

# Structure and stability of $\alpha$ - and $\beta$ -Ti<sub>2</sub>Se. Electron diffraction versus density-functional theory calculations

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The  $\alpha$  structure as well as the new  $\beta$  modification of Ti<sub>2</sub>Se were recently characterized by electron diffraction structural analysis of nanosize crystallites. In this study, both structures are investigated by means of total energy calculations within the non-local density-functional theory in order to validate the experimental results. The calculated parameters for both modifications are in excellent agreement with data determined from electron microscopy. From the calculated equation of states,  $\beta$ -Ti<sub>2</sub>Se is predicted to be a high-pressure modification. The present investigation proves by a well established non-crystallographic method that unknown structures, which are not accessible by other standard crystallographic techniques, can be solved and refined with high accuracy using electron diffraction data.

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## 1. Introduction

The determination of unknown structures using X-ray diffraction can be difficult if the material of interest is only available in small quantities or forms only extremely small crystallites. It has been repeatedly shown, however, that electron diffraction structure analysis (EDSA) is a powerful method to gain structural information even from minute crystals, often only a few tens of nanometres in size (Dorset, 1995; Zou *et al.*, 2001). Although several known and previously unknown structures have been determined from electron data, the widely used quasi-kinematical approach for solving and refining a structure is suspected to yield unreliable results since dynamical diffraction effects are totally neglected. This problem has prompted us to check results obtained from selected-area electron diffraction (SAED) by quantum-mechanical calculations within the density-functional theory (DFT), which enable an *ab initio* determination of lattice structures. Since the DFT calculations do not include empirical parameters and allow for full structural relaxation of both internal and external parameters, they are an appropriate and independent tool for verifying questionable structures. In this study, we compare theoretical structure parameters calculated for the  $\alpha$  phase and recently identified  $\beta$  phase of Ti<sub>2</sub>Se (Weirich *et al.*, 2000) with those determined by electron diffraction and single-crystal X-ray diffraction (XRD), respectively. Based on the calculated equation of states, we furthermore discuss the thermodynamic stability as well as the transition pressures between the two different phases.

## 2. Methodology

Total energy calculations were carried out in the framework of the density-functional theory (Jones & Gunnarson, 1989). All results reported here were obtained using the code *CASTEP* (Payne *et al.*, 1992) with non-relativistic ultra-soft pseudo-potentials (us-PP) (Lee, 1991). Exchange and correlation were included using the Perdew–Wang form of the general-gradient approximation (GGA) (Perdew & Wang, 1992). For both metallic structures, cells with 36 atoms were calculated using a cut-off energy of 310 eV, which was sufficient to get energy convergence better than 0.02 eV atom<sup>-1</sup>. The Monkhorst–Pack (1976) scheme was used for generating eight special *k* points. Additional calculations with a higher number of *k* points were carried out for the relaxed structures afterwards. Since both structures are metallic, partial occupancies were allowed for electronic bands close to the Fermi level. During the calculation, full relaxation of the lattice parameters *a*, *b*, *c* and internal coordinates were allowed. The structural relaxation was stopped when the energy gain per atom was less than  $2 \times 10^{-5}$  eV atom<sup>-1</sup>, the root mean square (r.m.s.) displacements were smaller than  $10^{-3}$  Å and the r.m.s. forces were smaller than 0.05 eV Å<sup>-1</sup>. Energy–volume data were then obtained by applying a uniform external stress to the unit cell, either compressive or tensile. The minimum energy, lattice constant, bulk modulus and pressure derivative of the bulk modulus were finally calculated by fitting the Birch–Murnaghan equation of state to the energy–volume data (Birch, 1978).

**Table 1**

Refined atomic coordinates of Ti<sub>2</sub>Se as obtained from XRD analysis (Weirich *et al.*, 1996) and EDSA (Weirich *et al.*, 2000) in comparison with theoretical results from DFT calculations for both  $\alpha$  and  $\beta$  modifications.

Note that  $z = 0$  for all atoms in  $\alpha$ -Ti<sub>2</sub>Se.

