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On the Residual *d*- and *f*-Contractions in s^2p^6-Closed Shell Ions over Rock-Salt-Type Compounds

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Residual size contractions, $\Delta(3d)$, $\Delta(4d)$, and $\Delta(4f + 5d)$, in the relevant series ions with the filled $2s^22p^6$-, $3s^23p^6$-, $3d^{10}4s^24p^6$-, $4d^{10}5s^25p^6$-, and $4f^{14}5d^{10}6s^26p^6$-electron shells have been demonstrated and evaluated over the rock-salt-series compounds. The obtained values range as follows: $\Delta(3d) = 1.44 \sim 1.59$ (Å/3*d* series), $\Delta(4d) = 1.30 \sim 1.45$ (Å/4*d* series), and $\Delta(4f + 5d) = 3.00 \sim 3.08$ (Å/4*f*-plus-5*d* series). Since similar residual size contractions, $\Delta(3d) = 1.49 \sim 1.70$ Å and $\Delta(4d) = 1.40 \sim 1.46$ Å, have been obtained for the inert-gas series crystals with *fcc* structure, alkali-metal series crystals with *bcc* structure, and IVb-element series crystals with diamond structure, these size contractions are attributed to the contractions in the cores of atoms and ions.

Introduction

A general decrease in ionic size with increase in atomic number for trivalent rare earth cations is well known as the lanthanide contraction. The cause of this contraction is believed to come from an aspherical, i.e., an incomplete, positive core shielding of the 4*f* electron shell against the increasing nuclear charge. The similar cause for size contraction via charge asphericity in *d* electron shell has been more rigorously interpreted by Hush and Pryce (*1*) for 3*d*-transition metal ions, and by Nakamura *et al.* (*2*) for 3*d*- and 4*d*-transition metal ions. The aim of this paper is to demonstrate the evidence of remanent *d*- and *f*-contractions in ions even after the outer sp^3-orbitals are filled up.

Figure 1 demonstrates the lanthanide contraction of Ln^{3+} ions, that is, the decrease in the average lattice parameters, defined by the cube root of the perovskite cell volume, of perovskite-type $Ln\mathrm{RhO}_3$ (*3*) and $Ln\mathrm{CrO}_3$ (*3*), plotted as a function of the number of 4*f* electrons in the Ln^{3+} ion.

Figure 2 shows the average lattice parameters of perovskite-type 3*d*-transition metal compounds $\mathrm{K}M\mathrm{F}_3$ (*3, 4, 15*) and $\mathrm{La}M\mathrm{O}_3$ (*3, 5–7*), plotted against the number of 3*d* electrons in M^{2+} and M^{3+} ions, respectively. Similarly, Fig. 3 shows the average lattice parameters of perovskite-type 4*d*-transition metal compounds $\mathrm{La}M^*\mathrm{O}_3$ (*3, 4, 8–10*) and $\mathrm{Sr}M^*\mathrm{O}_3$ (*3, 11–13*), plotted against the number of 4*d* electrons in M^{*3+} and M^{*4+} ions, respectively. The dashed lines in Figs. 2 and 3, respectively, denote the 3*d*- and 4*d*- contractions; that is, the sizes of 3*d*- and 4*d*-cations do not recover their initial values after filling up their *d*- electron shells.

Moreover, it is generally expected that such 3*d*-, 4*d*-, and 4*f*-contractions in the inner electronic shells remain even in the atoms or ions with the filled outer sp^3-electron shells.

Evidence of Remanent Contraction

The evidence for the mentioned remanent 3*d*-, 4*d*-, 4*f*-, and 5*d*-contractions in the closed electron shells is indicated in Figs. 4

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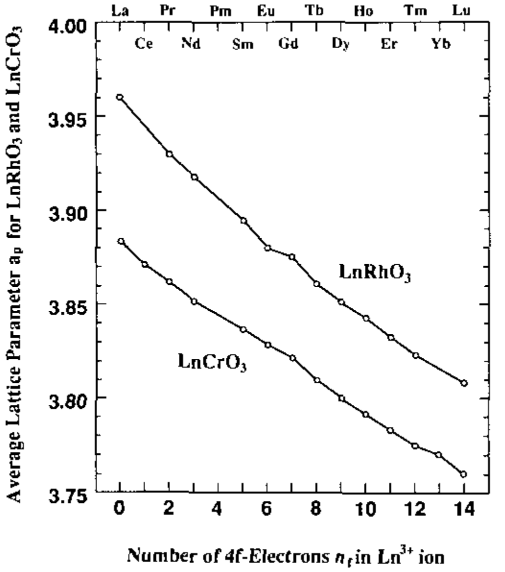

FIG. 1. "Lanthanide contraction" in perovskites $LnRhO_3$ and $LnCrO_3$. Average lattice parameters $a_p \equiv \sqrt[3]{V_p}$ for $LnMO_3$ (M = Rh, Cr) are plotted versus number of 4f electrons, n_f, in Ln^{3+} ions.

