

# Ions in crystals: the topology of the electron density in ionic materials. IV. The danburite ( $\text{CaB}_2\text{Si}_2\text{O}_8$ ) case and the occurrence of oxide–oxide bond paths in crystals.

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We have obtained the electron density of danburite by means of *ab initio* Perturbed Ion (aiPI) quantum mechanical calculations and fully characterized its topological features as required for the analysis of crystal bonding in the light of Bader’s Atoms In Molecules (AIM) theory. Our theoretical results are compared with the experimental determination by Downs and Swope (*J. Phys. Chem.* **96** (1992) 4834). Each B and Si ion is bound to its four nearest oxide ions in a deformed tetrahedral disposition, whereas Ca is bonded to seven oxide ions. What makes this mineral most interesting is a rich collection of O–O long distance bond paths. Their existence is examined in several crystalline oxides and gas phase molecules. The occurrence of bond paths is not simply due to the distance between atoms, but rather is a consequence of the molecular and crystal geometry. It is shown that the electron density at the bond critical point decreases exponentially as the distance between atoms increases. This relationship groups together molecules and crystals, neutral oxygen and oxide ions, bonds from 1.2 to 3.2 Å, both covalent and ionic.

## I. INTRODUCTION

From the first days of quantum mechanics, the chemical bond in molecules and solids has been interpreted in terms of concepts produced by the simplest MO-LCAO (Molecular Orbitals made as Linear Combinations of Atomic Orbitals) approximation. Whereas this approach has been a fruitful source of chemical insight, it is well known that many LCAO bonding concepts dissipate when large sets of basis functions (atomic or otherwise) are used, and even more when the molecular wavefunction is systematically improved in Configuration Interaction (CI) calculations. Furthermore, new powerful theoretical techniques generate wavefunctions that can explain experimental data without resort to the indirect approach of referring to molecular orbitals or the LCAO approximation. This situation has led several research groups to develop and use new approaches to the concept of chemical bonding, extracting the chemical information from the wavefunction itself, or from properties derived from it, as the electron density. This provides a sound definition for the chemical bonding concepts, since they become physical properties of the state of the system, in equal footing with other observables like the energy.

One of the most successful approaches is the work by Bader and collaborators,<sup>1–6</sup> and it is usually known as the Quantum Theory of Atoms in Molecules (AIM). The AIM theory is founded on the Lagrangian formulation of Quantum Mechanics<sup>7</sup> and, particularly, on Schwinger’s stationary action principle.<sup>8</sup> Through the generalization of this formulation to open subsystems (i.e. systems extending in a limited region of space), Bader was able to demonstrate that quantum mechanical laws don’t apply locally to arbitrary regions of the molecular systems. They apply if and only if the regions are chosen according to the criterion that the flux of the electron density through their limiting surfaces is null,  $\vec{\nabla}\rho \cdot \vec{n} = 0$ . In this case, each and every quantum mechanical law is lo-

cally satisfied, and each and every observable property is locally well defined. Accordingly, the atoms and functional groups of chemistry can be identified with regions of space whose properties are well defined, which additively contribute to the total properties of molecules, and that bind together providing an unequivocal description of molecular structure.

Although a review of all AIM studies done lies outside of the purpose of this work, we should mention that the extension of AIM concepts to crystalline solids has been analyzed in Refs.9–11. High-quality experimental densities of minerals,<sup>12–20</sup> covalent,<sup>21</sup> metallic,<sup>22</sup> and molecular crystals<sup>23–27</sup> have been analyzed in terms of AIM concepts. In addition, theoretical calculations on simple metals,<sup>28–30</sup> alloys and intermetallic phases,<sup>31–40</sup> molecular,<sup>10,30,41,42</sup> covalent and ionic crystals,<sup>11,20,21,30,43–49</sup> as well as impurity centers and defects<sup>50–53</sup> have been reported.

The electron density of danburite ( $\text{CaB}_2\text{Si}_2\text{O}_8$ ), a naturally occurring borosilicate, has been determined by Downs and Swope from x-ray diffraction experiments,<sup>14</sup> and analyzed in the light of the AIM theory. Even though the experimental noise precluded Downs and Swope from obtaining all topological features of the crystal, their data provide an excellent test for theoretical calculations of the crystal wavefunction and for ideas regarding bonding on ionic crystals.

Two of the results from Downs and Swope’s article are particularly appealing. First, danburite is shown to be an ionic crystal, all Ca–O, B–O and Si–O bonds presenting a local depletion of electron density ( $\nabla^2\rho_b > 0$ ) at the bond critical point. Second, the oxide ions are highly polarized and unspherical, extending  $0.937\pm 0.003$  Å in the Si–O bond directions,  $0.992\pm 0.015$  Å in the B–O, and  $1.246\pm 0.023$  Å along the Ca–O bond path.<sup>54</sup> This observation supports Pauling’s argument that the bonding radius of an atom should be inversely proportional to the electronegativity of the atom to which is bonded. It can also be viewed as an evidence of the polyhedral

shape of the ionic basins in crystals.<sup>11</sup>

On the other hand, recent works in ionic crystals,<sup>11,46</sup> hydrocarbons with large substituent functional groups,<sup>55–57</sup> and van der Waals aggregates<sup>58</sup> have shown the occurrence, in many instances, of long-range, low-density bonds. Some authors have raised doubts about whether these topological bonds should be considered as true chemical bonds or rather viewed as mathematical artifacts.<sup>55–57,59</sup> Danburite is a very interesting system in relation to this problem, because it has five non-equivalent oxide positions, each having a very different local environment. Unfortunately, the occurrence of O–O bonds in danburite has not been experimentally examined.

Our main objective in this work is to produce a complete characterization of all the topological features of danburite’s electron density. To this end we have used the techniques previously developed and applied to alkali halides and halide perovskites.<sup>11,46</sup> These techniques are briefly described in Section II. The topological properties of the electron density are presented and discussed in Sec. III. Section IV examines the shape and properties of atoms in the crystal. Finally, the occurrence of O–O bonds is addressed in Sec. V.

## II. THEORETICAL PROCEDURE

As in previous works,<sup>11,46,47</sup> the crystal wavefunction has been obtained by means of *ab initio* Perturbed Ion (aiPI)<sup>60–62</sup> calculations at the experimental geometry.<sup>14</sup> The aiPI method is a localized Hartree-Fock (HF) scheme<sup>60,63,64</sup> that has been extensively used to describe accurately the electronic structure, geometry and thermodynamical properties of ionic and partly ionic pure and defective solids.<sup>60,65–71</sup> The multi- $\zeta$  exponential basis sets by Clementi and Roetti<sup>72</sup> for Ca<sup>+2</sup>, B<sup>+3</sup>, Si<sup>+4</sup> and O<sup>-</sup> have been used in the present aiPI calculations.

In addition, Dovesi’s *et al.* CRYSTAL98<sup>73</sup> code has been used to obtain HF-LCAO (Linear Combination of Atomic Orbitals) electron densities on a collection of test crystals that provide independent validation of our aiPI results on danburite. Common practice techniques<sup>73</sup> have been used to truncate and adapt to the crystals double or triple zeta valence (DZV or TZV) gaussian molecular basis sets as described in Ref.30.

It is worth mentioning that aiPI and CRYSTAL98 wavefunctions do complement each other nicely for the purposes of this work. Whereas CRYSTAL98 provides a reliable description of the bond critical points with a significant electron density accumulation, aiPI works best at providing a good description of the low density regions and producing stable trends across families of compounds.

The electron densities obtained from the aiPI or CRYSTAL98 calculations has been the input to the critic program,<sup>74</sup> a code that automatically searches for all the independent critical points in a crystal lattice. Two dif-

ferent search methods have been used. The first method, previously described in Ref.11, is based on the recursive division of the irreducible wedge of the Wigner-Seitz polyhedron of the Bravais lattice and the minimization of  $|\vec{\nabla}\rho|$  within the edges, surfaces and interiors of the resulting tetrahedra. Even though this method works nicely in many simple crystals, it failed to find many critical points of danburite.

