dissociations at the fixed temperatures are very close to the expected values of the lithium metal. Additionally, it has been observed that Li_4 microclusters above 1000 K and Li_3 clusters above 700 K temperatures have steady structures in two different energy values.

Keywords: Dissociation; Interaction; Lithium cluster

1. Introduction

The structures of atomic solids, their phase transformations, their surface and defect characteristics, the nature of their microclusters, and their melting behavior all provide a rich source for experimental and theoretical studies. A question examined in many papers has been whether a potential energy function for the atomic interactions can rationalize the experimental findings [1]. The ground state geometrical structure of lithium clusters between four and eight atoms were interpreted using ab initio configuration interaction calculations [2]. The experimental values of the dissociation energies of small Li_n^+ had been compared with the dissociation energies of CI ab initio and Hückel type [3]. Recently, the investigation of the properties and dynamics of small clusters is a rapidly expanding field [4–9]. The structural properties of Li_n microclusters with the number of atoms $n = 3-10$ have been investigated by using molecular dynamics (MD) method [8,9].

In this work, the dissociation mechanism of Li_3 and Li_4 microclusters has been investigated for the first time by using a MD method. In the MD method, the molecules are allowed to move naturally under the influence of their own intermolecular forces. The positions and velocities of each molecule are followed in time by solving Newton's equation of motion (force equals mass times acceleration, a second order differential equation) using standard numerical methods. For the systems of non-spherical molecules the classical equation of rotational motion, involving the angular velocity and torque on a molecule, must also be solved. The macroscopic properties are calculated by averaging the appropriate functions of molecular positions and velocities over time [7]. Molecular dynamics simulations are limited largely by the speed and storage constraints of available computers.

In this study, we have investigated the steady structures and energies of Li_3 and Li_4 microclusters in different temperatures by the MD simulation methodology. We have also identified the temperatures of dissociation in the clusters. Li_3 and Li_4 clusters have been selected since they are most steady clusters in terms of energy. In this process, semi-experimental many-body potential energy function is used [10]. Considering $U_{ij}(r_{ij})$ two-body potential energy function and $W_{ijk}(r_{ij}, r_{ik}, r_{jk})$ three-body potential energy function,

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0022-4596/$ - see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/S0022-4596(03)00392-X

the total interaction potential energy is

$$\Phi = B_2 \sum_{i<j}^{N} U_{ij}(r_{ij}) + B_3 \sum_{i<j<k}^{N} W_{ijk}(r_{ij}, r_{ik}, r_{jk}). \quad (1)$$

In this formula, B_2 and B_3 are two-body and three-body interaction parameters respectively. Interaction potential between i and j atoms is

$$U_{ij}(r_{ij}) = A\left[\left(\frac{r_o}{r_{ij}}\right)^{2n} e^{-2\alpha(r_{ij}/r_o)^2} - \left(\frac{r_o}{r_{ij}}\right)^{n} e^{-\alpha(r_{ij}/r_o)^2}\right]. \quad (2)$$

Three-body interaction potential energy function is;

$$W_{ijk} = U_{ij}f_{ijk} + U_{ik}f_{ikj} + U_{jk}f_{jki}. \quad (3)$$

In this formula

$$f_{ijk} = e^{-(r_{ik}^2 + r_{jk}^2)}, \quad f_{ijk} = e^{-(r_{ij}^2 + r_{jk}^2)}, \quad f_{ijk} = e^{-(r_{ij}^2 + r_{ik}^2)}$$

are the Gaussian factors. The required parameters have been parameterized for lithium element [5].

Simulation process has been applied 25,000 MD steps where each step took 1.175×10^{-14} s. Temperature scaling has been applied for the first 15,000 steps and released for the last 10,000 steps. During the MD process temperature has been increased 100 K each time until 4000 K. Temperature increases are noted as 5 K for energy undulations. Mean influencing energy changes for Li_3 microcluster at 1300 K is shown in Fig. 1. In this simulation process, the triangular form, which is the energy wise steadiest configuration, has been used. Fig. 2 shows the mean kinetic energy change of Li_3 microcluster at 1300 K. Kinetic energy is becoming steady after 10,000 MD, in other words thermally balanced. The total energy is constant, kinetic and potential energy fluctuates; but these fluctuations must preserve the value of the total energy [6].

