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2001 J. Phys.: Condens. Matter 13 3699

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# Molecular dynamics simulation of superhard phases in RuO<sub>2</sub>

W Sekkal<sup>1,2</sup> and A Zaoui<sup>1,3</sup>

<sup>1</sup> INFN and Dipartimento di Fisica Teorica, Strada Costiera 11-34014, Trieste, Italy

<sup>2</sup> Condensed Matter Group, International Centre for Theoretical Physics, Strada Costiera 11-34014, Trieste, Italy

E-mail: zaoui@ts.infn.it

Received 18 November 2000, in final form 12 March 2001

## Abstract

We present a molecular dynamics simulation study of structural and thermodynamic properties of RuO<sub>2</sub> in the fluorite and  $Pa\bar{3}$  structures. Based on a three-body potential, our results are in agreement with experimental measurements and other *ab initio* calculations. The transferability of this potential model is tested by simulating the superhard phases of RuO<sub>2</sub> for varying temperature. Various thermodynamic properties including the Debye temperature, heat capacity, linear thermal coefficient, Grüneisen parameter, and melting point are predicted. Calculations are extended to simulate also the liquid phase of RuO<sub>2</sub> in the  $Pa\bar{3}$  structure.

## 1. Introduction

The search of new superhard materials has been extensive during recent years [1] and has focused particularly on simple covalent compounds of carbon, boron, and nitrogen [2–4]. Recently, a class of candidate hard materials: transition-metal dioxides has been suggested. It has been reported that the bulk moduli of the orthorhombic phase of ZrO<sub>2</sub> and the CaCl<sub>3</sub>-type phase of MnO<sub>2</sub> are 332 and 328 GPa, respectively. Another high-pressure dioxide phase, stishovite, rutile-type SiO<sub>2</sub>, has a hardness which is more than 50% greater than that of alumina [5]. Furthermore, the bulk modulus of cubic RuO<sub>2</sub> in the  $Pa\bar{3}$  structure was found to be 399 GPa [6] which is close to that of diamond, 442 GPa [7], the hardest material known.

Under ambient conditions, ruthenium dioxide (RuO<sub>2</sub>) crystallizes in the rutile structure ( $P4_2/mnm$ ) [6–8] and exhibits metallic conductivity at room temperature [9]. It transforms to a CaCl<sub>2</sub>-type ( $Pnmm$ ) structure at about 6 GPa and then to a cubic fluorite-type structure  $Pa\bar{3}$  at above 12 GPa. It is a metastable compound in the cubic fluorite structure. Nevertheless, it should not be too difficult to grow such a material. Due to the remarkable development in thin-film fabrication and epitaxial growth, it may be possible to stabilize films of these materials by means of growth on solid substrates of cubic crystals. If this could be achieved,

<sup>3</sup> Author to whom any correspondence should be addressed.

one would have a technologically very interesting system: a cubic substrate with a very hard coating on top.

Previous experimental measurements were investigated using neutron diffraction data in order to refine the high-pressure  $Pa\bar{3}$ -type phase of  $RuO_2$  [10]. Other theoretical calculations have been done within the local-density approximation using soft-core *ab initio* pseudopotentials and a plane-wave basis [11] in order to calculate the electronic and structural properties of  $RuO_2$ . A comparative study was done by Tse *et al* [13] using first-principles pseudopotential and full-potential linearized augmented-plane-wave methods to calculate the elastic and the electronic properties of superhard phases of  $RuO_2$ . A hypothetical  $Pbca$  structure has been investigated and it is found to be unstable. To the best of our knowledge, molecular dynamics (MD) calculations of the elastic and especially the thermodynamic properties have not yet been studied. In order to describe the habit of  $RuO_2$  under high pressure and temperature, we present in this paper an atomistic simulation based on a three-body potential, and we mainly use the Tersoff model to predict the different thermodynamical properties such as the Debye temperature, the heat capacity, the linear thermal coefficient, the Grüneisen parameter, and the melting point. We also aim to describe the liquid behaviour of the  $Pa\bar{3}$  structure of  $RuO_2$ .