	$\alpha$ -Ti <sub>2</sub> Se						$\beta$ -Ti <sub>2</sub> Se					
	EDSA		XRD		DFT		EDSA			DFT		
	<i>x</i>	<i>y</i>	<i>x</i>	<i>y</i>	<i>x</i>	<i>y</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Ti1	0.1561 (21)	0.0240 (15)	0.14659 (5)	0.02024 (4)	0.1450	0.0203	0.2311 (9)	3/4	0.7565 (20)	0.2291	3/4	0.75491
Ti2	0.0826 (20)	0.2647 (16)	0.09082 (5)	0.25983 (4)	0.0908	0.2602	0.3367 (11)	3/4	0.0473 (25)	0.3403	3/4	0.0390
Ti3	0.5887 (29)	0.0755 (20)	0.58487 (5)	0.07649 (4)	0.5879	0.0765	0.1463 (10)	3/4	0.0825 (21)	0.1472	3/4	0.0828
Ti4	0.4639 (26)	0.3967 (19)	0.47090 (5)	0.39209 (4)	0.4711	0.3909	0.3907 (9)	3/4	0.3514 (19)	0.3923	3/4	0.3504
Ti5	0.8040 (22)	0.2033 (19)	0.81077 (5)	0.20512 (4)	0.8129	0.2060	0.0325 (8)	3/4	0.3868 (16)	0.0304	3/4	0.3865
Ti6	0.8733 (36)	0.4112 (24)	0.88516 (5)	0.42551 (4)	0.8844	0.4256	0.5145 (13)	1/4	0.3844 (27)	0.5128	1/4	0.3882
Se1	0.4346 (17)	0.2092 (14)	0.43217 (3)	0.20689 (4)	0.4334	0.2058	0.2410 (9)	1/4	0.9641 (19)	0.2389	1/4	0.9687
Se2	0.2452 (13)	0.4152 (11)	0.24453 (3)	0.41382 (4)	0.2482	0.4133	0.4239 (11)	1/4	0.1600 (21)	0.4227	1/4	0.1625
Se3	0.6832 (16)	0.3481 (14)	0.68704 (3)	0.34980 (4)	0.6858	0.3498	0.1260 (10)	1/4	0.2796 (23)	0.1276	1/4	0.2811

**Table 2**

Lattice parameters of  $\alpha$ - and  $\beta$ -Ti<sub>2</sub>Se.

EDSA are the results from electron diffraction (Weirich *et al.*, 2000), DFT are the calculated values of the present study and XRD gives the results of the single-crystal X-ray diffraction (Weirich *et al.*, 1996).

$\alpha$ -Ti <sub>2</sub> Se ( <i>Pnmm</i> , No. 58)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
XRD	11.737	14.550	3.451
EDSA	11.708	14.668	†
DFT	11.752	14.534	3.453
$\beta$ -Ti <sub>2</sub> Se ( <i>Pnma</i> , No. 62)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
EDSA	17.934	3.453	9.526
DFT	17.923	3.455	9.517

† Not determined

### 3. Structural parameters

Metal-rich compounds of the early transition metals with *p* elements form a variety of complex structures with extended regions of metal–metal (*M–M*) contacts. These regions frequently contain octahedral *M*<sub>6</sub> clusters which are linked *via* common corners, edges or faces. The structures often have one short crystal axis of about 3.5 Å in common, which makes them perfectly suited for EDSA investigations, since all structural information can be extracted from a single electron diffraction pattern recorded along this axis.

The  $\alpha$  phase of Ti<sub>2</sub>Se is well characterized by XRD analysis (Weirich *et al.*, 1996) and it was therefore a natural starting point to compare its structural parameters with those obtained from EDSA and DFT. Similar to the structure determination described in Weirich *et al.* (2000), electron diffraction intensities of  $\alpha$ -Ti<sub>2</sub>Se were extracted from SAED patterns recorded on film. Symmetry-related reflections were merged and fed into the program *SIR97* (Altomare *et al.*, 1999) in order to determine the structure *via* conventional direct methods. By a subsequent (kinematical) least-squares structure refinement on  $|F_{hkl}|^2$  using the program *SHELXL97-2* (Sheldrick, 1998) we obtained the results given in Table 1. Comparison of the cell parameters in Table 2 shows that the lattice parameters determined from electron diffraction differ by 0.3% for the

*a* axis and 0.8% for the *b* axis from the XRD result, while the DFT calculations reproduce the XRD data within 0.1% for all three axes. A similarly good agreement was found for the corresponding atomic positions (Table 1). The difference between the previous structure solution from single-crystal X-ray diffraction and the refined atomic coordinates based on the electron diffraction data is on average 0.09 Å (maximum deviation 0.25 Å for Ti6). The atom positions determined by XRD and from DFT differ on average by only 0.02 Å (maximum deviation 0.04 Å for Se2).

The  $\beta$  structure of Ti<sub>2</sub>Se so far has only been synthesized in a multiphase powder and therefore only the structural solution from EDSA is available (Weirich *et al.*, 2000). The DFT calculations were started from this solution and served to validate the experimental result. As can be seen in Table 2, the calculated and measured lattice parameters agree within 0.1%, while the average deviation of the atomic positions is 0.04 Å (maximum deviation 0.10 Å for Ti2; see Table 1). The very good agreement of the structural models as obtained from DFT calculations and electron diffraction for  $\alpha$ - and  $\beta$ -Ti<sub>2</sub>Se is visualized in Fig. 1.

