The role of the inductive effect in solid state chemistry: how the chemist can use it to modify both the structural and the physical properties of the materials

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Abstract

The concept of the inductive effect, which is well known in organic chemistry, has been extended to solid-state chemistry. In solid ternary compounds, the cohesion energy of which primarily results from the electrostatic interaction between one type of anion X^{q-} and two types of cations M^{m+} and T^{z+}, the inductive effect of T on the M–X bond has been qualitatively assessed by the difference of electronegativity between M and T atoms, showing the limits of this concept. Several correlations between the inductive effect of the countercation T and physicochemical properties depending on the covalent character of the M–X bond have been reviewed: structural modification of oxides, stabilization of unusually high oxidation states of 3d transition elements in oxides and fluorides, vitrification conditions of materials, electrical conductivity of some perovskite oxides, cationic conductivity, magnetic properties, optical properties of divalent europium, Fe^{3+}/Fe^{2+} redox potential position in inorganic isostructural compounds and Mössbauer isomer shifts in FeO_x and FeF_n polyhedra.

1. Introduction

Many compounds have a bonding which is intermediate between the simple ionic and covalent extremes. Their structural and physical properties depend strongly on the degree of ionicity or covalency of the bonds. In the simple ionic model direct overlap between ions of the same kind is the only possible source of bandwidth, but as the degree of ionic character decreases, valence and conduction bands may also be broadened by the covalent overlap between anions and cations.

The aim of the present paper is to show how the chemist can modify the degree of ionicity or covalency of the bonds by using the concept of inductive effect, which is well known in organic chemistry [1], through cationic or anionic substitutions in inorganic materials.

2. Inductive effect in inorganic materials with essentially ionic bonds

Many inorganic solids can be pictured as a set of cations and anions, the cohesive energy resulting primarily from the electrostatic interaction between both species. This description implies that any bond between both species is polarized and that the definition of the inductive effect in organic chemistry is not literally applicable to such compounds.

The concept of the inductive effect was first extended to inorganic solids by Noll [2] in order to explain small differences in average Si–O bond lengths in silicates. Shannon [3] also interpreted average Ge–O distances in germanates according to the same principle.

For a binary compound $M_v^{m+}X_x^{q-}$ in which all cation–anion bonds are identical (cristobalite, for example), no inductive effect occurs. This situation may be regarded as parallel to that of ethane in organic chemistry. Let us now consider a ternary compound $T_u^{z+}M_v^{m+}X_x^{q-}$ in which each anion X^{q-} is coordinated only to a cation T^{z+} on one side and to a cation M^{m+} on the other one. If T^{z+} is more electronegative than M^{m+}, the anion X^{q-} will tend to share its electrons preferentially with T^{z+}. Less electron density will be available for covalency in the M–X bond. Conversely, if T^{z+} is an electron donor when compared with M^{m+}, an electron pressure will be exerted by T on the M–X bond in such a way that the covalent contribution to this bond is increased. By analogy with organic chemistry, the inductive effect of T on the M–X bond will be assumed to be positive if T^{z+} is more electropositive or electron donating than M^{m+} and negative in the opposite situation.

In summary, the inductive effect in such compounds is associated with the fact that the more covalent the T–X bond, the less covalent the M–X bond, and vice versa. For that reason, the bonds are often described as competing or antagonistic, and the cations as countercations.

The notion of a competing or antagonistic bond is easily defined in the simple case of an anion with a coordination number of two, as described previously. Such a situation occurs in several cases. For example, in TMX_6 phases with an ordered ReO_3 structure, each TX_6 octahedron shares its six vertices with a MX_6 octahedron, and vice versa. Similar behaviour for TX_4 and MX_4 tetrahedra is found in TMX_4 compounds with an ordered silica structure (*e.g.* $CrVO_4$ and $FePO_4$). In $Fe_2(SO_4)_3$, the SO_4 tetrahedra share their four vertices with FeO_6 octahedra and each FeO_6 octahedron is linked to six SO_4 tetrahedra [4].

However, in many cases the situation is less obvious. Even in a ternary compound TMX_3 with a simple perovskite structure, there is not one but four T–X bonds competing with any M–X bond, as well as another M–X bond. In $Na_3Fe_2(PO_4)_3$, whose structural network of PO_4 tetrahedra and FeO_6 octahedra is similar to that previously described for $Fe_6(SO_4)_3$, sodium cations must be introduced in the holes of the network in order to ensure electrical neutrality [5]. In such a case, both P–O and Na–O bonds can be considered antagonistic to the Fe–O bonds. The inductive effect of phosphorus on the Fe–O bonds should be negative, whereas that of sodium should be positive.

