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Local compressibilities in crystals

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An application of the atoms in molecules theory to the partitioning of static thermodynamic properties in condensed systems is presented. Attention is focused on the definition and the behavior of atomic compressibilities. Inverses of bulk moduli are found to be simple weighted averages of atomic compressibilities. Two kinds of systems are investigated as examples: four related oxide spinels and the alkali halide family. Our analyses show that the puzzling constancy of the bulk moduli of these spinels is a consequence of the value of the compressibility of an oxide ion. A functional dependence between ionic bulk moduli and ionic volume is also proposed.

I. INTRODUCTION

The partitioning of the observables of physical systems into additive microscopic contributions has always been one of the means by which complex sets of data are reduced to understandable components. This works surprisingly well in both the molecular and condensed matter realms. As chemists know well, a large number of properties — i.e., energies, electric and magnetic susceptibilities, electric dipolar moments — may be partitioned into atomic or group contributions, often with a precision similar to that of the experiments themselves, leading us inevitably to the concept of group or atomic property. It is also well known that quantum mechanics does not easily accommodate this picture. Well developed for around 20 years, the theory of atoms in molecules[1] (AIM) has proved to be a theoretical frame, completely rooted in quantum mechanics, that allows a smooth interpretation of these phenomena, recovering the concept of atoms and groups of atoms from a system's wave function. It is now routinely used in molecular quantum chemistry, and is being progressively applied to gain new insights in solid-state problems.[2,3] In this field, the theory provides a *de facto* geometrization of solids through finite quantum atoms or ions defined in physical three-dimensional space. We have previously shown that the sizes and properties of these atoms or ions are easily associated with those used empirically since the advent of solid-state physics.[4] Since all AIM atomic properties are additive and quantum atoms fill the space, bulk or thermodynamic properties may also be partitioned into atomic or group contributions, but work in this direction has been scarce. One field with interesting comparisons between existing knowledge and new AIM results is high-pressure solid-state physics.

Understanding the rules that govern the compressibility of simple solids has traditionally been a branch of geosciences, where insufficient knowledge of the behavior of minerals upon compression limits our models of the geological evolution of our planet.[5] Usually, crystalline bulk moduli are interpreted in terms of, on the one hand, the bulk moduli of cation-anion polyhedra and, on the other, the connectivity of these polyhedra across the lattices. The elemental units here are cation-centered anionic polyhedra whose bulk moduli are assumed to be constant. Since the 1920s, with a seminal paper by Bridgman,[6] through the 1979 paper by Hazen and Finger,[7] experiments have shown that polyhedral bulk moduli of minerals are inversely proportional to polyhedral volumes and are directly proportional to the product of both the formal charges of cations and anions and to an empirical ionicity measure. To a large extent polyhedral bulk moduli are constant. It has always been clear that these empirical magnitudes may be decomposed into atomic contributions, but to do so a well-defined atomic or group partitioning of the physical space is needed. The AIM theory provides it.

Local compressibilities or bulk moduli have also played an important role in the theory of the (mainly d-d) electronic spectra of substitutional transition metal impurities in compressed crystals. The empirical pressure variation of suitable spectral components has been used as a means to calibrate high pressure measurements.[8] However, to correctly understand these phenomena, it soon became clear that it was necessary to take into account the differential compression of host and guest ions. In 1961, Minomura and Drickamer[9] used these ideas, together with Bridgman's[10] equations of state (EOS), to show that the variation of the Dq values of several transition metal ions in MgO and Al_2O_3 demonstrated both the existence of differential compressibilities of impurities and host ions and of strong lattice relaxations around the impurities. Since then, a large amount of theoretical[11,12,15] as well as experimental work,[13,14] together with a wealth of new experimental techniques—electron paramagnetic resonance (EPR), extended x-ray-absorption fine structure, (EXAFS), x-ray appearance near-edge structure (XANES)—that allow the determination of local host-impurity distances have greatly extended our knowledge about these facts and produced a number of relevant results.[16] These may be summarized in the intuitive idea that differential compressibilities of impurities with respect to host ions are governed by the size difference and tuned by the formal charge mismatch between host and guest.

It is important to recognize that both the polyhedral and impurity local bulk moduli commented above are actually linear compressibilities. They are always obtained through pressure derivatives of interatomic distances, and this is a serious drawback if we try to use them additively. It is clearly not easy to avoid the problem unless we are able to divide this distances or volumes into atomic contributions.

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We show in this paper how the AIM theory applied to the problem of partitioning bulk moduli in crystals provides additive atomic-ionic compressibilities with properties fulfilling all physical and chemical requirements. These new objects may be compared to previous local measures of compressibility as well as applied to the *ab initio* prediction of bulk moduli of materials or to the interpretation of interesting empirical facts from an atomic point of view. To illustrate their behavior we have computed them in (i) a number of related oxide spinels, with very similar bulk moduli, and (ii) the alkali halides, whose widely different bulk moduli vary periodically on changing their constitutive cations and anions. We will show how these two strikingly different behaviors have the same origin, and how some general rules, both empirically and intuitively sound, arise from the amount of physical space (now a well-defined observable) occupied by the different kinds of atoms found in a crystal. The local bulk moduli here defined provide a quantitative measure of the ability of an atom or ion to deform *inside* a crystal. These magnitudes are, therefore, system dependent. As the alkali halide example will clearly demonstrate, it seems that this dependence is simple and basically dominated by the atomic volume.

