

On Some Features of the Scientific Hylorealistic Background of Crystal Chemistry

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Abstract — In this paper, we try to understand how Bunge's scientific hylorealism can fit with several crystal chemistry's objects and their properties. It is found that many of them, lying at the very core of this discipline, bring support to ontological emergentism. Building units, such as vacancies, their chemical potential, the non-stoichiometry, the crystal quantum number and many aspects of the spectroscopic properties of 4f electrons in ionic crystals, are presented as striking examples of emergent (or submergent) objects or properties encountered in the single crystal-line state. Among all the types of building units, vacancies are shown to be ontologically real and material.

Résumé — Dans cet article, nous essayons de comprendre comment l'hyloréalisme scientifique de Bunge peut s'accommoder avec plusieurs objets de la chimie des cristaux et leurs propriétés. Nous montrons que plusieurs d'entre eux, constituant le cœur de la discipline, soutiennent l'émergentisme ontologique. Les unités de construction, comme les lacunes, leur potentiel chimique, la non stœchiométrie, le nombre quantique cristallographique et plusieurs aspects des propriétés spectroscopiques des électrons 4f dans les cristaux ioniques, sont présentés comme des exemples remarquables d'objets ou de propriétés émergents (ou submergents) rencontrés dans l'état cristallin. Parmi tous les types d'unités de construction, nous montrons que les lacunes s'avèrent ontologiquement réelles et matérielles.

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There is a fact, or if you wish, a law, governing all natural phenomena that are known to date. There is no known exception to this law—it is exact so far as we know. The law is called the *conservation of energy*. It states that there is a certain quantity, which we call energy, that does not change in the manifold changes which nature undergoes. That is a most abstract idea, because it is a mathematical principle; it says that there is a numerical quantity which does not change when something happens. It is not a description of a mechanism, or anything concrete; it is just a strange fact that we can calculate some number and when we finish watching nature go through her tricks and calculate the number again, it is the same. (...) It is important to realize that in physics today we have no knowledge of what energy *is*. We do not have a picture that energy comes in little blobs of a definite amount. It is not that way.

RICHARD FEYNMAN, 1963

If you want to say that “God is energy,” then you can find God in a lump of coal.

STEVEN WEINBERG, 1992

Indeed, physics does not define the general concept of energy. This is why Richard Feynman claimed that physics does not know what energy is. Which suggests that the general concept of energy, like the general concepts of thing, fact, and law, is ontological.

MARIO BUNGE, 2006

In spite of both the scientific and technological importance of crystals for mankind since more than two millennia (Theophrastus 1956; Maitte 2014), Bunge did not write very much about these objects, their formation, their structural (multiscale) description and consequently, about their properties. In the thousands of pages of his *Philosophy of Physics* (1973), *Scientific Materialism* (1981), *Treatise on Basic Philosophy* (1974–1989), *Chasing Reality: Strife over Realism* (2006), and of his *Causality and Modern Science* ([1959] 2009), the occurrence of the term “crystal” is rather limited, a little bit anecdotal or exclusively associated with molecular crystal or related to molecular biology. The “chemical potential” and “vacancy” terms and concepts are totally absent of these works (while other “potentials” and the adjective “chemical” are abundantly used, and the concept of “quasiparticle” is evoked in

Philosophy of Physics (1973)). In *Philosophy of Physics*, the “*lattice plus the electron cloud*”, modeled by means of Bloch’s theory within the more general framework of quantum mechanics, is just said to constitute the “*model object*” of a crystal. X-ray diffraction pictures are mentioned as “*the main empirical tool of analysis for molecular biologists*” and, in order to emphasize the role of theory in telling us the meaning of “*natural signs*”, their patterns are said to “*bear no obvious relation to the spatial configuration of the atoms in the crystal*”. Diffraction patterns are schematically shown to arise from X-rays and molecular structure theory, and Bunge noted that quantum chemistry, which had “*been around for four decades*” was yet unable to deduce all the possible configurations that any given set of atoms could fit. In *Scientific Materialism* (1981), crystals are qualified—among other systems—as remarkable for the variety of their properties, and their properties of undergoing or causing change. Chemistry investigates not only the composition and the structure of chemical compounds, but also the formation and transformation processes of such compounds. He also stated that “*the very core of chemistry*” is constituted by chemical reactions. The 4th volume of his *Treatise on Basic Philosophy*, dealing with systemism and emergentism (1979), proceeds by increasing degree of assembly, from the atom to the molecule, to macro(bio)molecules, to cells, to multicellular organisms, and so on until human societies. In this broad and impressive ontological perspective, crystals stay completely out of the map. It looks like Bunge was a philosopher of science, grounded in theoretical physics, who liked to jump quickly from physics to biology², disregarding the atom to building unit and building unit to crystal-increasing degree of “assembly”. “*Crystals out of a solution*” are only quoted as an example of “*self-assembly by condensation of units of the same kind*”. The “*cooling of a liquid until it solidifies forming a crystal*” is used as an illustration of “*reorganization*” or “*restructuring*” as a “*change in the structure of the system, i.e., a change modifying some of the links among the system*”

² Especially from definition 2.4 page 51, to figure 2.6 page 63, where he seemed to completely disregard the crystallographic properties of sugars, proteins and many other biomolecules. More profoundly, if someday his ontology is to include crystals, it will need to be rewritten from the start, pages 46-47, by taking into account more than the atomic number Z alone as the “*root property*” of an atom, namely the electric charge and the nonequivalent crystallographic sites properties (coordinates and symmetry group), and probably, by paying more attention to the “*concatenation*” operations performed page 49 and following.

components though it may not alter appreciably the intrinsic properties of the said components". In the 6th volume of his *Treatise on Basic Philosophy*, dealing with epistemology and methodology (1983), Bunge wrote that "*one of the most spectacular successes of the reductionist program is contemporary solid state physics*", and to illustrate his judgment, he took the example of the copper wire, in which, while every one of the atoms that composes it can be accounted for, in principle, by the quantum theory of atoms, the body composed of these atoms has, however, bulk properties, which are emergent with respect to the component atoms. These properties (such as electrical conductivity) "*are not represented in the quantum theory of atoms, hence they cannot be explained by the latter without further ado. However, solid state physics explains those emergent properties on the basis of quantum mechanics, namely adding to it certain hypotheses concerning the copper crystal lattice, the electrons wandering through it, and the interactions among the copper ions and the electrons moving about in the lattice*". In the 7th volume of his *Treatise on Basic Philosophy* (1985), a comparative comment is found, which says that "*the grammar of a language is not detachable from the language itself, anymore than the structure of a crystal can be detached from the crystal*". Bunge also explained that "*according to classical statistical mechanics chance is neither in the individual system components nor in the eyes of the (blind) beholder, but in the nature of things: it is an emergent property on the same footing as other system properties such as entropy and temperature. (...) The simplest randomness (or chance) hypotheses in statistical mechanics concern the initial positions and velocities of the system components. But these are not the only ones. Thus the modeling of the crystallization process in a liquid calls for probabilistic hypotheses concerning the nucleation process. Since these events are random in space and time, neither the place nor the time of the emergence of the first crystal can be predicted exactly.*" In this volume too, he touched a few words on symmetry properties, warning against "*Platonic delusions*": "*(...) the theorist investigates the group-theoretic structure of that space: he conjectures, say, that the structure is an $US(2)$, $US(3)$, or some other symmetry group. Once he is done he glances at the 'particles' chart and, if lucky, discovers that nature does contain 'embodiments' of such conjectured symmetries; and if very lucky, he will predict one or two still unknown 'embodiments'. But this is no evidence for the power of pure mathematics to mirror the world: all such*

