Oxidation numbers as Social Security Numbers: Are they predictive or postdictive?

Hannes Raebiger, Stephan Lany, Alex Zunger, and Raffaele Resta

Cover note on the present contribution

In 2008, a Nature Letter was published by Raebiger, Lany, Zunger entitled "Charge self-regulation upon changing the oxidation state of transition metals in insulators" Nature **453**, 763-766 (2008)]. The paper dealt with a physicists-view on the peculiar phenomenon that the physical charge around a transition metal atom in covalent medium seems to be nearly constant, independently of the charge added to the system as a whole. A corresponding News &Views article entitled "Charge states in transition" was written in Nature by R. Resta, (ibid. p. 735).

These two papers have created significant interest in the chemistry community, including an Essay in Angewandte Chemie , published by Jansen and Wedig (JW), entitled "A Piece of the Picture - Misunderstanding of Chemical Concepts" (M. Jansen and U. Wedig, Angew. Chem. Int. Ed., 47, 10026-10029 (2008)]. In this essay, JW expressed opinions about our work, opinions which we find unwarranted if not unfounded. The authors of the Nature paper on which this Angewandte Chemie essay commented were not approached by the journal to solicit a comment or rebuttal. After the publication of the Essay, we have thus submitted to Angewandte Chemie a manuscript that provides our response to this criticism, and in fact attempts to go to the roots of the concepts of "Physical Charge" and "Oxidation State" underlying this controversy. The manuscript entitled: "Oxidation numbers as Social Security Numbers: Are they predictive or postdictive?" also includes new examples that illustrate our view of the difficulties created by the traditional chemistry concept of Oxidation States and the problem of assigning unambiguously oxidation numbers as prediction, rather than being a succinct way to designate ex-post-facto one's view on bonding once this information in gleaned from independent sources. The paper emphasizes that Charge Self-regulation, not charge-transfer is at work in such bonded systems. Our manuscript was, however, rejected by the Editor of Angewandte Chemie on the grounds that it is not of interest to the community. We beg to differ, and post it here to provide access for interested readers.

Oxidation numbers as Social Security Numbers: Are they predictive or postdictive?

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The Oxidation Number (ON) of an atom within a molecule or solid is a well defined quantity in chemistry (assuming a consistent set of rules are followed), with a long and distinguished history of usefulness. The question revisited recently [1–3] is whether it carries a predictive physical meaning in its own right beyond being an unquestionably convenient label. For example, whereas the color of compounds physically reflects the relative energetic positions of occupied vs. unoccupied, dipole-coupled energy levels, can the color be explained [4] by the oxidation state of the central ion? Can the different colors of various Mn compounds be predicted or explained in terms of their oxidation numbers [e.g. pink Mn(II) vs. black Mn(IV) vs. purple Mn(VII)], or does such understanding entail knowledge of the occupancy of the hybridized d bands, a knowledge not provided by the ON (but possibly labeled by it, once such understanding is independently acquired)? Also, the photoemission core shifts of an atom within a molecule (e.g. relative to a reference of the atom in its elemental form) physically represent the balance of all electrostatic charges in the system as felt by that atomic site. Can this balance be predicted or explained [1] by the oxidation number of the ion, or is the latter only a convenient short-hand notation (often assigned *ex post facto*) for an otherwise possibly nontrivial electronic structure? In other words, the central question here is whether the Oxidation Number is predictive, in its own right, or does it act functionally as a Social Security Number that conveniently labels a person, but by itself (e.g., without additional access to financial, medical, or educational records, or psychoanalysis) does not lead to understanding of the person.

