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# First-principles calculations of typical anisotropic cubic and hexagonal structures and homogenized moduli estimation based on the Y-parameter: Application to CaO, MgO, CH and Calcite $CaCO_3$

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ABSTRACT

X-ray method to test the material properties and to obtain elastic constants is commonly based on the Reuss model and Kroner model. Y parameter has been turned out to be an effective method to estimate elastic properties of polycrystalline material. Since Y-parameters of cubic polycrystalline material based on the certain uniform stress (Reuss model) has not been given, our work aims to complete this part of the theoretical analysis, which can effectively compare elastic constants measured by the X-ray diffraction method. The structural and the elastic properties of cubic structures (CaO and MgO) and hexagonal structures (CH and Calcite $CaCO_3$) are investigated by the density functional theory method. And then the credibility of Y parameters for determing elastic moduli of cubic structures is proved and elastic properties in typical crystallographic planes of [100], [110] and [111] are also calculated. Meanwhile, Young's moduli of CH and Calcite structure are 58.08 GPa and 84.549 GPa, which are all close to references. Elastic properties of cubic and hexagonal structures under various pressures are calculated and the surface constructions of elastic moduli are drawn, showing the anisotropy at various directions. The crystal structure investigated in this work are typical of some primary or secondary components of Hardened Cements Pastes and their homogenized elastic properties are needed in a hierarchical multi-scale modeling, such as the one developed by some of the authors of this paper.

## 1. Introduction

The development of computational methods to describe and predict the mechanical properties of cement-based materials is of obvious practical importance. The accuracy of the prediction of mechanical or, from a more general point of view, physical properties depend largely on the knowledge of the intrinsic properties of the various constitutive phases. Up to now, these properties have been solely obtained by experimental procedures. The tremendous increase of computational capabilities has largely favored the development of numerical modeling based on a realistic and multi-scale description of these kinds of materials. Since several years, some of the authors of this paper have been involved in the development of such numerical tools from the micro- to the macro-level (see for instance [1] or [2]). The intent is to assist the material developer by providing a rational approach to material development and concurrently assist the structural designer by providing an integrated analysis tool that incorporates fundamental material behavior. It is now clear that any realistic attempt to accomplish such an objective should be based on appropriate nano-structure / performance relationships, and also on an efficient method to up-scale the properties determined on the lowest level to the next higher one. This is the context of the work detailed in this paper.

An ab-initio plane wave pseudo-potential functional theory is first proposed to study various crystalline structures. The up-scaling to higher levels is then done by means of the Y-parameter theory which has been introduced by Zheng et al. [3,4] a few years ago to overcome the limits of X-rays diffraction methods and conventional Voigt-Reuss-Hill averaging, as it is recalled in the following of the introduction (Section 1.1), but which can be also seen as an efficient way to estimate homogenized properties.

### 1.1. Limits of X-rays diffraction methods and Voigt-Reuss-Hill averaging

X-ray method is commonly used to test the physical properties of materials. By satisfying the Bragg crystal diffraction conditions, the values, the shapes and the position changes of the diffraction peak are tested to calculate the distance between the crystal surfaces. Then the

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strain value at the normal direction of the crystal surface can be solved through the distance between the crystal surfaces mentioned above. Finally, by multiplying the relevant X-ray elastic constant and the strain value, the stress in the material can be thus obtained. Until now, for the commonly-used X-ray stress analyzer, the principle of X-ray diffraction is based on the uniform certain stress Reuss model. However, for the uniform certain strain Voigt model, there are still some difficulties in explaining its principle by X-ray diffraction method. Based on the content mentioned above, the concept of Y parameter is introduced on the basis of theoretical formulas' derivation to explain both Reuss and Voigt models.

Single crystals generally exhibit anisotropic mechanical behaviors, however, macroscopic averaging assuming a randomly distribution of initial crystals leads to isotropic mechanical properties such as Young's modulus. Polycrystalline materials which are composed of a single crystal, with a distribution probability depicting upward almost the same in three-dimensional space, exhibit an isotropic behavior at macroscopic scale.

X-Rays method is associated to the material surface, of which X-ray absorption and X-ray magnetic circular dichroism (XMCD) are very powerful tools [5]. Normally, elastic constants measured by X-Rays method contain the function of diffraction surface, which can be averaged within the total space to determine the macroscopic elastic properties of the material [6,7]. The mechanical elastic modulus of the macroscopic material is generally considered to be unrelated with diffraction surface material.

Y parameter can be seen as a function of the crystal plane index. Its theoretical derivation is thus relative to the type of crystal. Only cubic and hexagonal structures have been concerned by this concept. Y-parameter of cubic and hexagonal structures was firstly introduced and presented by Zheng et al. [3,4] in 2009. Based on the elastic constants of cubic and hexagonal crystals, the corresponding Y-parameter, as the new evaluation criteria, has been proposed. Elasticity of single crystal and mechanical properties of polycrystalline material has been closely integrated. By comparing various calculations method to determine homogenized moduli of the polycrystalline material composed of a single crystal, e.g. the certain stress of Reuss model [7], the certain strain of Voigt model [8] and Kröner-Voigt model [7] taking into account these two models and interaction between crystals, the Y-parameter, in the theoretical calculation to forecast the elastic modulus of polycrystalline material, has a highly consistency. Y parameter makes up the methodological disadvantage of X-Ray diffraction method (only the stress determined by strain). It can be used to estimate the homogenized properties under various crystal planes, which is the function associated with the crystal plane index.