symmetry groups are constructed on the basis of law statements such as commutation formulas for dynamical variables. Nor do symmetries hover over things, let alone produce them; in physics every symmetry is a property of either a physical entity, such as a crystal, or of a feature of a physical entity, such as the hamiltonian or the state function of a molecule. Melt the crystal, or dissociate the molecule, and the corresponding symmetry disappears". In his *Philosophical Dictionary* (2003), crystals are recognized as systems and also as "quantons", i.e. "a physical entity that quantum physics accounts for adequately and classical physics does not". He was fully aware of the existence of "defective crystals", as natural imperfections, which he used as an example contradicting "Intelligent Design"-like (pseudo-)arguments, and he defined chemistry as the science of molecular composition and transformation. A chemical system, or a reactor, is a system where chemical reactions occur. So much so that, according to him, when reactions are completed, the chemical reactor ceases to be a chemical system, and turns into a physical system, the components of which are necessarily atoms and molecules (Bunge 1979) (or radicals (Bunge 1982)). Here again, the repeated use of the "molecular" adjective, together with the emphasis put on "reactions", seem to discard crystal chemistry from the definition³. Indeed, so many crystals are not molecular at all (metals, salts, semiconductors), and chemistry also investigates state changes intimately "coupled" with chemical reactions (like, for instance, the growth of an incongruently melting crystal, or the growth of a crystalline thin film by chemical vapor deposition). In addition, as we shall see in this contribution, the most fundamental building unit at the atomic scale in crystal chemistry (and in chemistry *inside* crystals) are not atoms, nor molecules, nor radicals, but *vacancies*, a kind of quasi-particles which do not possess atomic number (hence, no box in the Periodic Table, and no electronegativity), nor mass number, nor very often electrical charge (absolute or relative) and does not relate to any of the elementary particles of the Standard Model either. In *Chasing Reality: Strife over Realism* (2006), Bunge gave a fair account of the strategy deployed to determine the crystal structure from a diffraction pattern analysis, in a dedicated section entitled "*Reading diffraction patterns*", a problem he

³ For a historical text on solid-state chemistry, at the French level, see Pierre Teissier, *Une histoire de la chimie du solide. Synthèses, formes, identités* (2014).

classified as “*inverse (or backward) cognitive problem*”. In *Causality and Modern Science* ([1959] 2009), classical crystallography is designated as an “*outstanding member of the class of noncausal and morphological theories*”, which need not contain a causal element, although they may turn out to be explainable in terms of a theory containing a causal element.

In this paper, we will confront crystal chemistry’s main objects, and some of their properties, to Bunge’s scientific hylorealism, the only complete philosophical system designed in the 20th century, which combines systemist and emergentist materialism with ontological, epistemological, semantic and methodological realism and scientism, at its ontological and epistemological levels and keeping the “analysis” broad, without axiomatization. The goal of this text is to convince that vacancies are real and material, and that more broadly speaking, building units, their chemical potential, the non-stoichiometry they generate, and some of their most elegant properties of properties (like crystallographic site symmetries), the crystal quantum number and many aspects of the spectroscopic properties of 4f electrons in ionic crystals, bring strong support to Bunge’s ideas on scientific hylorealism. It will also emphasize, by calling for a necessary clarification of the definition of the system components and of the corresponding levels of organization of reality, the interface where philosophy of chemistry and crystal chemistry itself exactly meet together.

But before we do so, we need to recall what “scientific hylorealism” stands for in Bunge’s philosophy, and also what a crystal is.

1] Scientific Hylorealism in a Nutshell

In Bunge’s ontological and epistemological views (1981; 1979; 2003), matter is the collection of all material entities, also called things. Only changing things can be considered as material. Being a collection, matter is conceptual, not material. A material entity is a thing capable of change. For example, its properties can change. A material entity does not necessarily possess mass. Mass is a property of only certain things, like protons and electrons, whereas photons do not have any mass, so that to possess a mass is sufficient but not necessary to be material. Gravitational and electromagnetic fields are examples of material things without mass. “To be able to change” means to be able to be in at least two different states, and

to change from one state to the other. In order to avoid verbal compulsions, Bunge insisted on the necessity of expressing this possibility of change by means of a mathematical theory which defines a state space containing at least two elements. Materialism is a group of ontological doctrines that have in common to postulate that all that really exists is material or, formulated negatively, that immaterial objects such as ideas have no independent existence on things (like brains that think them). Materialism postulates that reality is only made of material entities. Bunge coined the term *scientific materialism* because in his view, it is *the* ontology of science and technology, the ontology that gets inspired by science and which is tested as well as modified by the advancements of science. Anything that exists either in the outer world (independently on the subject) or in the subjective experience (because mental states are brain states) is considered as real. All natural things are real. Scientific realism states that things by themselves are existing and at least partially knowable. Realism is the epistemological view according to which knowledge, or at least scientific knowledge, seeks to represent reality. Scientific realism identifies reality with the collection of all material entities, that is, things that are likely to change in one way or another. It also implies that to grasp reality and take into account its complexity, mathematics-based theories, in addition to empirical data, are needed. This postulate of the independent existence of the outer world is a strong incentive to explore it and by doing so, to enrich and deepen our already acquired factual truths.

Energy is not a material entity, it is not a thing, but rather a property of it, which determines to which extent material entity changes or can change. It turns out to be the most universal property that real things possess, more universal than location in space-time. Hence, to be material means to possess energy. As energy is a property and not a thing, it does not exist by itself in the same way as matter does. The famous “ $E=mc^2$ ” theorem of relativistic mechanics which relates energy to the mass of a particle does not say that energy converts into matter and matter converts into energy. This is impossible because energy and mass are properties, and not things, and so any energy and mass are energy and mass of something. The combination of scientific materialism with realism can be summarized very simply:

- 1) all that *really* exists *is* material;

- 2) “to be material” means to be able to *change*, that is, to be *endowed with energy*.

Electrons, electromagnetic fields, atoms, and so on, are good examples of that, which sound familiar to the chemist. However, the properties of material entities, and the changes of these properties are only material indirectly, because they do not exist independently, outside of these material entities. Numbers have no energy and so they do not exist in the same way as atoms or crystals do: their existence is ideal, or fictitious. As Bunge puts it: there is matter without ideas, but there cannot be ideas without matter. Ideas are to be created or invented, but not discovered. One discovers the world, one invents ideas about the world as well as pure ideas which have no relation to it: “*Try to cut a brain with an idea or to divide a number with a knife*”, or, “*To repeat, energy is not just a property among many. Energy is the universal property, the universal par excellence. Moreover, energy is a universal in re: it inheres in things instead of being either ante rem (prior to them) or post rem (after them)*” (Bunge 2006).

Any structured ensemble can be conceived as a space. If this structure is endowed with a distance, then this space has a metric. Contrary to the diversity of mathematical spaces that can be invented, there is only one physical space, which is an important feature of the real world. A physical geometry is built by appropriately interpreting a mathematical geometry. While mathematical geometries are only tested against their internal and formal consistency, physical geometries must be submitted, in addition, to empirical tests. Physical geometry studies physical space, which is the basic structure of the collection of all material entities. Scientific materialism endorses a relational interpretation of physical space, which is made of the collection of things which change continuously and are related by the intermediarity relationship. Space (or rather space-time) is intimately related to matter. Without matter, there would be no physical space. The association of the collection of things and of their separation function can be called the space of things. So, real space turns out to be the basic structure of the collection of things. However, space is not the property of any particular thing. Like “public space”, it is common to everything, or said more specifically, the space relative to a reference frame is common to all the things that can be related to this reference frame. Things do not float in some space-time container, that would exist

independently on them. Rather, things have spatiotemporal (and changing) relationships which can be expressed with space and time concepts, and those relationships are just relationships (not bonds) between things and their changes. Space is neither a thing nor a property of a thing, and has no causal power. But even if space does not exist independently of things and their changes, it is no less real than any of the important properties of real things. Indeed, a relationship can be thought of as real if and only if it exists between real things, which is the case of spatial relationships. That coordinate values in a 3D Euclidean space just label points in a 3D space is true, but it does not imply this Euclidean space fails to represent the objective relationships among material entities, as shown by the absolute nature of some invariant distances. In fact, many invariant distances do not change upon the substitution of one coordinate system by another one, they do not depend upon the viewpoint, the location and the movement of the observer. Space has no autonomous existence, and from that no causal power either. No spatial relationship exists on its own, separated from the elements that are connected. They are real relations because they occur between real things. Space is the fundamental structure or framework of the real world. A physical theory must not only contain concepts with physical meaning, which means concepts referring to physical things. A theory of space should bring mathematical force, a close connection with contemporary physics, and clarification power.

