

Valence electron configurations of tellurium in its compounds, found from the x-ray-line chemical shift and the isomer shift

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The crystal-diffraction method is used to measure for twelve Te compounds the *K*-series x-ray chemical shifts (XCS) relative to the Te element. Atomic Dirac-Fock-Slater self-consistent-field (SCF) calculations are used to determine for different populations of the valence *5s*, *5p*, and *5d* levels the theoretical values of the electron density at the nucleus and the XCS, both in the frozen-orbital approximation and in the adiabatic-relaxation approximation. Using the obtained theoretical quantities, the valence configurations of Te in the investigated compounds are obtained in the effective-free-ion-field approximation from an analysis of the experimental XCS and of the published Mössbauer isomer shifts. It is shown that as the valence and the coordination number are increased, the *s*-character of the chemical bond increases in oxygen compounds and decreases in compounds of Te with Cl. A noticeable role in the chemical bond of oxygen compounds of tellurium is played by its *5d* orbitals. The role of the *5s*-orbitals in the bond increases in iso-electronic compounds in the Xe, I, Te series. An attempt is made to estimate the *sp* hybridization in metallic tellurium under the assumption that the bond in $(\text{NH}_4)_2\text{TeCl}_6$ is of pure *p*-character.

Despite the considerable recent advances in the quantum-mechanical description of the electronic structure of the condensed state, the description with the aid of the effective free ion has not lost its significance. The reason is not only the relative simplicity of this approach but also that not all the characteristics of the bound atom can be calculated with sufficient accuracy in polyatomic calculations, at any rate in those published to date. For example, an accuracy sufficient to describe the experimental x-ray line shifts has been achieved so far only in calculations of the energies of the internal levels of the atom. It seems unjustified, however, to use in the interpretation of the experimental results simple chemical-bond models that postulate, for example, a bond that is intermediate between purely ionic and purely covalent, as well as the definite valence-electron hybridization required by the localized-pairs scheme.

In this paper we use the effective-free-ion approximation for a joint interpretation of experimental results on the x-ray chemical shift (XCS) and the isomer shift in nuclear gamma resonance (NGR) in a number of Te compounds. It is assumed in the calculations that when the chemical bonds are formed a change takes place in the populations Q_{nl} of all the Te valence levels (*5s*, *5p*, and *5d*), i.e., the populations are not subjected beforehand to any constraints that follow,

e.g., from hybridization assumptions. The lower-level populations obtained in such a description admit of direct comparison with the results of the Mulliken analysis of populations in polyatomic calculations.

We obtain here the populations Q_{nl} of the valence levels *5s*, *5p*, and *5d*, and reveal the tendencies of their variation for isoelectronic compounds in the Te-I-Xe sequence, as well as the tendencies in the changes of the populations of the *5s* and *5p* levels of Te as functions of the number and nature of the ligands. The XCS measurement procedure used in the present study is close to that described in Refs. 1-3. The investigated Te compounds were synthesized by previously described methods.⁴⁻⁶ The composition of the compounds was monitored against the melting temperatures and by chemical and x-ray structure analysis. Measures were taken to prevent the air's moisture content from acting on easily hydrolyzed substances.

Table I lists the values of the XCS measured by us and the isomer shifts taken from the literature⁷⁻¹⁸ (with the exception of the shift for Mg_3TeO_6 , which was measured by us). All the shifts are referred to the elemental Te, and the shift errors are mean-squared. In the original papers the isomer shifts are cited relative to various references. Our analysis of the entire aggregate of experimental data on the isomer

TABLE I. Experimental chemical shifts of tellurium $K_{\alpha 1}$ and $K_{\beta 1}$ lines in its compounds, and Mössbauer isomer shifts (relative to elemental Te).