This result convincingly shows that this previously unknown structure, which has not been accessible by other diffraction methods, was solved and refined with high accuracy *via* EDSA.

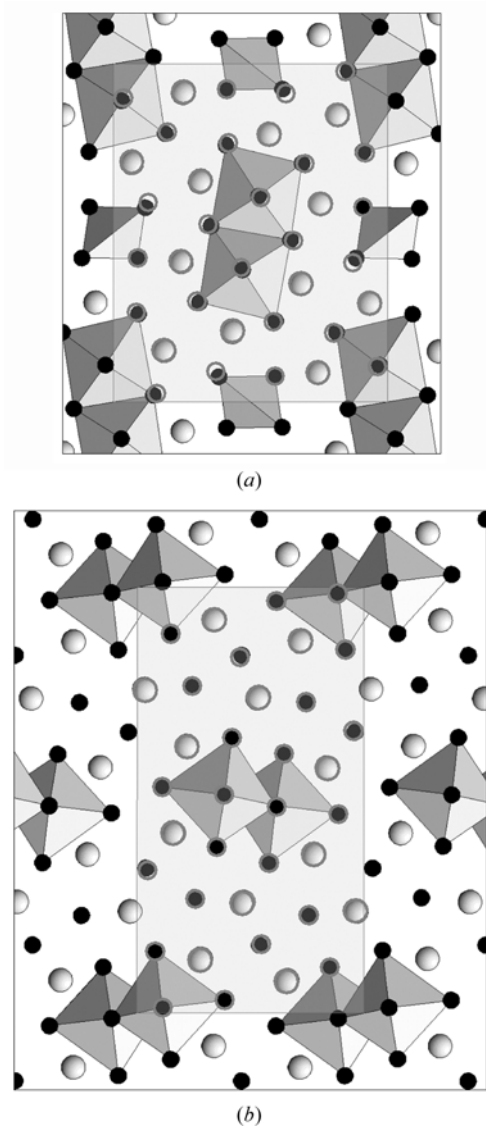
### 4. Phase stability and transition pressure

Since  $\alpha$ - and  $\beta$ -Ti<sub>2</sub>Se are observed in the same sample, it is interesting to investigate their relative phase stability. While allowing full structural relaxation, total energies for both modifications were calculated under uniform compressive and tensile stress. The equation of states and enthalpies of both structures at zero temperature were determined from the resulting energy–volume data (Fig. 2). According to the calculation, the  $\beta$  phase is almost isoenergetic to the  $\alpha$  structure, which is the thermodynamic ground structure of Ti<sub>2</sub>Se. Using eight special *k* points for both structures, the energy difference is only 20 meV/f.u. In an additional calculation of the relaxed configurations with 32 *k* points for the  $\alpha$  and 42 *k*

points for the  $\beta$  structure, we obtained a slightly higher value of 55 meV/f.u. Although this is about the magnitude of energy contributions from zero-point vibrations, the difference in the zero-point energies is presumably smaller and therefore does not alter this hierarchy substantially.

The bulk moduli and their pressure derivatives were determined from fitting the Birch–Murnaghan equation for both structures. Results obtained from the calculations are listed in Table 3. Since the bulk modulus of the  $\beta$  modification is lower than that of  $\alpha$ -Ti<sub>2</sub>Se, the energy–volume curves intersect and therefore  $\beta$ -Ti<sub>2</sub>Se is predicted to be metastable at ambient conditions.

From the intersection line, a transition pressure of about 10.5 GPa can be estimated. It should be noted, however, that this number sensitively depends on the energy differences of both structures. The corresponding tangent construction is



**Figure 1** Comparison of crystal structures as obtained from electron diffraction data (circles) and from DFT calculations for (a)  $\alpha$ -Ti<sub>2</sub>Se projected along the [001] direction and (b)  $\beta$ -Ti<sub>2</sub>Se projected along the [010] direction. Dark spheres show the Ti positions, grey spheres Se.

**Table 3**

Bulk modulus  $B$ , pressure derivative of the bulk modulus  $B'$ ,  $V_0$  volume per formula unit and energy difference  $\Delta E$  as obtained from fitting the Birch–Murnaghan equation to calculated  $E$ – $V$  data of  $\alpha$ - and  $\beta$ -Ti<sub>2</sub>Se.