Bunge's hylorealistic ontology does not stop here. It contains two important additional features: systemism and emergentism. A system is a complex thing each component of which is related to at least one other component. For instance, an atom is a physical system composed of protons, neutrons and electrons. To assess the systemic nature of something, Bunge proceeded to the so-called "CESM" analysis:

- 1) the *composition* of a system is the collection of its components (or parts), and it is defined at each level;
- 2) the *environment* of a system is the collection of things that act on the components of the system or upon which the components of the system act;
- 3) the *structure* of a system is the collection of relationships (in particular bonds or links) between the components of

the system, as well as between its components and elements of the environment;

- 4) the *mechanism* of a system consists of all the internal processes that make it work, that is, that make the system change upon some conditions, and not upon other conditions.

Only material systems have mechanisms. Any of these four features is likely to change with time.

A new system is said to be emergent if new properties of it can be identified and characterized. A property is emergent, as a static concept, if it is not the property of any of the system's component. The theoretical genesis of the emergence notion traces back to the epistemological distinction between a resultant effect and an emergent effect. While the former can be calculated from its causes, the latter cannot. If a system has a composition at a given level, then any property of the system is said to be resultant at this level if and only if it is possessed by all the components at the considered level of the system, and it is said to be emergent at this level if the property is not possessed by none of the components of the system at the considered level. If several causes produce one effect, or if we can predict their result from a law of composition of causes of classical physics, the effect will be said to be resultant. If the effect cannot be predicted that way, it will be said to be emergent. A phenomenon is qualified as emergent if it:

- 1) requires a certain amount of material constituents and/or preceding causes as necessary conditions of existence;
- 2) presents qualitatively new properties with respect to its preceding causes and/or its constituents;
- 3) remains unexplainable from the properties of the preceding causes and/or constituents of the said phenomenon, which raises the question of "unexplainability until now" or "unexplainability by principle".

The goal of a scientific study of a system is to explain its systemic (emergent) properties either from the point of view of the interaction between its components or from that of its history. Only systemism can account for emergent phenomena. Emergent materialism assumes that all material entities do not belong to the same level of organization of the reality. Instead, they are bunched in

several levels of organization: physical, chemical, biological, social and technical. A level of integration, or of organization of the reality, is made from a collection of material entities that possess common properties and laws. Entities of supraphysical levels are made of entities of preceding levels. Members of the superior levels have emerged with time by association or by development of members of preceding levels, and members of each level above the physical level are systems endowed with particular properties which emerge from the interaction of the components of these systems or the interaction between these components and their environment. Emergent materialism provides a strong incentive to the search for an explanation of emergence in terms of properties and processes from preceding levels. In a more recent book chapter (Kistler 2013), Max Kistler defines an ontological concept of emergence for a property, provided it is:

- 1) systemic, which is to say that none part of the system possess it;
- 2) qualitatively different from properties possessed by the system's parts;
- 3) consistent with physicalism, that is, completely determined by the properties of the system's parts, as well as by their mutual interactions and interactions with the environment;
- 4) stable or "robust", that is, unchanged by small perturbations in the underlying microscopic properties.

Bunge also pointed out that any sufficiently advanced scientific theory contains some conservation laws, for instance total mass conservation theorem, or of the total kinetic moment, or of the total energy, and so on. Such conservation laws state the invariance of a particular property of a certain type of material entity along the change it undergoes. These properties are constants of the movement or, broadly speaking, constants of the transformation of things. "*Ex nihilo nihil fit*", in other words, everything emerges from another thing and transforms into something else. This principle, due to Epicure and Lucrece, is the oldest and the most general statement of the conservation of matter principle.

2] What is a Crystal?

The crystalline state is a solid state of matter in which, ideally, all the atoms order periodically in the three directions of (the Euclidean) space. The crystal is “built” by translation along all the space directions of one specific block which is called the unit cell. This unit cell is chemically and geometrically defined by its atomic content and number of unit formulas, three vectors which describe the periodicity and give the crystallographic space its metrics, the set of symmetry operators which constitute the space group of the crystal and spatially relate the atoms to each other within the unit cell and from cell to cell, as well as the positions of atoms not related to each other by some symmetry operator within the unit cell. The crystal space group is the set of all symmetry operators which allow to “jump” from any point of the crystal to an equivalent point, for instance, when this point is occupied by an atom, to “jump” from this atom to the same atom elsewhere in the crystal. The International Union of Crystallography (IUCr) defines a material as being a crystal if it has essentially a sharp diffraction pattern, “essentially” meaning that most of the intensity of the diffraction is concentrated in relatively sharp Bragg peaks, besides the always present diffuse scattering. The main radiation sources currently used to collect diffraction patterns are X-rays, neutrons and electrons. Symmetry operators leave invariant an object or a structure when they are applied to them. They transform the object into itself, without modifications. The crystal structure describes the way atoms order themselves to form a crystal. A basic crystal structure model contains: a space group, lattice parameters (the vector lengths and angles between them), a number of unit formulas, a set of atoms and atomic coordinates, site fractional occupancies, site symmetry group and atomic anisotropic displacement parameters. The latter are directly related to their thermal agitation energy, which makes them vibrate around some equilibrium position, and the existence of which is a sufficient proof of their material and real existence. Inside the unit cell, atoms occupy specific positions, called block positions⁴. These positions are defined by a set of coordinates, a multiplicity factor, a fractional occupancy and a site symmetry group. General positions represent a collection of symmetry equivalent points which remain invariant only by the application of the

⁴ Or Wyckoff positions.

identity operator⁵. Special positions represent a collection of symmetry equivalent points which remain invariant by the application of at least two symmetry operations of the space group. The site symmetry group is the ensemble of symmetry operations which leave invariant the crystallographic site. This ensemble is determined exactly and exclusively by the unit cell content. All these informations can be obtained from the Rietveld analysis of an X-ray or a neutron diffractogram, which primarily gives the Fourier-transform of the electronic density of the atoms. X-rays lead to an average ideal crystal structure over typically ten-twenty thousand unit cell distances. But real crystals often possess local compositional and/or structural deviations from the ideal (average) model, as probed by different techniques such as Nuclear Magnetic Resonance (NMR), Mössbauer or Raman spectroscopies for middle range disorders (extending typically over hundreds of unit cells distances), high-resolution transmission electron microscope (HR-TEM), and Electron Paramagnetic Resonance (EPR), positron annihilation spectroscopy (PAS) or optical spectroscopy for short range disorders (at the level of the unit cell or so)⁶.

Now that we have worked out the broad strokes of both scientific hylerealism (matter, reality, energy, space, systems, emergence, components, levels of organization) and the crystalline state of matter, we can get to test Bunge's ontology to crystal chemistry.

3] Discussion

3.1] From Atoms to Structure Elements ... to Building Units

One thing is to “build” a crystal according to crystallographical geometry rules, the other thing is to do it with thermodynamically sound components. When it comes to model reactional equilibria and reaction-diffusion processes inside a crystal, one needs to identify a minimal set of independent components of the chemical system. This set allows us to apply Gibbs phase rule⁷ and to perform mass action law reasoning with components which have a well-

⁵ Their site symmetry group, or “point group” symmetry is symbolized as C_1 .

