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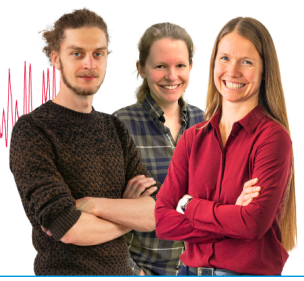

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ABSTRACT

The strongest driving forces for the formation of binary compounds (e.g., Na_2O, MgO, Al_2O_3, and SO_3) are related to the octet rule (formation of closed electronic shells) and charge redistribution as a result of electronegativity differences. Here, we investigate the driving forces behind the reactions of these binary compounds with each other, traditionally described in the language of acid-base interactions. For example, why do Na_2O and SO_3 (both of which have a closed-shell electronic structure) react with each other forming Na_2SO_4? In addition to Na_2SO_4, we also consider the processes of formation of Mg_2SiO_4 and $MgAl_2O_4$, tracking changes in chemical bonding characteristics and ionic charges of the constituent atoms. We show that in such acid-base reactions, electrons move from the atomic states with higher energies (from the basic oxide-forming element) to atoms with lower-energy states. This happens by changing the degrees of ionicity of bonds, without disrupting the closed-shell electronic structure.

I. INTRODUCTION

What are the driving forces of compound formation? Why do some elements (e.g., Na and Cl) form compounds while others (e.g., Mg and Fe) do not? The history of this question is more than 200 years old, and it started with the idea of Davy and Berzelius that "electropositive" (metals) and "electronegative" (nonmetals) elements tend to form stable compounds with each other. This idea has evolved into the concept of electronegativity, the idea being that a large difference in electronegativities stabilizes the chemical bond and two elements with very different electronegativities tend to form stable binary compounds. This becomes understandable because, according to Mulliken's definition, electronegativity is equal to minus the chemical potential of the electron in an atom: energy lowering due to electron transfer from atoms with lower electronegativity (higher chemical potential of the electron) to more electronegative ones stabilizes the compound.

We can upscale this question to more complex systems. What are the driving forces behind the formation of ternary and quaternary compounds from binary ones? Why does CaO react with SiO_2 to form $CaSiO_3$ and Ca_2SiO_4, while not reacting with Na_2O? Classical chemistry answers this by invoking the theory of acids and bases: CaO and Na_2O are both basic oxides, whereas SiO_2 is an acidic one: bases tend to react with acids, but not with other bases. Lewis' theory of acids (which he interpreted as entities accepting electrons) and bases (donating electrons) suggests, once again, that redistribution of the electrons is the key. It is possible to estimate the electronegativity of a compound as the arithmetic mean of the electronegativities of its constituent elements; indeed, oxides with high electronegativity (e.g., SiO_2) will be acidic and those with low

electronegativity (e.g., Na_2O and Ca_2O) will be basic. However, it is not immediately clear what kind of charge redistribution can occur between CaO and SiO_2, given that in the examples, these oxides and the resulting silicates are closed-shell. In other words, where can electrons go if all bonding orbitals are already occupied?

The nature of chemical bonding in compounds remains a complex and often ambiguous subject, lacking a definitive quantitative approach. Even for binary compounds, where only two types of atoms interact, accurately assessing the degree of ionicity or covalency in chemical bonds presents significant challenges. From a theoretical perspective, several methods have been developed to address this issue. These include straightforward calculations and analysis of electronegativities,[1] Löwdin or Mulliken population analysis, Bader's atoms in molecules method,[2] natural population analysis,[3] and Crystal Orbital Hamilton Population (COHP)[11,12] analysis. Each method has its strengths and limitations, varying in the degree of basis set dependence and applicability to crystals or molecules.

Recently, we have proposed a method[4] that, based on the results of first-principles calculations, allows the partitioning of the one-electron energy of a chemical bond into covalent and ionic components. Our method combines the advantages of Löwdin population analysis and COHP while addressing the issue of basis dependence by using Wannier functions—a rigorous and well-established framework for describing localized electronic states in crystals. This approach has been successfully applied to a series of binary compounds.[4]

In this study, we extend the application of our method to crystalline compounds composed of three elements. Our investigation focuses on the evolution of atomic charges and the degree of covalency of chemical bonds during the formation of ternary oxides from their binary precursors.

In particular, we examine three cases of ternary compound formation: Mg_2SiO_4 from $2MgO + SiO_2$, $MgAl_2O_4$ from $MgO + Al_2O_3$, and Na_2SO_4 from $Na_2O + SO_3$.

Our focus is not on predicting stable stoichiometries but on uncovering the electronic mechanisms that drive the formation of ternary compounds from binary oxides. This complements stability-based approaches by answering why certain reactions occur between already stable compounds.

By tracking charge transfer and evolution of bonding upon the formation of complex oxides or salts, we reveal how local bonding adjustments—without disrupting closed-shell states—drive these transformations. This complements stability-based approaches by addressing the fundamental 'why' behind the observed reactivity.

II. METHOD

In order to determine the degrees of ionicity and covalency of bonds, the Wannier function approach was used. This computational scheme has previously been successfully applied to study the properties of chemical bonds in a series of compounds.[4] The band structure calculations were performed using the GGA (generalized gradient approximation)[5] as implemented in the Quantum Espresso package.[6,7] We used pseudopotentials from the standard solid-state pseudopotential library set with the exchange–correlation functional in the PBEsol form (SSSP PBEsol Precision v1.3.0).[8] The energy cutoff for the plane wave function and charge density expansion was set to 50 Ry and 400 Ry, respectively. An effective Hamiltonian H_{DFT} was constructed using the basis of atom-centered Wannier functions, as described in Ref. 9.

