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Effective nuclear charge of an ion

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An analysis of the effective nuclear charge of ions based on linear relationships of the reciprocal of an ionic radius or the square root of ionisation energy and the nuclear charge of the ion has been carried out. It has been demonstrated that the effective nuclear charge of an ion is significantly different from its formal charge. The obtained character of the relationship indicates that the postulated parameter can be employed to determine differences in properties of ions. It has also been shown that the differences occurring in the calculated effective nuclear charges of the ion permit one to differentiate its states. Namely, values based on ionisation enthalpy characterise ions of a given coordination number in a crystal lattice.

Key words: *effective nuclear charge*; *formal charge; ions*

1. Introduction

A parameter which characterises any atom or ion is the so-called effective nuclear charge, lower than the actual nuclear charge. It results from the screening of the nuclear charge of the atom by electrons of an atom other than the considered one. The effect of the screening of the nuclear charge by electrons was for the first time taken into account in the Moseley law [1]. The effective charge has been widely applied in quantum mechanical atomic orbital calculations, which were first vperformed by Slater [2]. The rules put forward by Slater [2], Clementi and Raymondi [3], Burns [4] and others defined the above parameter with increasing precision, allowing an increasing precision of quantum mechanical calculations. Pauling [5] employed the effective nuclear charge for the calculation of ionic radii as early as in 1927, and Allred and Rochow [6] used it for determining the electronegativity of elements. In the eighties, rapid advances in the computational modelling of crystals created a possibility for determining parameters characterising single atoms or ions in a structure, as well as interaction energy and the like [7–9]. Despite the ever-growing computational abilities

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that we have now, our knowledge about the structure of solids is still unsatisfactory and does not allow quantum mechanics to be applied in a straightforward manner for the determination of properties of ions. The best results have been obtained with the density functional theory (DFT) which has become the theoretical method of choice in dealing with solid-state problems. However, even DFT requires a considerable amount of computing time, though much less than the Hartree–Fock methods. Thus there is a constant search for relatively simple parameters which would allow the properties of ions to be differentiated, and hence the properties of compounds to be determined.

Linear relationships between the reciprocal of the ionic radius or the square root of ionisation energy of ions and the atomic number, obtained in the previous work [10] for a relatively large number of ions of the same electronic configuration, exhibit a character analogous to the Slater equation [2]. They indicate that the difference between the nuclear charge of the ion and the parameter S in the equation can be treated as an experimental effective nuclear charge of the ion.

Because of a continuous transition from covalent bonding to an ionic one, a question has been posed in the present work, whether the proposed effective nuclear charge based on such values as ionic radii or their ionisation energies, determined according to the method proposed in [10], can really be related to a formal charge of an ion and whether it can constitute a basis for determining a scale which would differentiate ions with regard to their electrostatic properties (in crystals with dominating ionic bonding).

2. Effective nuclear charge of an isolated ion and the ion in a crystal lattice

The analysis [10] of the dependences of a parameter related to the ionisation energy of an ion, $\sqrt{E_{\mathrm{IE}}/R}$, (R being the Rydberg constant) and of the reciprocal of the ionic radius ($1/r$) on the nuclear charge of the ion, Z, demonstrated that for ions of the same electronic configuration the above relationship can be described by means of the following linear equations:

$$Z = a_{\mathrm{IE}}\sqrt{\frac{E_{\mathrm{IE}}}{R}} + S_{\mathrm{IE}} \tag{1}$$

$$Z = \frac{a_r}{\frac{r}{a_0}} + S_r \tag{2}$$

where: a_{IE} and a_r are constants, R is the Rydberg constant, r – ionic radius, a_0 is the Bohr radius ($a_0 = 5.29\cdot10^{-9}$ cm). It was also shown that the parameter S in the above equations can be treated as a screening constant and the difference between the nuclear charge and the screening constant ($Z - S$) = Z_{eff}, as the effective nuclear charge. Thus there exists a formal similarity between the Slater equation [2] and the 'experimental' relationships described by Eqs. (1) and (2) [10]. Despite the entire complexity of electron structures of atoms, a simple model can be used to describe a number of ions of a small charge. In the model, the outermost electron at a distance r equal to the 'ionic radius' is taken into account. An isolated ion interacts with the atom core (nucleus and the remaining electrons) with an energy equal to the ionisation energy and an ion in a crystal lattice or in a coordination compound with the energy of bonding of the outermost electron. It should be emphasized that the radii of ions forming the crystal lattice are treated formally in the above model. The radius defines a space occupied by the ion, the size of which results from the atom structure as well as from interactions of ions in the crystallographic structure of a given compound, resulting in optimum distances between the centres of mass of ions. The effective nuclear charge is therefore a parameter dependent on the space occupied by a given ion or accessible to it. As a result, the effective nuclear charge depends on the size of space attributed to a given ion. Furthermore, the concept of the effective nuclear charge assumes that the atom, despite the number of electrons being equivalent to its nuclear charge, is not 'electroneutral'. This is entirely consistent with the fact that atoms of elements, except for noble gas atoms, are in their unstable states and interact with each other forming determined bonds, i.e., they combine yielding molecules which occur in a gaseous or liquid state or form crystals.

