Final report

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Theoretical Studies of Zirconia and defects in Zirconia

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Abstract

Supported by this grant we have performed total energy electronic structure calculations for cubic, tetragonal, and monoclinic zirconia. The results of these calculations agree with the observed ordering of structures in the phase diagram. We have developed model potentials based on our total energy results. Molecular dynamics calculations using these model potentials give a good description of the phase transitions in and the thermal properties of zirconia.

Total energy electronic structure calculations.

The first part of the work performed under this grant used the full-potential linearized augmented plane wave method to perform total energy calculations for pure zirconia in the cubic, tetragonal, and monoclinic structure. The result for cubic and tetragonal zirconia are published [1,2]. In the remainder of this section I will describe the results for monoclinic zirconia [3].

The monoclinic unit cell for zirconia contains twelve atoms and is twice the size of the cell used for the tetragonal calculations. Fortunately, both cells are directly related and the tetragonal geometry is a special case of the monoclinic geometry. In order to compare the results obtained with tetragonal cells and monoclinic cells we have made a comparison of the total energy results for a tetragonal geometry using both types of unit cells. This showed that our total energy calculations were well converged, the differences between the two calculations are related to a larger degree of freedom of variational parameters in the monoclinic cell. A uniform shift in the total energy of 3 mRy (for twelve atoms!) in the tetragonal data was sufficient to bring all results in agreement. The value of this shift is very small, testifying that the convergence of our results is very good.

The monoclinic unit cell has 13 degrees of freedom to describe the geometry of zirconia. Four degrees pertain to the overall shape of the cell (the length of the sides in the a, b, and c direction and the angle between the a and c direction), while the remaining nine describe the positions in the unit cell of the Zr atoms and the two types of O atoms. We have calculated the total energy of monoclinic zirconia for about forty different combinations of these parameters.

Tight binding interpolation.

Theoretically, the best way to obtain information pertaining to phase transitions in zirconia is a combination of molecular dynamics and ab initio electronic structure calculations. If we perform both simultaneously, we have the best representation of the forces in the material. Unfortunately, for zirconia this is not feasible, since the ab initio calculations take too long.

Therefore, we tried to simplify the ab initio part by using a tight binding fit to the electronic band structure.

Martin Rosenbauer constructed a general method for obtaining tight binding fits in arbitrary crystals [4], based on results generated with our full potential linearized augmented plane wave algorithms. For each particular geometry of the tetragonal unit cell it is possible to obtain a good fit to the calculated energy bands [5]. In order to use the tight binding method in force calculations we also need a good description of the parameters in the tight binding model Hamiltonian as a function of geometry. This turned out to be impossible [5]. The dependence of the parameters in the model Hamiltonian on bond length should be very simple, but we did not find such a relation. Therefore, we gave up our idea of using a tight binding Hamiltonian in the electronic structure calculations for the interatomic forces.

Effective potentials.

An ab initio analysis of the monoclinic unit cell is almost impossible. To explore the total energy as a function of the 13 parameters describing the unit cell is a tremendous task. We simplified this task by modeling the forces between the atoms. Our effective interactions contain three terms, a Coulomb force, an induced dipole force, and a short range force. The parameters describing these effective interactions are found by fitting the total energy calculated with the effective interactions to the ab initio results. Good quality fits were obtained. Next, we used the model interactions to find the minimum in the total energy, and then performed an ab initio calculation at the predicted minimum to confirm the value of the total energy. The results are in agreement with experiment, and monoclinic zirconia has the lowest total energy. The equilibrium structure found in these calculations agrees with the experimental results.

Using the effective potentials it is also possible to find the reaction path between the monoclinic and tetragonal structure. These two structures are closely related and are both distortions from the cubic CaF_2 structure. The parent CaF_2 structure has layers of O atoms, in each layer the O atoms are situated on a simple square grid. The grids in the neighboring layers are on top of each other, there is no shift. In between the O layers there

are layers of Zr atoms, also arranged on a square grid. The grid of the Zr atoms is rotated, however, and the positions of the Zr atoms are in the centers of the O grids, with only half the number of centers occupied. There are two possible stackings for the Zr grid, and neighboring Zr layers have alternate orientations. The tetragonal lattice distorts the cubic grid by making the distance between the O layers different from the spacing in the planes, and moves the O atoms slightly out of their planes in a direction orthogonal to the planes. The monoclinic cell is more complicated. Half the O layers are still on a square grid, but alternating layers have a distorted grid. The distortion is very simple, however. If one groups the O atoms in squares containing four atoms, the distortion is a simple rotation of these squares in the layer. In addition, all atoms move perpendicular to the layers.

To our surprise the reaction path between the monoclinic and the tetragonal structure did not follow the simple recipe described above. The squares in the monoclinic lattice are obtained by transforming rhombi in the original lattice. The O atoms essentially rotate in groups of three around a Zr atom.

There are two factors that play a role in the stabilization of cubic zirconia. By substituting Zr with elements like Y one introduces vacancies in the O layers. As a result, the difference of the free energy of the monoclinic and cubic phase changes. The cubic phase becomes fully stabilized if the free energy of the cubic phase is lowest. A second effect of Zr substitution is a change in the energy barrier between the monoclinic and cubic phase. It is possible to create a situation where the monoclinic structure is still stable at low temperatures but where the energy barrier inhibits a phase transformation. In this case cubic zirconia is metastable.

