Tensor form of Vegard's law for crystals of low symmetry

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The rapid development of experimental methods for the analysis of solid solutions in the wide spectrum of chemical composition has opened a demand for constitutive modelling of the effect of composition on the resultant size of crystal lattice. This concerns the prediction of misfit of thin layers deposited in crystal growth processes, phase transitions, as well as many other problems. As of yet, Vegard's law seems to be the main mathematical tool for the quantitative assessment of the experimental data and the ab-initio results both in terms of their agreement with Vegard's law as well as in terms of deviations of such obtained results from this law, see e.g. Germini et al. (1999), Zhou and Usher (2001) among many others.

The classical form of Vegard's law states that the length of lattice vectors of a solid solution changes linearly with its chemical composition. Such a rule was observed in 1921 by Vegard to cubic crystals. Recently, this law is used widely for many other structures in which the crystallographic angles are fixed by symmetry. In the case of low symmetry crystals, the shape of resultant unit cell 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 the mentioned law can be generalized in different ways. Thus, a various generalizations were proposed in literature, see e.g. discussion in Peters et al. (2006). It is easy to show that all the generalizations mentioned do not determine uniquely the resultant size of unit cell for solid solutions in a triclinic lattice. For example, the use of Vegard's law for calculation of lattice vectors of a monoclinic solution $\mathrm{Mg}_y\mathrm{Cu}_{3-y}\mathrm{V}_2\mathrm{O}_8$ should not depend on the choice of the reference bound structure, $\mathrm{Mg}_3\mathrm{V}_2\mathrm{O}_8$ vs $\mathrm{Cu}_3\mathrm{V}_2\mathrm{O}_8$. As a matter of fact, from the stochiometric point of view, the monoclinic lattice (P 1 2_1/c 1) of $\mathrm{Mg}_y\mathrm{Cu}_{3-y}\mathrm{V}_2\mathrm{O}_8$ and $\mathrm{Mg}_{3-z}\mathrm{Cu}_z\mathrm{V}_2\mathrm{O}_8$ for $y = z = 1.5$ is one and the same $\mathrm{Mg}_{1.5}\mathrm{Cu}_{1.5}\mathrm{V}_2\mathrm{O}_8$ crystal structure.

Contrary to the previous finite strain generalizations a generalization of Vegard's law presented here is invariant with respect to the choice of the reference chemical composition of a triclinic lattice.

References

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