Let us consider a binary compound AB. Its binding energy, E_{bond}, is typically defined as the difference between the total energy of the compound per formula unit at its equilibrium volume V_0 and the sum of the energies of the free atoms A and B at infinity,

$$E^0_{\mathrm{bond}} = E^0_{\mathrm{AB}} - (E^\infty_{\mathrm{A}} + E^\infty_{\mathrm{B}}). \tag{1}$$

Solving the DFT problem, we obtain a set of electronic eigenvalues and eigenfunctions, $\varepsilon^\alpha_{\vec{k}}$, $|\psi^\alpha_{\vec{k}}\rangle$, and the electronic Hamiltonian can be expressed as

$$\hat{H} = \sum_{\vec{k}\alpha} |\psi^\alpha_{\vec{k}}\rangle \varepsilon^\alpha_{\vec{k}} \langle\psi^\alpha_{\vec{k}}|. \tag{2}$$

The corresponding density matrix operator is

$$\hat{\rho} = \sum_{\vec{k}\alpha} |\psi^\alpha_{\vec{k}}\rangle n^\alpha_{\vec{k}} \langle\psi^\alpha_{\vec{k}}|, \tag{3}$$

where $n^\alpha_{\vec{k}} = \theta(E_{\mathrm{Fermi}} - \varepsilon^\alpha_{\vec{k}})$.

Wannier functions $|W_i\rangle$ are calculated through a unitary transformation of the set of Bloch functions $|\psi^\alpha_{\vec{k}}\rangle$,

$$|W_i\rangle = \sum_{\vec{k}\alpha} |\psi^\alpha_{\vec{k}}\rangle \langle\psi^\alpha_{\vec{k}}|\varphi_i\rangle, \tag{4}$$

where $|\varphi_i\rangle$ are trial atomic wave functions, and thus, $|W_i\rangle$ also possess the same atomic orbital symmetry.

A basis set $|W_i\rangle$ defined by Eq. (4) is then orthonormalized. One can say that Wannier functions $|W_i\rangle$ are "natural" atomic orbitals for the electrons in a crystal, and index i runs over the atomic quantum numbers nl (1s, 2s, 2p, 3p, 3d, ...). Equation (4) is one of the possible choices for the unitary transformation of the Bloch function set $|k\rangle$, chosen to obtain Wannier functions having the symmetry of the atomic orbitals, as is usually done in the analysis of chemical bonds. It is known that Wannier functions are not uniquely defined. The projection procedure in Eq. (6) solves this problem, giving uniquely defined Wannier functions that are most similar to atomic orbitals, are fully compatible with both the atomic limit and solid-state calculations, and allow us to separate the atomic and bonding effects.

Wannier functions $|W_i\rangle$ from Eq. (4) are in real space representation. Sometimes, it is useful to define the reciprocal space representation $|W_{i\vec{k}}\rangle$ for them,

$$|W_{i\vec{k}}\rangle = \sum_{\vec{T}} \exp(-i\vec{k}\cdot\vec{T})|W_i\rangle, \tag{5}$$

where $\vec{T}$ is the translation vector, i is an atomic number in the crystal unit cell, and α is a band number.

One can define the Hamiltonian and density matrix in the Wannier functions basis,

$$\begin{aligned} H^{\vec{k}}_{ij} &= \langle W_{i\vec{k}}|\hat{H}|W_{j\vec{k}}\rangle, \\ \rho^{\vec{k}}_{ij} &= \langle W_{i\vec{k}}|\hat{\rho}|W_{j\vec{k}}\rangle. \end{aligned} \tag{6}$$

Then, the electronic energy E is

$$E = \mathrm{Tr}\,(\hat{\rho}\hat{H}) = \sum_{\vec{k}} \sum_{ij} Q_{ij}^{\vec{k}} H_{ji}^{\vec{k}} = \sum_{\vec{k}} \sum_{i} Q_{ii}^{\vec{k}} H_{ii}^{\vec{k}} + \sum_{\vec{k}} \sum_{ij, i\neq j} Q_{ij}^{\vec{k}} H_{ji}^{\vec{k}}. \quad (7)$$

To separate the electronic energy E in Eq. (7) into covalent and ionic parts is not a trivial task. While the interatomic term $\sum_{\vec{k}} \sum_{ij,i\neq j} Q_{ij}^{\vec{k}} H_{ji}^{\vec{k}} = \sum_{ij,i\neq j} E_{ij}$ is clearly a covalent energy, the diagonal term $\sum_i E_{ii} = \sum_{\vec{k}} \sum_i Q_{ii}^{\vec{k}} H_{ii}^{\vec{k}}$ contains both contributions: the covalent energy for all atoms of type i in the crystal and the ionic part of the energy. To separate them, let us introduce the average energy $H_i = \sum_{\vec{k}} H_{ii}^{\vec{k}}$ and the average occupancy $Q_i = \sum_{\vec{k}} Q_{ii}^{\vec{k}}$ for atom i. The ionic part can be defined as $E_i^{\mathrm{ion}} = Q_i H_i$, and the covalent part can be defined as $E_i^{\mathrm{cov}} = E_{ii} - Q_i H_i$. The electronic energy E in Eq. (7) can be written as

$$\begin{aligned} E &= E^{\mathrm{cov}} + E^{\mathrm{ion}}, \\ E^{\mathrm{ion}} &= \sum_i E_i^{\mathrm{ion}} = \sum_i Q_i H_i, \\ E^{\mathrm{cov}} &= \sum_{ij,i\neq j} E_{ij} + \sum_i E_{ii} - \sum_i Q_i H_i. \end{aligned} \quad (8)$$

