

s7.m26.o3 **A Re-Examination of the Bond Valence Model.** F. Liebau^a and X. Wang^{a,b}, ^aUniversität Kiel, Institut für Geowissenschaften, D-24098 Kiel, Germany, ^bUniversity of Houston, Department of Chemistry, Houston, TX 77204, USA. E-mail: liebau@min.uni-kiel.de

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The bond valence model (BVM) was introduced by Pauling [1] and extended by various others. Its present state has been extensively reviewed by Brown [2]. The basic equation of the BVM is

$$V_i = \sum_j s_{ij} = \sum_j \exp[(r_0 - D_{ij})/b], \quad (1)$$

with V_i the valence of the central cation A of a coordination polyhedron (CP) $[\text{AX}_n]$ or the central anion X of a CP $[\text{XA}_m]$, respectively. The s_{ij} are the bond valences of the A–X bonds and D_{ij} their experimentally determined bond lengths. Based on a statistical analysis of a large number of $[\text{AX}_n]$ polyhedra, Brown supposed r_0 to be a constant for each A–X pair. r_0 can formally be interpreted as the bond length of a single bond. It turned out that good fits could be obtained with $b = 0.37 \text{ \AA}$ for all A–X pairs, so that D_{ij} is the only variable in (1). For the vast majority of CPs, the bond valence sums (BVS) calculated with (1) and the values of r_0 and b deviate by less than ca. 0.1 v.u. from the integer number values of the stoichiometric cation valences, $^{\text{stoich}}V$. Sometimes, however, calculated BVS values deviate by up to 1 v.u. from the stoichiometric valences of the central ions A and, in particular, X, respectively.

Based on a statistical analysis of $[\text{LX}_n]$ CPs, where L is a cation with one lone electron pair, Wang and Liebau [3, 4] found that in special cases r_0 is a function of an averaged bond angle $\alpha_i = \angle \text{X-L-X}$ and, more generally, of an asphericity parameter $|\Phi_i|$ such that $r_0 = E|\Phi_i| + F$. (2)

This is in contradiction to the assumption $r_0 = \text{const}$ in the present BVM. The experimental quantities D_{ij} and $|\Phi_i|$ are the two variables for our modified BVM, giving

$$V_i = \sum_j s_{ij} = \sum_j \exp[(E|\Phi_i| + F - D_{ij})/b]. \quad (3)$$

It turns out that for $[\text{LX}_n]$ CPs, Brown's assumption of $r_0 = \text{const}$ restricts the range of applicability of the BVM to undistorted and, at most, slightly distorted CPs. The more distorted a CP the more its r_0 value deviates from being constant and the more its BVS deviates from $^{\text{stoich}}V$. Unfortunately, $|\Phi_i|$ does not describe distortions of the CPs unequivocally. Consequently, BVS values calculated with (3) and E,F values given in [4] occasionally deviate from $^{\text{stoich}}V$ considerably. Replacement of $|\Phi_i|$ by a complete and unequivocal distortion index, DI, will lead to a new basic equation of a general BVM (GBVM) that is applicable to CPs of any kind. At present, however, the mathematical form of DI is unknown. The BVS values calculated with the basic equation of the GBVM are interpreted as a measure of the actual bonding power of the atoms.

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 [4] X. Wang, F. Liebau, *Z. Kristallogr.* **211** (1996) 437.

s7.m26.o4 **Computation of Kinetic and Thermodynamic Characteristics for Close-Packed Crystalline Solutions from Diffuse Scattering and Phase Diagram Data.** T. Radchenko, H. Zapolsky, D. Blavette, V. Tatarenko*, UMR 6634 CNRS Faculté des Sciences de Rouen, Université de Rouen, 76801 Saint-Etienne-du Rouvray Cedex, France, *Institute for Metal Physics NASU, 36 Acad. Vernadsky Blvd., UA-03680, Kyiv-142, Ukraine. E-mail: Taras.Radchenko@univ-rouen.fr

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Microscopic approach is applied to use the data of measurements of time-dependent diffuse-scattering intensity of radiation in a solid solution for calculation of probabilities of elementary atomic-diffusion jumps per unit of time into the different sites of a lattice. Statistical models with one, two or three relaxation times can describe the kinetics of annealing relaxation of short-range order in a binary solid solution. As revealed by means of using the one-relaxation-time model for estimation of both the diffusion coefficient and equilibrium intensity values for Permalloy as an example, the magnetic contribution to the 'mixing' energy of substitutional atoms (in low-spin states) makes easier atomic ordering of this alloy. The presence of Ni and Fe atoms with essentially different spins induces its 'discontinuous-like' phase transition from a paramagnetic state into the magnetic one. As shown, the presence of interstitial C atoms in a substitutional f.c.c.-Ni-Fe alloy increases ferro-magnetic interaction between spins of Ni and Fe atoms, reduces ferromagnetic interaction between spins of Ni, and increases antiferromagnetic interaction between spins of Fe. Besides, statistical thermodynamics of f.c.c.-Ni-Fe and h.c.p.-Ti-Al solutions is investigated within the framework of self-consistent mean-field approach, etc. The method of static concentration waves is used to describe the distribution of substitutional atoms of these close-packed crystals. Energy parameters for Ni-Fe and Ti-Al are evaluated from the experimental data of time dependence of radiation diffuse scattering and phase diagram, respectively. Calculated phase diagram of Ti-Al is in a good agreement with an experimental one. Temperature dependence of long-range order parameter for Ti-Al alloy indicates that disorder-order transition from α phase to α_2 one is a first-order phase transformation.