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The incompressibility of atoms at high pressures

GERALD V. GIBBS¹, DAVID F. COX², AND NANCY L. ROSS¹,*

¹Department of Geosciences, Virginia Tech, Blacksburg, Virginia 24061, U.S.A.
²Department of Chemical Engineering, Virginia Tech, Blacksburg, Virginia 24061, U.S.A.

ABSTRACT

The structures of the silica polymorphs α-quartz and stishovite have been geometry optimized at highly simulated isotropic pressure within the framework of Density Functional Theory. The atoms of the high-pressure polymorph stishovite are virtually incompressible with the bonded radii for Si and O atoms decreasing by only 0.04 and 0.08 Å, respectively, at 100 GPa. In compensating for the increase in the effective interatomic potential associated with the compression of the Si-O bonded interactions, the electron density at the bond critical point between the bonded pair increases from 0.69 to 0.89 e/Å³. The bonded radii of the Si and O atoms for α-quartz decrease by 0.006 and 0.008 Å, respectively, between 1 bar and 26.4 GPa. The impact of simulated, isotropic pressure on the bonded radii of the atoms for three perovskites YAIO₃, LaAlO₃, and CaSnO₃ was also examined at high pressure. For the YAIO₃ perovskite, the bonded radii for Y and Al decrease by 0.06 and 0.05 Å, respectively, at 80 GPa, while the electron density between the bonded atoms increases by 0.12 and 0.15 e/Å³, on average. The calculations also show that the coordination number of the Y atom increases from 9 to 10 while the coordination number of the O₁ atom increases concomitantly in the structure from 5 to 6 at 20 GPa. Hence pressure not only promotes an increase in the coordination number of the metal atoms but also a necessary concomitant increase in the coordination number of the O atoms. The bonded radii, determined at a lower pressure between 0.0 and 15 GPa for LaAlO₃ and CaSnO₃, decrease a smaller amount with the radii for the La and Ca atoms decreasing by 0.03 and 0.04 Å, respectively, while the radii for the smaller Al and Sn atoms decrease by 0.01 and 0.02 Å, respectively. In general, O atoms are more compressible than the metal atoms, but overall the calculations demonstrate that the bonded radii for the atoms in crystals are virtually incompressible when subjected to high pressure. The reason that the bonded radii change little when subjected to high pressure is ascribed to the changes in the effective interatomic potentials that result in increased repulsion when the atoms are squeezed together.

Keywords: High pressure, bonded radii, silica polymorphs, perovskites

INTRODUCTION

To appreciate the impact of pressure on the structure and crystal chemistry of an oxide crystal, it is important, as argued by Prewitt and Downs (1998), that we understand the impact of pressure on the oxide anions, the bonded cations, and the cations containing coordination polyhedra. They also argued that coordinated polyhedra, containing large cations with small valences could be expected to be more compressible than those containing smaller cations with larger valences. Based on an examination of several experimental electron density maps determined by Sasaki et al. (1980), they also suggested that the atomic nuclei of the individual ions of an oxide crystal are shrouded by incompressible spherical cores of electron density that in turn are enclosed by more compressible, low lying shells. On the basis of this suggestion, they argued that the outer shells of the ions are ideal regions where the compressibility of a crystal may be accommodated. Based on these arguments, combined with results of Density Functional Theory (DFT) calculations for the silica polymorphs (Nicoll et al. 1994) and force constants estimated for the bonded interactions for several oxide molecules (Hill et al 1994), Prewitt and Downs (1998) developed guidelines as to how the sizes of the ions, the bond lengths, and the coordination numbers of the atoms of a material may be expected to respond to pressure. These guidelines include: (1) longer bonded interactions are more likely to decrease than shorter stronger ones; (2) the shared character of a bonded interaction increases with decreasing bond length; (3) the coordination number of a cation increases upon compression; and (4) oxygen anions are more compressible than metal cations. Grochala et al. (2007) have since examined the rules for a variety of materials, ranging from molecules to metals, with atoms that they considered to be in “very tight places,” that is, at pressures ranging up to that at the center of the Earth, 380 GPa. Despite the relative simplicity of the rules, they observed that the Prewitt and Downs (1998) rules are quite correct and serve as useful constructs for understanding how the structures and bonded interactions for various materials respond to high pressure.

In this study, we have determined the impact of pressure on the sizes of the bonded radii of the atoms and the polarization of the