In a general case with orbital indices $L = (l, m)$, Eq. (7) is

$$E = \mathrm{Tr}\,(\hat{\rho}\hat{H}) = \sum_{\vec{k}} \sum_{iL,jL'} Q_{iL,jL'}^{\vec{k}} H_{jL',iL}^{\vec{k}} = \sum_{\vec{k}} \sum_{iL,iL'} Q_{iL,iL'}^{\vec{k}} H_{iL',iL}^{\vec{k}} + \sum_{\vec{k}} \sum_{iL,jL'} Q_{iL,jL'}^{\vec{k}} H_{jL',iL}^{\vec{k}}. \quad (9)$$

For the binary compound AB, the binding energy [Eq. (1)] is

$$\begin{aligned} E_{\mathrm{bond}} &= E_{\mathrm{AB}} - (E_{\mathrm{A}}^{\infty} + E_{\mathrm{B}}^{\infty}) \\ &= E^{\mathrm{cov}} + E^{\mathrm{ion}} - (H_{\mathrm{A}}^{\infty} Q_{\mathrm{A}}^{\infty} + H_{\mathrm{B}}^{\infty} Q_{\mathrm{B}}^{\infty}). \end{aligned} \quad (10)$$

The following approximation could be useful:

$$\begin{aligned} H_A^{\infty} &= H_A = \sum_{\vec{k}} H_{AA}, \\ H_B^{\infty} &= H_B = \sum_{\vec{k}} H_{BB}. \end{aligned} \quad (11)$$

Then, from Eqs. (8) and (10),

$$\begin{aligned} E_{\mathrm{bond}} &= E^{\mathrm{cov}} + E^{\mathrm{ion}} - (H_A Q_A^{\infty} + H_B Q_B^{\infty}), \\ E^{\mathrm{ion}} &= E_A^{\mathrm{ion}} + E_B^{\mathrm{ion}} = Q_A H_A + Q_B H_B, \end{aligned} \quad (12)$$

$$E^{\mathrm{cov}} = 2E_{AB} + E_{AA} - Q_A H_A + E_{BB} - Q_B H_B. \quad (13)$$

Hence, the binding energy partitioning is

$$\begin{aligned} E_{\mathrm{bond}} &= E_{\mathrm{bond}}^{\mathrm{cov}} + E_{\mathrm{bond}}^{\mathrm{ion}}, \\ E_{\mathrm{bond}}^{\mathrm{ion}} &= E_A^{\mathrm{ion}} + E_B^{\mathrm{ion}} - (H_A Q_A^{\infty} + H_B Q_B^{\infty}) \\ &= (Q_A - Q_A^{\infty}) H_A + (Q_B - Q_B^{\infty}) H_B, \\ E_{\mathrm{bond}}^{\mathrm{cov}} &= E^{\mathrm{cov}} = 2E_{AB} + E_{AA} - Q_A H_A + E_{BB} - Q_B H_B. \end{aligned} \quad (14)$$

The covalent contribution to the binding energy $E_{\mathrm{bond}}^{\mathrm{cov}}$ in Eqs. (13) and (14) contains, by definition [see Eq. (8)], only off-diagonal terms of the Hamiltonian and density matrices in the basis of Wannier functions with atomic orbital symmetry Eq. (6). Hence, it directly corresponds to the common chemical understanding of a covalent bond between atomic orbitals. However, the ionic part is defined by the contribution from diagonal terms of those matrices minus the $H_A Q_A^{\infty} + H_B Q_B^{\infty}$ term. Hence, it contains not only the ion–ion interactions in the crystal but also the energy of intra-atomic electronic redistribution between different orbitals and the energy of formation of charged ions from neutral atoms.

It is important to note that the energy $E = \mathrm{Tr}\,(\hat{\rho}\hat{H})$ in Eq. (9) is not the total DFT energy but a sum over the occupied one-electron eigenvalues $\sum_{\vec{k}\alpha} n_{\vec{k}}^{\alpha} \varepsilon_{\vec{k}}^{\alpha}$ and so, unlike DFT total energy, it cannot be rigorously used to calculate energy differences (e.g., when computing energies of chemical reactions). Unfortunately, there is no way to split the total energy into such contributions as the ionic and covalent parts as done in Eq. (14). So, in the following, we use the definition of Eq. (14) for the ionic and covalent parts of the one-electron energy Eq. (9). It is also useful to calculate the covalent bond energy separately for certain pairs of atoms ij as $\sum_{L,L'} Q_{iL,jL'} H_{jL',iL}$.

III. RESULTS AND DISCUSSION

A. Mg_2SiO_4

Mg_2SiO_4 crystallizes in the olivine structure type, space group *Pnma* (no. 62). A schematic representation of its structure and DFT density of states are shown in Figs. 1(c)–1(f). This ternary oxide is formed from the binary oxides MgO and SiO_2 in the reaction 2MgO + SiO_2 = Mg_2SiO_4. During this process, the coordination numbers of magnesium and silicon do not change: in the binary oxide, magnesium has octahedral one with six neighbors [Fig. 1(a)] and silicon has tetrahedral coordination with four Si [Fig. 1(b)]. The density of states of all three compounds [Figs. 1(d)–1(f)] follows the same pattern. The top of the valence band of them is mainly formed by *p*-O states hybridizing with *s*– and *p*– states of Mg or/and Si, while the bottom of the conduction band, separated by an energy gap, consists mainly of *s*– and *p*– Mg(Si) states. Thus, this set of states was used to construct the Wannier function basis for these systems. The DFT total energy calculations indicate that the formation of Mg_2SiO_4 from binary oxides is favorable by 0.575 eV per formula unit (or 0.082 eV/atom). Curiously, the difference of one-electron energies gives the opposite sign.

