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Renormalization of bond valences: application to incommensurate intergrowth crystals

BY SANDER VAN SMAALEN

Chemical Physics, Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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Abstract. The bond-valence method may be renormalized to include all atom pairs instead of only nearest neighbours. It is shown that the difference between the present and the original method is very small when applied to conventional crystals. However, only the present method can be generalized to incommensurate crystals, where all interatomic distances beyond a certain minimum occur somewhere in the crystal. The method is applied to the incommensurate intergrowth compound $(LaS)_{1.14}NbS_2$. It is shown that several partial bonds exist between atoms of the mutually incommensurate subsystems.

The bond-valence method is a means of quantifying the relation between bond strengths and interatomic distances (Brown, 1981; O'Keeffe, 1989). The bond valence is usually given as (Brown, 1981)

$$\nu_{ij} = \exp\left[\left(R_{ij}^0 - d_{ij}\right)/b\right] \tag{1}$$

where $b = 0.37$ Å is a universal constant and the parameter R_{ij}^0 depends on the chemical type of the atoms i and j. The distance between atoms i and j is represented by d_{ij}.

The valence of each atom in a structure then follows from (Brown, 1981)

$$V_i = \sum_j \nu_{ij}. \tag{2}$$

The summation is usually restricted to nearest neighbours of i. For known crystal structures, with atoms to which a definite valence can be assigned, (1) and (2) can be used to obtain values for the bond-valence parameters R_{ij}^0. Recently, a compilation of R_{ij}^0 values has been made for a large variety of metal–non-metal pairs (Brese & O'Keeffe, 1991; Brown & Altermatt, 1985).

The restriction in the bond-valence method to nearest neighbours arises from the concept of the chemical bond. However, from consideration of the energy of the complete crystal, there is no reason to restrict oneself to nearest neighbours only (Donnay & Donnay, 1973). Therefore, the method can be redefined to include in (1) all atoms in the crystal. That is, for anion–anion or cation–cation pairs, ν_{ij} is set to zero whereas, for anion–cation pairs, ν_{ij} is given by (1). The rapid convergence of the integral of $r^2 \exp(-r)$ guarantees the convergence of the summation in (2)

To arrive at the same values for V_i, new values for R_{ij}^0 must be derived. As now all cation–anion pairs contribute to the valence, the effect will be to diminish the bond valences assigned to nearest neighbours, thus requiring smaller values for R_{ij}^0. The difference can be estimated from the function $d_{ij}^2 \nu_{ij}$ (the number of neighbours at each distance scales as d_{ij}^2). This function has a maximum at $d_{ij} = 2b = 0.76$ Å, a value much smaller than R_{ij}^0 or than the nearest-neighbour distance. It indicates that most of V_i is already obtained for nearest neighbours [(2)]. For the rock-salt-type structure of LaS and HoS (*Gmelin's Handbook of Inorganic Chemistry*, 1983), this has been con-

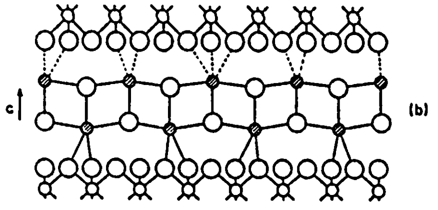

Fig. 1. Projection of the layer structure of $(LaS)_{1.14}NbS_2$ onto the *ac* plane. Large circles denote S atoms; small circles denote Nb atoms and hatched circles represent La atoms. The *a* axes of the subsystems are incommensurate, thus leading to an infinite number of different La—S coordinations. Several of these are indicated by broken lines.

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firmed by calculating the consecutive terms in (2). The terms beyond nearest neighbours together contribute approximately 0.4 and 0.7%, respectively, to V_i. The required correction to R_{ij}^0 will thus be of the order of 1%.

Applied to conventional three-dimensional (3D) translationally symmetric crystals, the difference between the nearest-neighbour bond-valence method and the variant proposed here is negligible, especially when new values for R_{ij}^0 are derived. Conversely, this means that the results obtained with the bond-valence method will not be changed when using the method presented here.

The importance of including more than nearest neighbours in the summation in (2) comes about when the bond-valence method is applied to incommensurate intergrowth compounds (Coppens, Cisarova, Bu & Sommer-Larsen, 1991). This type of crystal is characterized by different sets of atoms being arranged according to different, mutually incommensurate, unit cells (Janner & Janssen, 1980; van Smaalen, 1991*a*). The coordination of one atom is different in each of its unit cells (Fig. 1). A comprehensive description of the distances between atoms of different subsystems is obtained by plotting the interatomic distances as a function of the incommensurate parameter *t* (van Smaalen, 1991*b*). The resulting function is periodic in *t*, where all different coordinations occur in one interval.

As an example, the coordination is plotted of La in the inorganic misfit layer compound $(LaS)_{1.14}NbS_2$ (Fig. 1). There are five nearest-neighbour S atoms in their own subsystem (Fig. 2), but the distances from La to S of the NbS_2 subsystem vary continuously with *t* (Fig. 3). There is no way to classify S atoms of NbS_2 as nearest neighbours and beyond, because the maximum in the shortest La—S distance coincides with the minimum in the next-shortest distance and so on. This is a general property of incommensurate intergrowth compounds.