Even more complicated situations can occur. In many compounds, the various M–X bonds of a given MX_n polyhedron may be subject to different inductive effects because the nature and/or number of competing bonds is different for each bond.

Finally, we must emphasize that we shall only take account of the nature of the countercation T, not its topological location relative to the M–X bond. This problem is, of course, a different one which must not be overlooked. In some specific cases, it may be important to know whether the competition between the M–X and T–X bonds occurs via $\sigma - \sigma$, $\sigma - \pi$, $\pi - \sigma$ or $\pi - \pi$ orbitals.

Any tentative estimation of the inductive effect of T on the M–X bond in a ternary compound $T_u M_v X_x$ requires knowledge of the electronegativity difference between the T^{z+} and M^{m+} cations. Pauling first defined electronegativity as follows: "electronegativity is the power of an atom to attract electrons to itself" [6]. It is evident from this definition that electronegativity is not a property of the isolated atom but rather a property of an atom in a molecule, which depends on both its oxidation state and the nature of the surrounding atoms. Qualitatively it is simple to state that when a bond forms between two atoms, the bonding electrons will tend to move toward the atom of greater elec-

tronegativity, and thus, as the electron density shifts toward that atom, it will become negative and tend to attract electrons less. Conversely, the atom which is losing electrons becomes somewhat positive and more attractive to electrons than when it was neutral. This process will continue until the two atoms attract electrons equally. However, although the qualitative relationship between ionicity and electronegativity is clear, attempts to derive a simple quantitative relationship have been much less successful. The various methods can be arbitrarily divided into two groups. The Mulliken–Jaffé method [7–11], can be considered an absolute scale since it is based on ionization and electron affinity energies. All other scales are empirical and relative since they involve experimental data such as enthalpies of formation for Pauling's scale [6], size and charge of the species for both the Alled–Rochow and the Yonghe Zhang electrostatic scales [12, 13] and relative compactness for the Sanderson scale [14, 15].

Of the different electronegativity scales, the Mulliken–Jaffé seems the more satisfying since it is more fundamental and basic. The expression for electronegativity is $\chi = a + b\delta$ where a is the electronegativity of the neutral atom, b is the charge coefficient which measures the rate of change of electronegativity with charge when the atom is combined with another in a chemical bond and δ, which can be negative or positive, is the partial charge. The charge capacity of an atom, which is responsible for the well known inductive effect is the inverse of b, *i.e.* the ability of this atom to donate or to accept an electronic charge. Thus, for example, a small and slightly polarizable atom has a large b value and therefore a limited capability to donate or to absorb electron density. The charge capacity of an atom can be related, in one sense, to the hardness or the softness of acids and bases according to Pearson's classification [16]. It may be noted that hard species, of both acids and bases tend to be small and slightly polarizable (large b values) and that soft acids and bases (small b values) tend to be larger and more polarizable. In general, species having relatively high electronegativity are hard and those having low electronegativity are soft. This can be illustrated by Li^+, which is a hard acid having a high electronegativity due to its very high second ionization potential, and by Cu^+ or Ag^+ which are soft acids with low electronegativity.

However, it is worth mentioning that the different electronegativity scales must be used with great caution when accounting for the nature of the chemcial bond in a compound. This can be illustrated by two examples showing that the degree of ionic character of a bond is not governed by difference in the electronegativity of the elements alone. Thus the electronegativities (EN) of the Group IVB elements are the same (EN = 1.8) for Si, Ge, Sn, Pb on Pauling's scale. On the other hand,

the electronegativity of Ge is found to be greater than that of Si or Sn according to the electronegativity scales of Alled–Rochow, Sanderson and Mulliken–Jaffé. The difference in electronegativity between O and Si or Ge suggests that the Si–O bond should be more ionic than the Ge–O, what is not accurate since SiO_2 is a weakly acid oxide and GeO_2 a rather amphoteric oxide [17]. Nor is the difference in electronegativity a means of classifying crystal structures as ionic or covalent. Thus BeO and TiO crystallize in the blende and rocksalt structures respectively, although the electronegativity difference between Ti and O, and Be and O is the same on Pauling's scale. The Mooser–Pearson plots illustrate this behaviour well [18]. However, with Sanderson's electronegativity scale it is easy to see, by using the electronegativity difference between elements, that the Ti–O bond is more ionic than the Be–O, an observation which is consistent with the corresponding structural types. These apparent contradictions mean that we must be consistent and avoid picking the value of one element from Pauling, another from Alled–Rochow and a third from Sanderson and comparing the three. Anything can be proved by such a "judicious" mixing of systems.