The degree of covalency slightly increases in forming a ternary oxide: 62% for MgO, 59% for SiO_2, and 63% for Mg_2SiO_4.

Let us consider the atomic charges, which will allow us to characterize the flow of electrons between ions during the formation of a complex compound from simpler ones, using the data given in Tables. I and IV. The charge of Mg, computed as a trace over the corresponding density matrix, increases from Z_{Mg} = 1.21 in MgO to Z_{Mg} = 1.26 in Mg_2SiO_4. There are two ways to look at this. One way is to say that 0.05 electrons flow from magnesium (0.10 per formula unit). The charge of silicon decreases accordingly from Z_{Si} = 2.64 in SiO_2 to Z_{Si} = 2.41 in Mg_2SiO_4, that is, 0.23 electrons flow to silicon. The oxygen ion charge in Mg_2SiO_4 (−1.22/−1.28) is intermediate between the values in MgO (−1.21) and SiO_2 (−1.32). According to our Wannier Hamiltonian calculations, the energy of the Mg states is higher than that of the Si orbitals by ≈ 1 eV for

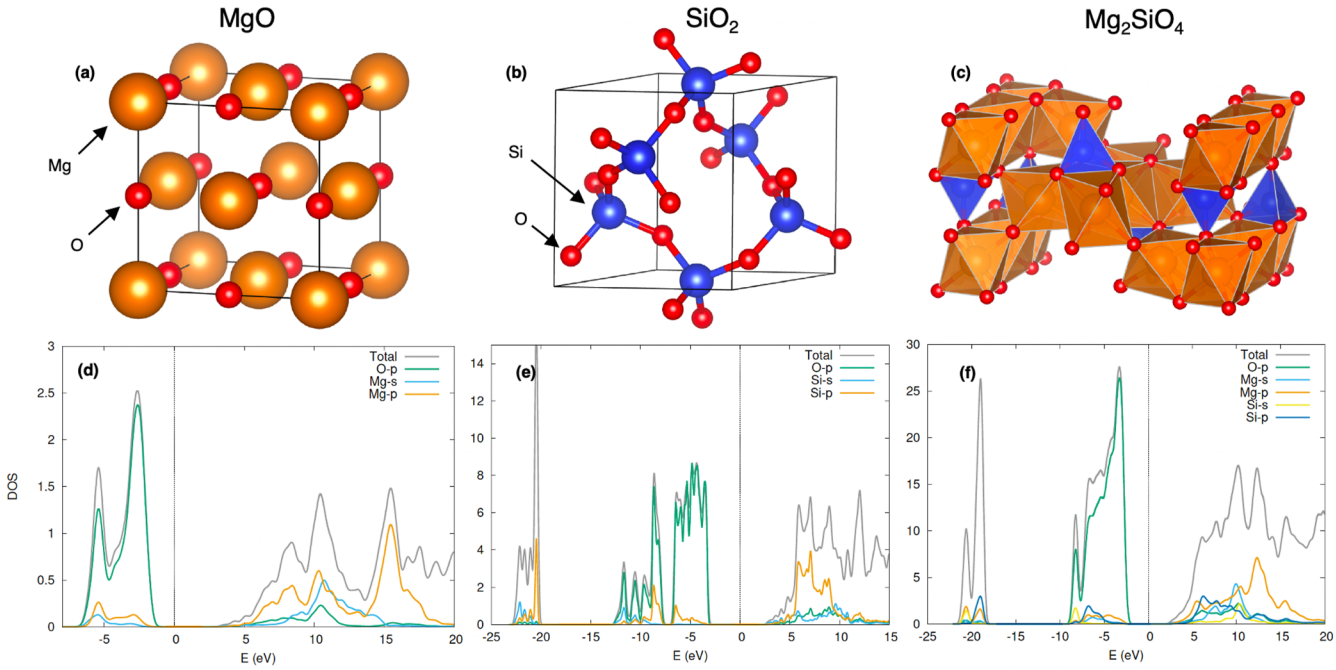

FIG. 1. Crystal structures of MgO (a), SiO_2 (b), Mg_2SiO_4 (c), and corresponding density of states [(d)–(f)] relative to the Fermi level. The orange, blue, and red spheres correspond to Mg, Al, and O atoms, respectively.

binary oxides MgO and SiO_2 and increases to ≈2 eV in Mg_2SiO_4. That fact explains the slight transfer of electrons from magnesium to silicon in the ternary oxide. The second way is less detailed, but (as we will see later) more universal: Looking at the atomic charges, we conclude that 0.055 electrons are transferred from 2MgO to SiO_2 during the formation of Mg_2SiO_4. This corresponds to the acid–base interpretation of compound formation.

The energy of one magnesium–oxygen bond $E_{Mg-O} = -2.93$ eV in MgO and $E_{Mg-O} = -3.096$ eV in Mg_2SiO_4 (Table I). For the silicon–oxygen bond, $E_{Si-O} = -8.267$ eV in SiO_2 and $E_{Si-O} = -9.359$ eV in Mg_2SiO_4. Thus, both bonds are strengthened in the ternary oxide compared to those in the binary oxides. This explains the favorability of the formation of the ternary oxide and agrees with the slight increase in covalency on going from binary to ternary oxides that was found in our Wannier calculations.

