

## COMPUTATIONAL ASPECTS OF CHEMO-ELASTIC PROBLEMS AND VEGARD'S LAW

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Vegard's law states that the length of lattice vectors of a solid solution changes linearly with its chemical composition. In 1921, such a rule was observed for cubic crystals by Vegard [2]. Recently, this law is used widely for many other structures. In the case of low symmetry crystals, the shape of resultant unit cell (spanned on the lattice vectors) depends not only on three lattice parameters,  $a$ ,  $b$ ,  $c$ , but also on three crystallographic angles which are not determined uniquely by the classical (scalar) form of Vegard's law.

The problem is that for lattice structures of low symmetry (arbitrary chosen repère) the mentioned law can be generalized in a different way. In result, various generalizations were proposed in literature, see e.g. a discussion in [1].

In many computational problems the scalar weighting functions are used for averaging of elemental lattice vector bases (Vegard's law), for example:

1. Projection of nodal distortions to Gauss points in the finite element method (FEM),
2. Projection of lattice vectors to the interfacial zone in the phase field method (PFM),
3. Calculation of lattice vectors for solid solutions (the classical application of Vegard's law).

As a matter of fact, it can be proved that all generalizations of Vegard's law proposed as of yet do not determine uniquely the resultant size of unit cell for low symmetry solid solutions. For example, the use of Vegard's law for calculation of lattice vectors of a monoclinic binary system  $Mg_yCu_{3-y}V_2O_8$  should not depend on the choice of the reference structure,  $Mg_3V_2O_8$  vs  $Cu_3V_2O_8$ . From the stoichiometric point of view, the lattice (P 1 2<sub>1</sub>/c 1) of  $Mg_yCu_{3-y}V_2O_8$  and  $Mg_{3-z}Cu_zV_2O_8$  for  $y = z = 1.5$  means one and the same crystal structure  $Mg_{1.5}Cu_{1.5}V_2O_8$ .

In the case of the  $n$ -ary system the strain tensor generalization of Vegard's law can be rewritten in the following form

$$(1) \quad \mathbf{e}_j = \left( \mathbf{1} + \sum_{i=1}^n x_i \boldsymbol{\varepsilon}_{i0} \right) \mathbf{e}_{j_{cr0}}$$

where  $\mathbf{e}_j$ ,  $x_i$ ,  $\boldsymbol{\varepsilon}_{i0}$  and  $\mathbf{e}_{j_{cr0}}$  denote the resulting lattice vectors for the solid solution, the weighting function of the  $i$ -th chemical compound, its strain tensor, and the lattice vectors of a crystal phase chosen as the reference (the reference repère), respectively.

With respect to different definitions of strain tensors and different choice of the reference lattice, the many different generalizations of Vegard's law were published. Contrary to the previous generalizations, the generalized form of Vegard's law presented here is invariant with respect to the choice of the reference chemical composition. From the view point of the projection the nodal distortions to Gauss points, this form of Vegard's law provides the indifference of the Gauss point distortion with respect to the choice of the reference repère. From the viewpoint of the phase field method, the generalization proposed means that the resultant values of the lattice parameters in the interfacial zone are independent of the choice of the reference phase.

#### References

- [1] L. Peters, K. Knorr, P. Schmid-Beurmann, and W. Depmeier. On the volume of solid solutions: an anisotropic approach. *Physics and Chemistry of Minerals*, 33(1):10–16, 2006.
- [2] L. Vegard. Die konstitution der mischkristalle und die raumfüllung der atome. *Zeitschrift für Physik*, 5(1):17–26, Jan 1921.