On the other hand we might expect that the Lewis acid strength of cations could be used instead of electronegativity to qualitatively estimate the degree of ionicity of a bond. This arises from the work of Drago and Wayland [19–22], who established that species (cations or anions) have a certain susceptibility to undergo electrostatic interaction ("ionic" or dipole–dipole) and to form covalent bonds. Thus different scales of Lewis acid strength have been proposed [23, 24] but none of them can really be used to account for the degree of ionicity of a bond. Their interest lies rather in predicting the stability of complexes formed between acids and bases through the empirical rule "hard acids prefer to bind to hard bases and soft acids prefer to bind to soft acids".

In making a qualitative assessment of the inductive effect of cations we shall use Sanderson's electronegativity scale, which seems to be more appropriate than the others for the group A, IB, IIB and IIIB elements.

In the following sections significant examples will be chosen to show how the chemist can manipulate the inductive effect concept of cations to explain some structural and physical properties of inorganic solids.

3. Correlation between inductive effect and feasibility of some inorganic compounds

The stability of several inorganic compounds, *e.g.* structural change in some oxides, unusually high oxidation states of 3d elements or the vitrification conditions of materials, is implicitly governed by the inductive effect.

3.1. Structural modification of the K_2MO_3 oxides

The K_2MO_3 oxides (M ≡ Zr, Hf, Sn, Pb) can be described schematically as a stacking of $(K_{1/3}M_{2/3})O_2$ layers separated by potassium in trigonal prismatic coordination, with the potassium and tetravalent elements belonging to the layers occupying octahedral sites with common edges.

Under the high pressure, those oxides with M = Zr, Hf are transformed into the β form in which potassium, between the $(K_{1/3}M_{2/3})O_2$ layers is in octahedral coordination [25]. This can be easily explained. The electrostatic repulsion between layers becomes greater as the bond in the layers becomes more ionic. Thus, the repulsion is stronger for compounds with M = Zr, Hf than for compounds with M = Sn, Pb, since the Zr–O or Hf–O bond is more ionic than the Sn–O or Pb–O (Zr and Hf are clearly less electronegative than Sn and Pb). When pressure is applied to these compounds, the layers are shifted in order to reduce the electrostatic repulsion. Such a structural modification is accompanied by a change in potassium coordination from trigonal prismatic to octahedral. This change under high pressure is all the easier as the repulsion between layers is already relatively higher for the compounds with M = Zr, Hf.

3.2. Stabilization of unusually high oxidation states of 3d transition elements in oxides and fluorides

Obtaining an unusually high oxidation state in a given 3d transition element M requires very large covalence in the M–X bond. The degree of covalency of the M–X bond can be enhanced by countercations with a strongly positive inductive effect, such as Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}, which we might suppose to form ionic bonds.

This principle was recently applied to stabilize pentavalent iron in the ordered perovskite $La_2LiFe^{5+}O_6$ [26, 27], tetravalent iron in $A_{0.5}La_{1.5}Li_{0.5}Fe^{4+}_{0.5}O_4$ (A = Ca, Sr, Ba) [28, 29] and tetravalent cobalt in $Sr_{0.5}La_{1.5}Li_{0.5}Co^{4+}_{0.5}O_4$ [30] with ordered K_2NiF_4- type structures. In these compounds, the MO_6 octahedra are separated from each other by LiO_6 octahedra.

It is also worthwhile noting that the conditions of preparation of either fluorides or oxides containing an unusually high oxidation state of 3d elements also depend on the inductive effect of the countercation(s). Increasing difficulty is expected with a decreasing inductive effect of the countercation, a law which is in the main verified.