## 2. Method of calculation

Two structures are studied in this paper: the cubic fluorite ( $Fm\bar{3}m$ ) and the cubic modified fluorite ( $Pa\bar{3}$ ) structures. In cubic fluorite structure, Ru atoms occupy (0, 0, 0) positions, while O atoms occupy  $\pm(u, u, u)$  positions, where the internal parameter  $u = 0.25$ . In the modified fluorite structure, oxygen atoms deviate from their positions in fluorite,  $u = 0.344$ . These parameters were obtained in previous works [13] by the plane-wave method and FLAPW calculations. It is also found, from first-principles calculations [12], that  $RuO_2$  has a strong covalent bonding between the ruthenium d state and oxygen p state in combination with the favourable geometry of the orbitals in the fluorite structure. This clearly shows the interest of using the Tersoff potential [14] and explains our goal in this paper of simulating the behaviour of this material under varying pressure and temperature. This three-body potential has been developed for covalent semiconductors and it is based on the concept of bond order: the strength of a bond between two atoms is not constant, but depends on the local environment. This idea is similar to that of the 'glue model' for metals: using the coordination of an atom as the variable controlling the energy. This potential model gives accurate properties of both elemental (C, Si [14–17]) and compound systems such as SiC, GeC [18] and BN [19]. The form of the potential energy  $E$ , between two neighbouring atoms  $i$  and  $j$ , is taken to be [14]

$$E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij} \quad (1)$$

with

$$V_{ij} = f_C(r_{ij}) [a_{ij} f_R(r_{ij}) + b_{ij} f_A(r_{ij})] \quad (2)$$

where

$$f_R(r) = A \exp(-\lambda r)$$

$$f_A(r) = -B \exp(-\mu r)$$

$$f_C(r) = \begin{cases} 1 & r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin \left[ \frac{\pi}{2} \frac{(r - R)}{D} \right] & R - D < r < R + D \\ 0 & r > R + D. \end{cases}$$

$b_{ij}$  is the many-body order parameter describing how the bond-formation energy is affected by the local atomic arrangement due to the presence of other neighbouring atoms (the  $k$ -atoms). It is a many-body function of the positions of atoms  $i$ ,  $j$ , and  $k$ . It has the form

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-1/(2n)} \quad (3)$$

with

$$\begin{aligned} \zeta_{ij} &= \sum_{k (\neq i, j)} f_C(r_{ik}) g(\theta_{ijk}) \\ g(\theta) &= 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos \theta)^2} \\ a_{ij} &= 1 \\ \eta_{ij} &= \sum_{k (\neq i, j)} f_C(r_{ik}). \end{aligned}$$

$\zeta$  is called the effective coordination number and  $g(\theta)$  is a function of the angle between  $r_{ij}$  and  $r_{ik}$  that has been fitted to stabilize the tetrahedral structure. The Tersoff parameters are determined by fitting to a database consisting of cohesive properties including the bulk modulus and the bond length. The adjusted parameters obtained are given in table 1.

**Table 1.** Adjusted Tersoff parameters for RuO<sub>2</sub> in the fluorite structure.

$A$ (eV)	6865.8
$B$ (eV)	409.5
$\lambda$ (Å <sup>-1</sup> )	3.4390
$\mu$ (Å <sup>-1</sup> )	1.7322
$n$	0.78734
$h$	-0.59825
$\beta$	$1.100 \times 10^{-6}$
$c$	$1.0039 \times 10^5$
$d$	16.217
$R$ (Å)	2.5
$D$ (Å)	0.15