Compound	$\Delta E_{K\alpha 1}$, meV	$\Delta E_{K\beta 1}$, meV	ΔE_{γ} , mm/s *	compound	$\Delta E_{K\alpha 1}$, meV	$\Delta E_{K\beta 1}$, meV	ΔE_{γ} , mm/s *
Te	0	0	0	TeCl_4	144(3)	213(6)	+0.46(6)
H_6TeO_6	193(2)	388(5)	-1.85(3)	TeCl_2	79(2)	127(4)	-0.04(7)
Mg_3TeO_6	238(3)	373(6)	-1.84(3)	ZnTe	-61(3)	-83(3)	-0.66(3)
$\alpha\text{-TeO}_3$	286(3)	374(4)	-1.73(3)	Ph_2TeCl_2	58(4)	64(4)	-0.1(1)
Na_2TeO_3	156(2)	217(5)	-0.42(4)	$(p\text{-Tolyl})_3\text{TeCl}$	43(4)	56(4)	-
TeO_2	186(2)	281(5)	+0.09(3)	$(\alpha\text{-Naphthyl})_2\text{Te}$	-19(3)	-22(3)	-
$(\text{NH}_4)_2\text{TeCl}_6$	141(2)	222(6)	+1.05(5)				

* Average data of Refs. 7-18.

shift in ^{125}Te has enabled us to recalculate all the shifts relative to elemental Te. We used the shifts of various reference sources that are in best agreement relative to $^{125}\text{I}(\text{Cu})$ (in mm/s):

$^{125}\text{Te}(\text{Pt})$	0.25 ± 0.02
$Z_n^{125}\text{Te}$	-0.06 ± 0.03
$^{125}\text{Te}_{\text{met}}$	0.63 ± 0.02

We did not use in the averaging the results of Ref. 19, despite the low statistical errors given by their authors, since in our opinion the isomer shifts cited there are shifted by $(+0.22 \pm 0.06)$ mm/s relative to the averaged results of other papers. The presence of a systematic error in Ref. 19 was noted also by Hartmann.²⁰

For each investigated compound we found the effective-Te-ion electron configuration for which the change of the energy of the $K_{\alpha 1}$ and $K_{\beta 1}$ lines and of the electron density in the nucleus, relative to the reference ion (with known electron configuration) agree with the experimental shifts. Just as in Ref. 3, we used here as a model a valence state of an atom with random directions of the valence-electron spins, i.e., absence of spin-orbit coupling for the valence electrons.

The theoretical values of the shifts can be obtained for an atom with definite electron configuration as a result of a self-consistent atomic calculation. This raises the question of taking into account the electron relaxation when vacancies appear in the electron shell in the initial and final states of the atom for an x-ray transition. In our opinion this problem is far from solved, although it is definitely postulated in a number of papers²¹⁻²⁴ that allowance for total relaxation improves the agreement of the self-consistent calculation results with experiment. In the present paper we calculate the XCS by two methods—without allowance for calculation and with adiabatic relaxation. In the first method, following a self-consistent Dirac-Slater calculation of an ion with a given configuration (the calculation program is described in Ref. 2), the x-ray transition energies E were calculated as the differences of the corresponding single-electron orbital energies ε_{nlj} , i.e., by using the Koopmans theorem. The XCS was calculated as the difference between the energies of the corresponding lines. For the $K_{\alpha 1}$ line, for example:

$$\Delta E_{K_{\alpha 1}} = E_{K_{\alpha 1}}^{\text{ion}} - E_{K_{\alpha 1}}^{\text{ref}} \\ = [\varepsilon(1s_{1/2}) - \varepsilon(2p_{3/2})]^{\text{ion}} - [\varepsilon(1s_{1/2}) - \varepsilon(2p_{3/2})]^{\text{ref}}. \quad (1)$$

This calculation method, used in Refs. 2 and 3, is not quite correct for a self-consistent calculation with statistical allowance for electron exchange,²⁶ since the Koopmans theorem is not exactly satisfied in this case. The error in the line energy in Eq. (1) (in the parentheses) is offset here mainly by subtraction of a second difference of like type for the other valence configuration.

In the second method, a self-consistent calculation was carried out for ions with vacancies on the corresponding levels. The x-ray line energies were taken to be the difference between the total energies with vacancies in the upper and lower levels of the transition. For the $K_{\alpha 1}$ line, for example, $\Delta E_{K_{\alpha 1}} = \{\mathcal{E}[1s_{1/2}] - \mathcal{E}[2p_{3/2}]\}^{\text{ion}} - \{\mathcal{E}[1s_{1/2}] - \mathcal{E}[2p_{3/2}]\}^{\text{ref}}$, (2) where $\mathcal{E}[nlj]$ is the total energy of an atom or ion with vacancy in the nlj group. This calculation method calls for a

large volume of calculations and the errors in the resultant shifts are significantly larger than in the calculation by Eq. (1). In the present paper, the calculation errors were reduced to 2 meV and to less than 1 meV for $\mathcal{E}[nlj]$ and ε_{nlj} , respectively.