Accordingly, we have turned to a brute force method that happened to be quite robust at getting all critical points of danburite. The method starts by recursively dividing the crystal cell into tetrahedra up to a recursion level previously fixed (usually 4 or 5 levels, which represents 425 or 1705 tetrahedra). Then, a Newton-Raphson search is done, starting from the baricenter of each tetrahedra, to find the solutions of the equation  $\vec{\nabla}\rho = \vec{0}$ . The value of the gradient at each end point must be checked to be below an appropriate threshold, as the Newton-Raphson search is not guaranteed to converge on a critical point. Most critical points, on the other hand, are reached many times, so the last step of the algorithm is replicating the points by symmetry and deleting the repeated ones. The final set must fulfill the Morse relationships:

$$n - b + r - c = 0, \quad (1)$$

and

$$n \geq 1, b \geq 3, r \geq 3, c \geq 1, \quad (2)$$

where  $n$ ,  $b$ ,  $r$  and  $c$  are the total number of nuclear, bond, ring and cage critical points of the electron density in the crystal cell, respectively.

On the other hand, we have also analyzed the occurrence of Si–O, Ca–O, B–O and O–O bonds on several small molecules to the end of comparing with the results on danburite. Those calculations have been done with GAMESS<sup>75</sup> using triple zeta valence plus diffuse and polarization functions at the Hartree-Fock level. The topological analysis of the GAMESS wavefunction has been done with the AIMPAC package.<sup>76</sup>

## III. TOPOLOGICAL PROPERTIES OF THE ELECTRON DENSITY IN DANBURITE

Danburite crystallizes in the orthorhombic system with space group  $Pnam$  and lattice parameters  $a = 8.0456(7)$ ,  $b = 8.7629(4)$  and  $c = 7.7341(7)$  Å at 300 K.<sup>14</sup> The location and properties of all theoretical bond critical points have been collected in Table I and compared with the available experimental values. Nuclear, ring and cage critical points have been also determined and are available upon request. We have found  $n = 52$ ,  $b = 164$ ,  $r = 136$ , and  $c = 24$ , which fulfill the Morse relations and can be compared with the experimentally known set of  $n = 52$  and  $b = 92$ .<sup>14</sup>

TABLE I: Theoretical (first row) and experimental (second row when available) bond critical points of Danburite. Ionic radii<sup>b</sup> ( $R_1$  and  $R_2$ ) are given in Å, bond densities ( $\rho_b$ ) in  $e/\text{Å}^3$ , bond Laplacians and curvatures ( $\nabla^2\rho_b$  and  $\lambda_3(b)$ ) in  $e/\text{Å}^5$ , and ellipticities ( $\varepsilon^b$ ) in %.

Wyckoff	Bond	x	y	z	$R_1$	$R_2$	$\rho_b$	$\nabla^2\rho_b$	$\lambda_3(b)$	$\varepsilon$
8d	Ca-O1	0.29145	0.07125	0.12505	1.2285	1.2713	0.1604	3.8317	5.2396	6.99
		0.2880	0.0733	0.1228			0.142(3)	3.23		
8d	Ca-O2	0.37890	0.97270	0.35269	1.2089	1.2460	0.1817	4.2908	5.9416	4.83
		0.3791	0.9709	0.3553			0.166(3)	3.73		
8d	Ca-O3	0.39243	0.19332	0.16563	1.2150	1.2526	0.1733	4.1484	5.7394	1.89
		0.3927	0.1949	0.1622			0.161(3)	3.57		
4c	Ca-O5	0.53289	0.07428	0.25000	1.1856	1.2153	0.2115	4.8858	6.8848	0.75
		0.5368	0.0736	0.25			0.184(5)	4.14		
8d	B-O1	0.22548	0.96781	0.94593	0.4836	0.9955	0.4832	26.7631	36.7152	1.28
		0.2205	0.9675	0.9406			0.93(6)	11.85		
8d	B-O2	0.21572	0.40190	0.03958	0.4886	1.0117	0.4525	24.9145	33.8588	1.99
		0.2139	0.3989	0.0438			0.99(3)	6.04		
8d	B-O3	0.30509	0.38463	0.07901	0.4798	0.9834	0.5092	28.4002	39.1935	1.52
		0.3052	0.3850	0.0784			1.13(5)	7.63		
8d	B-O5	0.23417	0.42207	0.13531	0.4778	0.9763	0.5265	29.1554	40.3686	1.18
		0.2432	0.4202	0.1358			1.15(5)	6.95		
8d	Si-O1	0.11201	0.14006	0.96627	0.6812	0.9375	0.6584	28.1712	39.6897	0.09
		0.1094	0.1385	0.9666			1.01(4)	17.56		
8d	Si-O2	0.08400	0.26499	0.94980	0.6825	0.9413	0.6484	27.7733	39.0528	0.23
		0.0856	0.2639	0.9515			0.95(3)	17.16		
8d	Si-O3	0.48862	0.30996	0.00066	0.6799	0.9351	0.6675	28.6467	40.3599	0.22
		0.4883	0.3129	-0.0009			0.95(4)	19.46		
8d	Si-O4	0.47498	0.68039	0.36237	0.6806	0.9352	0.6626	28.3908	40.0015	0.06
		0.4725	0.6802	0.3617			0.94(4)	18.30		
8d	O2-O1	0.28288	0.96603	0.48110	1.1624	1.1619	0.3127	5.0472	7.6690	3.35
8d	O2-O5	0.15642	0.39683	0.39658	1.1874	1.1871	0.2766	4.5689	6.7971	6.19
8d	O3-O5	0.29124	0.37154	0.33725	1.2021	1.2029	0.2554	4.3665	6.3211	15.09
8d	O3-O1	0.35147	0.44016	0.04131	1.2098	1.2102	0.2455	4.2252	6.1018	13.11
8d	O3-O2	0.26303	0.34093	0.01918	1.2148	1.2157	0.2396	4.1421	5.9560	12.06
8d	O5-O1	0.24577	0.49408	0.12393	1.2380	1.2376	0.2172	3.9563	5.2931	44.55
4c	O3-O3	0.39731	0.31448	0.25000	1.3275	1.3275	0.1336	2.4896	3.4534	12.13
8d	O3-O1	0.70470	0.80852	0.96251	1.3962	1.3978	0.0937	1.7990	2.4525	10.33
4c	O2-O2	0.37717	0.87129	0.25000	1.6063	1.6063	0.0336	0.7379	0.8526	88.98
4b	O2-O2	0.50000	0.00000	0.50000	1.5958	1.5958	0.0333	0.7073	0.9109	3.52
4c	O5-O4	0.41326	0.12770	0.75000	1.9157	1.9206	0.0065	0.1564	0.1725	4.96

<sup>a</sup>We define the ionic radius as the distance between the bond critical point and each corresponding nucleus.

<sup>b</sup>We define the ellipticity as  $\varepsilon = 1 - \lambda_2/\lambda_1$  rather than using Bader's definition ( $\lambda_1/\lambda_2 - 1$ ). The advantage of our definition is that  $\varepsilon$  lies in the range  $[0, 1]$ .