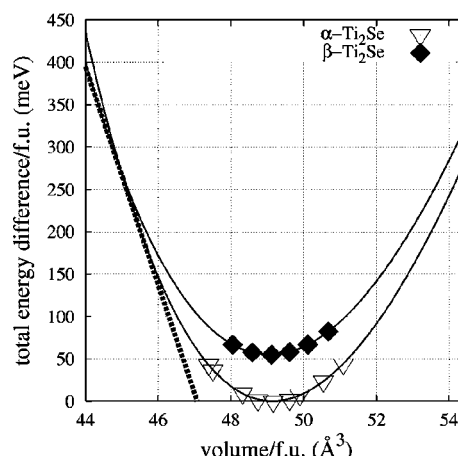
	$\alpha$ -Ti <sub>2</sub> Se	$\beta$ -Ti <sub>2</sub> Se
$B$ (GPa)	201 (2)	176 (1)
$B'$	6 (2)	1.5 (10)
$V_0$ /f.u. ( $\text{\AA}^3$ )	49.14 (3)	49.07 (3)
$\Delta E$ /f.u. (eV)	0	0.055

shown in Fig. 2. Although this calculation neglects zero-point vibrations and thermal contributions, it does indicate that the  $\alpha \rightarrow \beta$  phase transition in Ti<sub>2</sub>Se occurs only under extreme conditions.

Since the sample was synthesized at ambient pressure using a standard high-temperature preparation technique (Weirich *et al.*, 2000), it can only be assumed that reaction kinetics rather than energetics are responsible for the coexistence of both polymorphs in the same sample. Possibly, the  $\beta$  phase was formed by a peritectic reaction similar to that recently proposed for Zr<sub>2</sub>Te (Örlygsson & Harbrecht, 1999).

## 5. Conclusions

In the present study, we have compared structural parameters of  $\alpha$ - and  $\beta$ -Ti<sub>2</sub>Se from electron diffraction analysis and crystal X-ray diffraction with results of DFT calculations. Experimentally determined and theoretically calculated structures show excellent agreement with a deviation in the lattice parameters of about 1% and less than 0.1  $\text{\AA}$  in the atom coordinates. This again shows that electron diffraction structure analysis using the quasi-kinematical approach is capable under favourable conditions of determining unknown structures with high accuracy. The calculation of energy–volume data indicates that  $\beta$ -Ti<sub>2</sub>Se is thermodynamically stable under extreme pressures above 10.5 GPa. The reason for its occurrence in our samples, however, which have been produced by



**Figure 2** Total energy difference and volume per formula unit for  $\alpha$ - and  $\beta$ -Ti<sub>2</sub>Se. The solid lines show the corresponding fit to the Birch–Murnaghan equation. The dotted line depicts the tangent construction for determining the transition pressure.

high-temperature synthesis at ambient pressures, remains unclear.

In general, DFT calculations have become an extremely valuable standard tool for verifying and/or refining (rough) structure models that have been determined by crystallographic techniques.

Grants of computing time from the National Computational Science Alliance at UIUC and the National Energy Research Supercomputer Center are gratefully acknowledged.

## References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–118.
- Birch, F. (1978). *J. Geophys. Res.* **83**, 1257–1269.
- Dorset, D. (1995). *Structural Electron Crystallography*. New York: Plenum Press.
- Jones, R. & Gunnarson, O. (1989). *Rev. Mod. Phys.* **61**, 689–746.
- Lee, M. H. (1991). PhD thesis, Cambridge University, England.
- Monkhorst, H. J. & Pack, J. D. (1976). *Phys. Rev. B*, **13**, 5188–5192.
- Örlygsson, G. & Harbrecht, B. (1999). *Inorg. Chem.* **38**, 3377–3383.
- Payne, M., Teter, M., Allen, D., Arias, T. & Joannopoulos, J. (1992). *Rev. Mod. Phys.* **64**, 1045–1097.
- Perdew, J. & Wang, Y. (1992). *Phys. Rev. B*, **45**, 13244–13249.
- Sheldrick, G. M. (1998). *SHELXL-97-2. Program for Crystal Structure Refinement*. University of Göttingen, Germany.
- Weirich, T., Pöttgen, R. & Simon, A. (1996). *Z. Kristallogr.* **212**, 938.
- Weirich, T., Zou, X., Ramlau, R., Simon, A., Cascarano, G., Giacovazzo, C. & Hovmöller, S. (2000). *Acta Cryst.* **A56**, 29–35.
- Zou, X., Weirich, T. & Hovmöller, S. (2001). *Progress in Transmission Electron Microscopy*, Vol. 1. *Concepts and Techniques*. Berlin: Springer.