We determined the electron density at the nucleus for the same configurations for which the XCS were calculated. Using next the relation²⁷

$$\Delta E_{\gamma} = \frac{2}{3} \pi Z e^2 R^2 \rho \Delta |\psi(0)|^2 \quad (3)$$

we obtained the isomer shifts for different configurations of the effective Te ion relative to the ion with the reference configuration. In Eq. (3), Ze is the nuclear charge, $R = 1.2A^{1/3}$ is the radius of the nucleus, A is the mass number, $\rho = \Delta \langle R^2 \rangle / \langle R^2 \rangle$ is the relative change of the mean squared charge radius of the nucleus on going to the isomer state, and $\Delta |\psi(0)|^2$ is the change, relative to the reference, of the relativistic electron density in the nucleus for a given electron-shell configuration.

The NGR results were interpreted in Ref. 2 by assuming the configurations $5s^2 5p^6$ and $5s^2 5p^5$ for the ions I^- and I^0 , respectively. Thus, Eq. (3) and the experimental value of the isomer shift of elemental I_2 relative to I^- yielded an isomer-shift calibration that led to a value $\rho = 8.8 \cdot 10^{-4}$ for ^{129}I . This value, in conjunction with the ratio obtained in Ref. 11 for the values of ρ for the nuclei ^{125}Te and ^{129}I (assuming identical valence configurations of the isoelectronic compounds of Te and I), yielded the value $\rho = 2.7 \cdot 10^{-4}$ used by us in the present paper for ^{125}Te . The use of a somewhat different ratio of the values of ρ for ^{125}Te and ^{129}I , taken from Refs. 28 and 29, gives $\rho = 2.5 \cdot 10^{-4}$ for ^{125}Te . According to estimates of Ref. 11, the method of isoelectronic pairs can introduce an error of the order of 20% in ρ . It should be noted that our value of ρ is noticeably higher than previously proposed.^{20,32,20,27} The first two cited references (as well as most papers devoted to the determination of the values of ρ for ^{125}Te and not cited by us) make use of simple chemical-bond models, and this can lead to incorrect results. The result of Ref. 32 was severely criticized in Ref. 33.

The electron densities at the nucleus were obtained in Ref. 20 from a nonrelativistic cluster calculation by the $X\alpha$ method, with relativistic corrections introduced in the final result. The electron densities obtained in this manner and the experimental isotope shifts yielded $\rho = (1.75 \pm 0.11) \cdot 10^{-4}$ for the ^{125}Te nucleus. This differs noticeably from our present value. A serious problem in the $X\alpha$ method, however, is the choice of the minimal cluster for the calculation, and it is necessary to check the stability of the result to an increase of the cluster size. We shall show below how our present results are affected by variation of ρ .

Whereas in Refs. 2 and 3 the choice of the reference compound was no problem (it was natural to assume the configuration $5s^2 5p^5$ for I in a molecular crystal and $5s^2 5p^6$ for Xe in its clathrate), there was no such reliable reference in the case of Te compounds. The reference chosen was elemental Te, for which a configuration $\text{Te}^0 5s^2 5p^4$, was chosen, although it possible that the fact that the $5s$ and $5p$ levels are closer here than in Xe and I leads in this case to some sp hybridization. An estimate of this hybridization will be giv-

en below. The populations Q_{nl} of the valence levels of the effective ions in the compounds were calculated in the same manner as in Ref. 3. To this end, the numerical dependences of the shifts (of the K_{α_1} and K_{β_1} x-ray lines and of the isomer shift) on the populations, obtained from self-consistent calculations, was approximated by polynomials. The analytic relations obtained in this manner and the experimental values of the shifts were used to calculate the populations of the valence levels in the investigated compounds. The population errors were determined by the measurement errors of the shifts and by the errors of the approximating functions. The effective charges of the Te ion were calculated from the values of the populations, and the correlations between the population errors were taken into account in the calculation of the effective-charge errors.

The populations obtained in the frozen-orbital approximation (1) and in the adiabatic approximation (2), as well as the effective charges of the Te ions and ligands, are listed in Table II. The ligand charges were calculated from the molecule-electroneutrality condition. To verify this population-calculation method, an inverse calculation was carried out of the reference configuration by using the analytic dependences of the shifts on the populations.