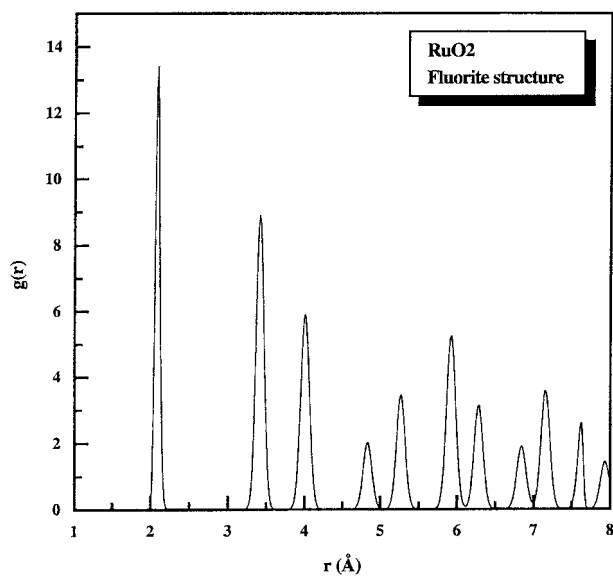
We ran MD calculations based on the Tersoff model: 20 000 steps, for a system of 216 atoms arranged in a cubic simulation cell with periodic boundary conditions. To integrate the equation of motion, a fifth-order Gear predictor–corrector algorithm was implemented with a 3.56 fs time step.

### 3. Numerical results

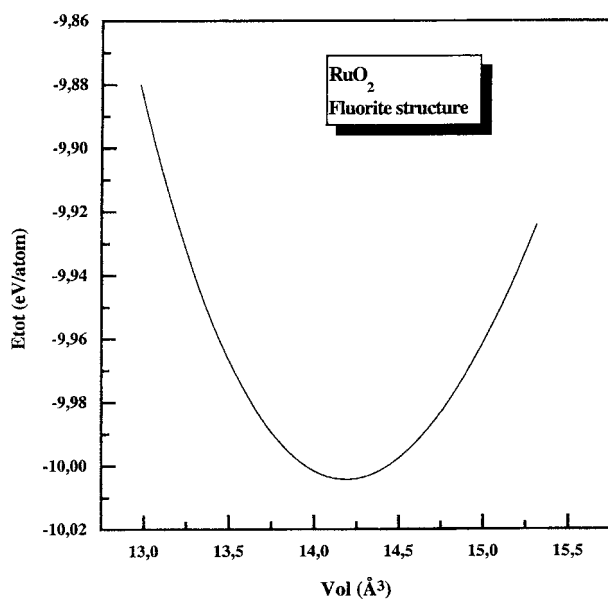
#### 3.1. Pressure effect

As a first step of our study, we want to test the validity of the potential model used and the adjusted parameters. In figure 1, we have plotted the pair distribution function  $g(r)$  for RuO<sub>2</sub> in the fluorite structure at  $T = 300$  K. The positions obtained for the successive peaks of  $g(r)$  are in excellent agreement with those expected in the crystal structure [13].

Figure 2 displays the cohesive energy versus volume. This curve is fitted to Murnaghan's equation of state [20] to obtain the equilibrium lattice parameter, the bulk modulus  $B$ , its derivative  $B'$ , and the cohesive energy.