A question thus arises, how does the magnitude of the effective nuclear charge of ions vary as a function of the nuclear charge of an isolated ion and of an ion placed in a structure of a given coordination number.

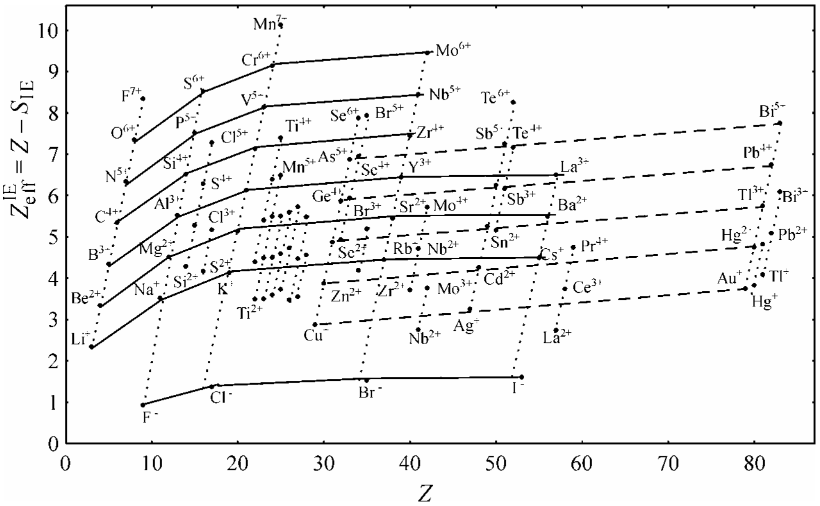

Fig. 1. Dependence of the effective nuclear charge of ions ($Z_{\text{eff}}^{\text{IE}}$), based on values of ionisation enthalpies of ions, on the nuclear charge of ion (atomic number) Z

Figure 1 presents a dependence of the effective nuclear charge of isolated ions, $Z_{\mathrm{eff}} = (Z - S_{\mathrm{IE}})$, on the nuclear charge, Z, calculated according to Eq. (1) based on the ionisation enthalpy of ions [11–14]. As can be seen, the dependences of the effective nuclear charge of ions of the same electron configuration on the nuclear charge are fitted very well by straight lines. It should be noted that if the ion radius is assumed to be inversely proportional to its effective charge, then the radii of valence shells of isolated ions of noble gas structure (filled (sp) shells) having the same formal charge are smaller than the radii of ions of filled (d) subshells (electron configurations of Ni, Pd and Pt atoms).

