

3-2002

Molecular Dynamics Simulations of Phase Transition in AgNO₃

Jianjun Liu

University of Nebraska-Lincoln, jliu@unlserve.unl.edu

Chun-Gang Duan

University of Nebraska-Lincoln, wxbdcg@gmail.com

M. M. Ossowski

University of Nebraska-Lincoln

Wai-Ning Mei

University of Nebraska at Omaha, physmei@unomaha.edu

Robert W. Smith

University of Nebraska at Omaha, robertsmith@unomaha.edu

See next page for additional authors

Follow this and additional works at: <https://digitalcommons.unomaha.edu/chemfacpub>

 Part of the [Chemistry Commons](#), and the [Physics Commons](#)

Recommended Citation

Liu, Jianjun; Duan, Chun-Gang; Ossowski, M. M.; Mei, Wai-Ning; Smith, Robert W.; and Hardy, J. R., "Molecular Dynamics Simulations of Phase Transition in AgNO₃" (2002). *Chemistry Faculty Publications*. 14.

<https://digitalcommons.unomaha.edu/chemfacpub/14>

This Article is brought to you for free and open access by the Department of Chemistry at DigitalCommons@UNO. It has been accepted for inclusion in Chemistry Faculty Publications by an authorized administrator of DigitalCommons@UNO. For more information, please contact unodigitalcommons@unomaha.edu.



Authors

Jianjun Liu, Chun-Gang Duan, M. M. Ossowski, Wai-Ning Mei, Robert W. Smith, and J. R. Hardy

Molecular dynamics simulations of phase transition in AgNO_3

Jianjun Liu^{a*}, Chun-gang Duan^b, M.M. Ossowski^a, W.N. Mei^b, R.W. Smith^c, J.R. Hardy^a

Department of Physics and Center for Electro-Optics, University of Nebraska, Lincoln, NE 68588-0111, USA
Department of Physics, University of Nebraska, Omaha, NE 68182-0266, USA
Department of Chemistry, University of Nebraska, Omaha, NE 68182-0109, USA

* Corresponding author. Tel.: +1-402-472-4522; fax: +1-402-472-2879.

E-mail address: jliu@unlserve.unl.edu (J. Liu).

Abstract:

Structural phase transition in AgNO_3 at high temperature is simulated by molecular dynamics. The simulations are based on the potentials calculated from the Gordon-Kim modified electron-gas formalism extended to molecular ionic crystals. AgNO_3 transforms into rhombohedral structure at high temperature and the phase transition is associated with the rotations of the NO_3 ions and displacements of the NO_3 and Ag ions.

Keywords: A. Inorganic compounds; C. Abinitio calculations; D. Phase transitions

Introduction

AgNO_3 has a crystal structure unique among metallic nitrates. At room temperature, AgNO_3 has an ordered orthorhombic structure [1] with space group Pbca which resembles neither the calcite nor the aragonite structure. At about 433 K it transforms into a rhombohedral form that is thought to be similar to the disordered high temperature phase of NaNO_3 [2]. This high temperature phase transition in AgNO_3 has been studied by Raman scattering [3], IR spectra [4], and thermal property [5], but the microscopic nature of the transformation has not yet been investigated. Specifically, there exists no theoretical study at the microscopic level of the phase transition in AgNO_3 .

In this paper, we describe molecular dynamics (MD) simulation of the high temperature phase transition in AgNO_3 using parameter-free potentials developed for ionic molecular solids. We have investigated the phase transition mechanism in KNO_3 using this method, but we did not get the correct high temperature phase of KNO_3 [6]. In the present work, we successfully simulated the phase transition in AgNO_3 and found that the high temperature phase is, indeed, similar to the disordered phase of NaNO_3 .

2. Interaction potentials and static relaxation

The interaction potentials were calculated using the method in Ref. [6], which is based on the Gordon-Kim modified electron-gas formalism [7] extended to molecular ionic crystals. We only outline the procedures related to AgNO_3 .