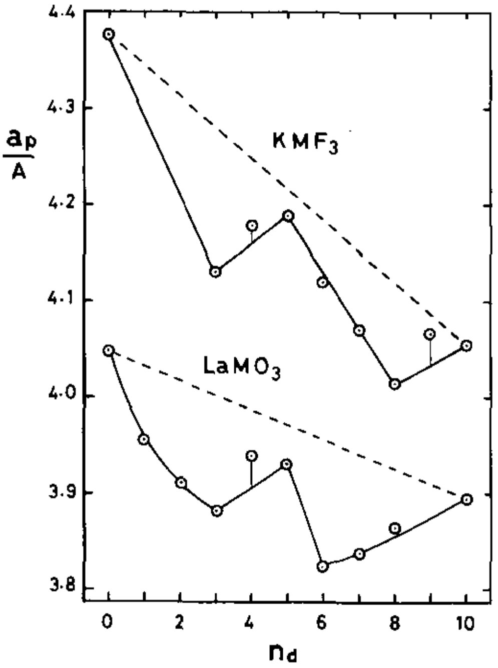

FIG. 2. "3d-contraction" in perovskites KMF_3 and $LaMO_3$. Average lattice parameters a_p are plotted versus number of 3d electrons, n_d, in M^{2+} (high-spin state) and M^{3+} (from high-spin state to low-spin state transfer between n_d = 5 and n_d = 6).

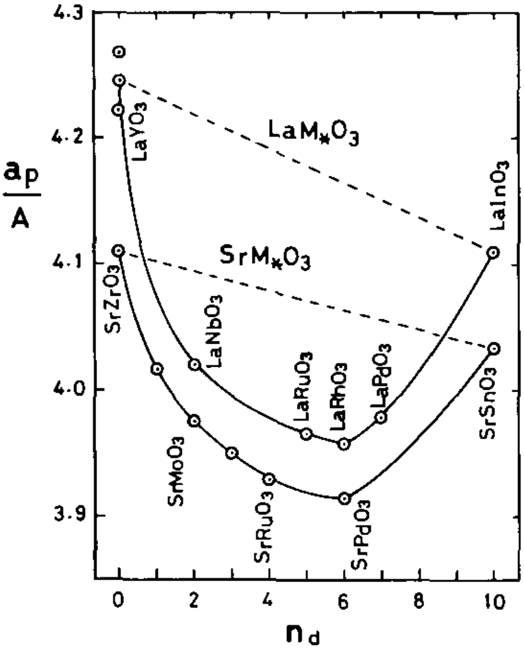

FIG. 3. "4d-contraction" in perovskites LaM_*O_3 and SrM_*O_3. Average lattice parameters a_p are plotted versus number of 4d electrons, n_d, in M_*^{3+} (low-spin state) and M_*^{4+} (low-spin state).

and 5. Lattice parameters in Å of the rock-salt-type compounds used in the figures are listed in Tables I and II, together with the file numbers of JCPDS Powder Diffraction Data. Figure 4 plots the lattice parameters of rock-salt-type compounds with the common s^2p^6-closed shell anions X^- (= F^-, Cl^-, Br^-, I^-) and Z^{2-} (= O^{2-}, S^{2-}, Se^{2-}) as a function of the total number of electrons n_c (= 2, 10, 18, 36, 54, 86) in the closed shell cations A^+ (= Li^+, Na^+, K^+, Rb^+, Cs^+, Fr^+) and M^{2+} (= Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+}). The solid squares in the figure are lattice parameters estimated from Shannon's ionic radii in the coordination number of six (*14*). The full curves which tie the open circles together for the common anion series in Fig. 4 demonstrate the two breaks at the same values n_c = 18 and n_c = 54. These breaks in curvature are interpreted as follows. Cations possessing no d-orbitals exist in the region $n_c < 18$, whereas those possessing 3d-orbitals and 4d-ortibals exist in the re-

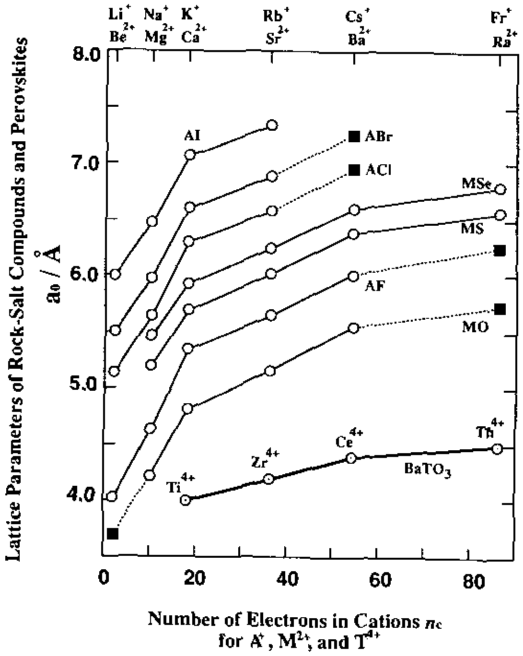

FIG. 4. Lattice parameter a_0 versus number of electrons n_c in cations A^+ and M^{2+} for rock-salt compounds AX and MZ with closed shell ions. Lattice parameter versus number of electrons in T^{4+} for perovskites $BaTO_3$ is also shown as a reference.