A simple geometrical argument is able to account for an increase in the energy barrier between the cubic and the monoclinic phase. Elements like Y and Ca have a larger ionic radius and hence it will become harder for the O atoms to rotate around these atoms from one structure to another, there is less space. If there is a substantial amount of substitutional impurities, this effect will be large enough to make cubic zirconia metastable. This has to be tested, of course, in realistic molecular dynamics calculations.

Molecular dynamics calculations.

In order to study the phase transitions in zirconia in more detail we used molecular dynamics calculations. The programs were developed by Mike Love, a PhD student supported under this program. His results are described in his thesis [6] and are being submitted. The model interactions between the atoms contain a Coulomb term, because it is believed that this type of interaction is important for the stability of monoclinic zirconia. Therefore, we had to develop methods to calculate the total energy including a Coulomb potential.

Mike Love has developed a scheme which is based upon the fast multipole method and includes a plane-wise summation. This method is linear in the number of atoms in the unit cell, in contrast to the standard Ewald method. A paper describing his results is submitted for publication [7]. An essential trick in these calculations is the inclusion of extra point charges on the faces of the molecular dynamics unit cell. In each cell these charges are chosen to compensate any dipole moment that might exist in a cell. Charges on opposite faces are equal in magnitude and opposite in sign, so neighboring cells compensate these extra charges. For a finite system one has a surface charge, but this term can be thrown out as unphysical. This method also makes it directly possible to compare Mike's results with the standard Ewald method.

Mike Love also incorporated the formalism that allows to perform the molecular dynamics calculations at constant temperature and pressure. We have carefully analyzed these schemes in order to study when they are applicable and how the convergence depends on the values chosen for the parameters describing the heat and pressure reservoirs. Mike Decker, a MS student partially supported under this grant, is defending his thesis [8] November 2, 1995. We made several interesting observations. For example, calculations at constant temperature can become unstable if the initial conditions are far away from equilibrium [9]. These effects are already present in the application of this method to a simple harmonic oscillator and are related to an oscillatory flow of energy between the system and the heat-bath. The presence of a pressure reservoir is very useful, it allows the study of phase transitions using a much

smaller number of atoms in the molecular dynamics unit cell than in traditional constant volume approaches.

Mike Love has performed a series of simple calculations using soft spheres to mimic zirconia [10]. Using a constant pressure and temperature simulation makes this calculation very easy, and a small molecular dynamics cell is sufficient. The results are very interesting. As a function of the ratio of the soft-sphere radii the crystal structure changes from cubic to tetragonal to orthorhombic back to cubic again. A soft-sphere ratio corresponding to the ratio of the ionic radii of Zr and O results in an orthorhombic structure. At high temperature this structure changes into a monoclinic structure. In our *ab initio* calculations we also find an orthorhombic structure with low energy and the fact that the monoclinic structure is most stable is related to chemical bonding effects that cannot be simulated by soft spheres. The soft-sphere model result at high temperature is not very realistic, since the volume has increased dramatically due to the absence of interatomic forces. Nevertheless, it is surprising to find a monoclinic structure at high temperatures. From these simple calculations we conclude that some aspects of the structure of zirconia can already be explained in terms of soft spheres, but that details have to be obtained by using realistic potentials.

The calculations using the model potentials based upon the *ab initio* results are performed by Yiqing Zhou, another student supported by the program. She is currently finishing her PhD (expected date early Winter 1996). She has used two sets of model potentials to describe the zirconia unit cell.

Our molecular dynamics calculations for zirconia show a phase transition from the monoclinic to the cubic structure around 800K and zero pressure. The model potentials are not sufficiently accurate to have an intermediate tetragonal phase. The thermal expansion coefficient of the material is close to the experimental value and the volume drop at the phase transition is also consistent with experiment. As a function of pressure we find transitions to a tetragonal and an orthorhombic phase. This is again similar to experiment, but we do not find all phases observed experimentally. Even though these calculations make use of model potentials, they are still time consuming.

When we slightly alter the parameters in our effective forces we find a different ordering in the phase diagram. The zero pressure ground state is now orthorhombic, but the thermal expansion is very similar. In addition, a phase transition to a cubic phase is found around 1000K. These results show that the differences in total energy between the various phases in zirconia are small, a necessary condition for the stabilization process to be possible. The advantage of using molecular dynamics with model potentials is now clear. Here we can vary the potentials and study how sensitive the results are to these changes. This allows for an interpretation of the results in terms of simple physical models. Ab initio molecular dynamics calculations just give you results, without any physical content.

Future work.

We plan to continue the work described in this report. By using larger molecular dynamics unit cells we will be able to study the phase transition from monoclinic to cubic zirconia in more detail. The main questions to be answered pertain to the role of impurities and the nature of the martensitic phase transformation.

It is easy to include impurity atoms, like Y, and O vacancies in our molecular dynamics unit cell. Using model potentials to describe the interactions of the impurities with the host atoms we can investigate the properties required of the model interactions for a stabilization of the cubic phase. This will lead to a better understanding of the nature of this process.

The investigation of the martensitic nature of the phase transition is harder, since it is unclear how large a cell we need in order to be able to describe processes like twinning. A preliminary study is necessary before a student's PhD thesis can be committed to this topic.

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Y. Ding	left 1989
M. Rosenbauer	MS, October 1991
M.J. Love	PhD, September 1993
M. Decker	MS, November 1995
Y. Zhou	PhD, expected Winter 1996.

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