We have organized the paper as follows. In Sec. II we define the concept of local atomic bulk moduli after a very brief account of the basics of the AIM theory. Section III presents the computational models used to obtain both the equations of state of the systems studied and the wave functions that feed the AIM topological analysis. Some numerical considerations about the precision of the several magnitudes used to obtain the local bulk moduli will also be made. Section IV will be devoted to discussing some experimental facts in oxo-spinels and alkali halides, as well as our computed local bulk moduli for both of them. We will also rationalize here our findings in terms of simple ideas. Finally, Sec. V will present our conclusions and some future prospects.

II. LOCAL COMPRESSIBILITIES IN CRYSTALS

The AIM theory[1] provides a sound and unique partitioning of physical space rooted in nonrelativistic quantum mechanics. It shows how Schwinger's stationary action principle[17] may be generalized to three-dimensional subsystems if some boundary conditions are assured on the surfaces separating them. Those surfaces are defined through the zero local flux condition of the electron density gradient vector field,

$$\nabla\rho(\vec{r})\cdot\vec{n}(\vec{r})=0, \tag{1}$$

where $\vec{r}$ is any point lying on the boundary surfaces characterized by exterior normal vectors $\vec{n}$.

The subsystems so defined satisfy Heisenberg equations of motion and turn out to be governed by the same dynamic laws as the whole quantum system. Moreover, the expectation values of every quantum mechanical observable $\langle\hat{O}\rangle$ are univocally defined for each quantum subsystem i,

$$\langle\hat{O}\rangle_i=\int_{V_i}dv\,\hat{O}(\vec{r}), \tag{2}$$

and quite evidently add up to the observable for the whole system. It is the topology of the electron density that warrants the existence of this kind of partitioning of the physical space. In the vast majority of cases, each quantum subsystem encloses one and only one nucleus, and we identify it with a quantum atom. These quantum atoms fill the space, and in crystals bear a finite volume. The peculiarities of the AIM theory as applied to crystals have been studied in detail in previous works.[3,4]

In this paper we are interested in the partitioning of observables into atomic contributions. Given a scalar electron density coming from either theory or experiment, the partitioning is assured if the associated gradient vector field may be computed with appropriate precision. To work out simple expressions, let us consider static thermodynamic conditions (zero temperature, no zero-point effects). In this case, the static compressibility (κ) and bulk modulus (B) of a condensed system are defined as

$$\kappa=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)=\frac{1}{B}. \tag{3}$$

If temperature is to be taken into account, then isothermal or isentropic magnitudes arise, according to which external degree of freedom is kept constant along the differentiation. These more realistic and complex cases might be studied if appropriate statistical averages of electron densities were available. In the following, only the static case will be considered.

Let us now topologically divide a unit formula within the crystal. This can be done by specifying a nuclear arrangement and analyzing the subsequent electron density of the system as summarized above. This procedure is always univocally defined, so the molar volume $\overline{V}$ may be written as a sum over atomic volumes V_i: $\overline{V}=\Sigma_i V_i$. We are now in a position to define static local bulk moduli B_i and static local compressibilities κ_i for each quantum subsystem within the system,

$$B_i=-V_i\left(\frac{\partial p}{\partial V_i}\right)=\frac{1}{\kappa_i}, \tag{4}$$

and using the volume partitioning, arrive at the following expression:

$$\kappa=\sum_i f_i\kappa_i,\quad \frac{1}{B}=\sum_i f_i\frac{1}{B_i}, \tag{5}$$

where $f_i=V_i/\overline{V}$ is the fractional volume occupancy due to quantum subsystem i in a unit formula volume.

This simple relation is the basis of all our following arguments. It shows that local compressibilities may be rigorously defined within the AIM theory and that the bulk compressibility of a condensed system is a volume-weighted sum of atomic or ionic contributions. Of course, the idea of reconstructing compressibilities of compounds from those of their constituents is not new, and has been applied repeatedly in the past. However, even in the simplest cases, the conceptual problems associated with partitioning space into local volumes introduced severe limitations to the approach. For example, the compressibility of solid solutions of different alkali halides never varies linearly with composition.[18] The present approach is physically sound and unique, and allows us to firmly root in theoretical grounds some well-known behaviors of materials and to rationalize others that are not well understood.

Given its simplicity, the analysis of Eq. (5) is straightforward. Only two factors enter in the construction of bulk compressibilities from our local magnitudes: (i) the relative volume occupied by a given quantum atom in the material's molar volume and (ii) its own local compressibility. Both factors, as we will see, run generally side by side, in agreement with the usual thinking. Large, bulky atoms or ions are usually more compressible than small, stiff quantum subsystems. Another interesting effect comes from the relative occupation factors, since if any quantum atom largely dominates the unit formula of a compound, the compressibility of the whole system will be dominated by its own contribution, no matter what the compressibility of its neighbors. This effect is greatly enhanced if the species dominating the unit formula is also the most compressible one.