Our method starts from performing abinitio quantum chemistry calculations for the whole NO_3 molecular ion. The calculations produce a realistic electron charge-density distribution that correctly takes into account the covalency within the NO_3 ion and, therefore, leads to a correct description of the intra-molecular interactions. We employ a harmonic expansion of the total energy of the NO_3 ion to describe the interactions within the NO_3 ion with the expansion coefficients also determined by the ab initio quantum chemistry calculations. We then decomposed the electron charge-density distribution of the whole NO_3 ion into approximate charge densities for the individual N and O ions in the spirit of a Mulliken population analysis [8]. Using these charge densities and the free ion charge density for the Ag ion [9], we computed the short-range pair potentials between these ions according to Gordon-Kim electron-gas model [7]. The long-range Coulomb interactions were calculated using the fractional Mulliken charges of N and O atoms of: +0.9917 and -0.6639, respectively, together with an ionic charge of +1 for the Ag ion.

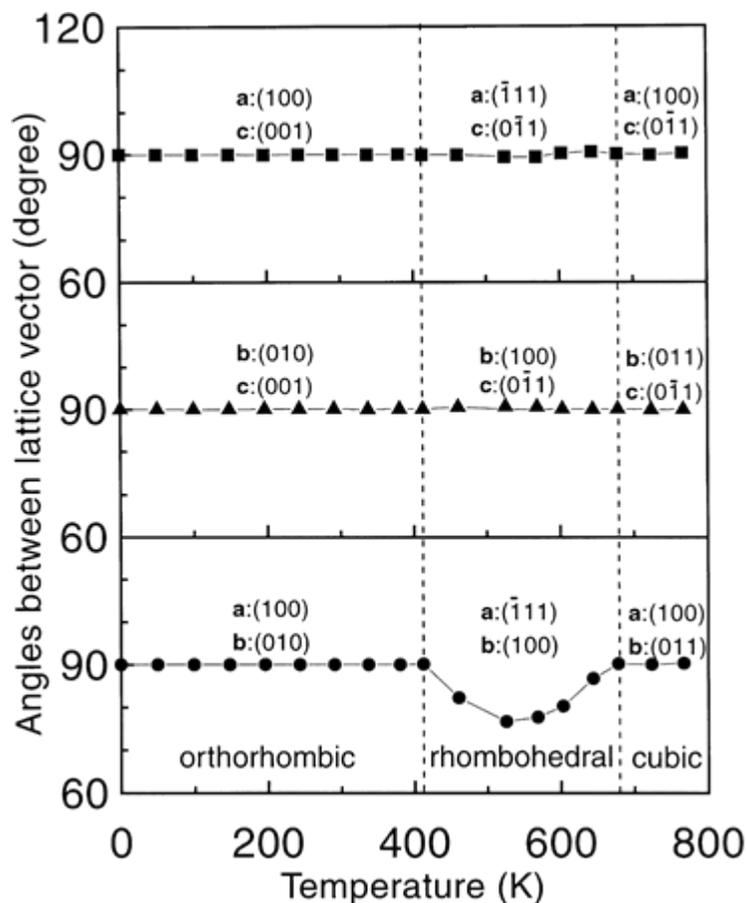


Fig. 1. Angles between lattice vectors a, b, and c as a function of temperature for the MD heating of AgNO_3 .

The quantum chemistry calculations were performed using the GAUSSIAN94 commercial package [10]. We used the standard 6-31G** basis set for N and O atoms. We performed a static relaxation for the room temperature structure of AgNO_3 using the foregoing potentials with and without the space group $Pbca$ symmetry constraints. This determines the positions of the atoms and lattice vectors that correspond to the minimum of the theoretical potential-energy surface. Our relaxation was performed for an infinite lattice by applying periodic boundary conditions, and followed a Newton-Raphson algorithm. The standard technique of the Ewald sum was used to calculate the lattice energy and forces, etc.

In both cases, we found the same minimum energy structure that was in good agreement with experiment. The parameters for the relaxed structures of AgNO_3 along with the experimental values [1] are given in Table 1. The overall agreement of our relaxed structure with the experimental structure indicates that our potentials are reasonable for the AgNO_3 crystal.