⁶ Needless to say, this list of techniques widely used to characterize crystals is not exhaustive at all.

⁷ Which dictates the number of chemical potentials which can be varied independently of each other.

defined chemical potential. Atoms, molecules, ions, ionic coordination polyhedra, so-called “building blocks” made of the latter’s assembly, embedded into a crystal, do not have well-defined calculable chemical potentials, neither computable nor measurable. This issue was solved when the concept of building units was introduced in crystal chemistry (Rickert 1982; Schmalzried 1995; Kröger, Stieltjes, and Vink 1959). Building units permit us to differentiate components of identical chemical nature (“*Z-equivalent atoms*” (Bunge 1979)) in a crystal. This differentiation is more specific than in gas, liquid or amorphous matter chemistries. Indeed, the site symmetry group applies to the hamiltonian of the atom (or the ion) located in its particular block position, and so it is relatively straightforward to understand that a chemical property, such as dissolution or solubility limit, may not be the same for two identical elements occupying two crystallographically nonequivalent sites. While the way Bunge insisted on not to characterize (and qualify) a system only by its composition and environment, but also by its structure and mechanisms, finds here a striking relevance, it is above all the remarkable finesse of his hylorealistic ontology of space⁸ that should be appreciated, for a site symmetry group contains symmetry operators which are noncausal properties of the most universal property possessed by chemical elements: energy.

Atoms occurring at particular site types, occupying certain lattice positions, are structure elements. Separated structure elements have no well-defined chemical potentials, because their numbers in a crystalline compound are not independent from each other. This is due to the fixed ratio of crystallographically nonequivalent sites in a crystal lattice. Hence, if one increases the size of the crystal or if one changes the number of atomic imperfections it contains, one must either add or withdraw a combination of structure elements. It is not possible to calculate the Gibbs free energy change due to the addition of a structure element, hence to calculate a structure element chemical potential. The latter equals the partial first derivative of the Gibbs free energy with respect to the number of particles of the considered structure element, at constant pressure, constant temperature and constant numbers of the other remaining structure elements (Rickert 1982). A structure element,

⁸ Bunge was neither a topodential, a topoclast, nor a topolatrous.

which is characterized by three kinds of “root” properties⁹ instead of only two in a gas or a liquid phase, does not exist outside the crystal lattice and is therefore not an independent component of the crystal in a thermodynamic sense (Schmalzried 1995). Two ways of describing crystal atomic imperfections are known to date:

- 1) the structure elements description, in which atomic imperfections are defined with respect to the empty space, in which lattice positions (and interstitials) are fixed with respect to an imaginary coordinate system;
- 2) the building units or relative building units description, in which crystal atomic imperfections are defined with respect to the ideal perfect crystal.

A building unit is a structure elements combination with a composition such that fixed relationships between the numbers of the varied site types, required by the crystal structure, remain unchanged upon addition of this combination to the crystal. The most obvious one is the “crystal molecule”, which is the smallest assembly from which the perfect crystal can be built¹⁰. When an infinite number of lattice molecules are stucked to each other in the three dimensions, we obtain an ideal defect-free crystal. The introduction of atomic imperfections (relative) building units in this ideal crystal produces a real crystal (Rickert 1982). Relative building units are defined with respect to the perfect crystal, and so they consist of differences between a structure element and a structure element corresponding to the normal occupancy of the same site (Kröger, Stieltjes, and Vink 1959). Corresponding to suitable combinations of structure elements, building units can be subtracted or added to the crystal independently of other building units. The number of types of building units necessary to describe the crystal is small: the lattice molecule, the interstitial particles, the vacancies and substitutional particles. A building unit belonging to a set of mutually independent building units can be considered as a component in the phase rule’s sense—the minimally sufficient set necessary to build any crystal without taking into account any internal equilibrium.

⁹ Chemical element, electric charge and type of (nonequivalent) crystallographic site (reduced coordinates and site symmetry group).

¹⁰ Building units were introduced by Wagner and Schottky in 1930 (Wagner & Schottky 1930). “*Gittermolekül*” is a poor choice of words, maybe the use of “asymmetric unit” (of the unit cell) would be better.

In the relative building units system, chemical atomic imperfections are defined with respect to the perfect and ideal crystal. Consequently, crystal chemistry forces one to formulate correctly the constraints which crystal structure and symmetry impose on their thermodynamic derivations (Schmalzried 1995). In principle, there are only three different types of irregular structure elements: vacancies on regularly occupied lattice sites, interstitial atoms (ions) on regularly unoccupied lattice sites, and impurity atoms (ions) present either on the interstitial lattice site or substituted for regular structural elements. In the simplest relative building units system, it is assumed that relaxation processes around the irregular structure elements are sufficiently fast so that thermodynamic state functions can be defined, that they keep the site symmetry group of the perfect crystal structure and that structure elements have no internal degrees of freedom¹¹. In a structure element, the effective electric charge is defined with respect to the perfect crystal. There is no experiment that permits the determination of a structure element's chemical potential, and so it is by subtraction that one can introduce a chemical potential. The "lattice molecule" introduced by Schottky corresponds to a formula unit, the chemical potential of which stands as the reference molar energy value and can arbitrarily and conveniently be fixed to 0¹². It is in equilibrium with all the vacancies distributed over all the types of crystallographic sites. These vacancies are the most necessary irregular structural elements to construct the crystal lattice¹³, and we shall come back to them in a forthcoming section.

In order to keep this concrete, we need to take an example which is not too simple (like monoatomic, or diatomic crystals with a 1:1 stoichiometry and atoms occupying only one block position in the structure) and not too complicated (like ternary compounds, or binary ones with so many crystallographically nonequivalent sites). Tb_2O_3 , an ionic crystal adopting the cubic bixbyite structure at room temperature (with Ia-3 space group), is likely to meet our purpose,

¹¹ The latter two assumptions are less frequently fulfilled.

¹² In diluted solutions, by the application of the Gibbs-Duhem relation, it is straightforward to show that the "lattice molecule" building unit's chemical potential can be approximated as the standard chemical potential of the compound in its Raoult reference state.

¹³ For a technical introduction to these problems, read: <https://hal.archives-ouvertes.fr/cel-00934568>.

because it contains only two elements, Tb and O, occupying three crystallographically nonequivalent sites.

3.2] O²⁻ Anions as Resultant Things

In a fully ionic crystalline oxide, the oxygen species is always found to be the O²⁻ anion. The “2-” oxidation state of the oxygen anion exists only because it is stabilized by the Madelung field, which is the crystalline electric field resulting from the electric charges of the cations and the anions located at crystallographic positions specified by a set of symmetry operators belonging to the crystal space group. The O²⁻ anion does not exist in the gaseous (or in the “free ion”) state. What exists in the gaseous state is the O₂ molecule with standard chemical potential -0.64 eV at 25°C, while that of the O atom at the same temperature amounts to +2.08 eV. The O atom first ionization potential is +13.6 eV and its second ionization potential is +35.1 eV, so that the dissociation and ionization energy costs for the existence of O²⁻ in the gaseous state are definitely prohibitive. This is a good example of resultant effect, because the crystal structure makes possible the Madelung field which is the cause of the stabilization of the O²⁻ anions, and this cause can be easily calculated by summing the electrostatic charges over the crystal lattice positions.

3.3] Components and/or Constituents?