**Figure 1.** The pair correlation function for the fluorite structure of  $\text{RuO}_2$ .



**Figure 2.** Cohesive energy as a function of volume for the fluorite structure of  $\text{RuO}_2$ .

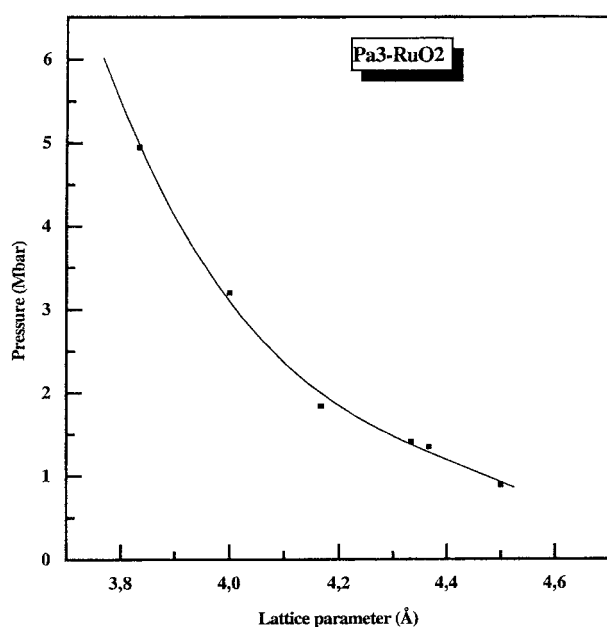
We have also calculated the elastic constants using the standard method of Mehl given in detail in reference [21]. The Voigt-averaged shear modulus  $G = (3C_{44} + C_{11} - C_{12})/5$  is also calculated. The results obtained are listed in table 2 and are compared to other first-principles calculations [13]. We note the small value of  $C_{44}$ , which reflects the very weak bond-angle forces in the potential. The calculated lattice parameters agree reasonably well with the GGA calculations (4.842 Å) rather than the LDA results (4.743 Å, with an accuracy of 2%). However, we found different values of the bulk modulus and our result agrees well with the GGA calculation of 3.36 Mbar, with an accuracy of about 3%. In view of these results, it would be interesting to test the transferability of this model under variation of pressure and temperature, keeping the same adjusted parameters.

**Table 2.** Equilibrium properties of RuO<sub>2</sub> in the fluorite and  $Pa\bar{3}$  structures.

	Fluorite structure		$Pa\bar{3}$ structure		
	Present work	Calculation	Present work	Other calculation	Experiment
Lattice constant (Å)	4.842	4.842; 4.743 <sup>a</sup>	5.00	4.884; 4.792 <sup>a</sup>	4.92 <sup>b</sup>
$B$ (Mbar)	3.28	3.36; 3.84; 3.51 <sup>a</sup>	3.92	3.80; 3.34; 3.46 <sup>a</sup>	3.99 <sup>b</sup>
$B'$	4.2	3.5; 4.1; 4.2 <sup>a</sup>	2.75	3.5; 3.9; 4.2 <sup>a</sup>	3.5 <sup>b</sup>
Cohesive energy (eV/atom)	-10.00427		-8.13614		
$C_{11}$ (Mbar)	4.106	4.35 <sup>a</sup>	3.919	4.50 <sup>a</sup>	
$C_{12}$ (Mbar)	2.866	2.27 <sup>a</sup>	1.209	1.89 <sup>a</sup>	
$C_{44}$ (Mbar)	0.620	1.52 <sup>a</sup>	1.36	1.47 <sup>a</sup>	
$G$ (Mbar)	0.62	1.33 <sup>a</sup>	1.358	1.40 <sup>a</sup>	

<sup>a</sup> Reference [13].<sup>b</sup> Reference [10].

First-principles plane-wave pseudopotential and FLAPW methods [13] showed that RuO<sub>2</sub> changes to a  $Pa\bar{3}$  structure at 0.89 and 0.97 Mbar respectively. Using MD simulations, we have examined the behaviour of  $Pa\bar{3}$ -RuO<sub>2</sub> under pressure ranging from 0.89 Mbar to 5 Mbar (see figure 3). In figure 4, we present the variation of the total energy versus volume for the  $Pa\bar{3}$  structure. The structural properties calculated using Murnaghan's equation of state are listed in table 2. The results obtained agree well with experiments [10] and other theoretical works [13]. We notice that the lattice parameter, 5.00 Å, is in good agreement with the experimental value of 4.92 Å, with an accuracy of 1.6%. The calculated value for the bulk modulus (3.92 Mbar) is found to be close to the experimental value of 3.99 Mbar [6], which is only 10% smaller than the one for diamond. Therefore,  $Pa\bar{3}$ -RuO<sub>2</sub> could be considered as a candidate for becoming a superhard material. A tentative of explanation of this high value was given by Lundin *et al* [12]. Their *ab initio* calculations show that the bonds are not ionic