Note that unphysical, negative Q_{5d} were obtained for certain compounds. They differ from zero, however, by not more than double the error. Comparison of the populations obtained for the same compounds in XCS calculations in accordance with (1) or (2) shows that the main difference is that allowance for the adiabatic relaxation (2) increases the values of Q_{5p} and accordingly lowers the charges of Te, the maximum difference amounting to $0.5e$ for hexavalent-Te compounds. The common trends of population variation on going from compound to compound remain the same, however. The use of (1) for the calculation could not yield a configuration corresponding to the experimental shifts at a negative effective ion charge in the case of ZnTe, since the negative XCS with maximum absolute values that could be obtained by this calculation method amounted to only one-half of the experimental values obtained for ZnTe.

At the same time, the use of (2) to calculate the XCS permits a choice of configuration also in this case. Exactly the same situation is encountered when the configuration of the iodine ion in KI is determined by the described method.² Here, too, the use of (2) to calculate the XCS leads to a configuration very close to $5s^25p^6$ for the XCS experimental values (-43 ± 4) meV and (-70 ± 10) meV (relative to

TABLE II. Configuration of effective Te ion in its compound. Calculations 1 and 2 are in accordance with Eqs. (1) and (2).

Compound	Calculation	Level populations*			Effective charges**	
		Q_{5s}	Q_{5p}	Q_{5d}	Te	ligand (O,Cl)
H_6TeO_6	1	1.22(1)	2.00(2)	0.73(11)	2.05(13)	-1.34(2)
	2	1.27(1)	2.50(2)	0.80(9)	1.42(12)	-1.24(2)
Mg_3TeO_6	1	1.24(1)	2.05(2)	0.88(15)	1.83(16)	-1.30(3)
	2	1.29(1)	2.56(3)	0.93(12)	1.22(15)	-1.20(3)
$\alpha\text{-TeO}_3$	1	1.26(1)	2.02(2)	0.82(12)	1.89(13)	-0.62(5)
	2	1.31(1)	2.53(2)	0.88(10)	1.28(12)	-0.42(4)
Na_2TeO_3	1	1.67(1)	2.45(2)	0.39(17)	1.49(19)	-1.17(6)
	2	1.72(1)	2.84(3)	0.47(11)	0.97(15)	-0.99(5)
TeO_2	1	1.76(1)	2.03(2)	0.08(13)	2.14(15)	-1.06(7)
	2	1.82(1)	2.41(2)	0.28(9)	1.49(12)	-0.74(6)
$(NH_4)_2TeCl_6$	1	2.06(1)	2.05(3)	0.09(18)	1.80(21)	-0.63(3)
	2	2.12(1)	2.40(3)	0.27(13)	1.21(17)	-0.53(3)
$TeCl_4$	1	1.91(2)	2.24(3)	0.29(20)	1.56(22)	-0.39(6)
	2	1.97(2)	2.61(4)	0.40(15)	1.02(19)	-0.25(5)
$TeCl_2$	1	1.85(2)	2.90(3)	0	1.25(2)	-0.62(1)
	1	1.83(2)	2.88(3)	-0.28(15)	-	-
	2	1.88(2)	3.14(3)	0	0.99(2)	-0.50(1)
	2	1.87(2)	3.13(4)	-0.02(8)	-	-
Te	1	2.00(1)	4.00(4)	0.00(6)	0.00(2)	-
	2	2.00(1)	4.00(1)	0.00(2)	0.00(2)	-
ZnTe	2	1.88(1)	5.36(6)	0	-1.25(7)	-
	2	1.87(2)	5.30(9)	0.57(25)	-1.74(17)	-
Ph_2TeCl_2	1	1.85(3)	3.33(4)	0	0.83(3)	-
	2	1.88(3)	3.52(4)	0	0.61(2)	-
$(p\text{-Tolyl})_3TeCl$	1	2	3.27(4)	0	0.73(4)	-
	2	2	3.46(3)	0	0.54(3)	-
$(\alpha\text{-Naphthyl})_2Te$	1	2	4.48(6)	0	-0.48(6)	-
	1	2	3.70(16)	1.22(71)	-0.92(44)	-
	2	2	4.28(3)	0	-0.28(3)	-
	2	2	4.04(8)	-0.36(17)	-	-

* The populations cited without errors were postulated.