Let us consider, for example, the nickel fluorides. $Cs_2Ni^{4+}F_6$, $Rb_2Ni^{4+}F_6$ and $K_2Ni^{4+}F_6$ are prepared by a simple fluorination under 1 bar pressure of a mixture of $2ACl + NiCl_2$ or preferably of A_2NiCl_4 or $A_2Ni(CN)_4$ [31–33]. However, the synthesis of $Na_2Ni^{4+}F_6$ requires a pressure of 350 bar and even in

these drastic conditions, the purity of the compound is questionable [34]. Under low pressures of fluorine, only trivalent nickel can be obtained with sodium, i.e. $Na_3Ni^{3+}F_6$ [35]. As for lithium with a still smaller inductive effect on the Ni–F bonds, $Li_2Ni^{4+}F_6$ has never been prepared and the synthesis of $Li_3Ni^{3+}F_6$ requries a pressure of 300 bar [36].

The oxides provide other verifications of this law. For instance, the average oxidation state of iron in the $AFeO_{3-x}$ (A = Ca, Sr, Ba) compounds prepared in the same conditions (1300 °C in air), depends on the electropositivity of the alkali earth cation. The phase obtained with calcium, $CaFeO_{2.5}$ (brownmillerite) contains only trivalent iron, whereas a large amount of tetravalent iron is present in the homologous compounds of strontium and barium [37].

3.3. Vitrification conditions of ternary oxides

A factor that is undoubtedly important in glass formation is the viscosity of liquids above the melting point of the system. Glass formation becomes easier as viscosity increases, as in the case of polymeric liquids. In other words, the greater the difficulty in breaking the bonds in polymeric groups the easier is glass formation.

According to the Rawson-modified criterion of Sun, the glass-forming tendency is related to the ratio of bond strength to melting temperature [38]. This ratio accounts for both the bond strength and the thermal energy available to break the bonds. The formation of glass becomes easier as the bond strength in the polymeric groups present in the liquid becomes stronger and the melting temperature lower. On the other hand, according to kinetics theory, the lower the critical cooling rate of the liquid, the easier is glass formation [39].

To illustrate the vitrification conditions of materials we have chosen the case of rare earth based compounds such as $LnAlO_3$ perovskites and $Ln_3Al_5O_{12}$ garnets. In the liquid state, as shown by nuclear magnetic resonance (NMR) spectroscopy, Al is mainly in tetrahedral coordination for both systems [36]. Glass formation becomes easier as the bond strength in the $(AlO)_n$ polymeric groups occurring in the liquid becomes stronger, i.e. when the Ln–O bond is more ionic. The ease of glass formation for the perovskite decreases from La to Sm, i.e. when the ionicity of Ln–O decreases and, consequently, when the covalency of the Al–O antagonistic bond becomes smaller. For yttrium and the heaviest rare earths, from Eu to Lu, the Al–O bond becomes less and less covalent and the critical cooling rate is probably too high to obtain glass under present experimental conditions [40].

On the other hand, rare earth garnets $Ln_3Al_5O_{12}$ form a glass with a critical cooling rate which increases

as the ionicity of the Ln–O bond decreases from Dy to Lu, i.e. as the covalency of the Al–O antagonistic bond decreases [40].

4. Correlation between inductive effect and some physical properties of inorganic materials

The physical properties of materials are often related to the degree of covalency of certain bonds. The inductive effect is thus expected to play a significant role in many cases.

4.1. Electrical conductivity of some perovskite oxides

Over a decade ago, Goodenough pointed out the influence of the competition between A–O and M–O bonds in perovskite oxides AMO_3 on the width of the π^* bands [41]. The strength of the competition, which was based on the acidity and the formal valency of the A cation, can easily be related to the inductive effect of A on the M–O bonds. The π^* bands are expected to narrow when the covalency of the M–O bonds decreases, i.e. when the inductive effect of A on the M–O bonds becomes less positive. The fact that $SrCrO_3$ and $SrFeO_3$ have a metallic-type conductivity [41] whereas $CaCrO_3$ [42] and $CaFeO_3$ [42] are semiconductors can be explained by means of this concept.

4.2. Cationic conductivity

Cationic conductivity results from the ability of a cation to move within a lattice when an external electrical field is applied. Topological considerations are, of course, very important in this process, which will be favoured by sheet or tunnel structures. It is also worthwhile noting that the moving cation always has a small polarizing power (i.e. Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+), which means that the bonds between the moving species and the host lattice must be weak. The inductive effect implies that for a specified mobile cation and crystal structure, conductivity should increase and activation energy should decrease when the cations present in the host lattice, which act as countercations, are more electronegative.