**Figure 3.** Pressure versus lattice parameter for the  $Pa\bar{3}$  structure.

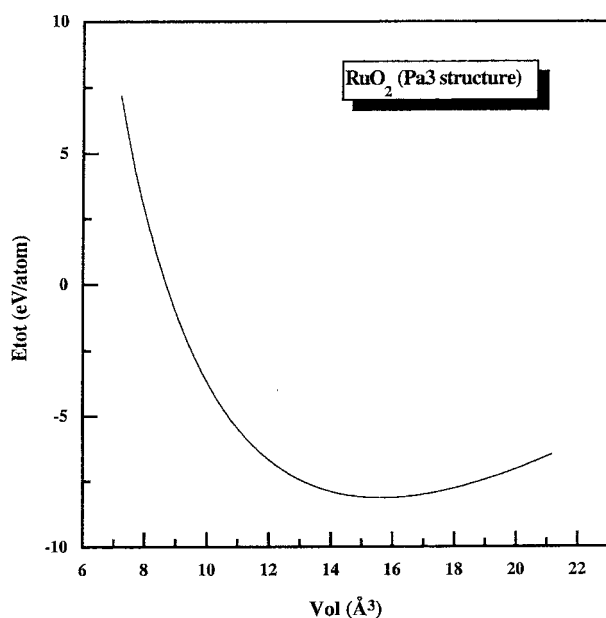


Figure 4. Cohesive energy as a function of volume for the  $Pa\bar{3}$ -RuO<sub>2</sub> structure.

since, compared to the neutral atom, oxygen in the solid has lost some of its electrons to the bond between Ru and O. Thus, a strong covalent bonding between ruthenium d states and oxygen p states is found in combination with the favourable geometry of the orbitals in the fluorite structure.

However, a high bulk modulus by itself does not directly imply high hardness. Hardness is related to a number of properties including linear compressibility and shear strength. A fundamental condition for high hardness is that a stress in a given direction should not be transmitted along a different direction, and therefore the shear moduli must also be high. We have, therefore, also calculated the shear modulus of the  $Pa\bar{3}$  structure. We notice that the value obtained agrees well with *ab initio* calculations [13]; however, it is found to be smaller than that of diamond.

The overall agreement confirms the validity of our adjusted potential parameters and the transferability of the Tersoff potential.

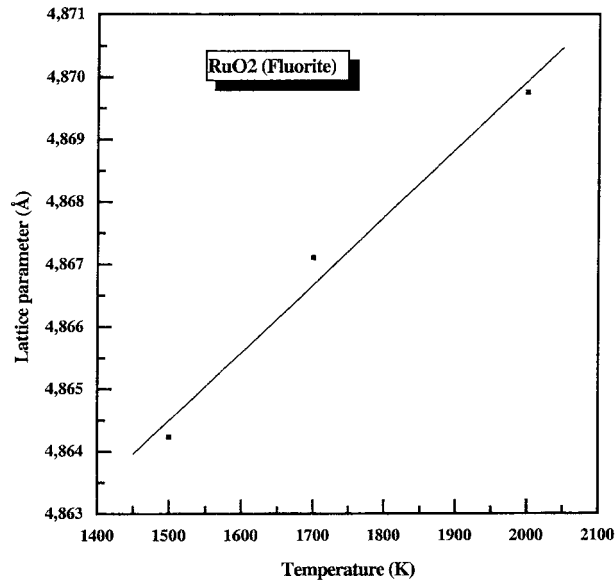
### 3.2. Temperature effect

Since the molecular dynamics method treats the motion of the atoms classically, it will correctly determine the thermodynamical properties above the Debye temperature ( $\theta_D$ ), where quantum effects can be neglected. Using the empirical relation taken from reference [22], we find that  $\theta_D = 1432$  K for RuO<sub>2</sub> in the fluorite structure and  $\theta_D = 1707$  K for RuO<sub>2</sub> in the  $Pa\bar{3}$  structure.