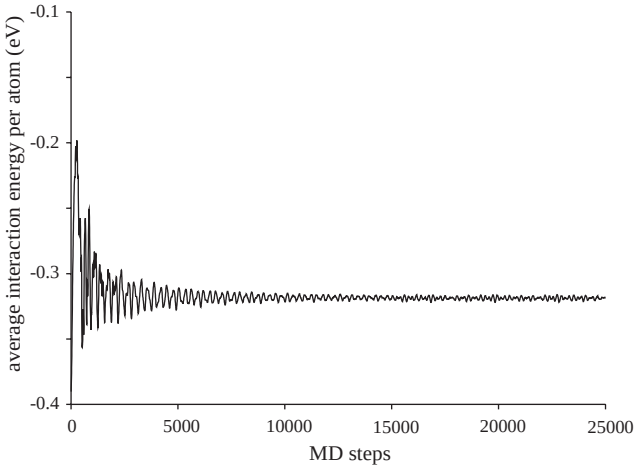

Fig. 1. Average interaction energy changes for Li_3 microcluster at 1300 K.

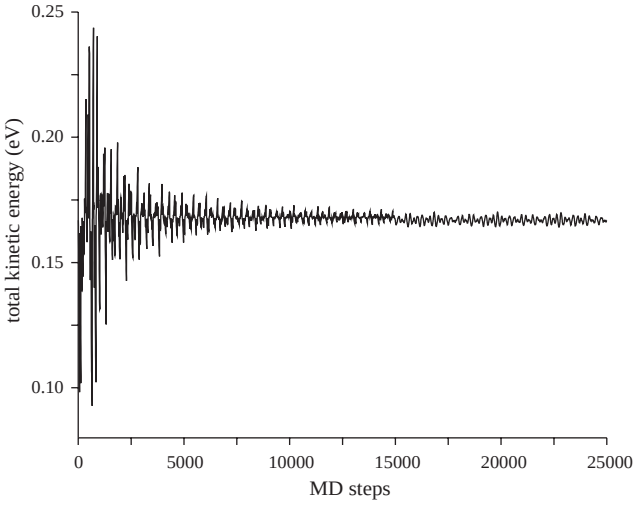

Fig. 2. Average kinetic energy changes for Li_3 microcluster at 1300 K.

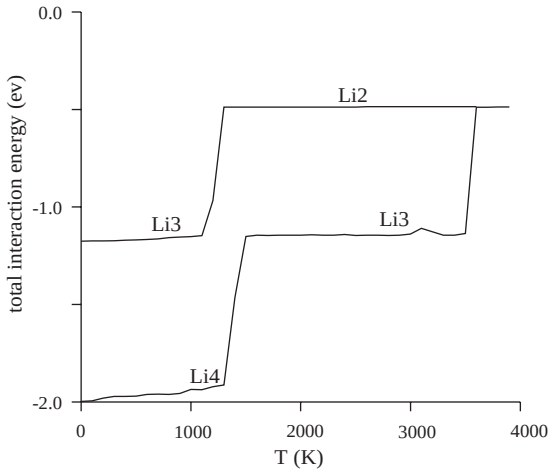

Fig 3. Total interaction energy changes of $Li_n (n = 3, 4)$ clusters in different temperatures.

2. Discussion and conclusion

Total interaction energy (TIE) of the microclusters versus temperature is given in Fig. 3. In the case of Li_3, the decrease in TIE within the temperature range of 1–1300 K is about 0.17 eV leading to an almost constant TIE. After 1300 K, the relative position of one of the atoms in the cluster changes considerably with respect to the others, and at 1350 K the distance of this atom to the other two atoms exceeds R_c. This is interpreted as the dissociation of this microcluster. The fluctuation in the interatomic separation of the remaining two atoms is relatively very small. This dissociation may be shown as $Li_3 \rightarrow Li_2 + Li$ ($T = 1300$ K) [4]. The early dissociation occurs in close temperatures. It has been observed that dissociation start after 1400 K temperature in Li_4 microclusters. TIE varies again smoothly between 1 and 900 K, the total decrease in this temperature range

