The Piezo-Spectroscopic Strain-Tensor: An *ab-initio* approach

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Abstract: Under a uniaxial stress, the equilibrium fractional alignment of anisotropic defects is controlled by their piezospectroscopic or stress tensors. These tensors have been measured for a number of defects by several spectroscopic techniques: magnetic resonance, infra-red electronic absorption, luminescence and vibrational mode spectroscopy. What has not been generally realised is that the tensor is easily evaluated by modern total energy methods which thus provide a simple and direct link with the principal methods used to characterise defects. We show how the tensor can be found, and compare the calculated and measured values for a number of oxygen defects in Si. These include: interstitial and substitutional oxygen, VO_2, C_iO_i, and several models of thermal double donors.

1. Introduction

The stress–tensor or strain–tensor (A or B), quantify the coupling between a defect and the host crystal.[1] The energy of a defect under stress is defined as

$$\Delta E = A_{lm} \cdot \sigma_{lm} = B_{lm} \cdot \epsilon_{lm}. \qquad (1)$$

Here A and B are connected through the elastic or stiffness constants. The compressive or tensile character of a defect along a particular direction, is stored in these piezo-spectroscopic tensors. Given the nature of these physical quantities, a total energy density functional approximation method is a suitable framework for modelling.

2. Experimental Procedure

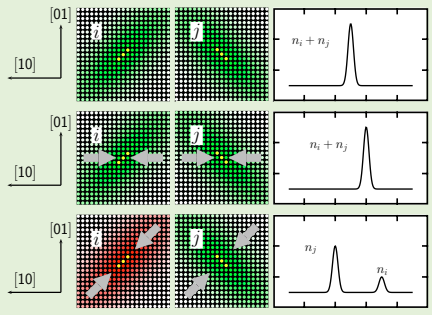
Under uniaxial stress at temperature T, an anisotropic defect aligned along i or j directions will be fractionally populated by

$$\frac{n_i}{n_j} = \exp\left[(\Delta E_j - \Delta E_i)/kT\right], \qquad (2)$$

with respective energies ΔE_i and ΔE_j. Here thermodynamical equilibrium must hold. Then, if n_i/n_j are observables, Equations 1 and 2 can be used to obtain the strain tensor.

Example in a 2D picture

The defective crystal distortion can be represented by an ellipsoid associated with B. This is schematically shown in the left side of Figure 1. Green and red show the energetically favoured and disfavoured orientations. Uniaxial strain is indicated by the arrows. On the right, a spectroscopic signal monitors the partial populations.



Zero strain
$B_{xx} + B_{yy} = 0$

$\epsilon_{lm} = \varepsilon\,\delta_{lx}\delta_{mx}$
$\Delta E_i = \Delta E_j$
$B_{xx} = B_{yy} = 0$

$\epsilon_{lm} = \frac{\varepsilon}{2}(1 - \delta_{lm})$
$\Delta E_i = -\Delta E_j$
$B_{xy} = \frac{kT}{2\varepsilon}\ln\left(\frac{n_i}{n_j}\right)$

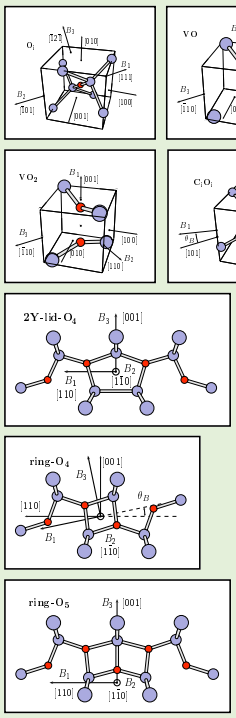
Figure 1. Strain tensor and spectroscopic signal (arbitrary units), for two possible orientations of a 2D defect in a square lattice.