The concept of Oxidation Number is connected with the idea of charge transfer [5]. It is commonly defined as [2]

$$\mathrm{ON(ion)} = Q(\mathrm{compound}) - \sum Q(\mathrm{ligands})\,. \qquad (1)$$

Here, the first term is the well-defined physical charge of the system as a whole. For molecules, it equals the net ionic charge, e.g $+1$ for $[NH_4]^+$ or -1 for $[BH_4]^-$; for solids such charges are commonly induced via carrier doping. The second term corresponds to the sum of the fictitious effective charges on ligands. Its magnitude could be guessed from the relative electronegativities of the ligand vs. central ion. For example, it is $+4$ for the hydrogen H_4 ligand in $[NH_4]^+$ and -4 for the hydrogen H_4 ligand in $[BH_4]^-$. The central problem surrounding the ON, which we discuss here, is already encoded in Eq. (1): It incorporates, as the first term a *physical* (observable) net charge, but the second term is a *fictitious* set of charges whose magnitude, as will be illustrated, lies to a large extent in the eyes of the beholder. Indeed, the determination of Q(ligand) might require sometimes a deeper understanding of the ligand-to-ion bonding than supplied by the electronegativities, since the thermochemically determined electronegativity may not always reflect the correct ligand vs central ion *orbital order*. Regardless of these ambiguities, the ON of Eq. (1) has proven to be a very useful construct in chemistry, having sufficient flexibility to accommodate rather sophisticated viewpoints and results. The discussion surrounding it does not question its usefulness, but rather if it can be interpreted simply in terms of a *physical* charge-transfer; in other words, is the ON pre-dictive or post-dictive?

In two recent contributions in *Nature* [6, 7] we have addressed the concept of oxidation number from a rather non-standard viewpoint (see, however, precursor work by Haldane and Anderson in Ref. 8). This induced the *Nature* journal's copywriter into advertising our conclusions as "heretical" and dispelling a "myth". Not surprisingly, articles decorated by such provocative copywriter headlines have triggered understandable reactions by some members of the chemistry community [1, 4]. What is surprising, is that our message has been regrettably missed. We thus take this opportunity to discuss the underlying concepts from our somewhat different point of view as physicists, with the hope that this cross-cultural discussion will enhance our mutual understanding of such important concepts.

Contrary to Jansen and Wedig's (JW's) claim, neither Raebiger, Lany and Zunger (RLZ) [6] nor Resta [7] were calling into question the usefulness of ON's. In fact, we are neither stating that "the concept of oxidation state is meaningless" nor that it doesn't "refer to something real", as our critics claim [4]; we do state—perhaps "heretically"—that the *real* experimental signatures associated with the oxidation number of a given element cannot be explained in terms of a charge-transfer model, not even as a first approximation. Indeed, we do question whether it makes sense to correlate atomic charges with oxidation states. While our answer is: "basically it doesn't", the answer of JW (Ref. 1) to the same question is: "yes, it does!" (exclamation point in the original). This answer, and the criticism embedded in it is fur-

ther cemented in JW's choice of the title of their paper ("...Misunderstanding of Chemical Concepts"), which is exciting, but does not have the additional virtue of being also true.

The fact that the ON may not represent a physical charge was indeed suspected by Pauling in 1948 [9] when he offered a postulate, saying "It has seemed to me likely that in general all of the atoms in the complex that constitutes stable chemical substances have resultant electrical charges smaller than those shown by these most electropositive and electronegative atoms in their compounds with one another, and I have accordingly formulated the *postulate of the essential electrical neutrality* of atoms; namely, that the electronic structure of substances is such as to cause each atom to have essentially zero resultant electrical charge." This postulate was eloquently phrased by R. Hoffmann in 2001 [10]: "Is there really a charge of +6 on the iron in the $[FeO_4]^{2-}$ and −2 charge in $[Fe(CO)_4]^{2-}$? Of course not, as Pauling told us... Such large charge separation in a molecule is unnatural." Such metaphysical expressions of what atoms really desire, and what's natural for them and what's not were frequently supported by quantum chemical calculations of atomic (e.g. Mulliken) charge [1, 2, 11]. Despite the frequently repeated disclaimers on the well-known arbitrariness in apportioning molecular charges into atomic constituents, such charges tend always to be much smaller than the oxidation numbers obtained by Eq. (1). Thus, formal Oxidation numbers are not physical entities. This is all well-known and not surprising; that oxidation numbers are formal quantities and not physical entities is indeed common undergraduate knowledge, and certainly not the subject of the recent paper in *Nature* [6].