3. Molecular dynamics simulation of the phase transition

Our molecular dynamics simulation follows a constant pressure ($P = 0$) algorithm [11]. Periodic boundary conditions are introduced to simulate an infinite lattice. We used a super-cell with 360 ions formed by tripling the orthorhombic unit cell in the a and c directions. Starting from the theoretical relaxed structure obtained above, we remove any residual kinetic energy by 'quenching' the supercell to 0 K and then, heated the supercell in 30 K stages. At each stage the average of the ion positions, energy, etc., were taken over 10 ps using a 1 fs molecular dynamics time step.

Fig. 1 shows the angles between lattice vectors a, b, and c as a function of temperature for the MD heating of AgNO_3 . One can see that the angles between b, c and c, a hardly change in the whole temperature range investigated. However, the evolution of the angle between a and b indicates that two phase transitions take place at 412 and 678 K, respectively. In the temperature range 0-412 K the system is stable in the orthorhombic structure, while the abrupt decrease of the angle between a and b at 460 K shows that the system transforms into a new phase. This phase transition corresponds to the phase transition in the real crystal observed at 433 K. The angle between a and b decreases with increasing temperature until its minimum at 525 K, then increases and returns to 90° at 678 K. At this last temperature, the system transforms into another phase which is not observed in experiment because the real crystal melts at 493 K.

Table 1

The structural parameters for the relaxed structure of AgNO₃ and experimental values at room temperature [1]

	Ag	N	O(1)	O(2)	O(3)
a	6.9441Åo (6.997Åo)	7.6271Åo (7.325Åo)			11.1264Åo (10.118Åo)
x	0.1427 (0.1352)	0.3816 (0.3472)	0.3975 (0.3938)	0.5028 (0.4960)	0.2445 (0.2537)
y	-0.0080 (-0.0112)	0.3636 (0.3627)	0.3088 (0.3239)	0.3261 (0.2941)	0.4560 (0.4711)
z	0.1435 (0.1308)	0.4177 (0.4112)	0.5204 (0.5244)	0.3419 (0.3240)	0.3902 (0.3678)

In order to know the structures of high temperature phases, we present the radical distribution functions of AgNO₃ at three different temperatures in Fig. 2. It can be seen that at low temperature the system is completely ordered so that the Ag-N, Ag-Ag, N-N and Ag-O distribution functions contain many very narrow, sharp peaks. Above 460 K, the Ag-N, Ag-Ag and N-N distribution functions clearly show that the Ag atoms and N atoms form a rhombohedral structure. The orientations of the NO₃ ions become disordered because the sharp peaks in Ag-O distribution function at low temperature change into several broad peaks at 460 K. At higher temperature, the system transforms into a NaCl structure as shown by the Ag-N, Ag-Ag and N-N distribution functions at 678 K.

The projections of the ion positions along the a, b, and c directions in the average structure at several different temperatures are illustrated in Figs. 3-5. In the plots, the lines connect the nitrogen atoms with their nearest oxygen atoms. The ovals centered about the atoms represent 'thermal ellipsoids' which indicate the root mean square (r.m.s.) deviation of atoms from their average positions. The isolated ellipses represent the Ag ions. From the cross sections of the average structures, we can obtain the relationship between different phases.