Up to 23 different bond critical points have been found in danburite's theoretical density. In the AIM framework, whenever there exists a bond critical point between two atoms these atoms are considered to be bonded, and the gradient line connecting both nuclei and the bond critical point is referred to as the *bond path* or simply the *bond* between the two atoms. Each Si and B are bonded to four oxide ions in a distorted tetrahedral configuration. Ca, on the other hand, is bonded to seven oxide ions in a configuration similar to a distorted octahedron with an extra bond appearing where an octahedron edge should be. This bonding pattern is the same as found experimentally and, in fact, there is an excellent agreement between the theoretical and the experimental positions of the *M-O* bond critical points<sup>14</sup> (see Table I). There is also agreement on the value of the density and the Laplacian at the *Ca-O* bond critical points. However, the aiPI

theoretical density at the *Si-O* bond critical point is only about 65% of the experimental value, and 45% for the *B-O* bond. The aiPI values for the Laplacians are also significantly larger than the experimental values, even if taking into account an estimated experimental error<sup>14</sup> of the order of 25%. This discrepancy on the *B-O* and *Si-O* bond critical properties is mostly due to the approximations incorporated within the aiPI technique, in particular the enforced radial symmetry of the electron density contributed by each ion. This approximation is expected to become poorer as the covalent accumulation of electron density increases. On the contrary, the use of a saturated exponential basis set is expected to work best on the representation of mostly ionic bonding, in addition to provide stability of the bond properties across families of compounds.

To provide an independent validation of our results we

TABLE II: Equilibrium geometry and bond topological properties of some reference molecules. The calculations have been done with GAMESS<sup>75</sup> at the Hartree-Fock level using a TZV+(3d1f) basis set. The topological analysis has been done with Bader’s AIMPACK suite.<sup>76</sup>

	State	$R_{AB}$ (Å)	$\rho_b$ (e/Å <sup>3</sup> )	$\nabla^2\rho_b$ (e/Å <sup>5</sup> )
SiO	X <sup>1</sup> Σ <sup>+</sup>	1.5097	1.26853	35.7156
BO	X <sup>2</sup> Σ <sup>+</sup>	1.205	2.09093	44.1469
CaO	X <sup>1</sup> Σ <sup>+</sup>	1.9426	0.68947	14.0227

have compared the aiPI and CRYSTAL98 electron densities for a representative collection of oxide crystals: ionic compounds like MgO, ZnO and CaO; polar crystals like  $\alpha$ -quartz, TiO<sub>2</sub> (both, rutile and anatase phases), AlBO<sub>3</sub>, and CaTiO<sub>3</sub>; and even molecular compounds like N<sub>2</sub>O<sub>4</sub>. The comparison shows that aiPI systematically underestimates the electron density accumulation in covalent and highly polar compounds. For instance, the ratio of aiPI to CRYSTAL98  $\rho_b$  values is about 74–76% on the Si–O bond critical points and 50% on the B–O ones. The agreement is much better in the *more ionic* cases: 80–95% on Ca–O, 83% on Ti–O, or 87% on Zr–O. More important, the CRYSTAL98 and aiPI calculations agree qualitatively on the occurrence of O–O bonds like those found on danburite, and quantitatively on the O–O bond point properties.

Furthermore, we can gain additional understanding on the crystal bonding and the aiPI results by turning to examine the electron density of SiO, BO and CaO diatomic molecules, as they provide a model of the electron density behavior when the interatomic distance changes. Table II presents the topological bond properties of the three molecules at their respective equilibrium distances. The calculations have been done with high quality basis sets at the Hartree-Fock level, and we have checked that the bond properties don’t change appreciably when correlation effects, up to a CI-SD level (Configuration Interaction including Single and Double excitations), are included. We can observe that bond lengths are consistently shorter in the molecule than in the crystal for the same pair of atoms, being the electron density and its Laplacian at the bond critical points much larger in the molecules.

To be able to compare molecular and crystal densities we need to put them in the same distance scale. Accordingly, we have represented the bond density *versus* the interatomic distance for the reference molecules in Fig 1. The most important thing to observe is that  $\ln \rho_b$  decreases linearly with the interatomic distance,  $R_{AB}$ , for a large range of distances that includes both the molecular equilibrium distance and the distances in danburite under normal pressure and temperature. The reason for this linear behavior is directly inherited from the properties of the radial electron density,  $\rho(r)$ , of the free atoms. Effectively,  $\ln \rho(r)$  decreases from the maximum cusp at the nucleus following linear steps, each step being re-

lated to one of the K, L, M, ... electron shells. Different linear steps, on the other hand, have different slope, and they are separated by rather curved arms. Those linear regimes are found to be essentially conserved on many molecules that we have analyzed, both diatomic and polyatomic. It is quite interesting to notice that  $\rho_b$  is a measurement of the bond strength and it has been observed to correlate with the traditional bond order,  $n$ , as  $n = \alpha\rho_b^\beta$  or  $n = \alpha \exp(\beta\rho_b)$  (Ref.4). We can then relate bond order and distance or, which is more striking, use a single and unified concept to deal with, say, the C–C bond on such molecules as C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>.

Fig 1 shows that the molecular values of  $\rho_b$  correlate quite well with the experimental values on danburite when the same interatomic distances are considered. This result suggests that the molecular and crystalline regimes are manifestations in a different distance range of an unique universal regime. The experimental densities on the crystal show, on the other hand, significant error bars that could, perhaps, be reduced if the molecular results were used to refine the analysis of the X-ray diffraction data. The aiPI densities for the Ca–O bond agree with the molecular results. Even more, the aiPI bond densities obtained in a collection of crystals that includes several phases of CaTiO<sub>3</sub> and CaO, as well as danburite predict exactly the calculated molecular bond density when extrapolated to the molecular distance. The same extrapolation, however, predicts densities on the diatomic Si–O and B–O bonds that are about half of what should be expected from the diatomic molecule calculations, owing to the more covalent character of these diatomics.

It appears, from the above analysis, that the aiPI wavefunction underestimates the electron density in tetrahedral bonds, but it is satisfactory representing bonds from higher coordination environments. This conclusion is in accordance with the lack of multipolar contributions to the energy and wavefunction in the present aiPI calculations.<sup>61,62</sup> These difficulties should be overcome in the next *generalized Perturbed Ion* method,<sup>77</sup> which is presently being coded.

#### IV. SHAPE AND PROPERTIES OF ATOMS

We can now turn to discuss the shape and properties of atoms in danburite. In a solid, we have shown<sup>11</sup> that the smallest proper quantum subsystems are the *primary bundles*. A primary bundle is the set of all points traversed by upward trajectories of the electron density gradient field that start at a given minimum and end at a given maximum. The collection of all bundles that have the same maximum as a common vertex form the *attraction basin* for that particular maximum. The integration of appropriate functionals over the basin gives the atomic properties, which are well defined for any quantum mechanical observable, are additive to give the total