Y parameters of hexagonal polycrystalline materials based on the Voigt model of the certain strain [3] and on the certain stress of the Reuss model [3,4] have been given. However, until now, for cubic polycrystalline materials, only Y parameter based on the Voigt model of a uniform certain strain has been derived.

In this work, it is firstly proposed to complete this part of the theoretical analysis and to obtain the definition of the Y-parameter based on the Reuss model. Here the expression form of the 6×6 matrix (36 parameters) is used instead of the four-rank tensor (81 parameters) in order to simplify the actual computing work and the derivation. In a second part, the methodology is applied to two typical cubic and two typical hexagonal structures, respectively CaO and MgO, and CH and Calcite $CaCO_3$. For that, a preliminary study by ab-initio plane-wave pseudopotential density functional theory method is performed for each of the considered crystalline structures.

The credibility of Y parameters for determing homogenized elastic moduli of CaO, MgO, CH and Calcite structure and studying their anisotropy is then proved.

### 1.2. Macroscopic mechanical behavior of CaO and MgO cubic polycrystals

CaO and MgO as the alkaline earth oxides have been used in civil engineering. CaO has the $B_1$–$B_2$ transition and the $B_2$ phase is stable to higher pressure region [9]. Besides, CaO turns to be transformed from the $B_1$ to the $B_2$ phases over a range of pressures [9] by shockwave measurements. By calculations using the outer-valence Green's function technique (OVGF), Nowiak et al. [10] found that the attachment of an alkali metal atom to any oxide MO (BeO, MgO, CaO) reverses its polarity, as the redirection of the dipole moment vector. Kalpana et al. [11] and Baltache et al. [12] also investigated this transition for CaO. Mehl et al. [13] predicted elastic constants and their pressure dependences of CaO using potential-induced breathing (PIB) models. The ab initio pseudopotential calculations with plane-wave basis (PWPP) and ab initio full-potential linear muffin-tin-orbitals (FP-LMTO) are used to study high-pressure elastic properties of CaO by Karki and Crain [14] and Tsuchiya and Kawamura [15], respectively.

In 1995, Duffy et al. [16] have found, for pressures up to 227 GPa, that B1-type MgO remained stable, while at 300*K* the stable pressure can reach up to 199 GPa. By Anvil hydrostatic test, Fei [17] has measured and got high pressure state equation as well as elastic modulus of MgO. By ultrasonic interferometry method, Chen et al. [18] have found that the elastic anisotropy of MgO structure decreases with an increase of pressure under normal temperature conditions, while the elastic anisotropy increases with temperature at high pressure. Jackson and Niesler [19] have obtained isothermal bulk modulus of MgO and its first derivative of pressure. Sinogeikin and Bass [20] have studied the pressure state equation of MgO by Anvil Brillouin scattering experiments. Zha et al. [21] have experimentally measured elastic properties with the pressure up to 55 GPa by scattering spectroscopy *X* Brillouin zone. Merkel et al. [22] have studied the pressure up to 47 GPa and measured elastic modulus, shear modulus and elastic anisotropy. Wolf and Bukowinski [23] have investigated the stabilization of the ionic charge densities in MgO and CaO crystals by an electron gas model. Matsui et al. [24] have calculated elastic constants and thermodynamic properties of MgO structure over a wide temperature and pressure range. High-temperature thermal expansion of lime, periclase. Fiquet et al. [25], through X-ray diffraction experiments with synchrotron radiation, have studied the thermal expansion of lime CaO and periclase MgO. Karki et al. [26] have used a plane wave qualitative study of the elastic properties of the potential B1 type MgO in the range of 0–25 GPa.

### 1.3. Macroscopic mechanical behavior of CH and Calcite polycrystals

Portlandite (CH) is one of the main and typical constituents of hydrated cementitious systems. CH represents 17–25% of the volume fraction of portland cement paste, and its Young's modulus is needed in the modeling of cement systems on the macro and micro scales [1,2]. Using this technic as well as Density Functional Theory (DFT), the present work aims to investigate the elastic properties of one specific crystal, Portlandite. These elastic properties influence the physical and mechanical properties as well as the durability of cement based materials. Speziale et al. [27] have investigated the elastic constants of Portlandite by Brillouin spectroscopy.

Calcium carbonate ($CaCO_3$) is the main component of limestone and marble, it naturally crystallizes in two major crystalline forms: aragonite and Calcite. Calcite has very large industrial applications in the field of civil engineering construction, and it can also be used as a flux in glass and in the field of metallurgy. Calcium carbonate ($CaCO_3$) is the most responded to the surface of the earth carbonate, several researchers have been interested in elastic constants of Calcite and its structure [28,29]. Zhang et al. [30] have investigated compressibilities of calcite-structure carbonates and confirmed the results found by Dandekar et al. [31] on the pressure dependence of the elastic