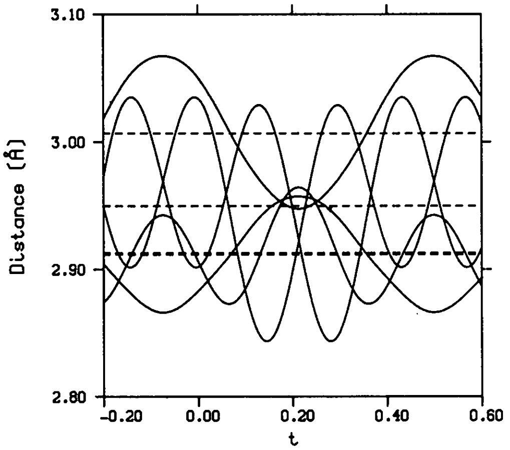

Fig. 2. Coordination of La by the five nearest-neighbour S atoms of the LaS subsystem of $(LaS)_{1.14}NbS_2$. The distance has definite values in the basic structure (dashed lines), but varies with *t* in the modulated structure (solid curves) (after van Smaalen, 1991*b*).

The bond valences corresponding to Fig. 3 are given in Fig. 4. It follows that the atoms with distances between nearest-neighbour distances and the second coordination shell, as usually found in ordinary crystals, do give an appreciable contribution to the total valence of La.

The classical bond-valence method cannot be generalized to intergrowth compounds. Restricting the summation in (2) to a particular number of neighbours (*e.g.* two or three in Fig. 4) will always lead to *t* values where only the contribution of one atom of a pair of atoms at equal distances is included (*e.g.* the coordination defined by points *C* in Fig. 3). The alternative formulation of the bond-valence method proposed here can be directly applied to intergrowth compounds, as all atoms are included in the summation in (2). For actual calculations, the rapid convergence of $r^2\exp(-r)$ makes it possible to use a cut-

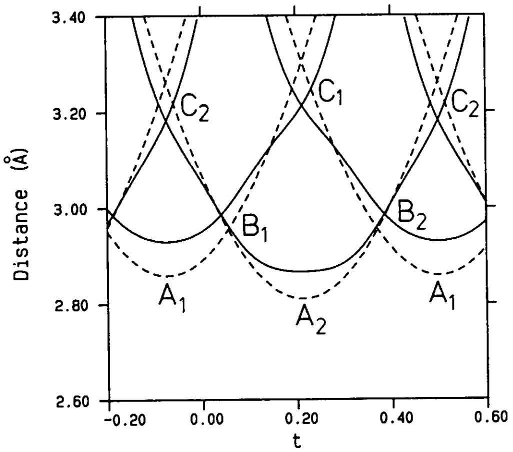

Fig. 3. Distance between La and S atoms of the NbS_2 subsystem. The incommensurateness defines a variation with *t* in the non-modulated structure (dashed curves). Distances in the modulated structure are represented by solid curves.

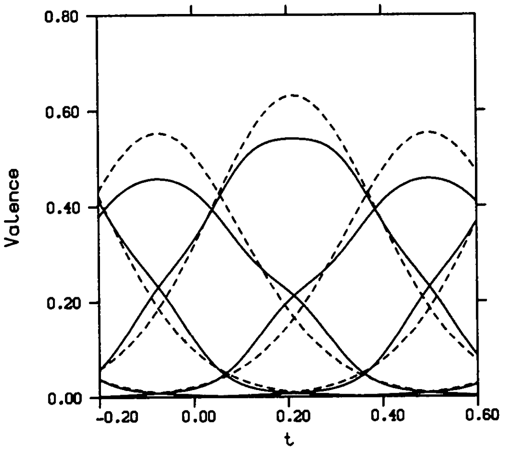

Fig. 4. Bond valences (equation 1) for the distances given in Fig. 3. The parameters R_{ij}^0(La—S) = 2.64 and *b* = 0.37 Å have been used (Brese & O'Keeffe, 1991).

off distance for terms included in (2). With such a cut-off of 5 Å, the valence of La in $(LaS)_{1.14}NbS_2$ is given in Fig. 5. The average value of 3.1 matches the expected valence very well. For renormalized R^0_{ij} values the valence will be even closer to 3.

The contribution from the intrasubsystem interaction to the valence of La adds up to 0.95. Fig. 4 shows that, instead of one or two bonded S atoms, the valence is distributed over three to four La—S interactions, while the fifth S atom still gives a contribution of about 0.01. It follows that the incommensurateness obscures the idea of coordination number. A single bond is replaced by several partial bonds, of varying interaction strength.

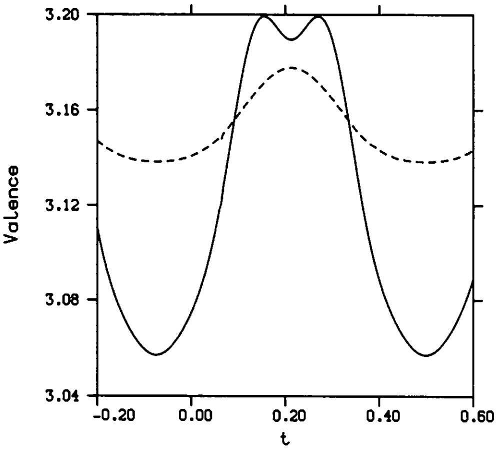

Fig. 5. Valence of La as a function of *t*, obtained by summation of all bond valences at constant *t* (equation 2). The summation includes both Fig. 4 and the bond valences corresponding to Fig. 2.

In conclusion, it is shown that the bond-valence method can be reformulated to include all atom pairs in the summation defining the valence of each atom [(2)]. The effect on the valence in conventional crystals is negligible. However, it makes it possible to define the proper generalization of the bond-valence method to incommensurate crystals.

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