What is surprising is that in a recent 2008 Essay in Angew. Chem. [1], JW suggest that "a specific oxidation state can be correlated to real properties". The authors further ponder the question "does it even make sense to correlate atomic charges with oxidation states?", and answer a resounding "yes". This is not the only recent assertion of the possible predictive significance of ON's vis a vis real properties: physical models of interacting point charges *constructed according to the ON's* are often employed to explain structural anomalies in solids [12–15]. Even Pauling, just after postulating in 1948 the electro neutrality principle, proceeds to describe the difference of white and gray tin as a literal transfer of electrons between different tin atoms [9]. JW say that RLZ "preach to the saved". Are some, perhaps still in need of saving?

Indeed, the discussion of JW of the uniqueness of ON determination leads them to a conceptual entanglement. After reviewing two centuries of chemistry, JW say that ON are defined by electron count, thus giving them actual physical meaning: "*it is possible to determine differences in oxidation states as whole numbers through redox titrations. A particular oxidation state of a transition metal can be attributed a specific number of unpaired electrons*". JW next continue to destroy the very physical meaning of ON, saying: "The only factor, then, that could lead to a change in oxidation state is the total electron count, *provided that the effect is localized on individual atoms*". Since, they recognize that the charge can not be fully localized on a given site except in ideal ionic limit, they say: "*Therefore, the allocation of different oxidation states for the transition metal atoms upon variation of the total electron count is highly questionable*". Can this statement be perceived as heretical to the Canon of chemistry? They giveth (a meaning to ON), then they taketh it away.

Given the sense of self-entanglement of some of the concepts surrounding the discussion of the physicality of ON, RLZ have taken [6] a somewhat different route: examine the physical charge PC around a central ion as a function of changing the system's charge Q(compound) of Eq. (1). Changing Q(compound) mimics what electrical doping of solids is doing—adding net charge via substitution of ionizeable impurities, thus shifting the Fermi energy. According to Eq. (1), a change of the electron count [i.e., a change of Q(compound)] necessitates that the ON(ion) of one ion must change. Will the physical charge PC(ion) around the ion change too? What RLZ have found was that PC(ion) stayed nearly constant as Q(compound) was varied.

The study of RLZ involves three significant ingredients that differ somewhat from analogous studies in chemistry.

First, RLZ look at actual charge distribution that resides around an ion, rather then at formal constructs such as ON. The standard objection that, the definition of a charge requires specifying a radius and that the latter is essentially non unique, is circumvented by considering [16] the Charge Accumulation Function $Q(R)$

$$Q(R) = \int_0^R \mathrm{d}r\ \rho(r)\ , \tag{2}$$

that tells you the amount of charge enclosed in a sphere of radius R, where R is a continuous variable, and $\rho(r)$ is the total charge density. $Q(R)$ for Cr in various oxidation states (+2, +3, +4, +5 in GaAs and +2, +3, +4 in MgO) is given in Fig. 1, and the reader may look at any R value he/she wants. (Luo et al. gave a similar plot for Mn with ON's +3 and +4 in $CaMnO_3$ and other materials, including the metallic bulk Mn [17].)

Second, RLZ focus on changes in such charge, for a system embedded in a reservoir. Even if the static charge around a bonded atom [such as Q(ligand)] is ill defined, the charge which flows in or out of the reservoir (such as Q(compound)) is well defined. Indeed, already in the very first lines of Ref. 7 we have stressed that, quite generally, charges in transit are robust while static charges are ill defined. This applies to both molecules and solids. In molecules, displaced charges (i.e. 'in transit') are measured by either "atomic polar tensors" or infrared charge tensors [11], and the concept is unambiguous.

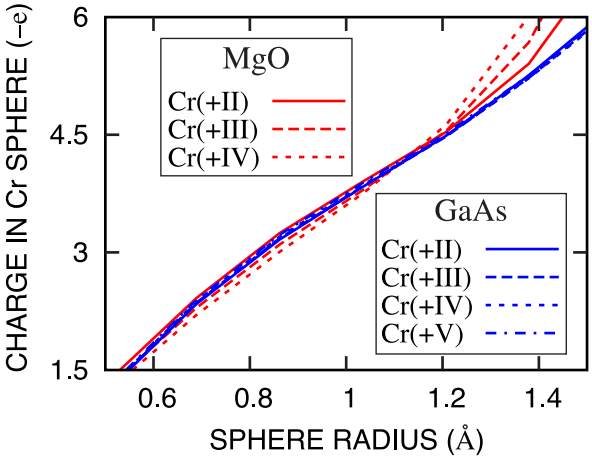

FIG. 1: Charge accumulation function $Q(R)$ for Cr in GaAs (blue) and MgO (red) in various oxidation states. Notice that, counter-intuitively, at large radii $R > 1.2$ Å, Q *increases* upon increasing oxidation numbers in MgO, due to the inward relaxation of the neighboring oxygen atoms.