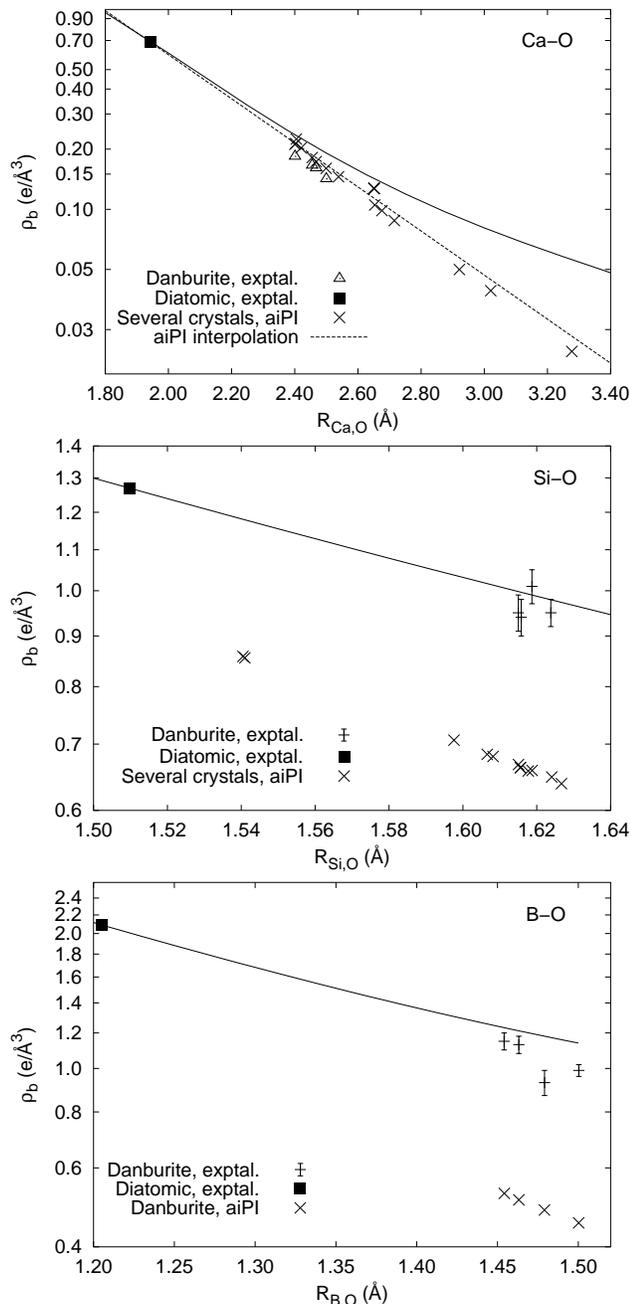


FIG. 1: Electron density *versus* interatomic distance for the Ca–O, Si–O and B–O bonds in danburite and the corresponding diatomic molecules. The solid lines correspond to the bond critical point densities ( $\rho_b$ ) of the corresponding diatomic molecules for a range of internuclear distances. Notice the logarithmic scale on the density.

property of the system, and are maximally transferable among systems up to the point that the basin shape is maintained.

The basin shapes of the ions in danburite are shown in Fig. 2. Basins are topologically equivalent to polyhedra, in the sense that they have faces, edges and vertices, and they satisfy Euler’s relationship (faces – edges + vertices

= 2). Unlike polyhedra, however, basins tend to have rather curved edges and faces. Each face is the attraction surface of a bond critical point, edges are the attraction lines of a ring, and vertices are minima of the electron density. Accordingly, ionic basins provide another way of looking at the crystal bonding.

Bonding in crystals is dominated by geometric factors. The existence of a bond path is not simply due to the distance between a particular pair of atoms, but it is rather the result of a complex balance among the basins of many neighbors. We have already observed that behavior on the rock-salt phase of alkali-halides and simple oxides ( $AX$ ): the ratio among anion and cation topological radii ( $r_X$  and  $r_A$ , respectively) on the  $A-X$  bond path is an exact predictor on whether there is ( $r_X/r_A > 1.15$ ) or not ( $< 1.15$ ) a  $X-X$  bond path.<sup>47,48</sup> Similar rules hold for the CsCl phase,<sup>47,48</sup> perovskites,<sup>46</sup> fluorites and other prototypical crystalline structures.<sup>49</sup>

Danburite presents some striking examples of this balance principle. Whereas B, Si, Ca and O1 ions are bonded to their nearest neighbors up to a given distance, the behavior of O2, O3, O4 and O5 ionic basins is quite different. O4 ions, for instance, being the bridge among two  $\text{SiO}_4$  tetrahedra, are bonded to both Si ions at 3.083 Å and to an O5 ion placed quite far away (6.353 Å), even though there are ten oxide ions and four B ions in the range 4.99–6.27 Å to which O4 ions are not bonded.

The most striking feature of ionic basins is, perhaps, their anisotropy and irregular shape as we can appreciate in Fig. 2. The distance from the nucleus to its basin’s surface is quite different depending on the direction. In addition, basin shapes on danburite reflect the low symmetry of the ions within the crystal. We could conclude, naïvely, that being the ion shape something completely different from a sphere the classical notion of ionic radius is not compatible with Bader’s AIM theory. However, our previous work has clearly shown us that the topological radii, defined as the distance from a nucleus to its bond critical points, can be compared to and have the predictive rôle of the empirical ionic radii.<sup>47,48</sup>

In agreement with this idea, the topological radii of cations show a very small variation among the different bonds in danburite:  $r_B = 0.483 \pm 0.005$  Å,  $r_{\text{Si}} = 0.681 \pm 0.001$  Å, and  $r_{\text{Ca}} = 1.213 \pm 0.014$  Å. Oxide ions, on the contrary, present a wide range of values: 0.935–1.921 Å. Quite interestingly, the radii of oxide ions are more or less constant when bonded to a particular cation —  $r_{\text{O}}(\text{Si-O}) = 0.937 \pm 0.003$ ,  $r_{\text{O}}(\text{B-O}) = 0.989 \pm 0.015$  and  $r_{\text{O}}(\text{Ca-O}) = 1.246 \pm 0.023$  Å — but show a large variability when bonded to other oxide ions:  $r_{\text{O}}(\text{O-O}) = 1.33 \pm 0.23$  Å. The image of hard cations versus soft, polarizable anions is a natural conclusion from these results. This image is clearly compatible with the description of ionic crystals traditional since Pauling.<sup>79</sup>

Regarding the basin shapes as we can see in Fig. 2, B and Si appear as slightly deformed tetrahedra, Ca is a heptahedron with bilateral symmetry, and the oxide basins have a very variable number of faces: 7 (O1), 8