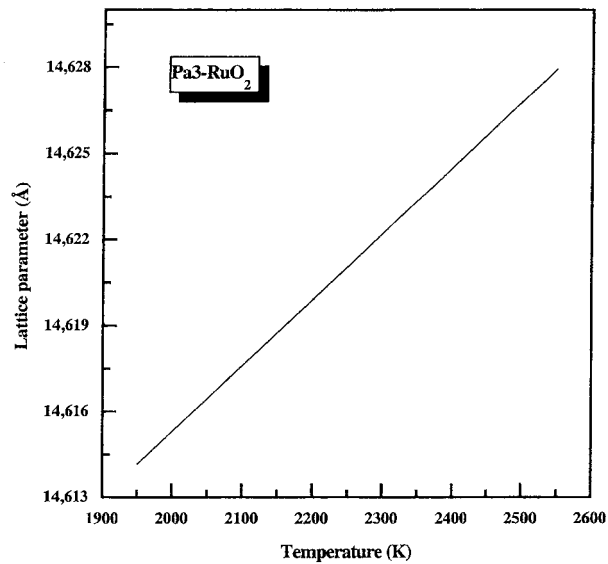
In MD simulation, the linear thermal expansion coefficient  $\alpha_l$  can be computed directly from the following relation:

$$\alpha_l = \left. \frac{1}{a} \frac{\partial a}{\partial T} \right|_p \quad (4)$$

where  $a$  is the lattice parameter. A molecular dynamics simulation is performed in an  $NVT$  ensemble, so at each temperature we do several runs for different volumes in order to find the corresponding zero-pressure lattice constant. In figures 5(a) and 5(b), we display the



(a)



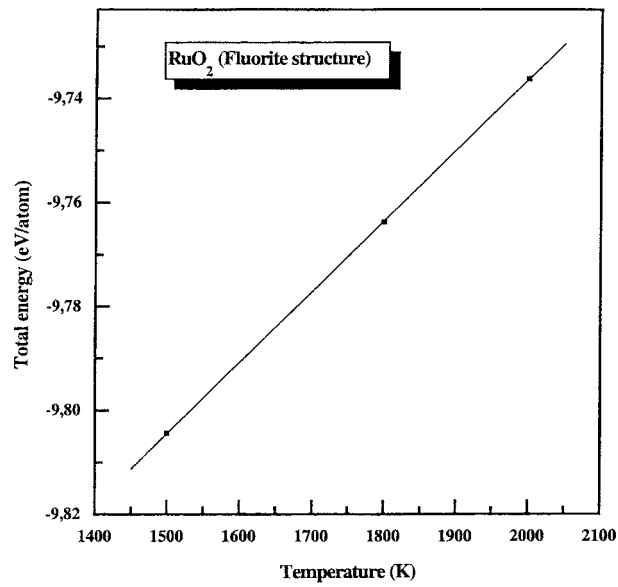
(b)

**Figure 5.** Lattice parameter versus temperature for the fluorite (a) and the  $Pa\bar{3}$  structure (b).

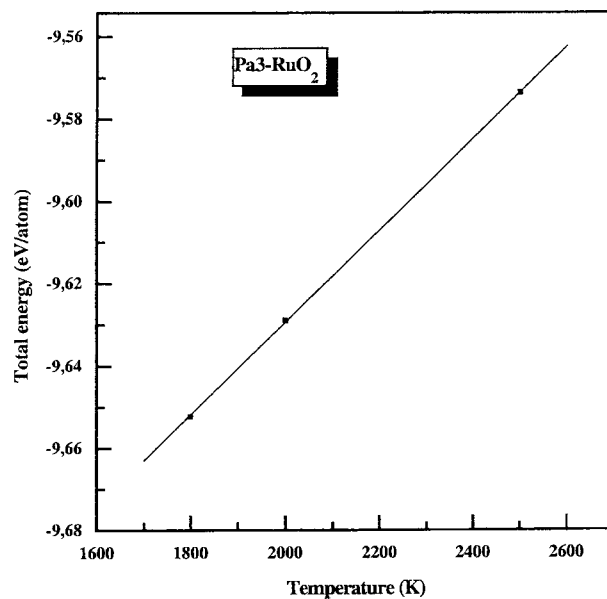
variation of the lattice parameter versus temperature for both structures. We found that  $\alpha_l = 6.83 \times 10^{-6} \text{ K}^{-1}$  for the fluorite structure. This value is smaller for the  $Pa\bar{3}$  structure and is equal to  $4.73 \times 10^{-6} \text{ K}^{-1}$ .