We have chosen two classes of systems to present our results. A few related inorganic spinels with very similar experimental bulk moduli will illustrate the decisive influence of the occupancy factors in global compressibilities. On the other hand, the alkali halide series will be used to assess the transferability of local compressibilities across compounds and to discover the main variables on which these new magnitudes depend.

III. COMPUTATIONAL DETAILS

The computation of static local compressibilities in pure crystals rests in the calculation of pressure derivatives of topologically partitioned quantum subsystems. Three basic ingredients are then needed. First, we need a method to compute reliable electron densities at selected nuclear configurations. These electron densities are to be fed into a code to determine zero-flux surfaces and integrate the unit density operator in Eq. (2) to obtain topological volumes. Second, these topologically partitioned densities are to be obtained at the thermodynamical equilibrium nuclear configurations of the system under study for a number of pressures in the range of interest, so a method to obtain the static EOS is needed. Finally, a suitable numerical differentiation is to be performed to obtain the atomic compressibilities. The whole process is numerically intensive.

As in other works, we have used the *ab initio* perturbed ion method (*ai*PI),[19–21] a localized, linear scaling quantum-mechanical scheme devised in our laboratory that has been successfully used to obtain the electronic structure and a wide range of properties in ionic and partially ionic solids. It usually gives equilibrium geometries within a few percent and bulk moduli within 10% of the empirical data. Densities are analyzed by our CRITIC program.[22] Integration of the unit operator within the atomic basins is done by numerical quadratures in spherical coordinates centered at the nuclei positions, the obtention of the zero-flux surface for each nucleus-centered ray being both the bottleneck and the main source of error in the algorithm. Usually, $90\times60\times60$ points in the radial, θ and ϕ coordinates are used, with atomic volumes converged to the mbohr^3.

EOS have been obtained by selecting a grid of crystalline molar volumes around the calculated unstressed equilibrium positions, minimizing the total crystal energy with respect to lattice and internal parameters at each volume. This involves a one-dimensional optimization of the internal parameter of the direct spinel structure and a single-point calculation in the alkali halide case. Volume-energy $(\overline{V},E)$ data are then fitted to Vinet's universal EOS (Ref. 23) with our GIBBS code.[24] This method provides us with the required $p(V)$ relation and the bulk modulus of the lattice, B, which enters Vinet's equation as a parameter. The procedure has proved to be extremely useful in avoiding numerical errors when computing second derivatives from $(\overline{V},E)$ data. Analysis of electron densities at each $\overline{V}$ point produces parallel V_i tables that have been also fitted to the Vinet EOS to give us local bulk moduli for each atomic subsystem.

Final data have been checked for consistency at each $\overline{V}$ point in a twofold manner: crystal compressibilities must fulfill Eq. (5), and local volumes must add to the whole lattice volume at each $\overline{V}$ point.

TABLE I. Zero-pressure structural properties of $MgAl_2O_4$, $ZnAl_2O_4$, $MgGa_2O_4$, and $ZnGa_2O_4$. Lattice parameters in Å .

	$MgAl_2O_4$	$ZnAl_2O_4$	$ZnGa_2O_4$	$MgGa_2O_4$
a	7.886	7.835	7.977	8.021
	8.0832 [a]	8.086 [a]	8.330 [a]	8.270 [b]
u	0.2688	0.2675	0.2673	0.2683
	0.2624 [a]	0.2636 [a]	0.2617 [a]	0.2614 [b]

[a] Experimental values from Ref. 37.

[b] Calculated values from Ref. 38.

IV. RESULTS

A. Spinels

Spinels are extremely versatile compounds with generic unit formula AB_2X_4, where A and B are cations and X denotes an anion. For a given X the structure may host a wealth of differently sized A or B cations. The ideal structure is usually described as a distorted cubic close-packed array of anions with one-eight of the tetrahedral and one-half of the octahedral interstices occupied by cations. In the normal, ordered distribution, the A divalent cations occupy the tetrahedral positions and the B trivalent cations the octahedral interstices. A large amount of cationic disorder, however, is allowed. Distortion of the ideally close-packed structure of the anions is measured by a single internal crystallographic coordinate u, equal to 0.25 in the ideal case. It is well known[25] that the empirical u parameter is controlled by the A,B cationic pair through relative size coordinates. Bulk moduli of many oxo-spinels have been determined and turned out to cluster around 200 GPa. Hazen and Finger[7] suggested that all oxide spinels might have such similar bulk moduli. Here we will focus in the four normal oxide spinels formed when $A=$Mg,Zn and $B=$Al,Ga. Computed and room-temperature experimental structural parameters at zero pressure are shown in Table I. A unit cell of a typical spinel is seen in Fig. 1.