Experimental results confirm this interpretation, which has already been proposed by several authors [43–47]. For example, the replacement of Mg^{2+} by more electronegative Zn^{2+} in the hollandite-type compound $K_2MgTi_7O_{16}$ leads to a decrease in the activation energy from 1.16 eV to 0.54 eV [46]. In the bidimensional oxides $K_{0.70}(T_{0.35}Sn_{0.65})O_2$, the room temperature conductivities are 4.5×10^{-7}, 1.6×10^{-6}, $7.5 \times 10^{-6}\,\Omega^{-1}\,cm^{-1}$ and the activation energies 0.54, 0.52, 0.45 (eV) for T = Ca^{2+}, Mg^{2+} and Zn^{2+} respectively [45].

4.3. Magnetic properties

The magnetic properties of an insulator strongly depend on the arrangement of the magnetic moments in the crystal structure. Besides the three-dimensional networks such as are found in perovskites, there exist various structural types allowing the magnetic ions to distribute themselves in only one or two directions in space, giving rise to a one-dimensional or a two-dimensional system.

Let us consider a two-dimensional system in which the long range magnetic ordering can be the result of either a finite J' exchange integral which characterizes the interlayer interaction or Ising-like behaviour.

An almost ideal two-dimensional system has been observed, *e.g.* in compounds with a K_2NiF_4 structure type. This can be illustrated by the solid solution $CaLa_{1-x}Y_xCrO_4$, which may be described schematically as intergrowth structure $(Ca, La, Y, O)_m$ $(Ca, La, Y, CrO_3)_n$ in which perovskite layers alternate with rocksalt layers along an [001] axis, Ca, La, Y being nine-fold coordinated. The separation between perovskite layers is almost twice the intraplanar distance between the two Cr^{3+} nearest neighbours.

The system magnetically studied for $0.4 \leqslant x < 1$ exhibits a strong two-dimensional magnetic behaviour (no magnetic ordering). For $CaYCrO_4$ ($x = 1$) a three-dimensional ordering temperature occurs. This effect results mainly from an increase in the covalency between oxygen and the nine-fold coordinated cations (Ca^{2+}, Y^{3+}, La^{3+}) leading to an increase of J' since Y is more electronegative than La. On the other hand, it is worthwhile noting that the magnetic interactions in the perovskite layers become weaker as the Y content increases since the $\pi(Cr-O)$ bonds, in competition with the $\sigma(Cu, La, Y)-O$ bonds, become less covalent in the absence of e_g electrons, which is revealed by a strong decrease of the intralayer exchange integral J/k [48, 49].

4.4. Optical properties of divalent europium

The excitation of Eu^{2+} in a host lattice can generally give rise to two types of emission, either a 4f–4f narrow one or a $(5d^14f^{n-1} \rightarrow 4f^n)$ broad one or both.

The 4f orbitals being internal, the influence of the crystal field on their energy level is small (the splitting of the J levels is of the order of a few hundred cm^{-1}). Consequently the 4f–4f emission involving the transition $^6P_{7/2} \rightarrow {}^8S_{7/2}$ depends weakly on the host lattice. On the other hand the 5d orbitals being external, the influence of the host lattice on the energy of the $4f^{n-1}5d^1$ levels is much more pronounced. The higher the covalency of the Eu–ligand bond, the lower the energy of the $4f^{n-1}5d^1$ excited levels.

Comparing the optical properties of Eu^{2+} in two host lattices in which Eu^{2+} is substituted for Ba ($BaLiF_3:Eu^{2+}$ and $BaSiF_6:Eu^{2+}$) and taking into ac-count the fact that Eu–F in $BaLiF_3:Eu^{2+}$ is more covalent than Eu–F in $BaSiF_6:Eu^{2+}$, we have observed that: (i) in $BaSiF_3:Eu^{2+}$, the lowest level of the $4f^65d^1$ excited configuration is far above the first excited level of the $4f^7$ configuration, $^6P_{7/2}$, and consequently the emission spectrum consists of intense lines originating from this level instead of the usual d → f [46]; (ii) in $BaLiF_3:Eu^{2+}$ the lowest level of the $4f^65d^1$ excited configuration is close to the $^6P_{7/2}$ level, and accordingly two emissions are observed at room temperature, a narrow one originating from the $^6P_{7/2}$ excited configuration, and a broad one originating from the $4f^65d^1$ excited configuration [50].