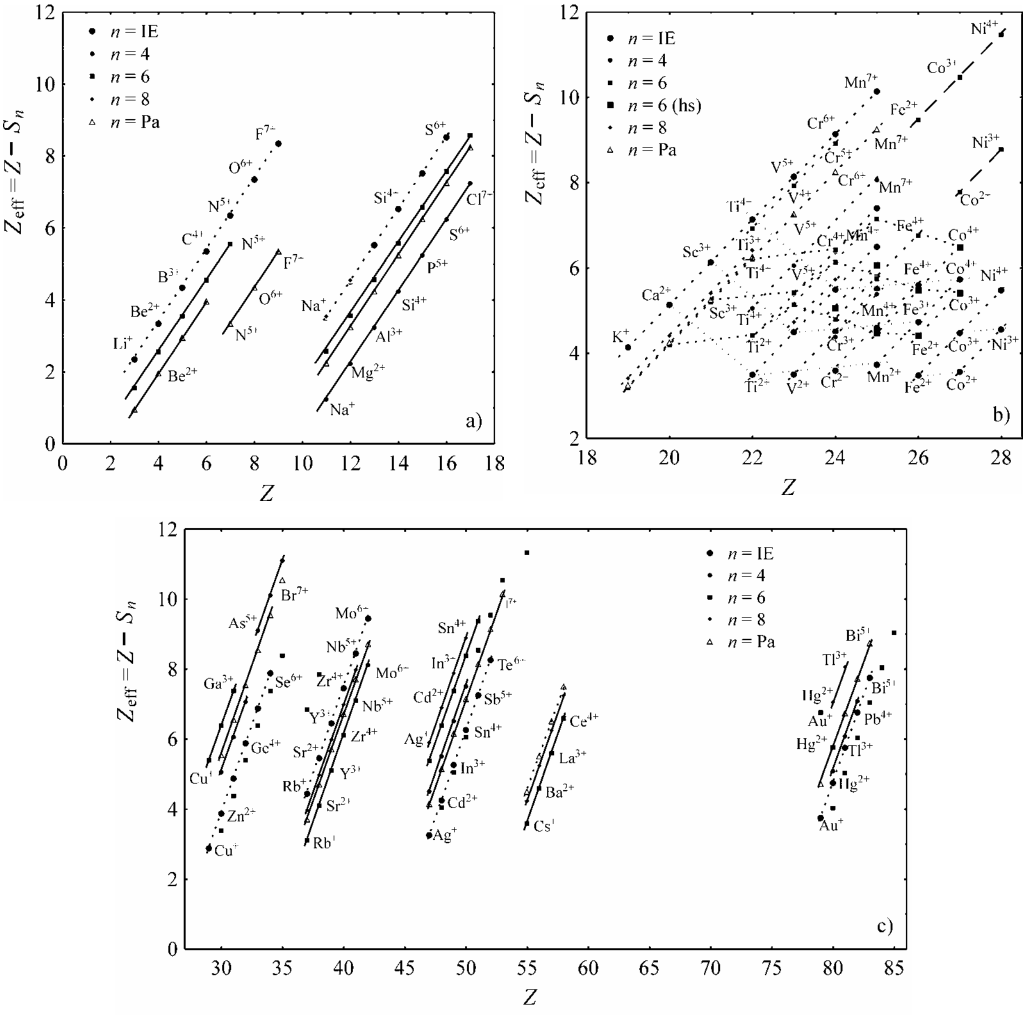

Fig. 2. Comparison of the effective nuclear charge of ion based on ionisation enthalpies of ions (subscript IE) and ionic radii for ions of the coordination number n = 4, 6 and 8, and Pauling's ionic radii (subscript Pa): a) for ions of electronic configuration of He and Ne atoms, b) for ions of 18-electron configuration (Ar) and 19–25-electron configurations (points (■) denote ions in high spin state), c) for ions of Ni, Kr, Pd, Xe, Pt atom configurations

Figure 2 shows a comparison of the effective nuclear charges of ions, calculated according to Eq. (2) based on ionisation enthalpies of ions and ionic radii [5, 14–16]. For comparison, Figs. 2a–c depict the effective nuclear charges of ions for ions of 2- and 10-electron configurations, for ions of 18–25-electron configurations and for ions of 28-, 36-, 46-, 54- and 78-electron configurations, respectively. As can be seen from the figures, the effective nuclear charges of isolated ions (of the same formal charge) are higher than the values based on ionic radii for a majority of ions of noble gas configurations. This indicates that the radii of isolated ions are smaller than the radii of the analogous ions in a crystal lattice. A reverse situation occurs in the case of ions of the electronic configuration of Ni, Pd and Pt atoms: for these configurations, the effective nuclear charges of isolated ions are smaller than for the analogous ions in crystal lattice. This in turn indicates that the ions in crystal lattice have smaller radii than the analogous isolated ions. These differences result from interactions between ions in crystal lattice: for the most part, the attraction between anions and cations and the repulsion between electron shells and ions of like charges. As a result, optimum distances between the centres of mass are established.

The effects mentioned can give rise to an increase in the radius of a sphere in which the ion is located, thus augmenting the ‘ionic radius’ in crystal lattice with respect to the radius of an isolated ion. The estimated radius of the space occupied by an ion in crystal lattice (at room temperature) includes also the effect of atom vibrations; it should therefore be bigger than the radius of the outermost electron shell of an ion. This is the case for ions of noble gas configurations, in which the valence shells are formed by (sp) orbitals. In the case of ions with the outermost shell formed by a filled (d) subshell, their polarisation interaction is significantly stronger than for ions of (sp) subshells, resulting in shortening of the distances between atoms. In such cases, both radii can be decreased. Otherwise, if a fixed anion radius is taken (which is assumed in a number of methods for radii determination), a decrease in the cation radius is found. A similar situation occurs in the case of radii of anions discussed in the previous work [10] which should be considerably larger, if they behaved as the cations of the same configuration. The aforementioned facts confirm the existence of a complex interactions of the ionic-covalent type.