We have obtained the static EOS of the four spinels in the range 0–80 GPa. A first indication of the differential behav-

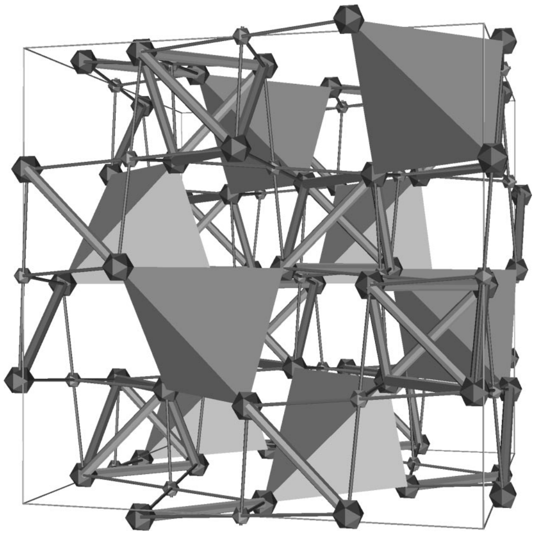

FIG. 1. Structural elements in the unit cell of a typical normal spinel. Divalent ions are not shown, hidden at the center of their coordination tetrahedra. Trivalent ions are displayed as small balls, at the centers of a clearly distorted oxide octahedron, while oxide ions are shown as large balls. Notice the perfect tetrahedra of empty oxide ions drawn in thick lines. The thinnest lines are just the boundaries of the cell.

ior of the A,B cations with pressure is obtained from the variation of the u parameter. As is usual in normal spinels, u decreases slightly with pressure: in our cases, about 0.002 units in the pressure range studied. Inorganic solids are usually described in terms of cationic coordination polyhedra. From elementary lattice calculations, the ideal octahedral (B^{3+}) and tetrahedral (A^{2+}) volumes are $v_{\mathrm{tet}}=8a^3(u-1/8)^3/3$ and $v_{\mathrm{oct}}=16a^3(u-3/8)^2u/3$. This gives an octahedral site that almost doubles the volume of the tetrahedral one at common u's. As can easily be seen from the above expressions, a decreasing u value with pressure means a progressively smaller $v_{\mathrm{tet}}/v_{\mathrm{oct}}$ ratio and, in some way, reflects the larger compressibility of the tetrahedral site with respect to the octahedral one. It has been customary to define polyhedral bulk moduli or compressibilities and try to rationalize the bulk compressibilities from the polyhedral ones.[7,25] A clear trend has been found from these studies: a given cationic polyhedron displays a mostly constant polyhedral compressibility. Hard linked structures (i.e., those with large amounts of face sharing or edge sharing polyhedra) display bulk moduli directly related to these polyhedral compressibilities. Soft linked structures do not. In spinels, it has been shown that bulk moduli are almost the arithmetic mean of the octahedral and tetrahedral bulk moduli,[26] and this fact has been algebraically understood only very recently.[27] We should bear in mind here, however, that polyhedral compressibilities are a mixture of anionic and cationic local contributions without quantum mechanical sense.

It may seem paradoxical, at first sight, that the intuitively smaller trivalent cations enter the structure at the largest polyhedral site. Some authors have tried to explain the site preference of cations in terms of electronic (crystal-field) effects.[28] Others even suggested a *rattling* model for the trivalent cation in its oxide ion cage.[29] However, closed-shell cations do show clear site preferences, and today it is commonly accepted that size is the main variable affecting these facts. A closer look allows us to understand this fact better. In a first spherical ion approximation, the cation-anion distance d shows an octahedral to tetrahedral ratio $d_{\mathrm{oct}}/d_{\mathrm{tet}}$ equal to 1.15 in the ideal spinel and about 0.94 for the u values found here, so the u distortion increases the size available to the divalent cation while decreasing that of the trivalent one. The u value at which the first neighbors of the oxide ions change from the divalent to the trivalent cations is $u=0.263$. Moreover, the oxide ion neighbor structure is only that of a more or less distorted cubic closed-packed lattice in a small u range going from 0.250 to 0.267. Another simple phenomenon is also driving the distortion. The Madelung energy of spinels peaks at about $u=0.281$, so there exists a strong electrostatic tendency towards large u values and small octahedral sites. Most direct spinels have u values significantly larger than 0.25 and clearly correlated with the classical size ratio between the A and B cations.

The topological features of the electron densities of these materials are simple. In all cases examined, there are just three kinds of bond paths: A and B to first-neighbor oxide ions and oxide ion to first neighbor oxide ions. Only when examining the complete topological graph do these spinels differ among themselves. As far as volume-dependent properties being studied, this fact is of no practical interest. Figure 2 shows the shape of the basins of all different ions bonded to a given oxide ion in the $ZnAl_2O_4$ system and the perfect tetrahedra of oxide ions formed by a given anion and its first anionic neighbors. This structural element will be extremely important in what follows, as its size determines the u parameter. Data come from our CRITIC code as rendered by GEOMVIEW.[30] As usual,[4] cations display convex ionic basins. Trivalent cations are homomorphic to cubes (sixfold coordination), while divalent ones are tetrahedra. No direct cation-cation contacts have been found, though the B cations may display almost bidimensional wings that avoid more oxide-oxide contacts. As found in most inorganic materials, the anionic basins are more complex than those of the cations. Oxides have C_{3v} symmetry, and three symmetry-related oxide ions together with three symmetry-related B cations bond to them on one side of the basin, while the other side gets fully occupied by a slightly convex interatomic surface that corresponds to the A-oxide ion bond. As sphericity of ions is concerned, it decreases in the order $B^{3+}>A^{2+}>O^{2-}$.