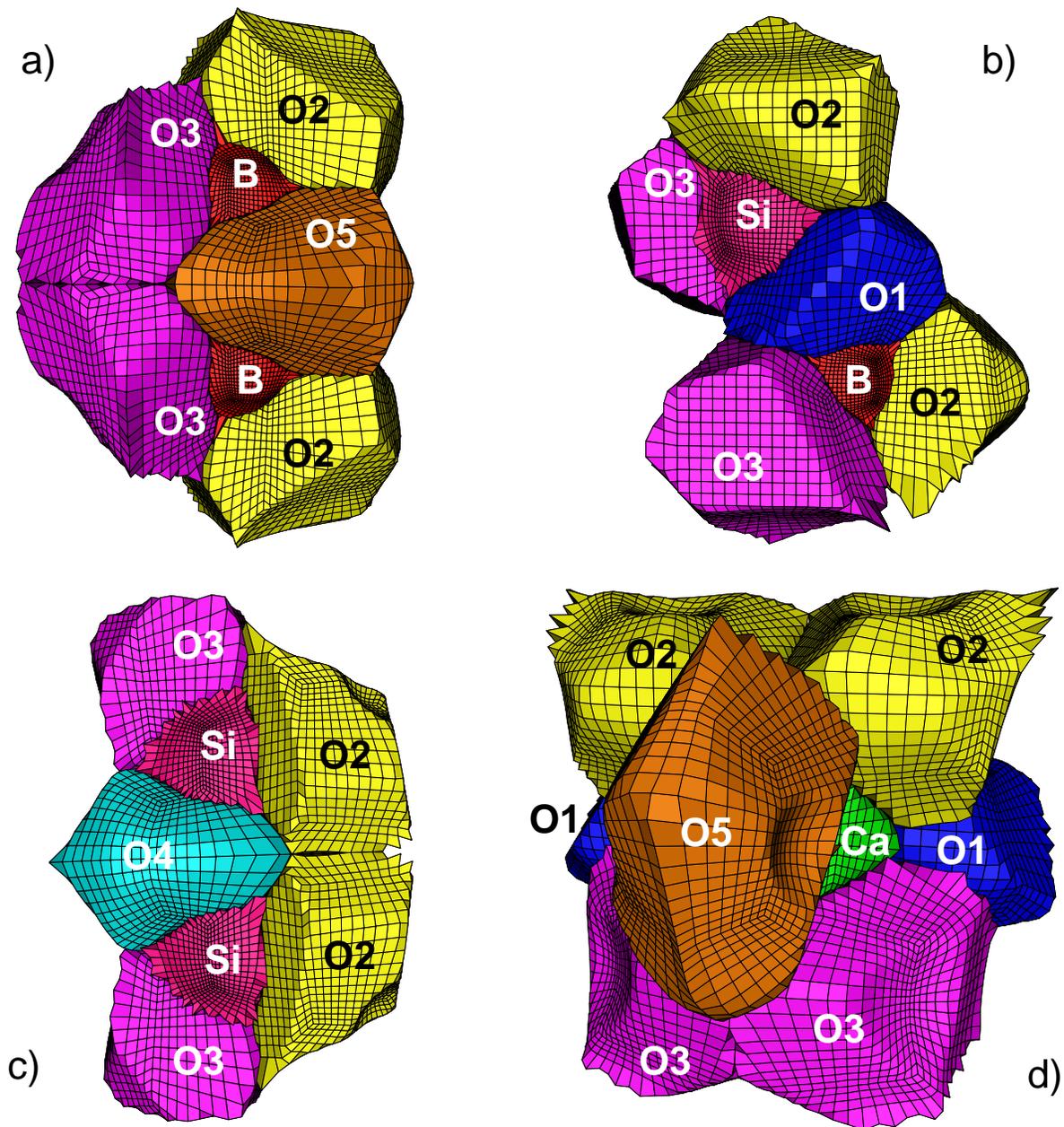


FIG. 2: Atomic basins for the ions in danburite. From left to right, up to down: (a) Two  $\text{BO}_4^{-5}$  groups united by a O5 bridge. Each B is surrounded by O1 (subtracted to show the B basin), O2, O3 and O5 atoms. (b) An O1 basin acts as a bridge between the  $\text{SiO}_4^{-4}$  (up) and  $\text{BO}_4^{-5}$  tetrahedra (O4 and O5 have been subtracted around Si and B, respectively). (c) The  $\text{SiO}_4^{-4}$  tetrahedra are bridged by an O4 basin. Each Si edge in the Si basin extends in the space as a nearly bidimensional wing, and is surrounded by O1 (subtracted to show the Si basin), O2, O3, and O4 atoms. (d) The Ca basin is heptacoordinated by two O2 basins (up), two O1 basins (middle), two O3 basins (down), and a single O5 basin (front). The figures have been created with Geomview.<sup>78</sup>

(O2 and O3), 3 (O4) and 10 (O5). The basin of O4 is, in fact, one of the strangest we have found in studying many kinds of crystals. Each O4 ion is only bonded to two equivalent Si ions ( $r_{\text{O4}}(\text{Si-O4}) = 0.935 \text{ \AA}$ ) and to a single O5 ion ( $r_{\text{O4}}(\text{O4-O5}) = 1.921 \text{ \AA}$ ). Accordingly, the O4 basin, which must show bilateral symmetry, has only three faces with a very large curvature (see Fig. 2).

The integration of appropriate functionals over the basins provides the properties of ions. Table III lists the basin volume and net charge of danburite's ions. As the integration is done numerically, it is relevant to indicate that the residual charge on the unit cell due to the integration errors is  $-0.018 e$ , and the absolute error in the cell volume is  $-0.125 \text{ \AA}^3$ , which represents a rel-

TABLE III: Volume and charge of ionic basins in Danburite. Shown as a comparison,  $\mathcal{R}$  is the radius of a sphere with the same volume than the basin, and  $\langle R \rangle$  is the average of the topological radii.

	$\mathcal{V} (\text{\AA}^3)$	$Q(e)$	$\mathcal{R}(\text{\AA})$	$\langle R \rangle(\text{\AA})$
Ca	12.183	+1.921	1.427	1.213
B	0.717	+2.874	0.555	0.483
Si	2.388	+3.735	0.829	0.681
O1	14.910	-1.890	1.527	1.173
O2	14.387	-1.896	1.509	1.246
O3	13.738	-1.900	1.486	1.190
O4	17.225	-1.862	1.602	1.264
O5	14.599	-1.909	1.516	1.234

ative error of  $-0.023\%$ . According to our calculations, the net charges of all ions are very close to their nominal oxidation states:  $Q_{\text{Ca}} = 1.9$ ,  $Q_{\text{B}} = 2.9$ ,  $Q_{\text{Si}} = 3.7$ , and  $Q_{\text{O}}^{av} = -1.9$ . Comparison with CRYSTAL98<sup>73</sup> calculations on simpler oxides<sup>30</sup> suggests that aiPI basin charges are slightly large and we should expect charges around 1.85 (Ca), 3.5 (Si),  $-1.75$  (O) and 2.6 (B). These atomic charges are very important components in the development of force fields, that allow for a fast estimation of the lattice energy on geometries not far away from the static equilibrium arrangement.

Basin volumes, on the other hand, show the trends that should be expected from the atomic number and oxidation state of the ions:  $\mathcal{V}_{\text{O}^{-2}} > \mathcal{V}_{\text{Ca}^{+2}} \gg \mathcal{V}_{\text{Si}^{+4}} > \mathcal{V}_{\text{B}^{+3}}$ . It is a little surprising the large variation among the volumes of oxide basins, from  $13.7 \text{ \AA}^3$  on O3 to  $17.2 \text{ \AA}^3$  on O4. This variability is related to the rôle that anions play on filling the space in the crystal. This large difference in the  $\text{O}^{-2}$  basin volumes is not, however, accompanied by an equivalent variability in the ion charge, and we can conclude that the additional volume on some basins corresponds to very low density regions. This is, probably, the reason for the rough correlation between basin volumes and average topological radii in danburite.

Once obtained, it is worth considering how the topological charges on the basins can be used. First of all, the charges provide a description, albeit a very limited one, of the distribution of electron density among the nuclei. It is possible, in principle, for two different electron densities to give equivalent descriptions of the critical points number and properties. The charges integrated over the basins give a different kind of information to distinguish them.

Furthermore, we can define an ionicity scale from the charges. We can compare, for instance, the topological charge,  $Q_i$  and the nominal oxidation state of an atom,  $Q_i$ , and define the *charge transfer index*<sup>80</sup> of the atom in the crystal as:

$$C_i = 1 - \frac{Q_i - Q_i}{Q_i} = \frac{Q_i}{Q_i}. \quad (3)$$

We have found, in all the crystals studied, that  $|Q_i| < |Q_i|$ . The  $C_i$  are then positive and lie in the range  $[0, 1]$ .

The charge transfer index of the crystal,  $\mathcal{C}$ , can be obtained as an average of the atomic values. On a binary compound,  $A_m B_n$ , the cell neutrality condition determines that  $\mathcal{C}_A = \mathcal{C}_B = \mathcal{C}$ . In the case of danburite, the  $C_i$  values range from 0.931 in O4 to 0.961 in Ca, with an average value of 94.7% for the whole crystal. This value is similar to those found in the alkali halides or simple oxides.<sup>30</sup> As a general rule, the charge transfer indexes defined in Eq. 3 are usually bigger than the ionicities obtained from Pauling's electronegativities.

## V. THE LONG-DISTANCE O–O BONDS

We have already shown the existence of topological oxide–oxide bond paths in danburite in addition to the typical metal–oxide bonds. We analyze now this evidence in detail and address the more general question of secondary (i.e. between second and further nearest neighbors) anion–anion bonds in crystals.

The occurrence of anion–anion bonds in ionic crystals has already been proposed several times: (a) Pauling discussed the importance of anion–anion contact in lithium halides.<sup>79</sup> He saw in this interaction the source of an additional repulsion, given the energy required to deform the anionic density. (b) O'Keefe and Brese<sup>81</sup> proposed a set of empirical rules to identify  $X-X$  bonds, where  $X$  is any of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{O}^{-2}$ ,  $\text{S}^{-2}$ , etc. (c) Göttlicher and Vegas<sup>82</sup> observed the existence of O–O *density bridges* in a very high-quality X-ray determination of magnesite ( $\text{MgCO}_3$ ), although later experiments on the same crystal by Maslen *et al.*<sup>83</sup> didn't reproduce this observation. (d) The topological features of anion–anion bond critical points were already detected in many historical high-quality measurements of the total electron density like Krug *et al.*<sup>84</sup> on LiF, Göttlicher<sup>85</sup> on NaCl, and Niederauer and Göttlicher<sup>86</sup> on  $\text{MgF}_2$ , to name just a few.