The effective nuclear charge depends quite substantially on the coordination number, the highest values being attained by ions of coordination number 6 and considerably lower effective nuclear charge being exhibited by ions of coordination number 4. This is in agreement with the findings of Pearson [17] and Philips [18] that compounds of coordination number 6 are highly ionic, whereas those of the coordination number 4 are more covalent. It is worth noting that the values of the effective nuclear charge of ion based on Pauling’s radii are most often close to the effective charge for ions of one of the coordination numbers.

The effective nuclear charges presented in Fig. 2b for ions of 18-electron (argon atom) configuration to 25-electron configurations allow the effective nuclear charges for ions of filled (sp) shells to be compared with ions of unfilled (d) subshells. As can be noticed, the points for the effective nuclear charges of ions of the same configuration (more than 18 electrons), lie on straight lines, practically parallel to the lines set for the 18-electron configuration. This applies to the lines calculated both by using the ionic radii and ionisation enthalpies. It should be emphasised that the values of Z_{eff} based on ionic radii are lower than the values of Z_{eff} based on ionisation enthalpy as in the case of ions of 18-electron configuration. Thus the values of Z_{eff} based on ionic radii are higher than those based on ionisation enthalpy for the configuration of more than 18 electrons (for ions of the same formal charge). These facts indicate that, similarly to the case of ions of filled (d) subshells, the ions of unfilled (d) subshells produce the effect of polarisation and their radii are smaller than those of isolated ions. It is worth noting that the effective nuclear charges of Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+} and Co^{4+} ions in their high spin states are quite well fitted by curves for ions of the same (formal) charge, whereas the values of Z_{eff} for the above ions in their low spin states are significantly higher (open circles in Fig. 2b) – even higher than the values for the Cr^{6+}, Mn^{7+} ions. These values can hardly be accepted as correct.

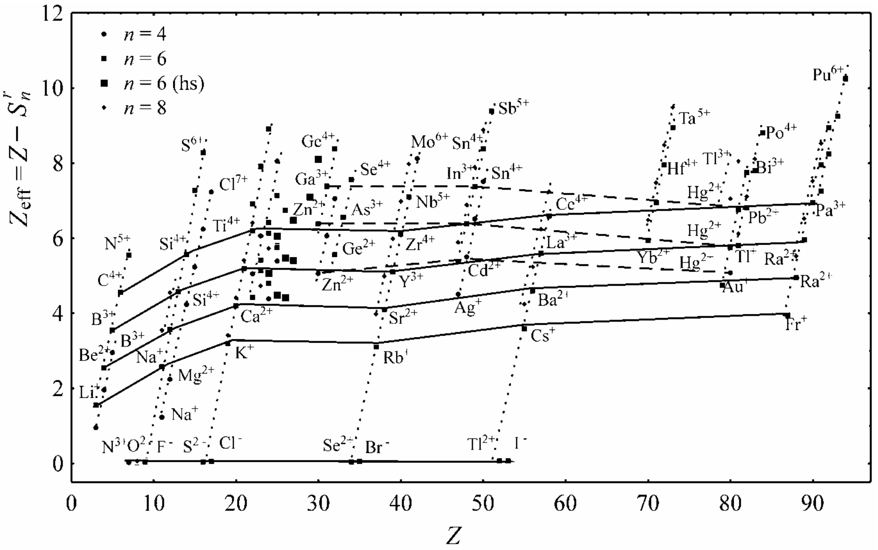

Fig. 3. Dependence of the effective nuclear charge of ions Z_{eff}^{n} of coordination number $n = 4, 6, 8$ on the nuclear charge of ion Z (points (■) denote ions in their high spin states)

Figure 3 summarises the effective nuclear charges based on their ionic radii, for ions of respective electron configurations and various coordination numbers. As can be seen, the character of the curves for ions of the same formal charge is similar as in the case of an analogous relationship of the effective nuclear charges of isolated ions calculated from the ionisation enthalpies (Fig. 1).