4.5. Fe^{3+}/Fe^{2+} redox potential position in inorganic isotructural compounds

The lithium may be inserted at room temperature either chemically or electrochemically in $Fe_2(XO_4)_3$ compounds with $X \equiv Mo$, W or S. $Li_2Fe_2(SO_4)_3$ appears to have an orthorhombic structure similar to that found for $Li_2Fe_2(XO_4)_3$ with $X \equiv Mo$ or W.

Where the lithiation has performed electrochemically, a 600 mV difference has been observed between the open-circuit voltage (OCV) of $Fe_2(SO_4)_3$ and that of a $Fe_2(WO_4)_3$ or $Fe_2(MoO_4)_3$. Such behaviour reflects the different positions of the Fe^{3+}/Fe^{2+} redox couple value with respect to that of the Li^+/Li^0 redox couple. The lithiation involves charge compensation of an inserted Li^+ ion by reduction of a Fe^{3+} ion to Fe^{2+}. The difference in the position of the Fe^{3+}/Fe^{2+} redox couple in two isostructural compounds of identical formal valence and similar lattice parameters can result from the strength of Fe–O π-bond covalent mixing since the minority-spin electron of a high-spin octahedral site $Fe^{2+}:t^4_{2g}e^2_g$ configuration occupies an antibonding t_{2g} orbital which only mixes with the nearest neighbour O–2pπ orbitals. As is well known, covalent mixing introduces a quantum-mechanical repulsion between the bonding and antibonding orbitals and consequently the energy of the minority-spin electron of a high-spin octahedral site $Fe^{2+}:t^4_{2g}e^2_g$, and hence the energy of the Fe^{3+}/Fe^{2+} redox couple, increases. Therefore the stronger the covalency of the Fe–O π-bond the higher the energy of the Fe^{3+}/Fe^{2+} redox couple and the smaller the OCV.

The countercation, which shares a common oxygen nearest neighbour with Fe in the Fe–O–X linkage ($M \equiv Mo$, W or S) determines the strength of the Fe–O covalency via the inductive effect. Comparing, *e.g.* $(SO_4)^{2-}$ and $(WO_4)^{2-}$ or $(MoO_4)^{2-}$, the covalency is the strongest in $(SO_4)^{2-}$ and consequently Fe–O is more covalent in $Fe_2(WO_4)_3$ or $Fe_2(MoO_4)_3$ than in $Fe_2(SO_4)_3$ [47].

In conclusion, such an example shows how we can manipulate the choice of countercation via its inductive

effect to change the position of a solid state redox potential in a solid.

4.6. ^{57}Fe Mössbauer isomer shifts in FeO_n and FeF_n polyhedra

Although all previous examples unambiguously support the reality of the concept of the inductive effect, none of them permits the derivation of a straightforward correlation between a physical measurement and the degree of covalency of a M–X bond when the countercation T changes from a very electronegative "ion" such as S^{6+} or P^{5+} to a very electropositive one such as Cs^+. A recent investigation of the systematic trends of the ^{57}Fe isomer shifts in FeO_n and FeF_n polyhedra has shown that this somewhat ambitious task can be partially achieved, at least for the Fe–O bonds [51].

The isomer shift of ^{57}Fe has long been to provide information about the covalency of the iron–ligand bonds. For a given oxidation state of iron, a correlation can be found between the isomer shift δ and the electronegativity of the ligand. For example, $\delta_{FeF_2} > \delta_{FeCl_2} > \delta_{FeBr_2} > \delta_{FeI_2}$. The same is true in trivalent iron: $\delta_{FeF_3} > \delta_{FeCl_3} > \delta_{FeBr_3}$. Moreover, it is generally admitted that for a given oxidation state and for identical ligands, a decrease in the coordination number leads to a decrease in the isomer shift. A typical example is provided by the yttrium (iron–gallium) garnet $Y_3Fe_3Ga_2O_{12}$ for which $\delta^{octa} = 0.37$ mm s^{-1} and $\delta^{tetra} = 0.16$ mm s^{-1} (all isomer shift values reported in this paper are experimentally derived values at room temperature, relative to α-Fe and taken from references included in [51]). Therefore, the isomer shift should a priori be a good indicator of the relative covalency of the Fe–X bonds.