If the O (and the Tb) atoms do not exist as such in the Tb₂O₃ crystal, i.e. without the properties they possess in the crystal lattice, it raises the question of the composition of the “physical level of organization of the reality”. Any atom occurring in a crystal formula is actually a constituent. A constituent is not a component, the major qualitative difference between them being that the latter has a well-defined chemical potential, while the former does not. Even if we assume that the “physical level of organization of reality” in the Tb₂O₃ crystal is composed of the three halves of the Tb³⁺ cations which have a C₂ site symmetry group, the one half of the Tb³⁺ cations which has a C_{3i} site symmetry group and the remaining three crystallographically equivalent O²⁻ anions which have a C₁ symmetry group, and if we consider them as structure elements, their chemical potentials in a crystal is not either definable in terms of statistical thermodynamics. There is just no way one can change the concentration of only one of them maintaining the 3/2:1/2:3 ratio

of crystallographic sites constant. To define the chemical potential of the oxygen (and the terbium) building units, one must comply with three conservation rules: the mass conservation, the charge conservation and the number of crystallographic sites conservation (Rickert 1982; Schmalzried 1995; Kröger, Stieltjes, and Vink 1959; Kröger 1964; Schottky, Ulich, and Wagner 1929). In our example, this leads to the following equilibrium between the Tb_2O_3 crystal lattice “molecule” and its building units, expressed in the modern Schottky notation: $Tb_2O_3 \leftrightarrow -3 |O|^{\bullet\bullet} - 3/2 |Tb(C_2)|^{\prime\prime} - 1/2 |Tb(C_{3i})|^{\prime\prime}$. Strictly speaking, the free energy variation of this reaction is 0, so that

$$\mu_{Tb_2O_3} = -3 \mu_{|O|^{\bullet\bullet}} - 3/2 \mu_{|Tb(C_2)|^{\prime\prime}} - 1/2 \mu_{|Tb(C_{3i})|^{\prime\prime}}$$

with μ symbolizing the chemical potential. The building units chemical potentials exist because of the constraints imposed on their definition by the number of crystallographic site conservation rule, which is itself related to the space group symmetries. These symmetry operators do not exist at the “physical” level (atomic, molecular). In fact, as the building units combine not only mass and electric charge properties of a chemical entity, but also the relational properties specific to a crystallographic site, it is a striking example of component that instead of being defined at the “physical” level, emerges at the crystal chemical level. Even if a crystallographic lattice site is clearly not the analog of a chemical element, only constitutive building units can be added to or withdrawn from the crystal structure in such a way that the crystal chemical potential remains constant, that is, without modifying the electric charge and lattice site equilibria. Consequently, only building units can be considered as genuine components in the Gibbs phase rule, which is not the case of individual atoms (ions) and related structure elements. Here, crystal chemistry imposes to distinguish components from constituents, and one is forced to recognize that what Bunge used to designate as components (or parts) are actually *constituents* in the chemical sense. This is a logical consequence of the fact that the energy concept, in his ontology, remains an extremely general concept, not as specific as in (crystal) chemical thermodynamics. Nevertheless, even if an atomic (ionic) constituent does not have a well-defined chemical potential, it still has an energy, and so it is a concrete thing. While the building units, which as components have a

chemical potential¹⁴, are atoms endowed with a relative combination of primary properties (mass—or Z —, electric charge) and of *invariance properties* of properties that turn out to be relational (crystallographic site symmetry group). Their chemical potential is a good example of emergent property, which exists only at the crystal chemical level and in addition, they constitute a core property of statistical thermodynamics¹⁵. While a mass and an electric charge have physical dimensions and can interact with a gravitational and an electric field, respectively, a crystallographic site is defined by reduced coordinates, a multiplicity factor, an occupancy fraction and its site symmetry group, i.e. pure numbers and symmetry operators¹⁶. Thus, it is unlikely—to put it mildly—to interact with some surrounding field. Note, however, that the change in bond strength with the nearest, second nearest and third nearest ions, and subsequent lattice positions relaxation (due to the change of mass and/or electric charge) upon the formation of the crystalline imperfection, induces an elastic strain and a stress field that decay over several unit cells, with which the associated building units can interact (including when this building unit is a vacancy). In addition, the relative building unit concept and related symbol bear the difference between two (equilibrium) states, the initial reference state, and the final state of the crystalline imperfection, which implies that the chemical potential discussed here is already a Gibbs free energy variation divided by the precise amount-of-substance variable quantifying the impurity, say $\Delta G/\Delta n$, possessing the three former properties. Leaving aside the trivial “lattice molecule”

¹⁴ And so a Gibbs free energy from which it derives.

¹⁵ The conceptual difficulties undergone by solid state chemists to define properly the structure elements chemical potentials led to a controversy between Schottky and Kröger in the 1950s (Kröger, Stieltjes, and Vink 1959), which is now part of the classical academic education, and the basic ideas were refined at the end of the 1970s to account for possible surface or dislocation specificity (Schmalzried 1976; Kröger 1980). The two formalisms, based on structure elements or on building units, are strictly speaking equivalent, but the former (Kröger-Vink’s one) leads to the definition of and search for *paired virtual* structure elements chemical potentials, which do not modify our conclusions in the sense that it is not possible to define, calculate and measure the chemical potential of a structure element *alone*.

¹⁶ The three of them, namely Z , electric charge and type of nonequivalent crystallographic site (reduced coordinates and site symmetry group), should be regarded as “*root properties*” in the very premises of any ontological theory of crystals for, so to speak, building units are the ontological “atoms” of the crystalline state of matter.

building units, relative building units, on the other hand, due to their relative subtractive nature, bear, in addition to the three already mentioned integrated properties, another property, namely the change itself, the change by chemical substitution, insertion, or removal of an atom (ion). What the $|O|^{**}$ symbol also means is: “on this specific crystallographic site, an O^{2-} anion escaped from the lattice and was not replaced by another ion”¹⁷.

3.4] “*There isn’t one in a hundred, and yet they exist*”...

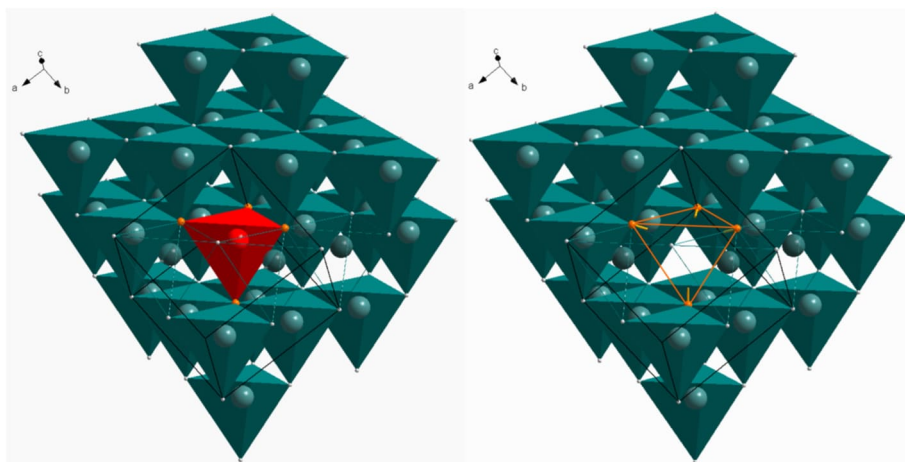
At $T=0$ K, an absolutely pure crystal is expected to be perfectly well ordered in terms of both cationic and anionic crystallographic sites occupancies. Nevertheless, when temperature becomes non-zero, which is the case for all practical situations, the second law of thermodynamics makes it necessary that, for instance, in a Tb_2O_3 crystal, a combination of Tb and O vacancies form. Indeed, if the Gibbs free energy of the crystal is to be found at a minimum, then there must be a nonzero vacancy concentration that permits minimizing, at concentrations such that they do not interact between themselves, the configurational entropy. As Bunge’s systemism so rightfully stresses, the crystal structure knowledge is necessary but not sufficient to describe, explain and predict how the crystal composition and structure will form and change under external constraints from its surroundings. This takes a bit of classical and statistical thermodynamics and of thermodynamics of irreversible processes, which contain causal elements of explanation and have predictive power¹⁸. Besides, the knowledge of the atomic (or ionic) constituents’ list of the crystal is also insufficient to discover and understand the mechanisms of crystal formation, of impurities dissolution and, more broadly speaking, of chemical reactivity. For the most fundamental component of a crystal, and of its crystal chemistry, at the angstrom scale of description, is not exactly a constituent, but rather a quasiparticle. These quasiparticles cannot be viewed as “impurities”¹⁹, they are not a chemical product one can

¹⁷ For instance, if a chlorine anion would substitute for it, then the symbol would become $Cl|O|•$.