In Figures 1 and 3, the values of the effective nuclear charges of anions are also included. Since the values of $\sqrt{E_{\mathrm{IE}}/R}$ or $1/r$ for anions deviate from the straight lines

Table. Values of effective charges of isolated ions $Z_{\text{eff}}^{\text{IE}}$ calculated on the basis of ionisation enthalpy (Eq. (1)) as well as ions of coordination number $n = 4, 6, 8$ (superscript) calculated on the basis of Shannon's and Pauling's radii (superscript Pa); (hs) denotes ions in their high spin states

Nuclear charge Z	Ion	Formal charge Q	Effective nuclear charge of ion					Nuclear charge Z	Ion	Formal charge Q	Effective nuclear charge of ion				
			$Z_{\text{eff}}^{\text{IE}}$	$Z_{\text{eff}}^{\text{Pa}}$	$Z_{\text{eff}}^{(4)}$	$Z_{\text{eff}}^{(6)}$	$Z_{\text{eff}}^{(8)}$				$Z_{\text{eff}}^{\text{IE}}$	$Z_{\text{eff}}^{\text{Pa}}$	$Z_{\text{eff}}^{(4)}$	$Z_{\text{eff}}^{(6)}$	$Z_{\text{eff}}^{(8)}$
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
3	Li	1+	2.348	0.967	0.957	1.555		22	Ti	2+	3.497			4.419	
4	Be	2+	3.348	1.967	1.957	2.555		23	V	5+	8.139	7.261	6.059		
5	B	3+	4.348	2.967	2.957	3.555		23	V	4+	5.401			7.917	4.733
6	C	4+	5.348	3.967		4.555		23	V	3+	4.497			5.419	
7	N	–3		0.024	0.023			23	V	2+	3.508			5.141	
7	N	5+	6.348			5.555		24	Cr	6+	9.139	8.261			
7	N	5+		3.354				24	Cr	5+	6.401		4.389	8.917	5.733
8	O	–2		0.029	0.025	0.029	0.069	24	Cr	4+	5.497			6.419	
8	O	6+	7.348					24	Cr	3+	4.508			6.141	
8	O	6+		4.354				24	Cr	2+	3.599			4.800	
9	F	–1	0.934	0.030	0.026	0.048		24	Cr	2+				(hs) 5.065	
9	F	7+	8.348					25	Mn	7+	10.139	9.261	8.059		
9	F	7+		5.354				25	Mn	6+	7.401		5.389		
11	Na	1+	3.521	2.252	1.237	2.574	3.552	25	Mn	5+	6.497				
12	Mg	2+	4.521	3.252	2.237	3.574	4.552	25	Mn	4+	5.508			7.141	
13	Al	3+	5.521	4.252		4.574		25	Mn	3+	4.599			5.800	
14	Si	4+	6.521	5.252	4.237	5.574		25	Mn	3+				(hs) 6.065	
14	Si	2+	4.286					25	Mn	2+	3.735			5.750	
15	P	5+	7.521	6.252	5.237			25	Mn	2+				(hs) 4.479	
15	P	3+	5.286			7.286		26	Fe	4+	5.599				
16	S	–2		0.044		0.044		26	Fe	3+	4.735			6.750	

Table cont.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
16	S	6+	8.521	7.252	6.237			26	Fe	3+				(hs) 5.479	
16	S	4+	6.286			8.286		26	Fe	2+	3.482			9.475	
16	S	2+	4.173					26	Fe	2+				(hs) 4.412	
17	Cl	–1	1.373	0.045		0.054		27	Co	4+	5.735				
17	Cl	7+		8.252	7.237			27	Co	4+				(hs) 6.479	
17	Cl	5+	7.286					27	Co	3+	4.482			10.475	
17	Cl	3+	5.173					27	Co	3+				(hs) 5.412	
19	K	1+	4.139	3.261		3.200	3.414	27	Co	2+	3.564			7.778	
20	Ca	2+	5.139	4.261		4.200	4.414	28	Ni	4+	5.482			11.475	
21	Sc	3+	6.139	5.261		5.200	5.414	28	Ni	3+	4.564			8.778	
22	Ti	4+	7.139	6.261	5.059	6.200	6.414	29	Co	2+				(hs) 7.103	
22	Ti	3+	4.401			6.917		29	Cu	1+	2.879				
30	Ni	3+				(hs) 8.103		52	Te	6+	8.260	9.155			
30	Zn	2+	3.879	5.554	5.061	6.385		52	Te	4+	7.169				
31	Ga	3+	4.879	6.554	6.061	7.385		53	I	–1	1.610	0.066		0.061	
32	Ge	4+	5.879	7.554	7.061	8.385		53	I	7+		10.155			
32	Ge	2+	4.943			5.563		55	Cs	1+	4.504	4.513		3.598	4.244
33	As	5+				12.406		56	Ba	2+	5.504	5.513		4.598	5.244
33	As	5+	6.879	8.554				57	La	3+	6.504	6.513		5.598	6.244
33	As	3+	5.943			6.563		57	La	2+	2.746				
34	Se	–2		0.051		0.051		58	Ce	4+		7.513			7.244
34	Se	6+				13.406		58	Ce	3+	3.746				
34	Se	6+	7.879	9.554				59	Pr	4+	4.746				
34	Se	4+	6.943			7.563		70	Yb	2+				5.949	6.484
34	Se	2+	4.196					71	Lu	3+				6.949	7.484
35	Br	–1	1.535	0.052		0.055		72	Hf	4+				7.949	8.484
35	Br	7+				14.406		73	Ta	5+				8.949	9.484