All Laplacians at bond points are small and positive, and all cations have lost their outermost electronic shell. Our four spinels are highly ionic compounds, and AIM ionic charges in the range 0–80 GPa are shown in Fig. 3. These charges are almost coincident with the nominal ones, the biggest fractional deviation being that of the Ga^{3+} ion, going from 0.10 to 0.11 on passing from 0 to 80 GPa. Deviations from nominal charge increase with pressure in all cases. Therefore, in some sense, ionicity slightly decreases with increasing pressure. It is clear from the figure that trivalent cations have almost constant charge at each p value, behaving themselves as hard species in a generalized chemical sense. Charge dispersion in the A cations is larger but still quite small and it is largest when the oxide ions are considered. The latter adapt their charges according to electroneutrality requirements. It is also interesting to notice that the charge

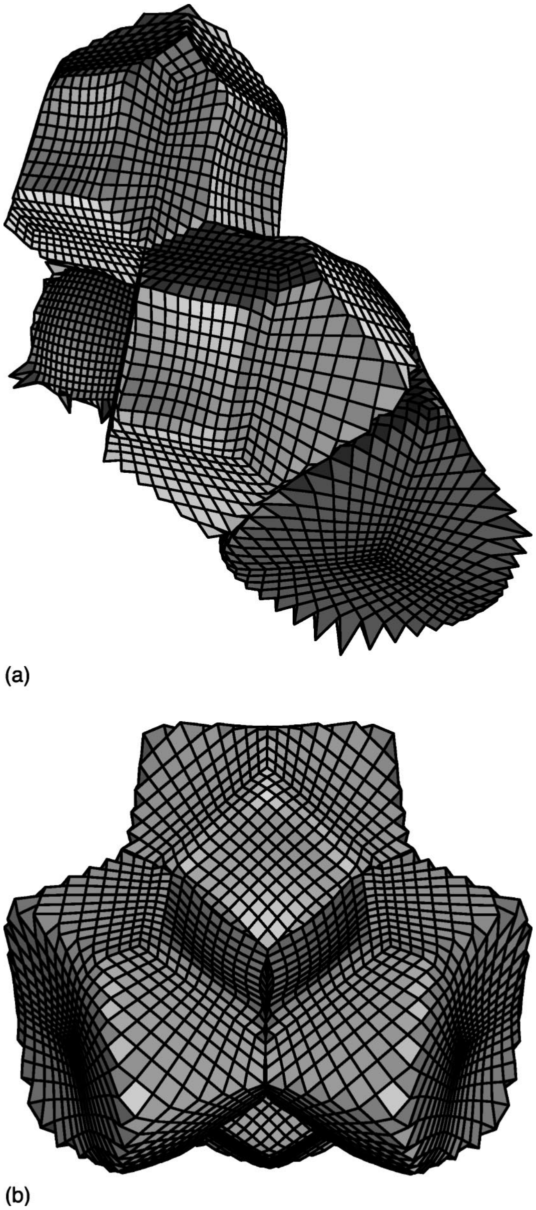

FIG. 2. (a) Ionic basins in $ZnAl_2O_4$ at zero pressure. We show here a central oxide ion surrounded by a Zn^{2+} cation (bottom, right), an almost cubic Al^{3+} (center, left), and another oxide ion (top, right). Notice the size difference among different basins, the convexity of the cation-anion contact faces, and the planar anion-anion contacts. (b) Perfect tetrahedron of oxide ions in the spinel structure as main structural element. We see the B^{3+} socket at the figure's center and the almost planar A-oxide ion interatomic surfaces in the outer sides.

variation of each cation has a clearly distinctive slope, whereas that for the anion is again dictated by electroneutrality. Moreover, the Zn^{2+} ion, a $3d$ system, is significantly different from the rest.

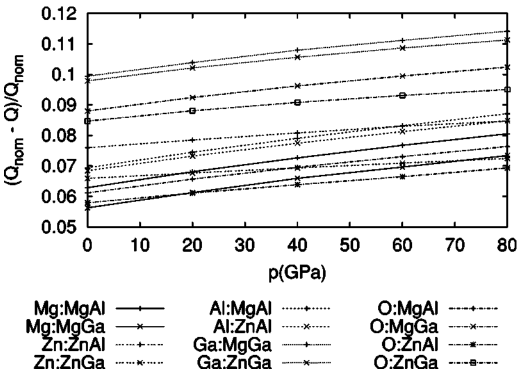

FIG. 3. Variation of AIM topological charges in the four spinels vs pressure. Relative deviations with respect to the ionic nominal charges (Q_{nom}) are represented.

Let us return to atomic volumes, shown in Table II. First we can observe that the oxide ions are much more voluminous than the cations. When weighted by the f stoichiometry factors, they outweigh the rest by far. The divalent cations are in both cases larger than the trivalent ones, being noticeable in that when the A and B volumes approach each other (like in the MgGa spinel), the observed structures turn out to be inverse or highly disordered. All ions display a rather constant volume at a given pressure, a very interesting result pointing towards the plausibility of a particular pressure behavior for each chemical species. We will comment on this later. On compression, ionic volumes decrease, but not uniformly. The size of the cations decreases about a 12% on going from 0 to 80 GPa, while that of the anions shrinks by a 25%. Oxides are much more compressible than cations. Furthermore, ionic charge and ionic volume turn out to be

TABLE II. AIM topological volumes (in a.u.) in the four spinels vs pressure.