The total energy of the system as a function of temperature is plotted in figures 6(a) and 6(b). From the slope of the energy-versus-temperature curve, we estimate the specific heat of the system to be  $C_v = 1.58k_B$  for the fluorite structure and  $C_v = 1.29k_B$  for the  $Pa\bar{3}$  phase at high temperatures. From these results, we have also predicted the value of the Grüneisen





(a)



(b)

Figure 6. Total energy versus temperature for the fluorite (a) and the  $Pa\bar{3}$  structure (b).

constant  $\gamma$  using the following equation:

$$\gamma = \frac{3BV\alpha_l}{C_v} \quad (5)$$

where  $V$  is the molar volume. We found that  $\gamma$  equals 4.39 and 4.73 for the fluorite and the  $Pa\bar{3}$  structures, respectively.

It is also interesting to test the behaviour of the superhard phase ( $Pa\bar{3}$ ) under high temperature. Using the following empirical relation of Fine *et al* [23] with the above calculations of the elastic constants, we have determined an approximate melting temperature of the  $Pa\bar{3}$ -RuO<sub>2</sub> structure:

$$T_m = 553 \text{ K} + (591 \text{ K Mbar}^{-1})C_{11} \pm 300 \text{ K}. \quad (6)$$

We found that  $T_m = 2869 \pm 300 \text{ K}$ .

Within the Tersoff potential model, we have run MD simulations at a number of temperatures ranging from 5000 K to 8000 K. The heating is performed using Andersen's method [24] for the temperature control. The pair correlation functions  $g(r)$  at  $T = 5000 \text{ K}$  and  $8000 \text{ K}$ , plotted in figure 7, exhibit sharp nearest-neighbour peaks and have an tail oscillating about the value of 1. It appears that this potential model also gives a qualitatively correct description for liquid  $Pa\bar{3}$ -RuO<sub>2</sub> between 5000 K and 8000 K. The same behaviour has been observed between 6000 K and 8000 K for carbon [15] and boron nitride [22] within the Tersoff potential.

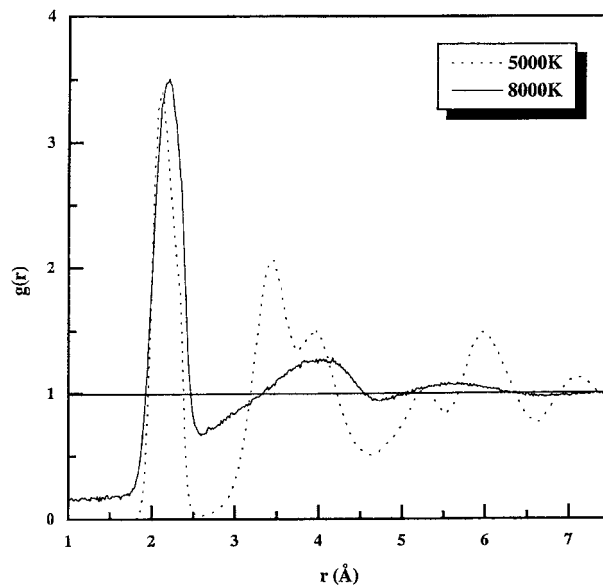


Figure 7. The pair correlation function for the  $Pa\bar{3}$  structure in the liquid phase.

#### 4. Conclusions

Superhard phases of RuO<sub>2</sub> are studied using molecular dynamics simulation based on the Tersoff potential. The structural and elastic properties for both fluorite and  $Pa\bar{3}$  phases are found to be in good agreement with *ab initio* calculations and experimental results. A high value of the bulk modulus for the  $Pa\bar{3}$  structure is found, which makes RuO<sub>2</sub> a good candidate for becoming a superhard material.

Since the Tersoff potential was found to be transferable, various thermodynamic properties are predicted. Our calculations show also that this model gives a qualitatively good description of  $Pa\bar{3}$ -RuO<sub>2</sub> in the liquid phase.

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