Table cont.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
35	Br	7+		10.554				79	Au	1+	3.756	4.740			
35	Br	5+	7.943					80	Hg	2+	4.756		5.081	5.757	7.059
35	Br	3+	5.196					80	Hg	1+	3.832				
37	Rb	1+	4.452	3.719		3.104	3.984	81	Tl	3+	5.756	6.740	6.081	6.757	8.059
38	Sr	2+	5.452	4.719		4.104	4.984	81	Tl	2+	4.832				
39	Y	3+	6.452	5.719		5.104	5.984	81	Tl	1+	4.097			5.806	6.115
40	Zr	4+	7.452	6.719	6.122	6.104	6.984	82	Pb	4+	6.756	7.740	7.081	7.757	
40	Zr	2+	3.724					82	Pb	2+	5.097			6.806	7.115
41	Nb	5+	8.452	7.719	7.122	7.104	7.984	83	Bi	5+	7.756	8.740			
41	Nb	3+	4.724					83	Bi	3+	6.097			7.806	8.115
41	Nb	2+	2.765					84	Po	4+				8.806	
42	Mo	6+	9.452	8.719	8.122			87	Fr	1+				3.955	
42	Mo	4+	5.724					88	Ra	2+				4.955	5.527
42	Mo	3+	3.765					89	Ac	3+				5.955	6.527
47	Ag	1+	3.260	4.155	4.511	5.380	5.894	90	Th	4+				6.955	7.527
48	Cd	2+	4.260	5.155	5.511	6.380	6.894	91	Pa	5+				7.955	8.527
49	In	3+	5.260	6.155	6.511	7.380	7.894	91	Pa	3+				7.253	
50	Sn	4+	6.260	7.155	7.511	8.380	8.894	92	U	6+				8.955	
50	Sn	2+	5.169					92	U	4+				8.253	
51	Sb	5+	7.260	8.155		9.380		93	Np	5+				9.253	
51	Sb	3+	6.169					94	Pu	6+				10.253	
52	Te	–2		0.064		0.064									

determined for cations of the same electronic configuration (see the detailed presentation in the preceding work [10]), hypothetical nuclear charges are assigned to anions. These charges are determined from a linear fit to the dependences of the charges on $\sqrt{E_{\mathrm{IE}}/R}$ or $1/r$ for cations of the same electronic configuration. Thus applying the screening constant to respective configurations, the effective charges of anions were calculated. In the table, the values of the effective charges of cations and anions are summarised.

It follows from the above calculations that, despite the experimental error, the values of the effective nuclear charges of ions based on ionisation enthalpies or ionic radii differentiate the ions with respect to electrostatic properties and, by means of them, different states of the ions can be described. The effective nuclear charges of isolated ions and of ions in crystal lattice are so different that they cannot be interchanged.

3. Conclusions

The analysis carried out in this paper demonstrates that the postulated parameter, effective nuclear charge of an ion based on ionisation enthalpies, characterises the isolated ion, whereas the effective nuclear charge based on ionic radii is the parameter characterising an ion of a given coordination number in a crystal lattice. It should be taken into account, however, that the real ion radius in a given compound is different from the tabulated value. This is why a more reliable value for determining the effective nuclear charge of ion would be the energy of the interaction of the electron with its core in crystal lattice, whose value is different from the ionisation enthalpy of the ion. The data of this type is relatively scarce.

The values of the effective nuclear charge as well as the character of the dependence of the effective charge on the formal nuclear charge indicates that it is a value that can be employed to characterise the ions with respect to their interactions.

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