The condensed-matter analogue is that, while the static atomic charges are ill defined, the charges displaced by any perturbation are unambiguous [18]. At the root of this is the continuity equation, and the fact that currents (either steady-state or transient) *are* well defined in condensed-matter theory. In some cases the charges in transit are quantized, as in electrolytic cells [19] or in the QHE [20], in some case are not, as for the Born effective charges in polar crystals [21], and, more generally, for the charge displaced in any dielectric phenomenon [18].

Third, RLZ used standard definitions [5] [formally Eq. (1)] to scan the ON of a transition metal impurity by changing the system charge on the compound. For example, in the case of a Cr impurity in MgO, the Mg and oxygen ions in pristine MgO have oxidation numbers of +2 and −2, respectively. Substitution of a single Mg in $Mg_{64}O_{64}$ by Cr produces a fully occupied valence band plus new impurity levels with t and e representations in the host band gap. (These orbitals are hybrid levels, and thus not associated with any single site such as Cr or O.) When these levels are occupied by 4 electrons (configuration t^3e^1), the system remains charge-neutral, meaning that no charge has flown in or out from the reservoir: hence Q(compound) is zero, and the ON of Cr is +2. We then remove an electron from the system by ionizing a gap level, thereby changing the integer physical charge Q(compound), which requires a change of the ON, according to Eq. (1). The question is, which atom accommodates the change. One may choose to change ON(Cr) from +2 to +3, ON(O) from −2 to −1, or ON(Mg) from +2 to +3. Obviously, changing either ON(O) or ON(Mg) breaks an octet, so ON(Cr) seems like the best guess. Note that there is no implication that this charge is removed from the TM site or any other site: the charge goes wherever the variational principle, implicit in all quantum calculations, tells it to go. The resulting calculated electronic configuration and lattice relaxation [6] tell us that, the crystal field resonances are occupied by 3 electrons (configuration t^3e^0), whereas the LUMO is mostly e like, the Cr magnetization has changed roughly by an integer from 4 to 3 Bohr magnetons, there was an inward relaxation shortening the Cr–O bond by ∼0.05 Å, and the average core electrostatic potential changes in accordance to XPS shifts for *known* [22] variations in ON(Cr), all in support of the guess that Cr changes its ON. Indeed, once the above *known signatures* are identified, one can assign ON's *ex post facto*, regardless of where the variational principle distributes *physical charges*.

It so happens that calculations of periodic solids require that each cell be formally charge neutral, or else the total (electrostatic) energy per cell diverges. JW were confused about this technicality, fearing it clouds the results. We emphasize here that the effect of the background is well-understood and robust [23], and that it does not cloud the calculated electron charge density. Image charge effects to total energies due to periodic boundaries [23–25] are naturally taken into account appropriately [23]. A Green's function calculation, for an isolated impurity in an otherwise infinite matrix [16, 26], or a cluster calculation (with appropriate termination) would provide the same results. Furthermore, the correction is actually implemented in the potential, not in the actual electron-density [23]. Therefore the calculated electronic charges do not contain any spurious contribution from the background. Thus, the only objection of JW regarding whether the calculation of RLZ amounts to changing the ON or not can be unambiguously resolved at the positive.