B. $MgAl_2O_4$

The compound $MgAl_2O_4$ has a spinel structure with the space group $Fd\bar{3}m$ (no. 227), as schematically represented in Fig. 2(b). The DFT density of states of Al_2O_3 and $MgAl_2O_4$ [Figs. 2(c) and 2(d)] also have the same structure similar to the oxides considered above. Therefore, the same strategy of choosing the states for design of the Wannier function basis was used during the projection procedure. Unlike Mg_2SiO_4, this ternary oxide does not have the same metal–oxygen coordination numbers as the binary oxides that form it. In particularly, while Al is octahedrally coordinated by oxygen atoms both in spinel and in Al_2O_3 [Fig. 2(a)], Mg atoms in spinel exhibit tetrahedral coordination, in contrast to the octahedral coordination in MgO. The Mg–O bond distances are also very different: 2.095 Å in MgO and 1.938 Å in spinel. Conversely, the aluminum–oxygen bond distance increases from an average value of

TABLE I. MgO, SiO_2, and Mg_2SiO_4 energies per formula unit.

	MgO	SiO_2	Mg_2SiO_4
Ionic energy	−12.466 eV	−23.690 eV	−44.387 eV
Covalent energy	−20.743 eV	−34.356 eV	−77.079 eV
Bond energy	−33.209 eV	−58.046 eV	−121.467 eV
Covalent/Bond energy ratio	62%	59%	63%
Covalent energy bond between Mg–O/Si–O atomic pair	−2.93 eV	−8.267 eV	−3.096/-9.359 eV
Ionic charge Z_{Mg}/Z_{Si}	1.21	2.64	1.26/2.41

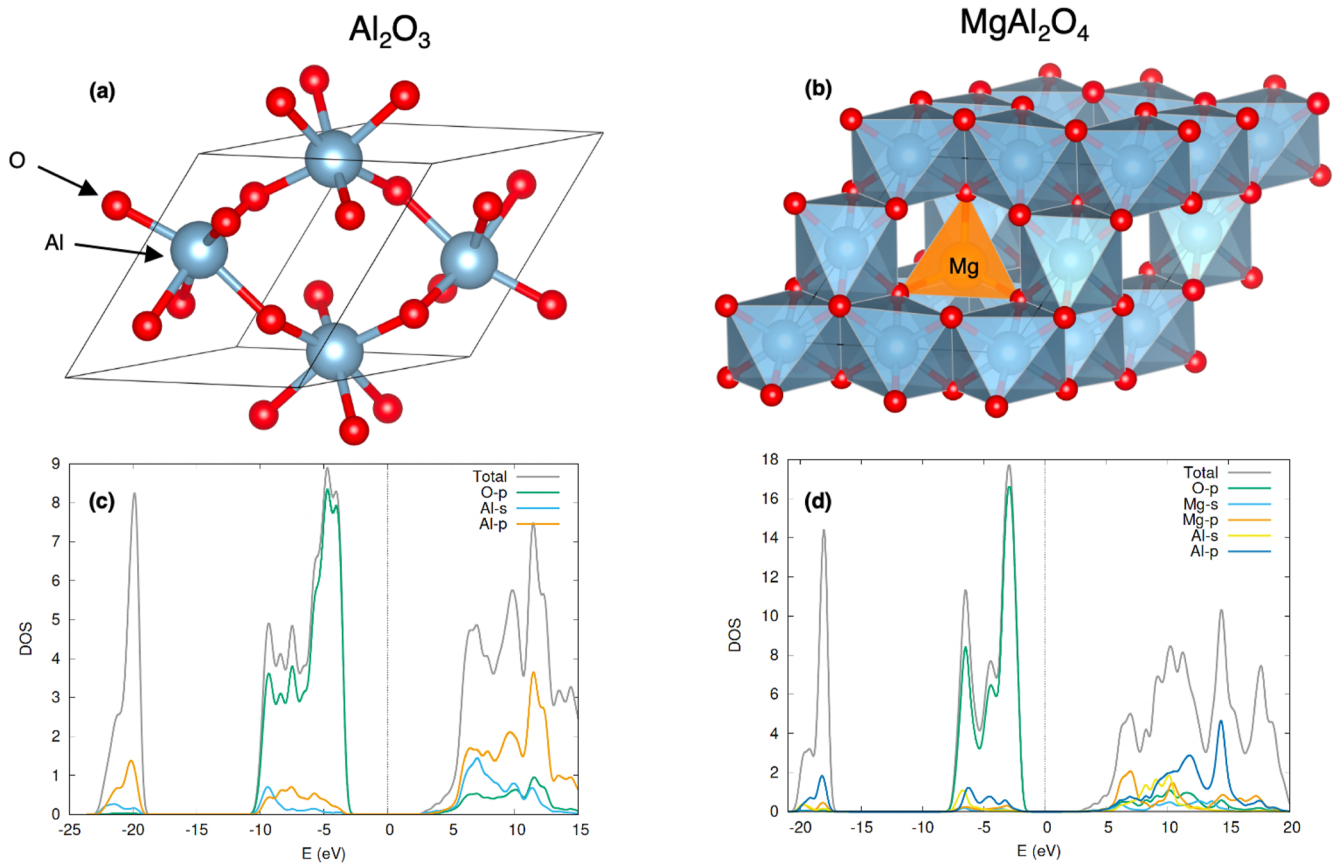

FIG. 2. Crystal structures of α-Al_2O_3 (a) and $MgAl_2O_4$ (b) and corresponding density of states [(c) and (d)] relative to the Fermi level. The orange, light blue, and red spheres correspond to the Mg, Al, and O atoms, respectively.

