Modelling the effective atomic number and the packing factor of polyatomic compounds: Applications to refractive index and dosimetry

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A B S T R A C T

In this work, based on fundamental physics and chemistry (charge distribution, electronegativity, induced dipole moment), we are introducing an analytical expression for Z_{eff} and a general way of calculating the *crystal packing factor*, p, of any ionic material. By using the average separation between the atomic and crystal(ionic) radii of the interacting ions, we are postulating an *effective distance* (R_{ij}) between the positive and the negative centre of charge. When compared to the available experimental data, predictions within 20% have been obtained to Z_{eff} of materials applied to dosimetry. In photonics, the increasing behaviour of the refractive index with Z_{eff} is confirmed. By combining crystal field and effective charge models, we have predicted Z_{eff} of the Eu_2O_3 within the range of available experimental data.

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1. Introduction

Over the years substantial efforts have been made in order to predict Z_{eff} of heterogeneous compounds [1,2]. Models discussing the behaviour of solid state materials in the presence of radiation should deal with interactions such as spin–orbit coupling and crystal field potential, each one with its own particular dependence on the atomic number [3–5]. For this, some concepts such as charge distribution, atomic/molecular polarizability (α), electronegativity (χ) of the constituents of the sample, its effective atomic number (Z_{eff}) and crystal packing factor (p) have to be discussed. In text books and in very recent papers, these two latter quantities have been described preferentially for monoatomic systems [3,6–8]. All these concepts are somehow related to each other. For instance, the spin–orbit interaction can be written in terms of Z_{eff} [3]; α can be written in terms of the electronegativity difference ($\Delta\chi$) of the interacting ions [9,10] or in terms of the induced dipole moment (μ) [11]; the charge distribution can be written as a function of (μ) [12]; and χ can be related to charge distribution, charge transfer and dipole moment in molecules [13,14].

There are four different scales of electronegativity, namely, Pauling, Mulliken, Allred-Rochow and Allen scales [15–18], each one based on different physical chemistry arguments. In addition, there are equalization methods of electronegativity and hardness (η). Such methods establish that the bonded species in the molecules have equalized its electronegativity/hardness. This is used in

density functional theory (DFT), and χ is defined as the negative of the chemical potential [19,20]. This gives an idea of how puzzled can be such investigation. We will try to bypass some intricate aspects of this subject to develop a simple but fundamental contribution to the analytical study of Z_{eff} and p of insulators.

Host materials used in photonics (laser, optical sensors and long lasting phosphorescence) and in medical applications (thermoluminescence and optically stimulated luminescence in dosimetry) are mainly ionic crystals and glasses, because suitable materials should have a band gap large enough to host metastable states and traps [21,22]. Intensity of the incident radiation and its range of energy are important features for photonics. The key point is the refractive index, n, which is directly related to Z_{eff} [6,23]. For dosimetry applications, ionizing radiation interacts with matter, and several effects can take place [2,3,24]. In the energy range of the Compton effect (200–1000 keV) all materials exhibits similar behaviour, clearly because this effect is the X-ray scattering by electrons, and the scattering does not depend on the material, but only on the angle of scattering. However, in the 10 eV to 200 keV energy range, where the photoelectric effect is dominant, each material responds differently, according to its Z_{eff} [24]. In this way, this is the most suitable experimental range to quantify Z_{eff}.

By using the Pauling scale, the interactions in ionic crystals and glasses are predominantly electrostatic. In this work we are using an effective coulomb type potential (U_{eff}) to describe the cation–anion interaction. As U_{eff} is an effective interaction, it is related to Z_{eff}, the effective atomic number of any ionic compound. It is being introduced the crystal packing factor, p, a way of calculating the packing factor of any compound, using the crystal(ionic) radii of the constituents. This is important because only incident radiation

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on matter should be considered. Another problem to be faced is that the potential U should contains an effective distance to describe the cation–anion interaction. Such interaction occurs between electronic clouds. Thus, we are postulating an *effective distance* (R_{ij}) between the positive and the negative centre of charge. By using the NaCl crystal as example, the 3s electron of the Na atom is completely transferred to the $2p^5$ orbital of the Cl atom. Thus, the Na^+ ion host a positive centre of charge and the Cl^- ion host a negative centre of charge. R_{ij} is the radial separation between them.

2. Theory

As the dominant interaction, U, that keeps the ions bonded in ionic crystals and glasses is coulomb type, the bonds are mainly σ-type in the cation–anion direction, and U can be assumed only with radial dependence. Thus, we can write:

$$\frac{dU}{dR} = -\frac{U}{R} \tag{1}$$

A similar expression has been obtained by Jørgensen [25] through many experimental evidences, partly from high-pressure experiments. In his work the constant appearing in the differential quotient is -7, because the potential is a short-range Van Der Waals type. Formally, U must depend on the atomic number of the interacting species. Thus, the effective potential, U_{eff}, must depend on Z_{eff}, and U and U_{eff} are assumed to respect the following proportional relations:

$$U \propto p Z_i Z_j \tag{2}$$

$$U_{eff} \propto Z_{eff}^2 \tag{3}$$

U is modified by the *crystal packing factor*, p, because only the incident radiation on matter must be considered. This p factor is obtained through the same expression used in solid state physics for monoatomic solids, but now using the crystal(ionic) radii of the interacting species. This is to be highlighted, because it is usual to find p only for monoatomic solids [7].