3. Modelling Method

In the present work, *ab–initio* total energy calculations (AIMPRO) using 64 – 128 Si atoms supercells were done. Details of the method can be found elsewhere.[2] The step below were followed for the B–tensor calculations:[3]

1. Volumetric relaxation of the defective supercell — with this step we ensure a traceless strain tensor;
2. Apply positive and negative uniaxial strain on the equilibrium cell. This is done along all symmetry independent Cartesian components, multiplying the unit vectors and atomic positions by $(\delta_{lm} + \epsilon_{lm})$. Everything is then relaxed again;
3. The strain tensor components are evaluated ($B_{lm} = \partial E/\partial\epsilon_{lm}$), and principal directions and values obtained by diagonalisation.

4. Results



		B_1	B_2	B_3	θ_B
O_i (D_{3d})	Obs	−15.2	7.6	7.6	
	Calc	−10.7	5.4	5.4	
VO^0	Obs	−11.1	6.1	4.9	
	Calc	−9.8	5.5	4.5	
VO^-	Obs	−8.4	8.8	−0.4	
	Calc	−6.8	7.8	−0.5	
VO_2	Calc	−11.1	5.9	5.9	
$C_iO_i^+$	Obs	8.6	0.2	−8.8	15
	Calc	8.5	2.4	−11.8	22
TDD_3^+	Obs	10.3	1.9	−12.2	
2Y-lid-O_4^{++}	Calc	10.1	1.9	−13.4	
ring-O_4^{++}	Calc	8.9	3.6	−12.4	15
ring-O_5^{++}	Calc	8.1	4.1	−12.4	

Table 1. Calculated and observed [1] B–tensor components (eV). When the principal directions are not aligned with the crystal, an angle (degrees) is given.

$\nu\,(^{16}O,^{12}C)$		$\Delta\nu\,(^{16}O,^{13}C)$		$\Delta\nu\,(^{18}O,^{12}C)$	
Obs	Calc	Obs	Calc	Obs	Calc
1116.3	**1137.6**	36.4	37.7	1.0	1.0
865.9	**876.1**	23.9	24.5	0.15	0.1
742.8	**759.6**	0.9	0.3	33.4	35.6
588	**593.4**	ND	0.1	3	3.2
539.9	**555.8**	0.2	0.3	0.3	0.2
ND	**544.7**	ND	0.1	ND	0.5
529.6	**544.2**	0.1	0.0	5.2	5.4

Table 2. Calculated and observed LVMs (cm^{-1}) for C_iO_i[5] along with downwards isotopic shifts (cm^{-1}). ND – Not Detected.

5. Conclusions

Several oxygen containing defects were investigated and its B–tensors calculated. We show that the strain tensor can be well reproduced using AIMPRO.

- In the VO defect, the occupation of an anti-bonding orbital on the Si···Si reconstructed bond makes it compressive along $[\bar{1}10]$, in contrast with the neutral defect;
- The strain tensor for VO_2 is reported for the first time;
- The strain tensor for the C_iO_i complex is well reproduced, local vibrational modes were also investigated. The O–relaxed mode at 742 cm^{-1} is only understood by the ring model;[4]
- Both C_{2v} TDD models have strain-tensor components in the right region. However in the ring-O_4, the principal directions are tilted by 15°, in conflict with observations. TDD_n with $n \geq 3$ are unlikely to have the ring-O_4 structure;
- The calculated strain-tensor for all three TDD structures, suggest that a sucessfull model will be composed of two mirrored staggered chains of O atoms with a central core — this arrangement seems to be responsible for the high compressive and tensile character of these aggregates along $[001]$ and $[110]$ respectively.

6. References

[1] G. D. Watkins, in *Early Stages of Oxygen Precipitation in Silicon*, Edited by R. Jones, NATO ASI Series, Vol. 17, p. 1 (1996).
[2] P. R. Briddon, *PhD Thesis*, University of Exeter 1990.
[3] J. Coutinho, R. Jones, P. R. Briddon, S. Öberg, submitted for publication.
[4] R. Jones, S. Öberg, Phys. Rev. Lett. **68**, 86 (1992).
[5] L. I. Murin, V. P. Markevich, *private communication*.