Density functional calculation of Raman intensity at high pressure in rutile phase of TiO_2 crystal

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Introduction

Intensity of Raman lines are important part of the information contained in the vibrational spectra of crystals. Due to the changes in the crystal structure as a response to external perturbation (pressure, temperature) the frequencies, as well as intensities of the Raman active modes change under external influence. The intensity of the Raman lines is important information about the properties of studied system, but is usually not used very much.

The Raman study of a oriented single crystal gives information about the components of Raman tensor for various Raman active modes. We calculate intensities of Raman modes of tetragonal rutile structure, space group $P4_2/mnm$ (Fig 1.) of TiO_2 crystal for different pressures. The ABINIT density functional program package [1] is used for the calculation of vibrational frequencies and Raman tensor components. The values given by calculations are in a fair agreement with the observed positions of phonons as a function of pressure. The possibility to use Raman intensities as additional tool in the study of phase transitions is discussed.

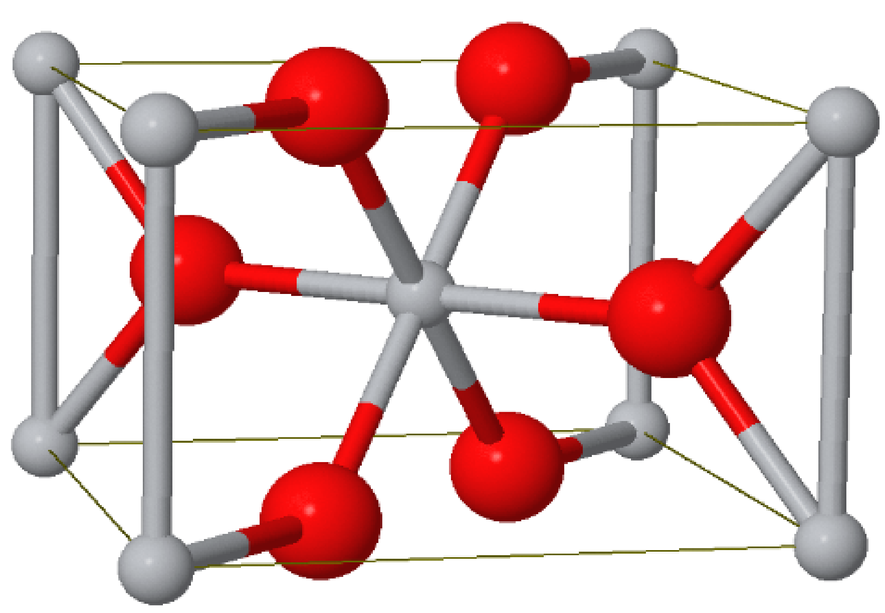

Fig 1

Method

Ab initio lattice dynamics calculations and calculation of higher order derivatives of energy were performed using the ABINIT program package [1], which is based on density functional perturbation theory (DFPT), use of pseudo potentials (PP) and plane waves [1]. Using the DFPT method it is possible to calculate phonons, elastic constants, Raman scattering efficiencies tensors, piezoelectric constants etc. The Raman scattering efficiencies tensors is calculated within DFPT as third derivative of energy twice with respect to electric field and once with respect to atom displacement [2].

Results

We have calculated Raman tensor of different modes of rutile structure of TiO_2 crystal using DFPT method [2].

The rutile structure of TiO_2 has four Raman active modes [3] with the frequencies: 826 cm^{-1} B_{2g} , 612 cm^{-1} A_{1g} , 447 E_g cm^{-1} and 143 cm^{-1} B_{1g}.

P=0 GPa	A_{1g}	E_g	B_{1g}	B_{2g}	P=5 GPa	A_{1g}	E_g	B_{1g}	B_{2g}
Frequencies cm^{-1} →	630	478	119	838		655	495	93	863
Raman tensor components ↓									
xx	-2.89		0.067			-2.77		0.057	
yy	- 2.89		-0.067			-2.77		-0.057	
zz	1.59					1.7			
xy				0.16					0.14
xz		**0.91**					**0.18**		
yz		1.2					1.5		

Table 1

Discusion

The present calculation shows that components of Raman tensors changes only slightly with pressures. The only exceptions are the Raman tensor components of the E_g mode. The table 1. shows the phonon frequencies at pressure of 0 and 5 GPa as well as components of Raman tensor. The calculated values show that the Raman tensor components for three modes (A_{1g}, B_{1g} and B_{2g}) do not change very much between zero and 5 GPa (Table 1.). The xy component of the Raman efficiency tensor for E_g modes changes substantially under the influence of pressure (Table 1.). The present calculations confirm the fact that intensities of some Raman lines are very sensitive to pressure. On the other hand, the strong change of observed Raman intensities is not necessary the indication of the phase transition, as it is often stated in the literature.

Literature

[1] The ABINIT code is a common project of Universite Catholique de Louvain, Corning Incorporated and other contributors **(**www.abinit.org**).**

[2] M. Veithen, X. Gonze and Ph. Ghosez, Phys. Rev. B **71** 125107 (2005).

[3] P. S. Porto, P. A. Fleury and T. C. Damen, Phys. Rev. **154**, 522 (1967).