Traditionally, O–O bonds have been described in a variety of forms: dioxygenil ion,  $\text{O}_2^+$ , as in  $\text{O}_2\text{PtF}_6$ <sup>87</sup>; neutral  $\text{O}_2$ <sup>88</sup> and  $\text{O}_3$ ; ozonides containing the  $\text{O}_3^-$  group, like  $\text{NH}_4\text{O}_3$ <sup>89</sup>; superoxides containing the  $\text{O}_2^-$  group, like  $\alpha\text{-KO}_2$ <sup>90</sup>; and peroxides having the  $\text{O}_2^{-2}$  group like  $\text{CdO}_2$ <sup>91</sup> and  $\text{H}_2\text{O}_2$ .<sup>92</sup> The O–O distances in these molecular and crystalline compounds range from 1.1 to 1.5  $\text{\AA}$ .<sup>93</sup> The oxide–oxide bond, on the other hand, would be described as an  $\text{O}_2^{-4}$  embedded group, and its O–O bond length would be 3.02  $\text{\AA}$  in  $\text{MgCO}_3$ <sup>82</sup> or 2.3–3.4  $\text{\AA}$  for the different O–O topological bonds in danburite.

Let us analyze the situation in danburite. Our topological analysis of the electron density indicates the existence of 11 different types of oxide–oxide bond critical points, with O–O bond lengths from 2.32 to 3.36  $\text{\AA}$ . The occurrence and spatial organization of oxide–oxide bond paths in danburite are shown in Figs. 3 and 4. Fig. 3 clearly shows that bond critical points do not simply appear when the O–O distance is below some threshold. Together, both figures indicate that bond formation is a consequence of the local geometry of the ions basins

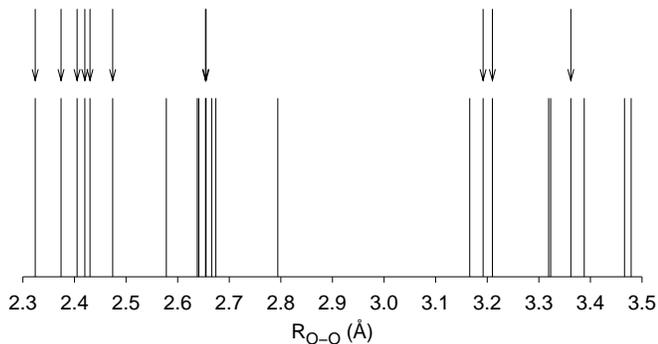


FIG. 3: Plot of the shortest O–O distances in danburite. The actual topological bonds are indicated by arrows.

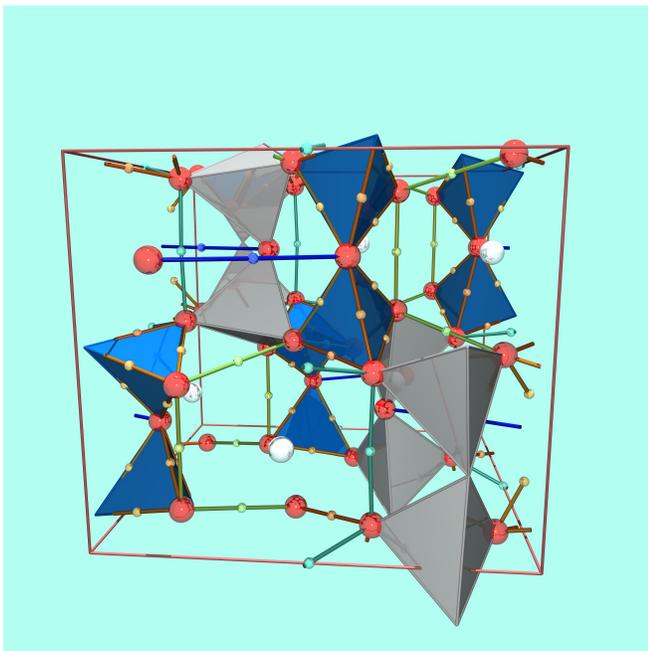


FIG. 4: Molecular graph of danburite illustrating the position of the O–O bond critical points (small spheres) and the O–O bond paths (sticks passing through the bond critical point). The dark tetrahedra correspond to the B coordination polyhedra, and the light ones are the Si coordination polyhedra. The plot has been designed with *tessel*<sup>94</sup> and rendered with *POVRay*.<sup>95</sup>

or, in other words, it is due to the competition among neighboring ions to attract electrons. The case of O4 is, again, the best example of what can happen in extreme cases. Effectively, O4, the bridge atom between two  $\text{SiO}_4^{-4}$  tetrahedra (see Fig. 2), is not bonded to its six  $\text{O}^{-2}$  neighbors in the tetrahedra, but it is bonded to its 9<sup>th</sup> neighboring shell: an O5 situated 3.362 Å away.

The different behavior of  $\text{SiO}_4^{-4}$  and  $\text{BO}_4^{-5}$  coordination tetrahedra is worth noticing. Whereas the oxide ions in the  $\text{BO}_4^{-5}$  tetrahedra are bonded together, those in  $\text{SiO}_4^{-4}$  are not. If we assume a regular tetrahedron and consider the ions as rigid spheres, the anion–anion

contact on the edges would happen only if the cation to anion radii ratio is:  $r_c/r_a \leq 1/\sqrt{2} \approx 0.707$ . Using the average topological radii along the B–O and Si–O bonds we find  $r_B/r_O = 0.489$  and  $r_{\text{Si}}/r_O = 0.727$ . Thus, a simple rigid ion argument correctly predicts the existence of O–O bond paths on the  $\text{BO}_4^{-5}$  tetrahedra and their absence on the  $\text{SiO}_4^{-4}$  tetrahedra.

There is evidence supporting that the O–O bond paths are not a quirk in the aiPI wavefunction. As we have remarked before, both aiPI and CRYSTAL98 agree on the prediction of O–O bonding in a collection of representative oxide crystals. For instance, according to both techniques, they will be present in MgO but not in CaO due to the different cation to anion ratio size.<sup>30</sup> The aiPI to CRYSTAL98  $\rho_b(\text{O–O})$  ratio varies between 60% to 130% for the representative set of crystals already cited. This may amount to a significative difference, but it must be taken into account that the gaussian bases used on the CRYSTAL98 calculations are commonly not saturated and optimized differently for each crystal instead. This produces a nonnegligible error bar on the low density regions that varies from a crystal to another. We need, accordingly, a different test on the O–O density trends.

We have already seen, in the case of  $M\text{–O}$  bonding, that the bond properties of small molecules, when extrapolated to the distances found in crystals, can serve as a valid reference for the crystalline regime. We will try again this strategy to further analyze O–O bond critical points. Several reference molecules have, consequently, been selected:  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_2\text{F}_2$ , and the planar and non-planar configurations of  $\text{C}(\text{NO}_2)_3^-$ . Hartree-Fock (HF) calculations have been done at the theoretical ( $\text{C}(\text{NO}_2)_3^-$ ) or experimental (the rest of molecules) equilibrium geometries. In the case of  $\text{O}_2$ , we have done HF calculations on the  $^3\Sigma_g^-$  ground state from 0.8 to 4.2 Å, taking great care to keep the same electronic state at all distances. The effect of basis sets has been analyzed extensively, but only the best results using a TZV+(3d) basis consisting of a triple zeta valence,<sup>75,96</sup> diffuse sp functions<sup>97</sup> and three d polarization functions,<sup>98</sup> will be discussed here (a TZV+(1d) basis set in the case of  $\text{C}(\text{NO}_2)_3^-$ ). Correlation effects, up to a CI-SD level, were found to have a negligible influence on the topology of the electron density of  $\text{O}_2$ .