1.913 Å (comprising three shorter bonds at 1.855 Å and three longer ones at 1.972 Å) to 1.944 Å.

From the total energies, we find that the formation of $MgAl_2O_4$ is favorable by 0.2328 eV per formula unit (or 0.033 eV/atom), which is a rather small value indicating a small driving force for the formation of a complex oxide. The difference of the one-electron energies again gives an effect of an opposite sign.

The degree of covalency defined as the ratio of the covalent component to the binding energy also varies very slightly. For Al_2O_3 it is 65%, for MgO 62%, and for the ternary oxide $MgAl_2O_4$ again 65%.

It is interesting to follow the change in the value of ionicity, which characterizes the flow of electrons between ions during the formation of a complex compound from simple ones (Tables II and IV). The charge of the aluminum ion changes from Z_{Al} = 1.84 in Al_2O_3 to Z_{Al} = 1.77 in $MgAl_2O_4$, i.e., 0.07 electrons flow to aluminum (0.14 per formula unit). At the same time, the charge of the magnesium ion increases from Z_{Mg} = 1.21 in MgO to Z_{Mg} = 1.28 in $MgAl_2O_4$. This means that 0.07 electrons flow to the two aluminum ions from the magnesium ion, and the remaining electrons transfer from the oxygen ions average ionicity of which decreases: Z_O = −1.235 in Al_2O_3, Z_O = −1.21 in MgO, and in $MgAl_2O_4$ Z_O = −1.20

TABLE II. α-Al_2O_3 and $MgAl_2O_4$ energies per formula unit.

	α-Al_2O_3	$MgAl_2O_4$
Ionic energy	−33.782 eV	−43.322 eV
Covalent energy	−62.982 eV	−81.020 eV
Bond energy	−96.764 eV	−124.342 eV
Covalent/bond energy ratio	65%	65%
Covalent energy bond between Al–O/Mg–O atomic pairs	−5.514 (−4.383) eV	−5.064/-3.345 eV
Ionic charge Z_{Al}/Z_{Mg}	1.84 eV	1.77/1.28

(Table II). This agrees well with the fact that the calculated Wannier energies of Al are lower than the corresponding Mg states by ≈ 1–2 eV.

Let us follow the change in the covalent bonding energy of the metal–oxygen pairs. In Al_2O_3, this value E_{Al-O} = −5.514 eV for three short bonds and E_{Al-O} = −4.383 eV for three long bonds. This energy becomes equal to E_{Al-O} = −5.06 eV in $MgAl_2O_4$, where all six bonds have the same length. As the average bond energy in Al_2O_3

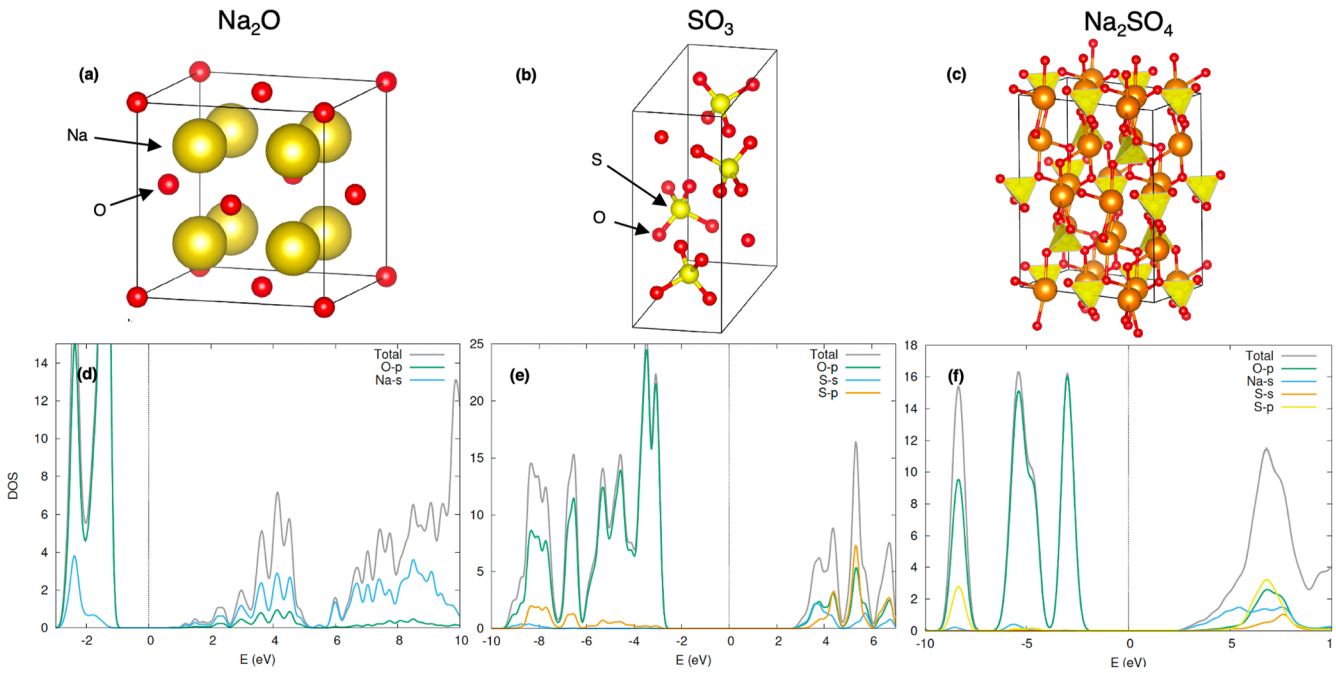

FIG. 3. Crystal structures of Na_2O (a) SO_3 (b) and Na_2SO_4 (c) and corresponding density of states [(d)–(f)] relative to the Fermi level. The orange, yellow, and red spheres correspond to the Na, S, and O atoms, respectively.