¹⁸ In some sense, the periodicity of Mendeleev’s Table of elements and the (chemical) process—(multiscale) structure relationships prevail over the crystal lattice periodicity and structure-property relationships in determining the kind of chemical bonds, non-stoichiometries and crystal structures likely to be obtained.

¹⁹ They are called crystalline imperfections.

purchase on the market and get delivered with a certificate of purity warranted by the vendor. They do not form a gas (they actually have no vapour pressure (Schmalzried 1995)), nor some liquid phase, not even a powder, beads or chips one can handle on the bench, with spatulas or pairs of tweezers, a mortar and a pillar, and this, in spite of the fact that they do belong to the *solid* state of matter. They have no mass (no atomic number : no proton, neutron nor electron²⁰), very often they have no electric charge (relative, effective or absolute), they have no (nuclear, electronic) spins, no parity, no isospin, no rotational nor internal vibrational degrees of freedom, ... We are, of course, talking about vacancies²¹ (Figure 1).



²⁰ In transport by diffusion theory though, it might be possible to define a generalized effective mass, scaling in fraction of the missing atom mass, but this is another concept of mass in solid state physics, which does not lead to molar mass in chemistry.

²¹ Random vacancies are not to be confused with interstitial sites, gaps, voids, pores, crystallographic cages, porosities, and so on and so forth.

Figure 1. Simplified and stylized drawing of the sphalerite structure (cubic, space group F-43m) adopted at ambient temperature and pressure by many crystals whose standard formula is “AB” and with a predominantly covalent bond (such as InP, AlAs, InSb, etc., much studied in optoelectronics, high frequency electronics, among others), therefore being able to form electrically neutral vacancies. Atoms are represented by spheres of arbitrary dimensions and of different color depending on whether the atom is “A” (grey) or “B” (green). All “A” atoms are crystallographically equivalent to each other (tetrahedral point group -43m), and all “B” atoms are also equivalent to each other (with the same point group) but not to “A” atoms. The drawing shows that the atoms “A” nearest neighbors of the atom “B” form a tetrahedron, and that these tetrahedra pile up by their vertices in the three directions of the crystallographic space defined by the reference frame (a, b, c). The figure on the left highlights in red an atom “B” surrounded by four atoms “A” in orange inside the unit cell (cubic) represented in solid black lines, and oriented in such a way as to put the whole perspective. The figure on the right shows exactly the same structure but with the “B” atom missing, and the broken chemical bonds with the “A” atoms in the form of truncated yellow lines: this is a (random) “B-vacancy”. Strictly speaking, this drawing should show that the atoms nearest to and following the missing atom “B” shift a little bit from their initial positions (adopted in the figure on the left) by a distance which decreases with the distance to the initial “B” atom. This local deformation, which may or may not modify the initial point group of the vacancy site, is at the origin of the middle range elastic stress field which propagates in the real crystal, and with which another vacancy located further away can interact.

In their intrinsic regime of formation, their concentration remains very low²², and their volume is delimited—in the simplest case—by the set of the outer shells electrons of the nearest atoms immediately surrounding them. To put it metaphorically, vacancies form the most important “active minority” of a crystal, the most systemic and emergent one that shakes up the “established order”²³ and always forces the crystal to evolve (provided changes of external constraints are made). One very interesting thing about these crystal chemical objects which do not refer to any chemical species is that not only the same line of reasoning that applied in the previous sections to the definition of building units chemical potentials applies now to that of their chemical potentials ($\mu_{|O|^{**}}$, $\mu_{|Tb|^{***}}$), but above all, that they can be discarded as constituents at some “physical level of organization of reality”. While the existence of an atom,

²² Typically less than $\sim 10^{20} \text{ cm}^{-3}$, for instance in the disorder-prone β -AgI crystals, intrinsic vacancy concentrations range from $\sim 8 \times 10^{16} \text{ cm}^{-3}$ at 25°C to $\sim 1.5 \times 10^{20} \text{ cm}^{-3}$ at 770°C.

²³ But that, not without a sense of irony, also gives rise to the propagation of the crystal structure by generating dislocation-based crystal growth sources.

an ion, a molecule, a free radical can only make sense at the latter level, the existence of a vacancy makes sense only at the crystal chemical level. In a 1982 paper which, we believe, might stand as Bunge's most original contribution to the philosophy of chemistry, he explained that "*what is physical about a chemical system is its components rather than the system itself (...). The composition of a chemical system is then a set of atoms or molecules, each of which may be regarded as a physical system. (...) And the composition of a chemical system is included in the reference class of physics.*" (Bunge 1982)²⁴. How can a Z-less, electrically neutral, inner structureless thing fit in "*the reference class of physics*"? Vacancies are entities of their own in the crystal lattice reference system, which must be taken into account when calculating the partition function of the crystal. Schottky's symbol for a vacancy building unit means "withdrawal of an atom" and has the significance of a "negative atom", or "- atom" ("minus one atom"). In the symbol for a vacancy structure element, the suffix represents only the site type and not "some atom has been withdrawn". Consequently, the vacancy structure element is to be looked upon as a "zero particle" or "nil particle". When building units symbols are used to describe them, vacancies simultaneously have the significance of a "negative particle", whereas *a vacancy as structure element has no material significance*. Vacancies have no vapour pressure but they surely have a chemical activity, they are thermalized by the crystal lattice vibrations and they locally undergo a "pressure" (a stress) on the order of magnitude of the crystal's shear modulus. Their related building units having a chemical potential, they necessarily have an energy (of formation, of interactions, of thermal agitation, and so on): vacancies are as real as material. Full-fledged matter! Which leads us to a somewhat funny observation that in the $|O|^{**}$ building unit symbol, an O^{2-} anion escaped from the crystal lattice not being replaced by anything but rather by *some* thing... Vacancies can introduce narrow electronic energy levels in an insulator or a semiconductor bandgap. They can

²⁴ Moreover, two of the "*extra assumptions*" he thought must be added to make quantum chemistry follow from quantum mechanics are not completely true when extrapolated to a crystal, namely that "*all the interactions among the components of a molecule are electromagnetic*" and that "*every chemical reaction consists of either the combination or the dissociation or the substitution of atoms or polyatomic systems, such as molecules and radical*". These claims neglect mass effects for instance, in the lattice relaxation processes, and in isotopic phase segregation phenomena.

interact by coulombic (long range) and elastic (middle range) interactions resulting from their relative electric charge and the crystallographic distortions arising from the atomic (ionic) neighbours position relaxation, respectively. They can pair, and when their concentration increases, they can order (by adopting periodic crystallographic positions instead of being randomly distributed through the crystal lattice) and lead to new structural types. They can also help forming clusters, as in the well-known Koch-Cohen cluster in wustite Fe_{1-x}O ²⁵, or dislocations²⁶, and can even trap mobile electrons and form so-called polarons²⁷. In doing so, they behave like a system *per se* inside the crystal which in turn is to be viewed as the reactor for crystalline imperfection reactions. They also have a tremendous technological importance (Gunkel et al. 2020; Debuisschert 2021). Due to the modification of the bond strength arising from the mass and electric charge variations entailed by the removal of an ion, the presence of a vacancy implies that the nearest ionic neighbours are shifted with respect to their positions in the normal ideal crystal, so that in the vicinity of the vacancy some lattice distortion occurs, producing a specific contribution to the vacancy formation enthalpy variation (in the form of elastic stress and strain) and entropy variation (resulting from the local lattice vibration frequencies modifications). Nevertheless, at longer range—at several lattice sites away from the vacancy, the crystal lattice remains unchanged. One may identify at least two ways vacancies (and their properties) bring about emergent (or submergent) features:

- 1) Bunge firmly defined the composition of a system at a certain level as the set of parts of the system belonging to the considered level. The molecular composition of a body of water is the set of its H_2O molecules, and the atomic composition of the same body is the set of H and O atoms that

²⁵ According to Robert Collongues (1973), it is iron protoxide which "from 1927, drew the attention of chemists and appeared as the archetype of non stoichiometric compound", and "the first attempt at demonstrating a non random distribution of vacancies in a non stoichiometric compound was performed by Bertaut" in a pyrothine crystal Fe_7S_8 .