** The ligand charges were calculated by postulating a + 1 charge for the H, Na, and NH_4 ions and a + 2 charge for the Mg ion, and also by using the molecule electroneutrality condition.

elemental I_2 for the $K_{\alpha 1}$ and $K_{\beta 1}$ lines, respectively). This increase of the absolute value of the XCS is understandable, for in the calculation of (2) using the total ion energy self consistency of the ion with the vacancy is carried out in the inner shell, i.e., with a charge larger by unity than in the Koopmans calculation of (1).

To obtain the valence configurations of compounds for which there are no published isomer shifts, it was necessary to make some additional assumptions concerning the populations of the $5s$ and/or $5d$ levels. Note the similarity of the CXS dependences on Q_{5s} and Q_{5p} . Therefore in the case of relatively large experimental errors the problem of finding Q_{5s} and Q_{5p} separately from the values of the XCS for the $K_{\alpha 1}$ and $K_{\beta 1}$ line, without resorting to NGR data, is mathematically untenable. It was just in these cases that we additionally postulated the values $Q_{5s} = 2$. However, the summary $5s$ and $5p$ populations, which determine the effective Te charge, are calculated with sufficient accuracy.

We consider now the laws governing the population variation in compounds of Te with oxygen. For H_6TeO_6 , Mg_3TeO_6 and TeO_3 , both the experimental shifts and the valence structures are very close. This is natural, in view of the similarity of the nearest environment of the Te atom in the lattices of these compounds.⁶ For the pair Na_2TeO_3 and TeO_2 , the nearest surroundings of the Te atoms are substantially different, and the valence structures are likewise different. The part played in the bond by the $5s$ electrons of Te is appreciable in all the oxygen compounds, and increases with increase of the formal valence (and of the coordination). In compounds of Te with Cl, however, the role of the $5s$ electrons in the bond is small and, in contrast to oxygen compounds, decreases with increasing valence (and coordination) of the Te atom, from $TeCl_2$ to $TeCl_4$ and $(NH_4)_2TeCl_6$.

For the latter compound, Q_{5s} has an unphysical value somewhat larger than 2. We shall attempt below to explain this fact.

The described variation of Q_{5s} with change of the coordination of the Te atom can be explained qualitatively as follows: Whereas for $TeCl_2$ one can assume ordinary two-center and two-electron bonds with a certain degree of sp hybridization, for $[TeCl_6]^{2-}$, which is has the same electron valency as XeF_6 , the bands can be described as three-center and four-electron, with Te using each of the three $5p$ orbitals to bind two Cl ligands, and with an angle 180° between the bonds. The $5s^2$ pair turns out in this case to be stereochemically inactive. The case of $TeCl_4$ is intermediate. The participation of the $5d$ electrons in the bond is significant in the cases investigated by us only for oxygen compounds of Te that have maximum formal valency.

The electron populations obtained in the present study depend on the employed value of ρ . An increase of an assumed value of ρ alters the configurations listed in Table II more the larger the isomeric shift of the compound relative to the references, with Q_{5s} and Q_{5d} decreasing for positive isomeric shifts, and Q_{5p} decreasing. Thus, when the assumed value of ρ is increased by 20% the largest changes are observed for H_6TeO_6 ($\Delta Q_{5s} = +0.08$; $\Delta Q_{5p} = -0.08$;

$\Delta Q_{5d} = +0.05$) and $(NH_4)_2TeCl_6$ ($\Delta Q_{5s} = -0.04$; $\Delta Q_{5p} = +0.04$; $\Delta Q_{5d} = -0.04$), while the configuration of TeO_2 is practically unchanged. It can be seen from Table II that a reasonable increase of ρ is incapable of shifting into the physical region the value of Q_{5s} for $(NH_4)_2TeCl_6$. The published experimental values of the isomer shift for this compound are contradictory. It should be noted that the use of the customarily cited value from Gibb's paper¹⁹ makes Q_{5s} larger by 0.06 than in Table II. The value of Q_{5s} shifts to the physical region, however, if a small sp hybridization is assumed in the elemental Te that serves as the reference. For example, if the reference is chosen to be the configuration $5s^{1.90}5p^{4.10}$, all the values of Q_{5s} are lowered by 0.08–0.09, while all the Q_{5p} are increased by the same amount. Such an assumption concerning the reference configuration is reasonable: The difference $|\epsilon(5p) - \epsilon(5s)|$, decreases in the Xe-Sn sequence, and this should lead to greater participation of the $5s$ electrons in the bond.^{34,35} Calculations³⁶ of the band structure of elemental Te also favor the foregoing assumption concerning the configuration of the reference.