is equal to −4.948 eV that means overall strengthening of Al–O covalent bonding upon the formation of the ternary compound. For the Mg–O bond, E_{Mg-O} = −2.93 eV in MgO and E_{Mg-O} = −3.35 eV in $MgAl_2O_4$ however, one must remember that in $MgAl_2O_4$, there are only 4 such bonds per Mg atom (and 6 in MgO). Again, from the computed atomic charges, we see that in the reaction of the formation $MgAl_2O_4$ each MgO unit donates 0.07 electrons to the Al_2O_3 unit, again in perfect agreement with the expectations of the acid–base theory.

C. Na_2SO_4

Sodium sulfate Na_2SO_4 [Fig. 3(c)] is a rather simple and clear chemical compound. It is an almost purely ionic crystal formed by the ions Na^+ and $(SO_4)^{2-}$. However, in the $(SO_4)^{2-}$ ion itself, a strong covalent bonding of sulfur and oxygen is present. The ternary oxide Na_2SO_4 is formed from the binary oxides Na_2O [Fig. 3(a)] and SO_3[Fig. 3(b)]. While Na_2O is an ionic compound, SO_3 forms a polymeric crystal structure where a predominantly covalent character of chemical bonding is expected. Computing the total energy differences, we see that the formation of Na_2SO_4 is favorable by a large amount, 4.914 eV per formula unit (or 0.702 eV/atom). The difference of one-electron energies for this compound correctly reproduces the sign and large magnitude of this energy difference (overestimating it, however, by more than 2 times).

The structure of the density of states in the region of the Fermi level for Na_2O, SO_3, and Na_2SO_4 is qualitatively similar to that of the systems considered above, except that the contribution of Na is limited only by the *s*− states [Figs. 3(d)–3(f)]. Therefore, the *p*− O, *s*−, *p*− S, and only the *s*− states of sodium for these oxides were used in the construction of the Wannier function basis.

It is useful to follow the change in the value of ionicity, which characterizes the flow of electrons between ions during the formation of a complex compound from simple ones (Tables III and IV). The charge of the Na atom increases from Z_{Na} = 0.735 in Na_2O to

TABLE III. Na_2O, SO_3, and Na_2SO_4 energies per formula unit.

	Na_2O	SO_3	Na_2SO_4
Ionic energy	−8.576 eV	−16.317 eV	−35.713 eV
Covalent energy	−6.811 eV	−53.094 eV	−60.597 eV
Bond energy	−15.384 eV	−69.411 eV	−96.31 eV
Covalent/bond energy ratio	44%	76%	63%
Covalent energy bond between Na–O, S–O atomic pair	−0.741 eV	−10.204 eV	−0.375/-13.137 eV
Ionic charge Z_{Na}/Z_S	0.735	3.35	3.49/0.85

TABLE IV. Atomic charges in studied compounds.

–	O	Mg	Si	Al	Na	S
MgO	−1.21	1.21	⋯	⋯	⋯	⋯
SiO_2	−1.33	⋯	2.66	⋯	⋯	⋯
Al_2O_3	−1.23	⋯	⋯	1.84	⋯	⋯
Na_2O	−1.47	⋯	⋯	⋯	0.73	⋯
SO_3	−1.07/−1.15	⋯	⋯	⋯	⋯	3.35
Mg_2SiO_4	−1.22	1.26	2.41	⋯	⋯	⋯
$MgAl_2O_4$	−1.20	1.28	⋯	1.77	⋯	⋯
Na_2SO_4	−1.30	⋯	⋯	⋯	0.85	3.49

$Z_{Na} = 0.85$ in Na_2SO_4, that is, 0.115 electrons flow from sodium (0.23 per Na_2O unit), and each SO_3 unit gains 0.23 electrons. This again is in accordance with the acid–base theory.

The charge on sulfur increases from $Z_S = 3.35$ in SO_3 to $Z_S = 3.49$ in Na_2SO_4 when the $(SO_4)^{2-}$ ion is formed. This is interesting—contrary to expectations, the electrons attracted by the sodium atoms are not redistributed to the orbitals of S, but to the orbitals of O. The oxygen ion charge $Z_O = -1.30$ in Na_2SO_4 is between $Z_O = -1.47$ in Na_2O and $Z_O = -1.07/1.15$ in SO_3.

Let us consider how the covalent binding energy of the sulfur–oxygen complex changes during the formation of the ternary oxide using the data shown in Table III. SO_3 has three pairs of S–O bonds, each with a covalent bond energy of $E_{S–O} = -10.2$ eV. Meanwhile, in the ternary oxide Na_2SO_4, the number of pairs increases to four, and the energy of each S–O bond becomes $E_{S–O} = -13.14$ eV. Thus, in this example, the strengthening of individual S–O bonds does not occur because the energy per bond decreases from −3.4 to −3.28 eV. Thus, the formation of the ternary oxide Na_2SO_4 from binary compounds cannot be explained by the strengthening of each individual sulfur–oxygen bond, but rather by the formation of a more stable S–O complex $(SO_4)^{2-}$ than (SO_3).