²⁶ Extended one-dimensional defects which stem from periodically missing atoms.

²⁷ Mobile electrons (or holes) are, with vacancies, the only two known quasiparticles in a crystal which do not refer to a chemical species. When an electron is trapped on a vacancy site, it generates an additional distortion that stabilizes it on the crystal lattice, and so the electron plus the local distortion it carries is called a classical (dielectric) polaron.

compose it. In Bunge's words, a chemical system is one whose components are reacting chemicals (atoms, molecules or radicals). The axiomatized formulation of this definition completely excludes the recognition of the interdependencies between the constituents, so it is abundantly clear from his writings that what he calls a component is in fact a constituent in the chemical thermodynamics sense²⁸. A way to circumvent the difficulty could be to define the "physical level" by means of some sort of building unit composition of the crystal system, which could, of course, include the vacancies building units. After all, quasiparticles should "fit in the reference class of physics". However, in that case, it would also mean that the immediately preceding level of organization of the crystal would less be defined objectively than *ad hoc*²⁹, that is, with respect to constraints imposed by its structure. Vacancies suggest a new criterion for qualifying a thing as emergent: anything that is a component of a system which cannot be as well referred to as a constituent (or a part) is ontologically emergent. Neutral vacancies are examples of real and material things, the emergent nature of which is completely related to their type of (non-equivalent) crystallographic site, namely their space location (in the crystal lattice reference frame) and set of spatial relationships with other building units in the crystal (site symmetry group);

- 2) the crystallographic site symmetry group is the set of symmetry operators that leaves invariant the crystallographic site, as well as the hamiltonian and the wavefunction of any particle or quasiparticle that occupies it. Hence, it is a property of the most universal properties of things: their energy and their location in spacetime. It just so happens that due to ionic positions relaxation processes at play in the formation of a crystalline imperfection, this site symmetry group, which in the perfect ideal

²⁸ It is obvious from volumes 3 and 4 of his *Treatise*, that he uses both terms almost as synonymous.

²⁹ Although fully consistently with the exact definition 1.8, page 13 of the volume 4 of his *Treatise*.

crystal is determined exclusively by the unit cell content, can change. Some new symmetry operators can emerge, while some others can submerge, and it is even possible that emergent and submergent behaviours occur during the same transient regime leading to equilibrium. We shall see some examples of this in the next section³⁰.

3.5] Spectroscopic Properties of RE³⁺ Cations in Insulating Dielectric Crystals

Because the crystal-field possesses the same symmetry operators as the electric charges, dipoles, quadrupoles, etc., that give rise to it, the study of the optical spectra of several rare-earth 3+ (RE³⁺) cations dissolved in crystals permits us to characterize the crystallographic site symmetry group properties. In the case of Eu³⁺ cations, symmetry “trees” have been established that allows us to quickly identify from optical absorption and/or luminescence spectra their site symmetry group. Let us have a look at sesquioxides TM₂O₃ (TM=Sc,Y,Gd,Lu,In) doped with Eu³⁺ cations. In these

³⁰ Actually, there might be an additional way vacancies bring about submergent features, but the topic would deserve a full article of its own. The phenomenological (macrochemical) equation describing the formation kinetics of Schottky vacancy pairs, which is a law of chemical kinetics, i.e. a property possessed by the population of vacancies, is not symmetrical by time inversion (nor is the law describing the related entropy increase). On the other hand, at the microscopic level, the Schrödinger’s equation describes the spatiotemporal trajectories of the vacancies, and it is well-known that this equation is invariant with respect to the time reversal operation $t \rightarrow -t$. To the best of our knowledge, two physics theoreticians (Léon van Hove (1955) and Joseph Seiden (1957)) were the first to firmly establish the mechanisms of relaxation towards equilibrium, in different systems, with different assumptions, and to ground the entropy increase at the microphysical level (we mean, to establish Boltzmann’s H-theorem—including the loss of the “invariance by time inversion” property—starting from the Schrödinger’s equation), for a specific class of initial conditions. They demonstrated that it is fully possible to get rid of arguments and concepts of statistical nature or *ad hoc* (Gibbs ensembles, phase space, ergodicity, molecular chaos, random phase approximation, Dirac’s method of constant’s variation, etc.) to establish “mechanistically” the relaxation towards the equilibrium state of a system with a very large number of particles: internal molecular movement (semi-rotation of chlorine in molecular crystals containing – CCl₃ molecular groups)—strong coupling, quadrupolar interaction mediated coupling to the Brownian motion of molecules in a liquid—weak coupling, phonon-phonon, magnon-phonon and/or magnon-magnon collisions—weak coupling. These works hold “only” for a specific class of initial conditions and so far (and not by principle), the time reversal symmetry loss upon passing from Schrödinger’s equation to macrochemical kinetics equation can still be viewed as a submergent property, and the full reduction of the latter to the former does not seem to be a piece of cake.

crystals, there are two new building units that are dissolved in very small amounts, and their well-defined chemical potential $\mu_{\text{Eu}|\text{TM}(\text{C}_2)}$ and $\mu_{\text{Eu}|\text{TM}(\text{C}_{3i})}$ ³¹. As explained before, in the cubic crystallographic form of this oxide, TM^{3+} cations occupy two crystallographically nonequivalent sites in a $\frac{1}{4}(\text{C}_{3i})\text{-}\frac{3}{4}(\text{C}_2)$ proportion³². The majority site bears no inversion operation so that it is said to be noncentrosymmetric. This induces odd components of the crystal-field which force electric-dipole allowed optical intraconfigurational transitions between crystal-field sublevels. These sublevels, constituting the so-called “fine structure” of the Eu^{3+} cations’ 4f electrons in cubic TM_2O_3 ’s, arise from the degeneracy lifting, by the crystal-field, of the spin-orbit multiplets of the Eu^{3+} cations 4f⁶ electronic configuration. In the gaseous state, or in the “free ion” state (of atomic physics), where no (odd and even) crystal-field components exist around the Eu^{3+} ions, such transitions are strictly electric-dipole forbidden, and no visible absorption and luminescence are observed. So, these specific (and possibly polarized) absorption and luminescence, are emergent properties at the crystal chemical level, which do not exist at the “physical level of organization”. The electronic energy level diagram is also *partly* an emergent one, because the degeneracy of the free ion spin-orbit multiplets is lifted by the crystal-field, which gives rise to crystal-field sublevels that are labeled by the crystal quantum number (Margerie 1965; Hellwege 1948). The crystal quantum number, which is related to the atomic or free ion quantum number L for angular orbital momentum but not reducible to it, expresses the group theory properties and, in the crystal-field theory, all its possible values correspond to one of the irreducible representations of the site symmetry group. Hence, its

³¹ To which the same considerations as those developed in the previous sections apply. Since its concentration remains very small, the chemical potential of the building unit formed by the lattice molecule TM_2O_3 is taken as the standard chemical potential of this compound in its Raoult’s reference state.