being 0.04 eV. TIE within the temperature range of 900–1400 K is about 0.49 eV. TIE varies very small between 1500 and 3500 K, the total decrease in this temperature range being 0.05 eV. The second atom has been dissociated around 3500 K of temperature for Li_4 cluster as shown in Fig. 3. This can be explained as because of the tight connection of the Li_4 atoms [4]. The TIE versus temperature characteristics of product Li_3 between 1500 and 3500 K shows the same behavior of Li_3 microcluster. Additionally, the Li_4 cluster becomes steady in two different energy values after 1000 K. Similarly, the Li_3 microcluster also creates steady structure in two different energy values after 700 K. These structures are equilateral triangle and isosceles triangle. Li_3 microcluster, which has the equilateral triangle geometry, is steadier in terms of energy when compared with isosceles triangle. The equilateral triangle geometry is the unique geometry, which can occur in FCC net among the three neighbor atoms, although, the isosceles triangle geometry is the geometry that can occur in BCC net among the three neighbors. There is a crystallographic phase transition from FCC to BCC structure in Li_3 microclusters within this working temperature interval. Total interaction energy versus characteristics of product Li_3 at 1330 K shows the same behavior of Li_3 microclusters. Li_4, even it is seen as steady in different values in terms of energy after the first dissociation in its cluster, configurationally behaves same as the Li_3 microcluster.

The last product dimers (Li_2) of the both Li_3 and Li_4 microclusters have nearly the same interaction energy values. It has been seen that the interaction energy of the formed geometry ($Li_4 \rightarrow Li_3 + Li$) of the Li_4 microcluster after the first dissociation is close to the interaction energy of the Li_3 microcluster. This is the expected result. But, it shows that the Li_4 cluster has more tight connection since these values occur at different temperatures. In other words, more energy is required for the dissociations in large clusters. The fusing points of the microclusters are lower than the bulk materials [11]. The melting temperature is strongly dependent on the size, even the addition or removal of one atom, instead of monotonic variations with size. Also the phenomena of dynamic coexistence strongly depends on the cluster size [12]. The melting temperature increases with increasing cluster size [13]. Dissociation energies of the lowest dissociation channel for Kn_n^+, Na_n^+ and Li_n^+ exhibits the sawtooth behavior as illustrated in Ref. [14]. In our MD simulation calculations, the amplitude of dissociation energies is as follows:

$$Li_3 \rightarrow Li_2 + Li \quad (0.6\,eV) \quad \text{and} \quad Li_4 \rightarrow Li_3 + L_2 \quad (0.68\,eV)$$
$$\downarrow$$
$$Li_3 \rightarrow Li_2 + Li \quad (0.67\,eV)$$

These values are near to the experimental values. Also the phases in Li single crystals change in terms of temperature [3]. In this work, Li_3 microcluster has isosceles triangle geometry within the temperature range of 700–850 K. This result is in agreement with Ref. [3].

We conclude by pointing out that this type of study can be valuably used in studies on dissociation mechanisms of the lithium and other microclusters.

References

[1] H. Cox, R.L. Johnston, J.N. Murrell, J. Solid State Chem. 145 (1999) 517–540.
[2] J. Blanc, V. Bonačić-Koutecký, M. Broyer, J. Chevaleyre, Ph. Dugourd, J. Kouteckỳ, C. Scheuch, J.P. Wolf, L. Wöste, J. Chem. Phys. 96 (3) (1992) 1793–1809.
[3] W. Pichl, M. Krystian, Mater. Sci. Eng. A 273–275 (1999) 208–212.
[4] Ş. Katircioğlu, Ş. Erkoç, Mol. Simul. 4 (1989) 247–250.
[5] N. Kolsuz, Ş. Erkoç, M. Çivi, Mod. Phys. Lett. A 10 (2) (1995) 125–131.
[6] J.M. Haile, Molecular Dynamics Simulation: Elementary Methods, Wiley Professional Paperback Series, Wiley, New York, 1997, pp. 489, ISBN 0-471-18439-X.
[7] K.E. Gubbins, N. Quirke, Molecular Simulation and Industrial Applications: Methods, Examples and Prospects, Gordon and Breach Science, Amsterdam BV, 1996, pp. 537.
[8] I. Kara, N. Kolsuz, J. Phys. Chem. Solids 63 (2002) 861–867.
[9] I. Kara, N. Kolsuz, J. Phys. Chem. Solids 61 (2000) 689–694.
[10] Ş. Erkoç, Phys. Stat. Sol. (B) 152 (1989) 447.
[11] M.H. Güven, M. Eryürek, Phys. Stat. Sol. (b) 213 (1999) 283–295.
[12] Y. Joo Lee, R.M. Nieminen, E.-K. Lee, S. Kim, Comput. Phys. Commun. 142 (2001) 201–205.
[13] M. Ma, W. Lu, J. Huang, J. Solid State Chem. 165 (2002) 165–289.
[14] C. Bréchignac, H. Busch, Ph. Cahuzac, J. Leygnier, J. Chem. Phys. 101 (8) (1994) 6992–7002.