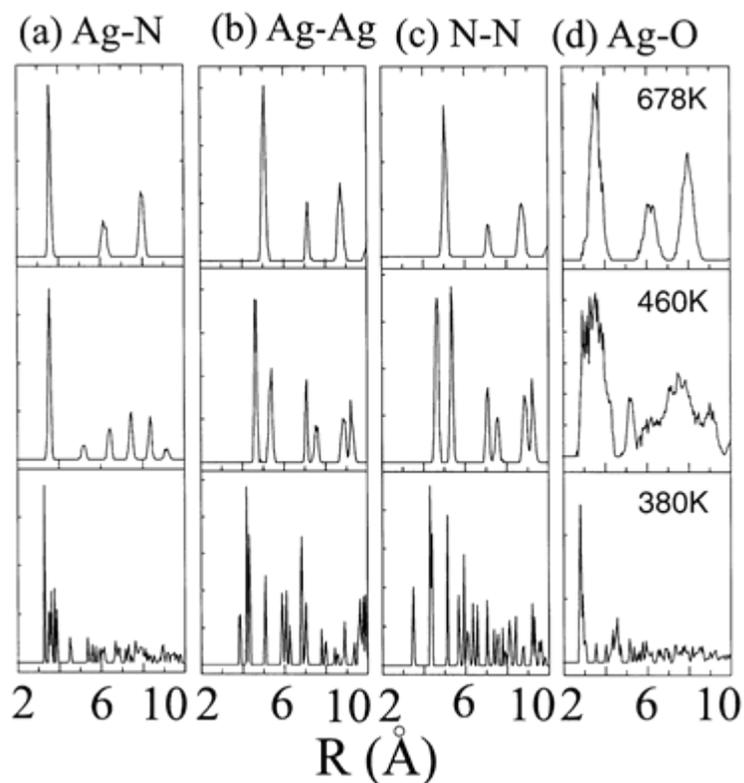


Fig. 2. Radical distribution functions of AgNO₃ at three different temperatures.

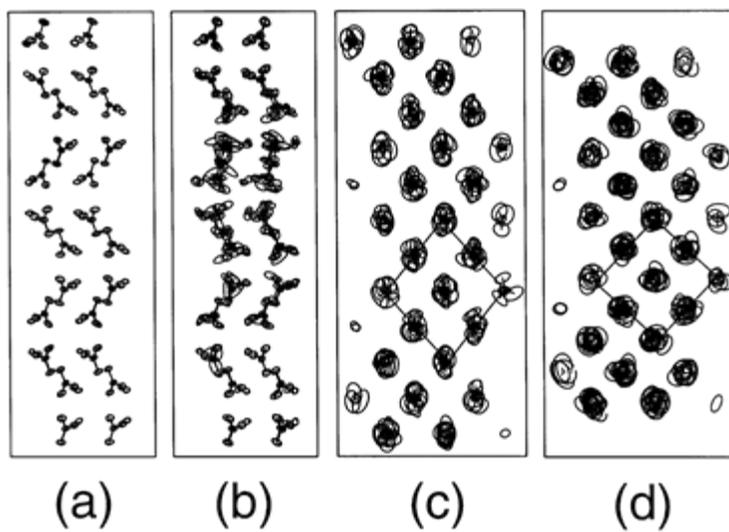


Fig. 3. Projections of average structure along a direction at (a) 380 K, (b) 412 K, (c) 460 K, (d) 678 K.