$MgAl_2O_4$	Mg	Al	O	p (GPa)
	34.413	19.151	78.879	0
	32.389	18.187	72.415	20
	30.897	17.470	67.718	40
	29.720	16.899	64.046	60
	28.751	16.426	61.043	80
$MgGa_2O_4$	Mg	Ga	O	p (GPa)
	35.456	33.135	75.742	0
	33.309	31.313	69.457	20
	31.444	30.042	65.019	40
	30.511	29.115	61.523	60
	29.499	28.339	58.740	80
$ZnAl_2O_4$	Zn	Al	O	p (GPa)
	54.073	19.018	76.674	0
	50.393	18.083	70.437	20
	47.682	17.387	65.892	40
	45.555	16.838	62.343	60
	43.714	16.409	59.436	80
$ZnGa_2O_4$	Zn	Ga	O	p (GPa)
	56.405	32.809	73.615	0
	52.549	31.104	67.507	20
	49.736	29.885	63.146	40
	47.534	28.950	59.787	60
	45.733	28.202	57.082	80

TABLE III. Fractional occupancy factors (f) in the four spinels studied at zero pressure.

	$f(A)$	$f(B)$	$f(O)$
$MgAl_2O_4$	0.0886	0.0987	0.8127
$MgGa_2O_4$	0.0876	0.1638	0.7486
$ZnAl_2O_4$	0.1356	0.0954	0.7690
$ZnGa_2O_4$	0.1354	0.1576	0.7070

largely correlated, so that the charge hardness previously introduced is actually related to compressibility. Figures 1 and 2(b) can now be reinterpreted. The primary tetrahedra of oxide ions in the structure are the basic structural units that support deformation. Both the internal stress, coming from the hardness of the cations, and the external one, coming from applied pressure, transmit themselves to these tetrahedra, which shrink or expand on need, fixing the observed u distortion. As we are starting to see, the oxide ions are plastic constituents of these spinel structures.

Local bulk moduli have been calculated as explained in Sec. III. Fractional occupancy factors at zero pressure are shown in Table III. It is clear from the data that the bulk compressibility of these crystals is to be dominated by the anionic contribution and that a given cation has an almost constant volume occupancy, the oxide ions behaving like volume buffers. Local and global bulk moduli are found in Table IV. In reasonable agreement with experiment, the global B values cluster around 213 GPa, and not surprisingly, those of the oxide ions gather around 200 GPa. All species show basically constant B values in different compounds. This fact, together with the charge and volume constancy noted before, points towards a very interesting transferability of atomic properties among compounds. Cations are quite less compressible than oxide ions, and a clear relation among the local bulk moduli and both the atomic volumes and topological charges is found, in agreement with previous empirical models already cited.[31,7]

Several interesting particular comparisons are due. For example, among the B cations, which display a local B around 300 GPa, Ga^{3+} is clearly more compressible than Al^{3+}, while among the divalent cations, Mg^{2+} is less compressible than Zn^{2+}, in agreement with chemical intuition. Pressure derivatives of local bulk moduli (B_i') are also informative, being again determined by the most compressible component: the B cation. In this way, the two Gallium spinels show a large B' due to a large trivalent component. Fine details are also easy to rationalize. Ga^{3+} and Al^{3+} are less compressible in the presence of the larger Zn^{2+} ion than in the Mg^{2+} compounds. The contrary is true for the dipositive cations: Zn^{2+} and Mg^{2+} are less compressible in the Al compounds than in the Ga ones. This means that the size available for trivalent cations controls their compressibility, while other factors, notably the large polarizing ability of Al^{3+}, control the size of divalent ions. As already noticed, oxide ions accommodate their size to lattice constraints. Nevertheless, this variation does not affect much their compressibility. This is probably true in any system with large compressible oxide ions, where not too large volume variations will induce negligible compressibility changes, but will turn progressively wrong as the oxide ion volume decreases. The latter situation is expected in rocksalt oxides like MgO, and its halide equivalent will be discussed in the next subsection.

TABLE IV. Local and global bulk moduli (GPa), together with their first pressure derivatives, for the spinels under study at null pressure.

Spinel	B	B'	B_B	B_B'	B_A	B_A'	B_O	B_O'
$MgAl_2O_4$	215.2	3.81	331.9	6.00	282.1	5.18	201.6	3.5
$MgGa_2O_4$	211.2	4.38	283.9	7.69	261.2	5.45	196.1	3.8
$ZnAl_2O_4$	214.8	3.84	335.2	6.56	246.0	4.14	203.3	3.5
$ZnGa_2O_4$	213.3	4.28	308.6	7.22	241.2	4.48	195.7	3.8

TABLE V. Computed unit formula and ionic volumes (a.u.) in alkali halides at null pressure. Fractional occupancy factors are also given. Notice that not all of these $B1$ phases are the thermodynamically preferred ones.