The O–O bond properties calculated on a collection of crystals and gas phase molecules are presented in Table IV. The results shown there clearly indicate that the occurrence of O–O bond critical points is not uniquely due to the O–O distance. The trinitromethanyde ion,  $\text{C}(\text{NO}_2)_3^-$ , provides a clear illustration of this point. The shortest O–O distance is 2.084 Å between the two oxygens in a  $\text{NO}_2$  group, but there is no bond path among them. The electron density gradient vector field of the molecule, depicted in Fig. 5, shows how each N basin interposes as a barrier between the two oxygens in its  $\text{NO}_2$  group, preventing the existence of a bond path among them. The oxygens in different  $\text{NO}_2$  groups, however, have no such limitation and even though their distance

TABLE IV: Topological properties of O–O bond critical points in a collection of crystals and gas phase molecules. Crystal calculations have been done with the aiPI method at the experimental geometries, using a large STO basis set. Molecular calculations have been done at the experimental geometry using a HF/TZV+(3d) method, except the trinitromethynide ion, for which the geometry has been optimized at the HF/TZV+(1d) level using both a  $D_{3h}$  (planar) and a  $D_3$  (non-planar) configuration. Distances ( $d_{OO}$ ) are given in Å, bond densities ( $\rho_b$ ) in  $e/\text{Å}^3$ , bond Laplacians and curvatures ( $\nabla^2\rho_b$  and  $\lambda_3(b)$ ) in  $e/\text{Å}^5$ , ellipticities in %, and angles in degrees. In those crystals where there is no O–O bond,  $d_{OO}$  corresponds to the shortest O–O distance.

System	$d_{OO}$	$\rho_b$	$\nabla^2\rho_b$	$\lambda_3(b)$	$\epsilon$	O–b–O
$\alpha$ -Al <sub>2</sub> O <sub>3</sub> Ref.99	2.361	0.28222	4.82771	7.20722	1.79	179.56
	2.464	0.21608	3.89050	5.62176	4.27	180.00
	2.606	0.14988	2.87932	3.96931	5.97	178.54
BaO Ref.100	(3.917)					
CaO Ref.100	(3.402)					
CaTiO <sub>3</sub> ( <i>Cmmm</i> ) Ref.101	(3.273)					
CaTiO <sub>3</sub> ( <i>Pbnm</i> ) Ref.101	3.350	0.02510	0.56632	0.61187	71.51	180.00
CaTiO <sub>3</sub> ( <i>Pm3m</i> ) Ref.99	(2.715)					
Danburite Ref.14	2.325	0.31272	5.04725	7.66895	3.35	179.38
	2.374	0.27661	4.56888	6.79706	6.19	178.98
	2.405	0.25536	4.36646	6.32111	15.09	178.72
	2.420	0.24550	4.22524	6.10181	13.11	178.41
	2.430	0.23957	4.14210	5.95601	12.06	178.31
	2.474	0.21716	3.95629	5.29305	44.55	176.29
	2.655	0.13362	2.48964	3.45335	12.13	178.21
	2.793	0.09373	1.79897	2.45253	10.33	179.15
	3.192	0.03327	0.70730	0.91093	3.52	180.00
	3.210	0.03361	0.73790	0.85261	88.98	175.45
	3.831	0.00648	0.15640	0.17255	4.96	173.70
Li <sub>2</sub> O Ref.100	(3.266)					
MgO Ref.100	2.977	0.07288	1.22060	1.61606	21.48	180.00
SiO <sub>2</sub> (Tridymite) Ref.101	(2.515)					
SiO <sub>2</sub> ( $\alpha$ -Cristobalite) Ref.99	3.962	0.00418	0.10338	0.12098	45.78	177.36
SiO <sub>2</sub> ( $\alpha$ -Quartz) Ref.99	3.299	0.02490	0.53186	0.68368	5.17	179.84
	3.563	0.01242	0.28051	0.34630	2.34	179.30
	3.578	0.01221	0.27834	0.33136	21.81	176.71
SiO <sub>2</sub> ( $\beta$ -Cristobalite) Ref.99	(2.616)					
SiO <sub>2</sub> ( $\beta$ -Quartz) Ref.99	3.420	0.01856	0.40390	0.50463	5.61	180.00
	3.477	0.01586	0.34943	0.43378	2.02	178.14
SrO Ref.100	(3.649)					
TiO <sub>2</sub> (anatase) Ref.99	1.892	0.70115	15.74348	24.93740	0.27	179.95
	2.050	0.43932	11.97492	16.36836	33.40	179.56
	3.473	0.00756	0.01253	0.02506	0.00	137.85
TiO <sub>2</sub> (rutile) Ref.102	2.536	0.17930	3.50806	4.67155	43.41	180.00
	3.325	0.02166	0.53788	0.62560	14.78	180.00
ZnO Ref.103	(3.209)					
ZrO <sub>2</sub> (cubic) Ref.100	2.545	0.18207	3.25165	4.60648	15.29	180.00
O <sub>2</sub> (g)	1.208	3.63513	−22.08444	47.08056	0.00	180.00
F <sub>2</sub> O <sub>2</sub> (g)	1.217	3.60353	−24.45509	47.62489	0.72	
O <sub>3</sub> (g)	1.278	2.96936	−8.97505	29.35337	11.10	
H <sub>2</sub> O <sub>2</sub> (g)	1.452	1.91704	−2.75818	27.67977	5.25	
C(NO <sub>2</sub> ) <sub>3</sub> (planar)	2.453	0.17165	3.22675	4.65489	12.07	
C(NO <sub>2</sub> ) <sub>3</sub> (nonplanar)	2.689	0.10126	1.91329	2.42346	39.02	

(2.453 Å) is larger than within a NO<sub>2</sub> group, the molecule presents three O–O bonds. Similarly, the topological analysis of simple and highly symmetric crystalline structures has made clear that the occurrence of secondary anion–anion bond critical points (or cation–cation bonds in some cases) is regulated by the ratio of topological radii along the main cation–anion bond paths.<sup>11,46,47</sup> The analysis of low symmetry crystals or molecules is more difficult, but the same principles should apply and we could say that the occurrence of secondary bonds between two atoms is controlled not by the distance but

rather by the size of the nearest neighbors’ basins around both atoms.

On the other hand, the electron density at the O–O bond critical point decays exponentially with the O–O distance, as we can see in Fig 6. This behavior is closely followed by molecules and crystals, for distances from 1.2 to 3.2 Å, and for bonds whose densities range from 5 to 0.005  $e/\text{Å}^3$ . As we had expected, the behavior of the bond in the O<sub>2</sub> molecule with the distance passes through the actual values of the other molecules and crystals, therefore representing an appropriate model for the

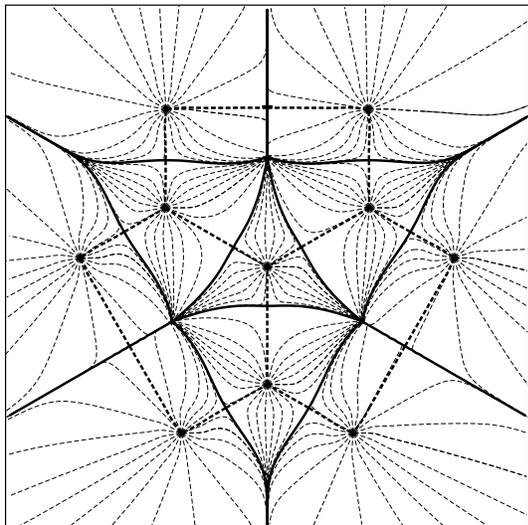


FIG. 5: Electron density gradient vector field of  $C(NO_2)_3^-$  at the optimal HF/TZV+(1d) planar geometry. In addition to the expected C–N and N–O bond critical points, the molecule presents O–O bonds connecting neighbor  $NO_2$  groups, and ring points within each ONCNO pentagon. It is readily seen that O–O bonds occur only between  $NO_2$  groups, as the N basin extends through the two oxygens in each  $NO_2$  group. The topology of the non-planar optimal configuration is identical, albeit less simple to visualize.