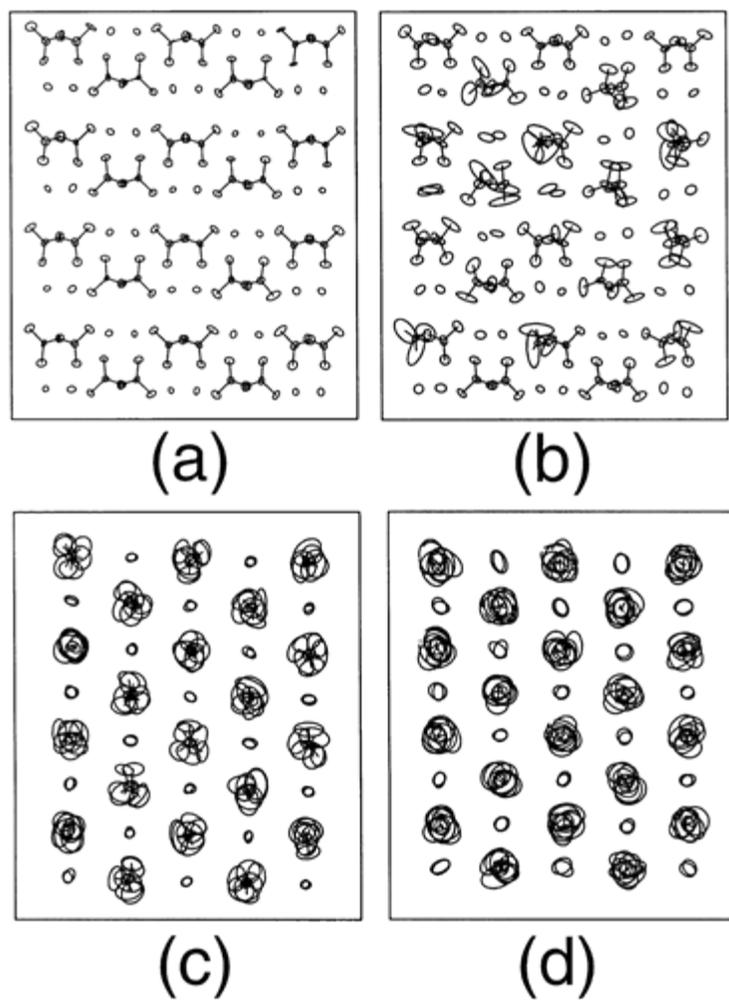


Fig. 4. Projections of average structure along b direction at (a) 380 K, (b) 412 K, (c) 460 K, (d) 678 K.

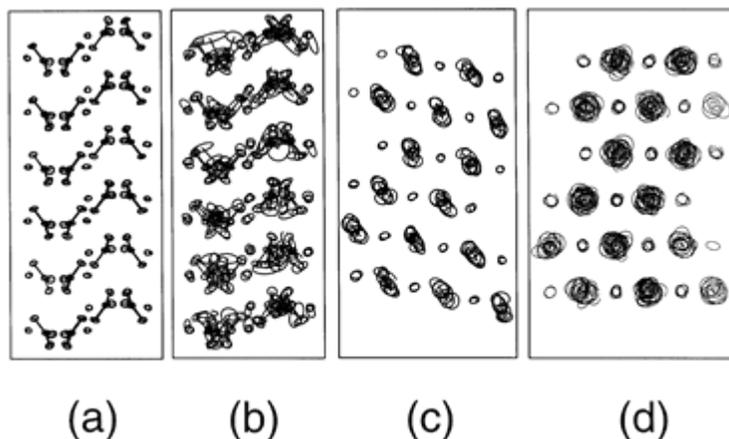


Fig. 5. Projections of average structure along c direction at (a) 380 K, (b) 412 K, (c) 460 K, (d) 678 K.

At low temperature orthorhombic structure (Figs. 3(a)-5(a)), the orientations of NO_3 ions are completely ordered. Near the first transition temperature the NO_3 ions become partially orientationally disordered. Some NO_3 ions begin to hop 120° about their triad axes to their equivalent positions (Figs. 3(b)-Fig.5(b)), but the system still remains in the orthorhombic structure. With increasing temperature, the Ag ions and NO_3 ions undergo displacements to form a rhombohedral structure at the first transition. The orthorhombic a , b and c axes transform into rhombohedral $[111]$, $[100]$ and $[011]$ directions (Figs. 3(c)-5(c)), respectively. The angle between a and b decreases from 90 to 82.26° at 460 K. One can see from Figs. 3(c)-5(c) that the thermal motions of NO_3 ions in rhombohedral structure are anisotropic. The normals of all the NO_3 ions seem to be along one direction and the thermal motion of the in-plane rotations is much larger than that of the out-of-plane rotations. This means that the rhombohedral phase of AgNO_3 has the same structure as that of disordered phase NaNO_3 . For comparison we present the projections of the ion positions along $[111]$, $[100]$ and $[011]$ directions in the average structure of disordered phase NaNO_3 in Fig. 6. The average structure of disordered phase NaNO_3 was obtained by MD using the same method. Figs. 3(c)-5(c) are similar to Fig. 6(a)-(c) except that the out-of-plane motion of AgNO_3 is larger than that of NaNO_3 (c.f. Figs. 5(c) and 6(c)).

