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Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



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



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ARTICLE INFO

ABSTRACT

Article history: Received 26 October 2015 Received in revised form 29 February 2016 Accepted 3 May 2016 Available online 7 May 2016

Keywords: Polyatomic compounds Effective distance Crystal packing factor Effective atomic number

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

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http://dx.doi.org/10.1016/j.jpcs.2016.05.003 0022-3697/© 2016 Elsevier Ltd. All rights reserved. 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 Eu₂O₃ within the range of available experimental data.

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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 cationanion 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

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:

$$U \propto p Z_i Z_j$$
 (2)

$$U_{eff} \propto Z_{eff}^2$$
 (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

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

where 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 $R_i^I(R_i^I)$ are ionic radii of the i(j)-th interacting species, respectively:

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

Therefore, we emphasize that \bar{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 $p_C(p_l)$, 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_l . By comparing with the packing factor of monoatomic systems, we have the p_C of the SiO₂ similar to the diamond structure, which is the less dense structure, and the p_l of the Al₂O₃ 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 $p_C(p_l)$ 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	Ta	ble	1
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Packing factors calculated using the crystal (p_c) and ionic (p_l) radii. In each case, the R_{ij} are specified. The references are from where we have taken each structure type.

Structure	$p_C/R_{12}(R_{13})$	$p_l/R_{12}(R_{13})$	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 ₂ O 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]

Table 2 Theoretical Z_{eff} obtained with the crystal (*C*) and ionic (*I*) radii, and the available experimental data.

Structure	$Z_{eff}\left(C\right)$	$Z_{eff}\left(I ight)$	$Z_{eff}(exp)$
BeO	7.176	7.498	7.2 [41]
LiF	7.999	7.679	7.74 [1], 7.87 [42], 7.65 [43]
Al_2O_3	13.786	14.448	11.72 [42], 10.27 ± 0.47 [44]
MgO	13.683	13.458	10.042 ± 1.365 [45]
NaF	14.372	13.251	9.897 ± 1.885 [45]
SiO ₂	9.958	10.531	10.79 [42], 12.64 ± 0.56 [44], 10.74 [43]
CaF ₂	19.952	19.086	$16.979, 14.569 \pm 1.853$ [45], 16.70 ± 0.77 [44],
			15.30 [43]
V ₂ O ₃	19.623	19.558	20.97 [46]
ZnO	24.636	23.517	25.03 [47]
Li ₂ B ₄ O ₇	9.892	10.115	7.04 [43]
CaSO ₄	22.144	22.193	14.408 [1], 15.698 ± 1.281 [45], 17.04 ± 0.76 [44],
			14.02 [43]



Fig. 2. *n* versus Z_{eff} for the (0.7-x)NaPO₃–0.3WO₃–xBi₂O₃ glassy system. The behaviour is similar to *n* versus Bi₂O₃ concentration in Ref. [23].

predictions of Z_{eff} for diatomic and polyatomic systems using the crystal and ionic radii.

For photonics, we find results of monoatomic or covalent materials [6,49]. In both works the hard X-ray region is investigated. This is the domain of the photoelectric effect, but Eq. (4) is not applicable in the case of non ionic systems. However, for the (0.7 - x)NaPO₃–0.3WO₃–xBi₂O₃ glassy system, as x increases (which means Bi₂O₃ replaces NaPO₃), the refractive index, n, increases [23]. With such replacement the ionic character of the glass increases, because the Bi–O bond is more ionic than the P–O bond. Eq. (4) gives 17.3 and 37.5 for the Z_{eff} of the NaPO₃ and Bi₂O₃, respectively. Thus, the Z_{eff} of the glass increases from 20.81 to 24.85 ($Z_{eff} = \sum_i x_i Z_{eff}^i$, *i* running over the glass components) with the Bi₂O₃ concentration, which confirms that *n* increases with Z_{eff} (Fig. 2).

For the Eu₂O₃ system we can amplify the discussions, because we can use the simple expression connecting Δ_{χ} (Pauling scale), μ and R_{*ij*} as follows [9]:

$$\Delta \chi = \frac{\mu}{D} = \frac{ge \kappa_{ij}}{D} \tag{6}$$

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valid for diatomic systems. *D* is the Debye factor, R_{ij} is our postulated *effective distance. ge* is the charge devoted to the Eu–O bond, *g* being the charge factor. We picture this frame as an electric dipole moment, μ , formed by two opposite charges of equal magnitude. The Eu³⁺ ions in this oxide have two sites, both with coordination number (CN) 6. In order to estimate a reasonable range

of g, for the minimum we used the average by dividing the Eu^{3+} valence by 6, and $g_{min}=0.5$. For the maximum, we have obtained g_{max} = 0.708 by dividing by 6 the Eu ion charge calculated by the Batista-Longo improved model (BLIM) at the Eu–O middle distance [50], combined with the method of equivalent nearest neighbours (MENN) [51-53]. The MENN is a method which attempts to systematize the simple overlap model [54,55]. The MENN and the BLIM have been published for compounds with CN 8 and for coordination compounds. However, the shielding of the 4f orbitals by the 5s and 5p filled shells is valid no matter the host, and this leads to very similar energy level positions no matter the host. So, even though in an inorganic oxide, the europium charge distribution must be similar. Using the limits of g we found $0.659 \le R_{ii}(\text{\AA}) \le 0.933$. $R_{ii}(\text{\AA}) = 0.727(0.866)$ for crystal(ionic) radii calculated from Eq. (5) is in this range. Thus, using $p_c(p_I)$ we found $Z_{eff} = 26.5(26.05)$. In related literature we find Z_{eff} from 18 to 50 approximately, obtained by different techniques [56].

The radial effective charge (REC) model uses the Pauling scale of electronegativity in a different way in order to describe magnetic and spectroscopic properties of lanthanide ions coordinated by halides [57,58]. The effective charges obtained by the REC model are comparable to our predictions.

By the side of dosimetry, different experimental procedures lead to different Z_{eff} in the same region of ionizing energy for some compounds. The available experimental ranges and uncertainties of Z_{eff} are listed in Table 2. Our predictions for all diatomic systems are in good agreement, the relative errors $\leq 20\%$. It can be noted that Eq. (4) predicts quite similar Z_{eff} for compounds with cations inside the same family of the periodic table, each one with its own R_{ij} . For the two polyatomic systems, CaSO₄ and Li₂B₄O₇, our predictions show relative errors around 41% (28%) by using the crystal (ionic) radii, respectively, for both crystals. The S–O and B–O bonds have 78% and 57% of covalent characters, respectively. This explains such errors, since Eq. (4) applies to ionic systems.

4. Conclusions

In summary, we are announcing an analytical expression to predict the effective atomic number (Z_{eff}) of any ionic compound. For this, it is being introduced a way of calculating the crystal packing factor (p) for any compound, which is compared to the fractional electron content, and an *effective distance* (R_{ij}) between the negative and positive centre of charge. In photonics, the increasing of the linear and nonlinear refractive indexes with the Bi₂O₃ concentration in the (0.7 – x)NaPO₃–0.3WO₃–xBi₂O₃ glassy system has been satisfactorily explained. In the case of the Eu₂O₃, we have found Z_{eff} in the range of available experimental data. In dosimetry, for diatomic systems the predictions of Z_{eff} are less than or equal to 20%, in good comparison to the available experimental data. For the two available polyatomic crystals, the greater relative errors are associated to the covalent character of the S–O (78%) and B–O (57%) bonds.

Acknowledgements

The authors strongly acknowledge the financial support of the Inct-INAMI, CNPq, CAPES, and FAPITEC Brazilian agencies.

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