The central result of the study of RLZ was *not* that PC(ion) is different from ON(ion), as suggested by the *Nature* copywriter offering [7] in Resta's cover piece the headline "*Transition metals come in different oxidation states with different electric charges. So at least we are told at school. Detailed calculations lead to a heretical conclusion—those variable charge states are a myth...*" "*What is the relationship between static electric charges and oxidation states? None.*" Indeed, the central result of the RLZ study was that there exists a feedback mechanism that balances the physical charges in response to changing the net charge Q(compound) of the system. The change (re-hybridization) is so as to compensate this perturbation, i.e. it is a self-regulating response (in the Le Chatelier sense). Charge self-regulation, not charge transfer is the appropriate description of what happens when the system charge is altered. The change of the ON is generally not reflected by a change of the physical atomic charges. The fact that ON's often correlate with interatomic distances, Jahn-Teller distortions, photoemission core shifts, etc., is coincidental rather than causal.

TABLE I: Properties of the neutral (Q(compound)$= 0$) and charged (Q(compound)$= -1$) Mn acceptor in zincblende GaN and GaSb: The point group symmetry, the sphere-integrated (R = 1.36) local magnetic moment and local charge, and the ON deduced from these properties. [These calculations were done in GGA+U with standard parameters for Mn (U = 4eV, J = 1eV)].

	symmetry	m [μ_B]	Q [e]	ON
GaN:Mn^0	tetragonal (D_{2d})^a	3.8	5.9	+III
GaN:Mn^{-1}	tetrahedral (T_d)	4.4	5.9	+II
GaSb:Mn^0	tetrahedral (T_d)^b	4.4	5.6	+II
GaSb:Mn^{-1}	tetrahedral (T_d)	4.4	5.6	+II

^{a} the aspect ratio of the tetragonal distortion is 0.94 (-6%)
^{b} approx. T_d symmetry with a non-symmetric distortion of less than 1%.

This study of RLZ highlights the fact that the ON is pre-dictive only to the extent that the second term in Eq. (1), the fictitious charges on the ligands *can be assigned a priori*, rather then post-dicted *after* the Schrödinger's equation has been solved. We give here a few examples illustrating how ON's can be assigned *only after* electronic structure calculations revealed what's happening.

Example 1, Mn in GaN and GaSb. Here we consider substitution of the cation site of common, fourfold coordinated zincblende materials by Mn. In both cases, this leads to a partially-occupied t_2 impurity level in the band gap [6, 27]. Additional occupation of this level, (e.g., by doping with donor impurities such as Se or Cl) creates the "negatively charged $\mathrm{Mn}_{\mathrm{Ga}}^{-}$" for which we obtain ON = +2 from Eq. (1). Without such additional doping of this gap level, we have the "charge-neutral $\mathrm{Mn}_{\mathrm{Ga}}$ impurity", for which, using Eq. (1) and applying common rules [5], one would assign ON = +3 for Mn in both GaN and GaSb .

However, contrary to this generic picture, electronic structure calculations [6, 27] reveal an important difference between the behaviors of Mn in GaN vs GaSb. As shown in Table I, in GaN, the expected change of the ON due to adding electrons to the entire system [i.e., changing Q(Compound) from 0 to -1] is reflected by a change of the point group symmetry of $\mathrm{Mn}_{\mathrm{Ga}}$ and the local magnetic moment of Mn, consistent with a change of the Mn ON from +3 (d^4) to +2 (d^5). In GaSb, however, such a change does not occur, and from the symmetry and the magnitude of the local moment, we must conclude that the ON of Mn is +2, irrespective of the change of Q(compound). Thus, in order to accommodate this realization by Eq. (1), we then need to assume a -2 ligand charge for Sb, instead of the usual -3 ligand charge. Thus, GaSb:Mn can be described has a "d^5+ hole" configuration, in contrast to the d^4 configuration of GaN:Mn [27]. We see that *ex post facto*, Eq. (1) can accommodate the knowledge gained from electronic structure calculations, but this truth is not forced upon us a priori by the intrinsic concept of ON itself.

Example 2, substituting Mg by Li in MgO. Here, Mg, Li, and O are elements, which by convention [5] rarely exist in oxidation states other than +2, +1, and -2, respectively. In the charge neutral case, however, the sum of these "normal" ONs in the supercell $(\mathrm{Mg}_{n-1},\mathrm{Li})\mathrm{O}_n$, does not add up to Q(compound)$= 0$, and one needs to either (arbitrarily) pick one atom to have a non-standard oxidation number, or assume a delocalized (free carrier like) hole state in the MgO host. Experiment [28] and theory [29] tell us that in the charge neutral case, one of the six oxygen atoms around the Li site is oxidized to ON(O)$=-1$ in the charge neutral case, whereas all other O atoms remain in the "natural" ON(O)$=-2$. Here, electron doping then leads to changing the ON of this one O ligands from ON(O)$=-1$ to ON(O)$=-2$.