The dependence in Eq. (2) on p shows that the fraction of the atoms that will interact with the incident radiation is a increasing function of p. Consequently, the greater will be the cross section. Thus, solving the differential equation in (1) through the method of separation of variables, and using (2) and (3) as the limits of integration, we obtain

$$Z_{eff} = \left(\sum_{i \neq j} p Z_i Z_j \left(\frac{\overline{R}_{ij}}{R_{ij}} \right) \right)^{0.5} \tag{4}$$

where $\overline{R}_{ij}$ is the sum of the ionic radii of the interacting ions [26] or the cation–anion distance. R_{ij}, the *effective distance* between the negative and positive centre of charge, is obtained by the average difference between the atomic and crystal(ionic) radii of interacting ions (Fig. 1 and Eq. (5)). In Fig. 1, $R_i^A (R_j^A)$ are atomic radii and $R_i^I (R_j^I)$ are ionic radii of the $i(j)$-th interacting species, respectively:

$$R_{ij} = (|R_i^A - R_i^I| + |R_j^A - R_j^I|)/2 \tag{5}$$

Therefore, we emphasize that $\overline{R}_{ij}$ can never be equal to R_{ij}. A similar idea has been used in Ref. [27]. Currently, there are at least two well known ways of calculating Z_{eff} of polyatomic compounds, the first one based on phenomenological procedures [2], and the second one, numerical codes [28]. Both procedures, however, do not take into account the cation–anion interaction, even dealing with solid state materials.
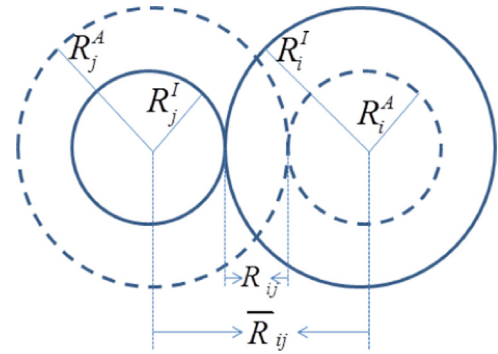

Fig. 1. Region of interaction between the electronic clouds.

3. Results and discussions

In polyatomic systems the radii of the cations and anions can be quite different. Therefore, p is being calculated based on the structure type and on the occupation number of cations and anions of the unit cell. For comparison, we are using the crystal and ionic radii. The contribution of each ion is taken into account in the calculation of the hard sphere volume. Crystal and ionic radii can be really different. In Ref. [26] it is argued that the crystal radii correspond more closely to the physical size of the ions in a solid, because it varies very slightly from crystal to crystal. We have entered both radii in our predictions, and dealt with compounds with available experimental Z_{eff} (to the authors' knowledge).

Table 1 shows the $p_C(p_I)$, the packing factor calculated by the crystal(ionic) radii, and the references are from where we have taken each structure type. p_C is always smaller than p_I. By comparing with the packing factor of monoatomic systems, we have the p_C of the SiO_2 similar to the diamond structure, which is the less dense structure, and the p_I of the Al_2O_3 is greater than the face centred cubic (FCC) or face centred hexagonal (FCH), which have the most dense crystal lattices [7,48]. The Z_{eff} expression is sensitive to small variations of p, and its accurate calculation is very important for a good prediction. When applied to dosimetry, p is a factor which contains the same spirit of the fractional electron content (f_i), used in the phenomenological calculations [2,24], because the crystal/ionic radii take into account the electronic clouds of the interacting ions. In this way, with $p_C(p_I)$ it is being introduced a formal way of considering the f_i factor.

In order to use Eq. (4), a detailed analysis has to be developed. For diatomic systems, $i=1$ and $j=2$, i standing for the anion, Z_{eff} depends on only one variable, R_{12}. For polyatomic systems, it depends on at least two variables, $i=1$ and $j=2, 3$, namely, R_{12} and R_{13}. These variables are calculated through Eq. (5) and indicated by the overlap of the electronic clouds in Fig. 1. Table 2 shows the

Table 1
Packing factors calculated using the crystal (p_C) and ionic (p_I) radii. In each case, the R_{ij} are specified. The references are from where we have taken each structure type.

Structure	$p_C/R_{12}(R_{13})$	$p_I/R_{12}(R_{13})$	Ref.
BeO	0.600/0.615	0.804/0.755	[29]
LiF	0.624/0.550	0.721/0.69	[30]
Al_2O_3	0.595/0.617	0.804/0.767	[31]
MgO	0.580/0.63	0.685/0.77	[32]
NaF	0.524/0.59	0.551/0.73	[33]
SiO_2	0.344/0.625	0.471/0.765	[34]
CaF_2	0.532/0.585	0.604/0.725	[35]
V_2O_3	0.539/0.52	0.679/0.66	[36]
ZnO	0.573/0.485	0.673/0.625	[37]
Eu_2O_3	0.434/0.727	0.502/0.866	[38]
$Li_2B_4O_7$	0.516/0.55(0.605)	0.670/0.69(0.745)	[39]
$CaSO_4$	0.509/0.595(0.64)	0.629/0.735(0.78)	[40]