At higher temperature, the rhombohedral phase of AgNO_3 transforms into a NaCl structure simply by contracting along its 3-fold symmetric axis. The rhombohedral $[111]$, $[100]$ and $[011]$ directions change into cubic $[100]$, $[011]$ and $[011]$ directions. Meanwhile, the thermal motions of NO_3 ions become isotropic so that the NO_3 ions have the spherical distribution. There is no experimental report of this phase because it is preempted by melting of the real crystal.

In our simulation, we do not consider the free surfaces so we cannot simulate the melting of the sample. However, we find that if AgNO_3 did not melt at the observed melting point, its most stable structure would be NaCl structure at high temperatures, just like RbNO_3 . RbNO_3 has three high temperature phases. It first transforms into a CsCl structure, then into rhombohedral phase, and finally into the NaCl structure [12]. Ag^+ ion exhibits unusual behavior in a number of compounds, particularly silver halides. Our method seems slightly simplistic in modeling of Ag^+ ion, but it works very well and is justified by the success of the simulation of the phase transition.

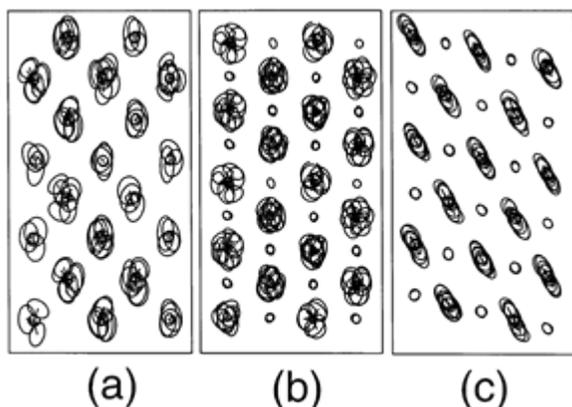


Fig. 6. Projections of average structure of disordered NaNO_3 along (a) $[111]$, (b) $[100]$, and (c) $[011]$ directions.

4. Conclusion

We have simulated the high temperature phase transition in AgNO_3 by using our parameter-free potentials. We find that the high temperature phase of AgNO_3 has a rhombohedral structure similar to the disordered high temperature phase of NaNO_3 . Moreover, AgNO_3 would transform into NaCl structure if it did not melt at the melting point.

Acknowledgements

This work was supported by the US Army Research Office under Grants Nos. DAAG 55-97-1-0106 and DAAG 55-98-1-0273. The computer facility was supported by Nebraska-EPSCoR-NSF Grant EPS-9720643.

References

- [1] P.E. Lindley, P. Woodward, *J. Chem. Soc. A* (1966) 123.
- [2] W.L. Fraser, S.W. Kennedy, G.F. Taylor, *Acta Crystallog.* B33 (1977) 311.
- [3] K. Balasubrahmanyam, G.J. Janz, *J. Chem. Phys.* 57 (1972)4084.
- [4] F. El-Kabbany, Y. Badr, M. Tosson, S. Taha, S. Mahrous, *Phys. Stat. Sol. A* 94 (1986) 35.
- [5] F. El-Kabbany, Y. Badr, G. Said, S. Taha, S. Mahrous, *Phys.Stat. Sol. A* 95 (1986) 127.
- [6] H.M. Lu, J.R. Hardy, *Phys. Rev. B*44 (1991) 7215.
- [7] R.G. Gordon, Y.S. Kim, *J. Chem. Phys.* 56 (1972) 3122.
- [8] R.S. Mulliken, *J. Chem. Phys.* 23 (1955) 1833.
- [9] E. Clementi, C. Roetti, *At. Data Nucl. Data Tables* 14 (1974)177.
- [10] M.J. Frish, A. Frish, J.B. Foreman, GAUSSIAN94, Gaussian, Inc, Pittsburgh, 1994.
- [11] M. Parrinello, A. Rahman, *Phys. Rev. Lett.* 45 (1980) 1196.
- [12] M. Ahtee, A.W. Hewat, *Phys. Stat. Sol. A* 58 (1980) 525.