Example 3, Fe in In_2O_3. Without additional doping ("charge neutral") $\mathrm{Fe}_{\mathrm{In}}$ in $\mathrm{In}_2\mathrm{O}_3$ exhibits a "d^5 configuration" and the corresponding ON = +3. Additional doping by acceptors [i.e, lowering Q(Compound) by removing electrons from the entire system] shows that there exists also a positively charged $\mathrm{Fe}_{\mathrm{In}}$ state [30], for which one might assume ON = +4 according to Eq. (1). However, similar to the $\mathrm{Mn}_{\mathrm{Ga}}^{0}$ case in GaSb, here $\mathrm{Fe}_{\mathrm{In}}^{+}$ in $\mathrm{In}_2\mathrm{O}_3$ largely maintains its d^5 configuration, and the hole added to the system by additional acceptor doping is located mostly in the dangling-bond-hybrid state [6] at the oxygen ligands.

These examples illustrate that, an unambiguous assignment of oxidation states requires a detailed analysis of the electronic structure, and that in many cases the ON based on an ad hoc assumption of the ligand charge leads to an even qualitatively wrong picture.

Example 4, transition metal borane complexes. Such difficulties in a priori assignment of ON's arise also in the chemistry of transition metal borane complexes, where, as described by Parkin [3], ON's lack an unambiguous definition. Assigning the ON's, one needs to heterolytically chop up the compound into ions, which turns out to be far from simple in the case of a covalent bond between a trivalent BX_3 ligand and a transition metal atom M: should the two electrons from the covalent bonding orbital be assigned to M or BX_3? Assigning the (fictional) charges, one may (i) give the two electrons to the more electronegative atom, or (ii) decide to remove the ligand in a closed shell configuration. Even more ambiguity is added to (ii) by the fact that $[\mathrm{BX}_3]$ exists in two reasonable closed shell configurations, and to (i) by the fact that Boron's electronegativity of 2.0 lies between e.g. Co (1.8) and Rh (2.2), which could be expected to behave very similarly, but would be assigned different ONs.

Example 5, Ba_3Pt_2, as discussed by JW. Similar examples regarding the need to figure out the detailed electronic structure before an ON label can be properly assigned was given by by JW in their Essay, when they

explain how the ON was deduced for Pt salts, saying: "*the actual Oxidation states of the elements are not at all intuitive; only a precise analysis of the bands at the Fermi surface (e.g delocalized electrons in the interlayer region of Ba_2Pt) and the covalent interactions between Pt atoms (one dimensional chains in $BaPt$,Pt_2 dumbbels in Ba_3Pt_2) lead to a consistent description*".

Thus, in answering the question posed at the top of this paper about the physical meaning of the ON, we find that the a priori assigned ON often does not reflect the electronic structure of the transition metal and its immediate neighbors (ligands), which largely determines properties like color, bond distances and coordination geometry. However, once the (often nontrivial) electronic structure is understood in its own right, the ensuing insights can then be baptized under the label ON.

JW express an ideological distrust of quantum mechanics with its underlying use of wavefunctions both because "*the exact wavefunctions as a solution to the Schrödinger equation is practically impossible to determine*", and because it is difficult to determine system-to-system trends because "*each chemical system is described by its own wavefunction*". However, as illustrated by the examples above, a quantum mechanical calculation based on a reasonably good approximation to the exact Hamiltonian it is often indispensable to understand even the basic chemistry of the compound, including the assignment of ON. As Pauling put it in his 1948 prophetic paper, "*If scientific progress continues, the next generation may have a theory of valency that is sufficiently precise and powerful to permit chemistry to be classed along with physics as an exact science.*"