Compound	$\overline{V}$	V_A	V_X	$f(A)$	$f(X)$
LiF	100.4	16.93	83.41	0.1687	0.8312
LiCl	234.2	25.38	208.9	0.1083	0.8916
LiBr	279.1	25.61	253.3	0.0918	0.9081
LiI	395.3	29.62	365.6	0.0749	0.9250
NaF	155.4	49.69	105.5	0.3201	0.6798
NaCl	295.9	61.34	234.5	0.2073	0.7926
NaBr	352.7	62.25	290.3	0.1765	0.8234
NaI	474.2	68.61	405.6	0.1447	0.8553
KF	258.8	136.5	121.9	0.5282	0.4717
KCl	470.5	167.9	301.9	0.3574	0.6425
KBr	529.7	163.3	365.6	0.3087	0.6912
KI	679.3	173.8	505.2	0.2560	0.7439
RbF	263.5	159.6	103.5	0.6066	0.3934
RbCl	512.4	217.6	294.0	0.4252	0.5747
RbBr	582.6	214.2	367.6	0.3682	0.6317
RbI	745.2	228.1	516.1	0.3064	0.6935
CsF	229.3	156.6	72.30	0.6841	0.3158
CsCl	514.5	274.2	239.4	0.5339	0.4660
CsBr	573.6	268.2	304.5	0.4682	0.5317
CsI	776.6	302.3	473.2	0.3897	0.6102

The whole set of ideas presented here forms a very easy to grasp frame under which many structural aspects of these compounds may be understood in a compact manner. Site preference, u distortion, bulk moduli, cell size, etc., turn out to be mainly controlled by atomic size and its resistance to variation.

B. Alkali halides

The alkali halides (AX) in the rocksalt ($B1$) phase constitute a class of compounds whose behavior upon compression is very different to that of oxo-spinels. It is well known that their bulk moduli, as well as their lattice parameters, show a gradation on running over both cations and anions.[32] Using our *ai*PI technology, theoretical analyses of their electronic structure, EOS, global B values, and their first pressure derivatives, phase transitions, and other thermodynamical

TABLE VI. Global and local bulk moduli (GPa) for the 20 rocksalt alkali halides at zero pressure. Pressure derivatives of bulk moduli are also shown.

Compound	B	B'	B_A	B'_A	B_X	B'_X
LiF	80.93	4.68	94.16	5.53	78.59	4.53
LiCl	31.58	3.86	35.91	4.24	31.15	3.82
LiBr	29.41	4.27	34.30	5.15	28.98	4.20
LiI	17.23	4.21	20.20	5.18	17.03	4.14
NaF	65.83	4.33	82.46	5.52	60.45	3.84
NaCl	28.67	4.77	35.49	5.81	27.40	4.53
NaBr	26.75	4.71	32.69	6.47	25.79	4.41
NaI	17.28	4.52	22.19	6.16	16.63	4.31
KF	30.34	4.36	33.66	4.69	27.31	4.00
KCl	15.69	4.29	19.93	4.77	14.03	4.00
KBr	15.64	4.66	18.95	5.60	14.49	4.30
KI	11.48	4.78	13.25	6.32	11.01	4.35
RbF	27.18	3.82	29.24	4.08	24.51	3.45
RbCl	15.01	3.84	18.54	4.42	13.15	3.45
RbBr	14.21	4.26	16.89	5.15	13.00	3.83
RbI	11.03	4.39	13.13	5.39	10.29	4.02
CsF	31.25	3.76	31.49	3.74	30.74	3.79
CsCl	10.14	2.97	11.61	3.24	8.84	2.66
CsBr	10.83	4.12	12.17	4.57	9.86	3.76
CsI	7.60	3.90	8.82	4.53	6.97	3.57

properties have already been presented.[21,33] A study of these systems under the AIM formalism, with topological schemes, ionic shapes, etc., has also been reported,[4,34] so we will focus here just on atomic volumes and local compressibilities. All AX's are extremely ionic as measured by topological charges, with values exceeding 0.94 electrons.

The 1:1 stoichiometry of the alkali halides, together with the general ideas of Sec. II, suggests in general that now volume is shared more equally than in the spinels and that we should expect the observed B gradation. Table V confirms this. Neither cations nor anions have constant volumes, a fact that is well known from the study of empirical and theoretical ionic radii.[4] Cationic volumes evolve with a common pattern: they are much smaller in the fluoride salts than in the rest of the halides, where they have almost constant values. This head of the group anomaly is found in every chemistry textbook, and depends on the large polarizing power of the fluoride ion. Halide volumes display a more complex behavior, with a maximum on increasing the atomic number of the cation. This is likely to be related to a competition between anion-anion and cation-cation interactions.