The above "rules", however, suffer from many unexplained exceptions. For instance, according to any scale of electronegativity, the Fe–F bonds should always be more ionic than the Fe–O bonds for an identical oxidation state and coordination of iron. Yet some ferric compounds in which Fe^{3+} is located in an octahedron of oxygen such as $FeBO_3$ ($\delta = 0.41$ mm s^{-1}), $Ca_3Fe_2Si_3O_{12}$ ($\delta = 0.41$ mm s^{-1}), Fe_2PO_5 ($\delta = 0.43$ mm s^{-1}), $Na_3FeP_2O_7$ ($\delta = 0.45$ mm s^{-1}), $Na_3Fe_2(PO_4)_3$ ($\delta = 0.45$ mm s^{-1}) and $Fe_2(SO_4)_3$ ($\delta = 0.49$ mm s^{-1}) have isomer shift values in the range of those found for Fe^{3+} in a fluorine octahedron (0.41–0.50 mm s^{-1}).

Because of these anomalies, the relationship between isomer shift and covalency has remained somewhat controversial. In order to obtain a better understanding of this relationship, an investigation of some 300 published isomer shift values [52] was carried out by Ménil. This study clearly demonstrates both previous trends (the general decrease of δ with decreasing electronegativity of the ligand and decreasing coordination num-

ber) as well as their limits (unexplained spread of the isomer shift values for most $Fe^{m+}X_n$ series and consequent overlapping of several series).

The second-order Doppler shift, which contributes to δ and may vary from one compound to another, was first ruled out as a possible factor leading to the large spread of values observed in some specified $Fe^{m+}X_n$ series (a very pessimistic estimate yields a spread of 0.05 mm s^{-1} due to this factor). Moreover, the correlation of the isomer shift with the interatomic Fe–X distances, which was proposed by several authors to explain the spread of values within a specified series, turned out to be groundless.

There is an interesting comparison between ferric sulphate $Fe_2(SO_4)_3$ and ferric molybdate $Fe_2(MoO_4)_3$ and similar structures of $Fe^{3+}O_6$ octahedra sharing all vertices with $T^{6+}O_4$ tetrahedra and vice versa. Their isomer shifts are 0.49 mm s^{-1} and 0.42 mm s^{-1} respectively. Such a difference is expected from the electronegativity of Mo as compared to that of S. The increase in the covalency of the Fe^{3+}–O bond in the molybdate has been confirmed directly by the covalency sums obtained from the Fe^{3+} moments determined by neutron diffraction: 9% for the molybdate instead of only 6% for the sulphate.

A comparison between the ferric sulphate α-$Fe_2(SO_4)_3$ and the fluoride K_2FeF_5 also illustrates how the inductive effect of a countercation can modify the covalency of a bond. In both compounds, the Fe–O and Fe–F distances are very close ($d_{Fe-O} = 1.95$–2.04 Å; $d_{Fe-F} = 1.80$–2.05 Å) and Fe^{3+} is located in octahedral sites. A Mössbauer study shows that the ^{57}Fe isomer shift is larger in the sulphate ($\delta_{300 K} = +0.49$ mm s^{-1}) than in the fluoride ($\delta_{300 K} = +0.42$ mm s^{-1}). This clearly means, taking the inductive effect into account, that the Fe–F bond in K_2FeF_5 is more covalent than the Fe–O bond in α-$Fe_2(SO_4)_3$ since the K–F competing bond is more ionic than the S–O bond.

5. Conclusion

The purpose of this paper is to demonstrate unambiguously the reality and generality of the concept of the inductive effect in solid-state chemistry. We have mainly dealt with compounds containing the most electronegative anions (fluorine and oxygen) as these materials are the most familiar. However, since the concept of the inductive effect applies on the one hand to essentially covalent compounds (organic compounds) and on the other to compounds containing essentially ionic bonds (M–F or M–O), there is obviously no apparent reason why it should not apply to materials containing ligands which are less electronegative than oxygen or fluorine.

The inductive effect of the countercation is by no means a second-order effect on the covalent character of the M–X bond. According to Mössbauer data, the magnitude of the increase in the covalent character of the Fe–O bond when the countercation changes from S^{6-} to Cs^+, all other things remaining the same, can be compared with the increase in covalency which results from a reduction of the iron coordination number from 6 to 4 in a compound containing both octahedral and tetrahedral sites. The apparent paradox that the Fe–O bonds in sulphates should be more ionic than the Fe–F bonds in some fluorides is a clear illustration of the importance of the inductive effect concept.

The various examples presented in this paper indicate that the reality, generality and importance of the concept of the inductive effect in solid-state chemistry is an irrefutable fact.

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