Traditional *ab initio* thermodynamics methods (involving the convex hull construction and implemented, e.g., in the USPEX[10] code) can routinely predict the stoichiometry of stable compounds (e.g., whether MgO and SiO_2 will react to form $2MgO \cdot SiO_2$ or $MgO \cdot SiO_2$ or something else). Instead, the method used here addresses the question "why"—why MgO and SiO_2 react in the first place, and what are the electronic driving forces behind this reaction and formation of complex compounds. This bridges the gap between traditional acid–base concepts and quantum-mechanical bonding analysis.

IV. CONCLUSIONS

This paper explored, using our latest tools in the theory of chemical bonding, a fundamental chemical question: what are the driving forces for the formation of ternary and more complex compounds from simpler ones? Given that chemistry is the science about the behavior of the electrons in atoms, molecules, and condensed matter, the key should be in the redistribution of the electrons. We took as examples the formation of Mg_2SiO_4, $MgAl_2O_4$, and Na_2SO_4 from binary oxides. Binary oxides already have the closed-shell electronic structure, so why do they react? Obviously, oxidation states do not change. Classical chemistry describes such reactions in terms of acid–base interactions, where in Lewis' theory acids and bases are viewed as acceptors and donors of electrons. Using the Wannier function formalism, we have found that the electrons are indeed transferred from the high-energy orbitals of the base to the lower-energy orbitals of the acid (e.g., from Na_2O to SO_3 in the reaction $Na_2O + SO_3 = Na_2SO_4$). This is accomplished without changing the oxidation states of the atoms, but simply by changing the degree of ionicity of the bonds. The arithmetic mean of the atomic electronegativities is a reasonable measure of acidity/basicity, increasing in the series $Na_2O–MgO–Al_2O_3–SiO_2–SO_3$. Indeed, the largest exothermic effect is produced by the reaction of the strongest acid (SO_3) and strongest base (Na_2O) in this series, and the weakest effect is in the reaction of MgO and Al_2O_3. We have shown that these acid–base charge redistributions lead to an overall bond strengthening in ternary oxides.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Dmitry Y. Novoselov: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Dmitry M. Korotin**: Formal analysis (equal); Investigation (equal); Software (lead); Writing – review & editing (equal). **Mary A. Mazannikova**: Formal analysis (equal); Investigation (equal); Writing – review & editing (equal). **Vladimir I. Anisimov**: Conceptualization (equal); Formal analysis (equal); Methodology (lead); Writing – review & editing (equal). **Artem R. Oganov**: Conceptualization (equal); Formal analysis (equal); Funding acquisition (lead); Investigation (equal); Project administration (lead); Supervision (lead); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

REFERENCES

[1] C. Tantardini and A. R. Oganov, "Thermochemical electronegativities of the elements," Nat. Commun. **12**, 2087 (2021).
[2] R. F. W. Bader, "A quantum theory of molecular structure and its applications," Chem. Rev. **91**, 893–928 (1991).
[3] A. E. Reed, R. B. Weinstock, and F. Weinhold, "Natural population analysis," J. Chem. Phys. **83**, 735–746 (1985).

[4]V. I. Anisimov, A. R. Oganov, D. M. Korotin, D. Y. Novoselov, A. O. Shorikov, and A. S. Belozerov, "First-principles definition of ionicity and covalency in molecules and solids," J. Chem. Phys. **160**, 144113 (2024).
[5]J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," Phys. Rev. Lett. **77**, 3865–3868 (1996).
[6]P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, "Quantum espresso: A modular and open-source software project for quantum simulations of materials," J. Phys.: Condens. Matter **21**, 395502 (2009).
[7]P. Giannozzi, O. Baseggio, P. Bonfà, D. Brunato, R. Car, I. Carnimeo, C. Cavazzoni, S. de Gironcoli, P. Delugas, F. Ferrari Ruffino, A. Ferretti, N. Marzari, I. Timrov, A. Urru, and S. Baroni, "Quantum espresso toward the exascale," J. Chem. Phys. **152**, 154105 (2020).
[8]G. Prandini, A. Marrazzo, I. E. Castelli, N. Mounet, and N. Marzari, "Precision and efficiency in solid-state pseudopotential calculations," npj Comput. Mater. **4**, 72 (2018).
[9]D. Korotin, A. V. Kozhevnikov, S. L. Skornyakov, I. Leonov, N. Binggeli, V. I. Anisimov, and G. Trimarchi, "Construction and solution of a wannier-functions based Hamiltonian in the pseudopotential plane-wave framework for strongly correlated materials," Eur. Phys. J. B **65**, 91–98 (2008).
[10]C. W. Glass, A. R. Oganov, and N. Hansen, "Uspex—Evolutionary crystal structure prediction," Comput. Phys. Commun. **175**, 713–720 (2006).
[11]V. L. Deringer, A. L. Tchougréeff, and R. Dronskowski, "Crystal orbital Hamilton population (COHP) analysis as projected from plane-wave basis sets," J. Phys. Chem. A **115**, 5461–5466 (2011).
[12]R. Dronskowski and P. E. Blöchl, "Crystal orbital Hamilton populations (COHP): Energy-resolved visualization of chemical bonding in solids based on density-functional calculations," J. Phys. Chem. **97**, 8617–8624 (1993).