Comparison of the populations obtained for of the iso-electronic compounds Te, I, and Xe in the present paper and in Refs. 2 and 3 demonstrate clearly the tendency of the $5s$ electrons to assume a larger role in the bond (compared with the $5s$ electrons) on going from Xe to Te (in the sequences $H_6TeO_6-Na_3H_2IO_6-Na_4XeO_6$ and $Na_2TeO_3-KIO_3 - XeO_3NaOH$).

The charges of the ligands O and Cl in Te compounds are close to those obtained for them in I and Xe compounds, with the exception of TeO_3 . The reason for the low charge on the oxygen atom in this compound may be that all the O atoms are apparently act as bridges, i.e., they are connected to two Te atoms each. Just as in high-valency oxygen compounds of I and Xe, the $5d$ -population in oxygen compounds of hexavalent Te is relatively high, so that one can state definitely in this case that the $5d$ electrons of Te participate in the chemical bonds with the O atoms.

Sumbaev has already published in his review³⁷ the measured XCS on the $K_{\alpha 1}$ lines of TeO_2 and TeO_3 , while Makarov *et al.*³⁸ have used these results to obtain the effective charge of the Te ion in these compounds. The XCS in Ref. 37 are somewhat lower than in the present paper, since the data-reduction procedure used at that time underestimated (by $\sim 5\%$) the XCS values. The effective charges were calculated in Ref. 38 under the assumption that $Q_{5d} = 0$ and that the XCS on the $K_{\alpha 1}$ line has the same dependence on Q_{5s} as on Q_{5p} . The last assumption is quite close to reality. The effective charge calculated by us from the XCS of the $K_{\alpha 1}$ line under these assumptions yield values very close to those of Ref. 38 if the XCS are calculated from Eq. (2). On the other hand, the charges listed in Table II are noticeably lower, since allowance for the $5d$ populations lowers the effective charges.

Nuclear quadrupole resonance on ^{35}Cl in the compound $(NH_4)_2TeCl_6$ was used to determine the Cl charge and from it in turn the Te charge,³⁹ found to be close to that in Table II [calculated from Eq. (1)]. Cheyne¹⁷ deduced from an analysis of experimental data on NGR on ^{125}Te and

NQR on halogens³⁹ a pure *p*-bond for the compounds (NH₄)₂TeHal₆ (Hal = Cl, Br, I). A joint analysis of the chemical shifts of the levels and of the x-ray electronic spectra and the NGR isomer shifts of ¹²⁵Te in a sequence of Te compounds⁴⁰ yielded estimates of the relative contribution of the 5s electrons to the effective charge on Te. These estimates agree well with those obtained in the present paper for the same compounds, provided that the values of Q_{sd} are neglected in the calculation of the effective charge.

Hartmann *et al.*²⁰ used calculations by the $X\alpha$ scattered-wave method, for a number of Te compounds. It is impossible in principle to compare directly the *nl* populations of an effective ion with the fractions of the charge of *l*-valent electrons in a certain bounded sphere assigned to the atom in the $X\alpha$ method. This multicenter calculation of the valence structure of a bound atom is preferable to the one-center method, but is subject in practice to uncertainties connected, for example, with the choice of the sphere radius and of the cluster size. Nonetheless, the valence configuration obtained in the present paper for Te in its oxygen compounds are close enough to those obtained in Ref. 20, particularly when it comes to Q_{sd} . For (NH₄)₂TeCl₆ and ZnTe the difference is appreciable. Thus, for example, in ZnTe the charge on the Te atom was found in Ref. 20 to be positive (+ 1.42e), a doubtful result.

It must be noted that description of an atom in a molecular system by means of an effective ion whose properties are determined by one-center calculations becomes more correct the higher the effective charge of the ion, inasmuch as at high binding energy of the valence electrons the influence of the nearest-environment charges becomes relatively less significant.

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