Rocksalt alkali halides display a full range of f factors. On the one hand, we have systems like LiI where the cations occupy a mere 7.5% of the total volume. In these extreme cases our previous discussion concerning the spinels should apply directly. KF, on the other hand, shows an almost equal partitioning of volume between ions and, finally, other systems like CsF belong to a rather strange class of materials dominated by cationic volume (almost 70%). Global and local bulk moduli obtained from our EOS are shown in Table VI. All of our general principles are here playing together to construct lattice compressibilities, and need not be further commented on. Li^+ and Na^+ are far less compressible than the rest of cations, which cluster around a constant B value. The same happens for anions when fixing the cation, the head of the group, F^-, being clearly different from the rest. All anions are more compressible than the corresponding cations on a given crystal, whereas this is not so when compared across a series.

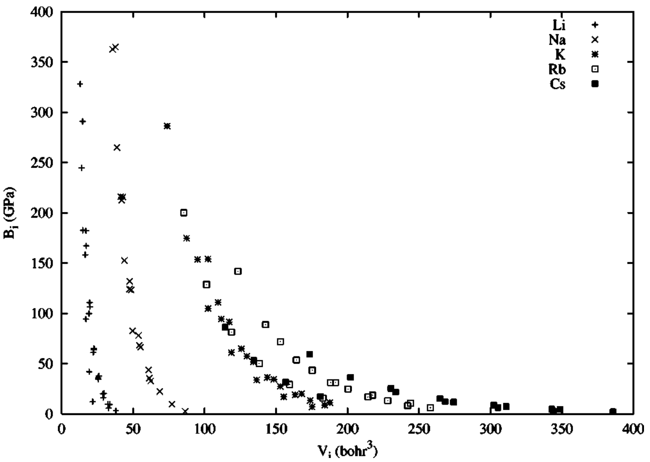

FIG. 4. Variation of the cationic bulk moduli vs the cationic volumes for all the cell sizes of our grids in the various alkali halides.

Some other interesting facts arise, however. There is a general softening of the systems as the lattice volume increases, together with a noticeable tendency towards the equalization of cationic and anionic bulk moduli. For example, cationic, anionic and global bulk moduli in LiF are 94, 79, and 81 GPa, respectively; 20, 17, and 17 GPa in LiI; and 9, 7, and 8 GPa in CsI. We have not found a successful explanation for this fact at the moment, but we think that some general mechanism lies behind these equalization forces, and that this fact deserves further study.

Tables V and VI show a very interesting correlation. It seems as if each ion might display a common B at a given ionic volume. Were this confirmed, it would mean that the general compressibility of an atomic-ionic species would be basically a function of its volume. Atoms or functional groups would be transferable on a generalized diagram and, given a volume, atomic properties would be fixed. Figure 4 shows a collection of all cationic B values obtained not only at zero pressure, but for all the cell volumes and pressures of our computational grids. Taking into account numerical errors, it is clear that the alleged correlation exists. Exceptions do occur for all the cations, however, as two kinds of curves appear for each of them. A closer examination reveals that the leftmost curves are always associated with fluorides. The effects of the head of the group anion preclude a complete transferability, but in the absence of this strongly polarizing anion, the alkali ions follow well-defined B versus V curves. Similar correlations, with somewhat greater dispersion, are found for the anions.

V. CONCLUSIONS

We have shown in this paper how the AIM theory may be used to partition static thermodynamic properties in condensed systems as applied to the particular problem of bulk moduli. The local basin properties so defined add up to the bulk observable and behave in a physical and chemically sound way. Transferability of basins together with their properties among compounds seems feasible, provided that certain volume requirements are met.

As bulk moduli are concerned, we have shown that bulk compressibilities are just a weighted average of atomic compressibilities, the weight factor being the fractional volume occupancy in a unit formula of the species considered. A very simple, intuitive limit emerges from this finding. Whenever a particular constituent dominates the unit formula (as is common in natural, oxygen-rich minerals), the bulk compressibility will be very near to that of the dominant atom or ion. The similarity of the compressibilities of related spinels is not a puzzle, then. It is related to the dominance of oxide ions in retrieving the bulk modulus of the crystals. This is actually what we have found in the examples studied. The bulk modulus of an oxide ion in these compounds is about 200 GPa, and this should be a rough estimate valid for the bulk moduli of oxygen-rich oxides, as found empirically. Our analyses do not only show the ability of a particular ion to deform under pressure. They provide other clues to understanding empirical facts. Oxides in spinels and anions, in general, are quite bigger and more compressible than cations, particularly those with a high charge. Their basins used to deviate largely from sphericity, filling interstices in a glue-like manner. Oxides do form closed packings, not of tangent spheres, but of entities that occupy the largest amount of space possible and that, at the same time, are very easily deformed, controlling the overall compressibilities and cell sizes. This description is closer to the ideas of Burdett[35] than to the classical ones. Distortion of spinels (and likely of other compounds) from ideal structures turns out to be controlled by the size and compressibility of cations on distorting the underlying oxide ion array.

When volume is more equally shared, compressibilities vary widely from one compound to the other. This is the case found in alkali halides. What is interesting here is the plausibility of an ion displaying a well-defined B-V correlation and the implications of this fact for transferability purposes.

We think that these sets of ideas should be of wide applicability to general condensed matter theory and to high-pressure research in particular. In this respect, the definition of local pressures within the AIM theory, successfully explored by Bader and Austen,[36] remains to be applied to actual solid-state electron densities. Work in this direction will clearly contribute to clarify the effect of pressure on solids.

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