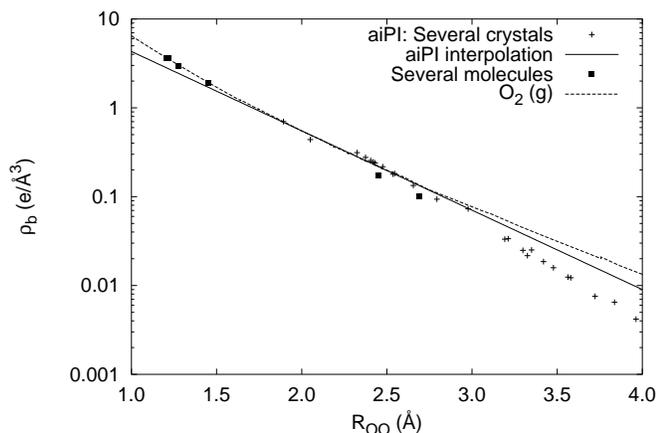


FIG. 6: Electron density at the O–O bonds, in a collection of molecules and crystals, represented against the O–O distance. The electron density for the  $O_2$  molecule has been obtained on a wide range of distances rather than at a single geometry like in the case of the other systems. The  $\rho_b$  value for the crystals has been represented by the best fit exponential law,  $\rho_b(r_{OO}) = A \exp(-\alpha r_{OO})$ , where  $A = 33.692 \text{ e}/\text{\AA}^3$  and  $\alpha = 2.0569 \text{ \AA}^{-1}$ . Notice the logarithmic scale used on the vertical axis.

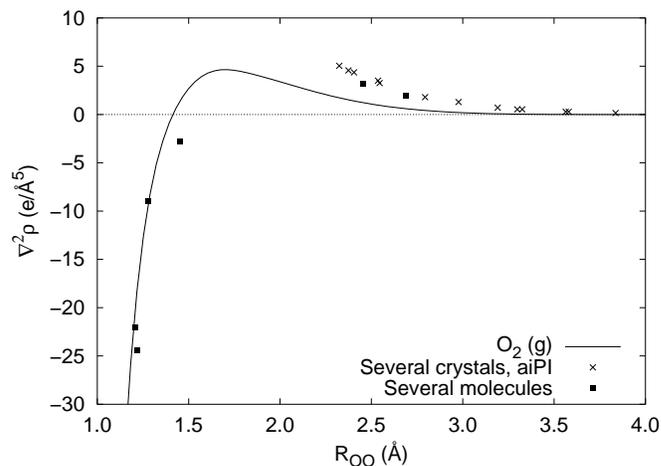


FIG. 7: Laplacian of  $\rho_b(O-O)$  for a collection of molecules and crystals. The value of  $\nabla^2 \rho_b$  of the  $O_2$  molecule has been obtained in a range of internuclear distances, and it provides an approximate model for all the compounds.

O–O bond.

The  $O_2$  molecule also provides an appropriate model for the Laplacian of the electron density at the O–O bond critical point, although it is less precise than in the case of the bond density. We can observe in Fig 7 that the bond character changes from mainly covalent ( $\nabla^2 \rho_b < 0$ ) to mainly closed-shell like ( $\nabla^2 \rho_b > 0$ ) as the O–O distance passes from below to above 1.5  $\text{\AA}$ , respectively. Accordingly, the O–O bond is clearly ionic (or closed-shell) in most crystals, whereas it can be either covalent or ionic in the molecules.

The above results show, in our opinion, a clear evidence in favor of the real occurrence of O–O secondary bonds in many crystals, and they also show the continuity in the bond properties of the O–O dumbbell from the molecular to the crystal regime, the internuclear distance being the main control parameter.

Several authors, on the other hand, have raised legitimate concerns about the physical meaning of anion–anion bonding in crystals,<sup>59</sup> “sterically interacting” atoms<sup>57</sup> or long-distance nonclassical bonds in general.<sup>55,56,104</sup>

Abramov,<sup>59</sup> for instance, based his main argument on a particular decomposition of the lattice energy into coulombic and short range repulsive terms by using Bader’s basin charges within a simple electrostatic formula that assumes point-like ions. According to this partitioning scheme, the anion–anion interactions (or the cation–cation ones) could only destabilize the crystal by raising the Coulomb energy. It must be noticed, however, that atomic basins are far from being spherical and point-like, and that quite important multipolar interactions do exist, as it has been demonstrated by Popelier.<sup>105,106</sup> A thorough analysis of whether the local distribution of electron density of the anion–anion interaction line represents a bonding or antibonding net contribution in the

energetic sense could be done using Berlin’s methods.<sup>107</sup> Such analysis has been used extensively, to the best of our knowledge, only on simple diatomic molecules<sup>108–112</sup> and its generalization to more complex molecules and even crystals could be described as a nightmare (see however Ref.113).

Cioslowski *et al.*<sup>55–57,104</sup> have tried to classify long distance, weak topological bonds into true chemical bonds (like those appearing in van der Waals interactions<sup>114</sup> and hydrogen bridges,<sup>115,116</sup> for instance) and interactions appearing only for “steric reasons”. The O–O bond in the planar configuration of the trinitromethanyde ion,  $C(NO_2)_3^-$ , is proposed as a typical example of molecule with steric interactions.<sup>57</sup> It could be argued, however, that the “steric crowding” is eliminated in the nonplanar optimal geometry of  $C(NO_2)_3^-$  by the rotation of the  $NO_2$  groups around the C–N axes, but the fact is that the O–O bonds do not disappear by this relaxation of the symmetry (see Table IV). In addition, as we have shown previously, the topological properties of O–O bond paths display a clear continuity from their occurrence as *strong bonds* in many molecules to the *weak* second and longer range interactions appearing in many crystal oxides, the *effective bond order* being determined by the O–O distance.

More fundamentally, the occurrence of closed-shell weak bonds in molecules and crystals has been discussed by Bader.<sup>117</sup> After examining the atomic and local theorems governing atomic interactions, Bader concludes that the presence of a (3, –1) critical point of the electron density and its associated atomic interaction line in a stationary state of a molecule or crystal is both necessary and sufficient for the two atoms to be bonded to one another in the usual chemical sense of the word. In addition, “there are no repulsive contributions to the total potential energy locally nor from atoms or ions within a system” and “only an excess electronic kinetic energy

can lead to repulsions within the system”, the electronic potential energy being always stabilizing.<sup>117</sup> Finally, even though the Lewis model of bonding in terms of the formation of one pair of electrons per bond is clearly unable to deal with bonding in closed-shell systems, this idea can be generalized to include less than complete pairing. Accordingly, closed-shell interactions (either weak or strong) and shared interactions are, both, due to the pairing of the densities of opposite spin electrons.

## VI. CONCLUSIONS

To conclude, we want to stress the usefulness of comparing high quality electron densities from experiments and theoretical calculations to further improve our knowledge of chemical bonding in the light of the new paradigm provided by the Atoms in Molecules Theory. An universal indication of a bonding interaction between two atoms, for short as well as long distances is the occurrence of a bond critical point and its associated bond path connecting both atoms. The extrapolation of bond properties from small molecules to the solid state regime appears as a promising auxiliary technique that should be further explored.

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