³² It was found recently that the statistical distribution of Eu^{3+} cations dissolved in a flux-grown Y_2O_3 crystal, does not follow the 25-75 % “share” of the crystal structure, but a shifted 16-84 % distribution in favour of the crystallographic site endowed with C_2 symmetry group. This illustrates our previous remark on the necessary differentiation of “*Z-equivalent*” cations in a crystal structure. Another example is that of chrysoberyl Cr^{3+} -doped BeAl_2O_4 crystals, in which the Al^{3+} cations occupy octahedral sites and Be^{2+} ones occupy the tetrahedral sites. The two crystallographically nonequivalent Al^{3+} sites in this structure occur in equal numbers, but ~80% of Cr^{3+} impurity ions occupy the C_s mirror sites, which play an exclusive role in laser action.

possible values are constrained by site symmetry. It just so happens that in cubic TM_2O_3 's, there is a difference between the site symmetry group and the (kind of) “molecular” dominant symmetry that can be inferred from a continuous symmetry analysis of the crystal structure at an intermediate level, between the crystal chemical and the so-called “physical” levels, which might be defined by the nearest neighbours coordination sphere of the Eu^{3+} cations. While the former is C_2 , the latter is quasi- C_{2v} (Krupke 1966; Linarès 1968)³³. If one would perform a very simple calculation of crystal-field parameters by lattice summations based on the multipole expansion of the electrostatic interaction between ions in this crystal structure, one would expect that the parameters imposed by the C_2 symmetry, namely iB_{42} , iB_{44} , iB_{62} , iB_{64} , iB_{66} , are almost systematically nil, which would lead to the *a priori* conclusion that the crystal-field parameterized hamiltonian must be invariant by the C_{2v} site symmetry group operations. In fact, it was firmly established by means of combined experimental spectroscopic energy levels determination and parameterized crystal-field hamiltonian calculations, that these imaginary crystal-field parameters are far from being negligible (Antic-Fidancev, Hölsä, and Lastusaari 2002). This proves that the site symmetry C_2 , lower³⁴ than C_{2v} , which results in measurable and computable spectroscopic properties of the 4f electrons, is truly an emergent symmetry non-deducible from the atomic physics level nor from some kind of intermediate level between the atomic and the unit cell level. Thus, the value of the crystal quantum number labelling each of these crystal-field sublevels is (at least partly) an emergent property. While the number of crystal-field sublevels arising from the degeneracy lifting of the spin-orbit multiplets of the Eu^{3+} cations, and the allowance of forced electric-dipole optical intraconfigurational transitions (absorption, luminescence, including polarization effects), are to some extent emergent properties of the 4f configuration electrons at the crystal

³³ Another example where the dominant “molecular” or “polyhedral” symmetry group is of higher order than the actual site symmetry group is in the $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ herbertsmithite crystal structure, around the $\text{Cu}^{2+}(2)$ cationic site: while the former is D_{4h} , the latter is D_{2h} . The fourfold rotation axis is lost upon addition of the unit cell atomic content beyond the first coordination sphere.

³⁴ Interestingly, when the degree of “assembly” increases here, from the O^{2-} second nearest neighbours of the Eu^{3+} cations to the full content of the lattice unit cell, the vertical mirror symmetry operator disappears, which can be qualified as a quasi-submergent phenomenon.

chemical level, the energy splitting between the sublevels, the strengths and cross-sections of these optical transitions are resultant properties. One should be dissuaded from thinking that an inversion symmetry operator has a causal power³⁵. One way to understand this is to realize that under the parity conservation general principle and the Wigner-Eckart theorem application, there is a separation between the features of these spectroscopic properties which depend only on spatial relationships (site symmetry group) and those which depend on the details of the multipolar electrostatic interactions between ions (Weissbluth 1978)³⁶. Some transition selection rules are rigorously deduced from symmetry considerations, some others depend on the angular momenta specific coupling scheme. Moreover, optical spectroscopy of Eu^{3+} cations (and of some other RE^{3+} cations) is also helpful in demonstrating that site symmetry group properties may emerge and/or submerge during the relaxation processes taking place during their dissolution in the crystal structure. For instance, the dissolution of Eu^{3+} cations in crystallographic sites of the KPb_2Cl_5 structure that bear only the identity operator (C_1 group) leads to the emergence of higher order symmetry operators, like a threefold rotation axis or a vertical mirror (C_3 and C_{2v} groups) (Cascales, Fernández, and Balda 2005). The same happens when Eu^{3+} cations are dissolved in orthorhombic α' - Sr_2SiO_4 crystals: while the two Sr^{2+} cations crystallographically nonequivalent sites have a C_1 symmetry group, Eu^{3+} cations adopt a C_{2v} and a C_{3v} site symmetry group when substituting for the ninefold coordinated Sr^{2+} cation and for the tenfold coordinated one, respectively (Gupta, Kadam, and Pujari 2020). While, on the other hand, the dissolution of the same cations in α - and β -forms of NaYF_4 crystals is accompanied by a loss of many symmetry operators, characterized by the decrease in symmetry order from O_h (α -form) or C_{3h} (β -form) to C_2/C_s symmetry groups (You et al. 2018). In $\text{Ca}_2\text{La}_3\text{Sb}_3\text{O}_{14}$ (Srivastava et al. 2014) and SrZrO_3 (Gupta, Kadam, and Pujari 2020) crystals, the same chemical reaction on centrosymmetric crystallographic sites leads to the submergence of the inversion point symmetry (as evidenced by visible emission spectra), as in CsCdBr_3 , where two Eu^{3+} cations form an associated complex with a Cd^{2+} -vacancy and lower the site symmetry from D_{3d} to C_{3v}

³⁵ Electrons have, through their charge, angular momentum, and so on.

³⁶ Check for example pages 159-167, 500-504 and chapter 28.

(submergence of an inversion point, three perpendicular twofold rotation axes and a sixfold improper axis) (Pellé et al. 1995).

4] Conclusions

We hope we have been convincing in trying to establish that relative building units and their chemical potential illustrate the fact that crystal chemistry is not reducible to atomic and lepton physics. While the existence of O^{2-} anions, or the magnitude of the crystal-field parameters are examples of resultant effects, vacancies, and more broadly speaking relative building units, are examples of ontologically emergent objects, and the building units chemical potentials, the crystal quantum number (itself an undefinable quantum number at the atomic or free ion level of description), are other examples of emergent properties poorly reducible to microphysics. Relative building units constituting, at the angström-scale of description, the “atomic” basis for non stoichiometry, it is straightforward to understand that the latter, which, to quote Robert Colongues, expresses the existence of a composition variation of a single phase in a solid, in contradiction with the Proust-Dalton laws, is an emergent property of crystals.

We have argued that vacancies³⁷ are ontologically as real as material. Note that the discussion about the O^{2-} anion might be generalized to all ions said to exhibit unusual oxidation states and that crystal chemistry may supply the philosophical reflection with other interesting objects such as clusters embedded in crystals and dislocations patterns, likely to illustrate ontological emergentism at play in condensed matter processes. We have also seen that crystallographic site symmetry properties that are (invariance) properties of properties of things (like energy, wavefunctions), may also be viewed as emergent (or submergent) properties. In this discussion, we have been concerned with properties that are not only well-defined, but also at the very core of statistical thermodynamics (the chemical potential) and quantum mechanics (the crystal quantum number which labels the eigen wavefunctions and upon which the hamiltonian algebra directly acts) of crystal chemistry, and we believe that makes our arguments much stronger than if we had manipulated vague, non-dimensional and purely qualitative properties as is sometimes the case in the philosophical literature on reduction

³⁷ Including electrically neutral vacancies.

and emergence. Perhaps a strategy to find emergent objects and properties could be to look for symmetries that appear only at some level of organization, resulting in closely related conservation rules necessary to define root properties, and then to look for intrinsic (and local) deviations from these symmetries and their impact on the preceding level. In the ontology and epistemology of crystal chemistry, this leads for instance to the distinction between a component and a constituent, and the recognition of the vacancy as a strikingly emergent thing.

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