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[1] M. Jansen, U. Wedig, *Angew. Chem. Int. Ed.* **2008**, 47, 10026.
[2] G. Parkin, *J. Chem. Ed.* **2006**, 83, 791.
[3] G. Parkin, *Organometallics* **2006**, 25, 4744.
[4] P. Ball, *Chemistry World* **2009**, Vol 6, No 1.
[5] http://goldbook.iupac.org/O043565.html
[6] H. Raebiger, S. Lany, A. Zunger, *Nature* **2008**, 453, 763.
[7] R. Resta, *Nature* **2008**, 453, 735.
[8] F.D.M. Haldane, P.W. Anderson, *Phys. Rev. B* **1976**, 13, 2553.
[9] L. Pauling, *J. Chem. Soc.* **1948**, , 1461.
[10] R. Hoffmann, *American Scientist* **2001**, 89, 311.
[11] J. Meister, W. H. E. Schwarz, *J. Phys. Chem.* **1994**, 98, 8245.
[12] E Wawrzyńska, R Coldea, E. M Wheeler, T Sörgel, M Jansen, R. M Ibberson, P. G Radaelli, M. M Koza, *Phys. Rev. B* **2008**, 77, 094439.
[13] E Wawrzyńska, R Coldea, E. M Wheeler, I. I Mazin, M. D Johannes, T Sörgel, M Jansen, R. M Ibberson, P. G Radaelli, *Phys. Rev. Lett.* **2007**, 99, 157204.
[14] X. S Xu, M Angst, T. V Brinzari, R. P Hermann, J. L Musfeldt, A. D Christianson, D Mandrus, B. C Sales, S Mcgill, J.-W Kim, Z Islam, *Phys. Rev. Lett.* **2008**, 101, 227602.
[15] M Angst, R. P Hermann, A. D Christianson, M. D Lumsden, C Lee, M.-H Whangbo, J.-W Kim, P. J Ryan, S. E Nagler, W Tian, R Jin, B. C Sales, D Mandrus, *Phys. Rev. Lett.* **2008**, 101, 227601.
[16] A. Zunger, U. Lindefelt, *Solid State Commun.* **1983**, 45, 343. and A. Zunger in Solid State Physics Vol. **39** (eds Seitz, F., Turnbull, D. and Ehrenreich, H.) 275–464 (Academic, New York, 1986).
[17] W. Luo, A. Franceschetti, M. Varela, J. Tao, S. J. Pennycook, S. T. Pantelides, *Phys. Rev. Lett.* **2007**, 99, 036402.
[18] R. Resta, *Rev. Mod. Phys.* **1994**, 66, 899.
[19] J.B. Pendry, C.H.J. Hodges, *J. Phys. C* **1984**, 17, 1269.
[20] D.J. Thouless, *Topological Quantum Numbers in Nonrelativistic Physics* (World Scientific, Singapore, 1998).
[21] Ph Ghosez, J.-P Michenaud, X Gonze, *Phys. Rev. B* **1998**, 58, 6224.
[22] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Handbook of X-ray Photoelecetetron Spectroscopy*, Ed. J. Chastain (Perkin-Elmer, Eden-Prairie 1992).
[23] S. Lany, A. Zunger, *Phys. Rev. B* **2008**, 78, 235104.
[24] M. Leslie, M.J. Gillan, *J. Phys. C* **1985**, 18, 973.
[25] G. Makov, M.C. Payne, *Phys. Rev. B* **1995**, 51, 4014.
[26] G.A. Baraff, M. Schluter, G. Allan, *Phys. Rev. Lett.* **1983**, 50, 739.
[27] P. Mahadevan, A. Zunger, D.D. Sarma, *Phys. Rev. Lett.* **2004**, 93, 177201. P. Mahadevan, A. Zunger, *Phys. Rev. B* **2004**, 69, 115211.
[28] O.F. Schirmer, *J. Phys.: Cond. Matter* **2006**, 18, R667.
[29] C.R.A. Catlow, P.H. Poole, P.G. Wolynes, J.L. Finney, *Phil. Trans. R. Soc. A* **2005**, 363, 913.
[30] H. Raebiger, S. Lany, A. Zunger, *Phys. Rev. B* **2009**, 79, 165202.