gions 18 $<n_c<$ 36 and 36 $< n_c <$ 54, respectively. Therefore, the first break in the slope at n_c = 18 comes from the remanent 3*d*- and 4*d*- contractions, as exemplified by Figs. 2 and 3. The second break in the slope at n_c = 54 comes from the remanent 4*f*- and 5*d*-contractions, because the cations within the region 54 $< n_c <$ 86 have 4*f*- and 5*d*-orbitals, successively. Lattice parameter versus number of electrons n_c in T^{4+} for perovskite-type oxides $BaTO_3$ (*11, 16, 17*) is also indicated in Fig. 4.

Quite similarly, the two breaks appear in the slope at n_a = 18 and n_a = 54 in Fig. 5, where the lattice parameters of rock-salt-type compounds with the common closed shell cations A^+ (= Li^+, Na^+, Rb^+) and M^{2+} (= Ca^{2+}, Sr^{2+}, Ba^{2+}) are plotted against the total number of electrons n_a (= 10, 18, 36, 54, 86) in the s^2p^6-closed shell anions X^- (= F^-, Cl^-, Br^-, I^-) and Z^{2-} (= O^{2-}, S^{2-}, Se^{2-}, Te^{2-}, and Po^{2-}).

Evaluation of Remanent Contraction and Discussion

In order to recognize the mentioned remanent contractions, substantive values of contractions Δ(3*d*), Δ(4*d*), and Δ(4*f* + 5*d*) have been evaluated relative to the slope of the lattice parameter,

$$\text{slope} = \frac{a_0(3s^2 3p^6) - a_0(2_s^2\, 2p^6)}{18 - 10} \qquad (1)$$

based on the geometry given in Fig. 6. Figure 6 shows a typical a_0 versus n relationship, together with the related residual contractions Δ(3*d*), Δ(4*d*), and Δ(4*f* + 5*d*). Writing the lattice parameters as

$$\begin{aligned} a_0(2s^2 2p^6) &\equiv a_1 \\ a_0(3s^2 3p^6) &\equiv a_2 \\ a_0(3d^{10} 4s^2 4p^6) &\equiv a_3 \\ a_0(4d^{10} 5s^2 5p^6) &\equiv a_4 \\ a_0(4f^{14} 5d^{10} 6s^2 6p^6) &\equiv a_5, \end{aligned} \qquad (2)$$

the three residual contractions are given

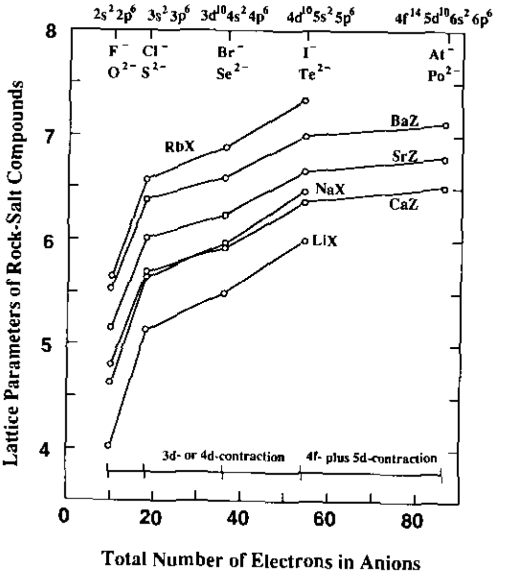

FIG. 5. Lattice parameter a_0 versus number of electrons n_a in anions X^- and Z^{2-} for rock-salt compounds AX and MZ with closed shell ions.

TABLE I

LATTICE PARAMETERS IN Å OF MONOVALENT ROCK-SALT-TYPE COMPOUNDS, TOGETHER WITH THE FILE NUMBER OF JCPDS POWDER DIFFRACTION DATA, SWARTHMORE (1991)

	$2s^22p^6$	$3s^23p^6$	$4s^24p^6$	$5s^25p^6$	$6s^26p^6$
	F^-	Cl^-	Br^-	I^-	At^-
Li^+	4.0270	5.1396	5.5013	6.00	
$1s^2$	(4-857)	(4-664)	(6-319)	(1-592)	
Na^+	4.63329	5.6402	5.97353	6.473	
$2s^22p^6$	(36-1455)	(5-628)	(36-1456)	(6-302)	
K^+	5.34758	6.2917	6.6005	7.0655	
$3s^23p^6$	(36-1458)	(41-1476)	(36-1471)	(4-471)	
Rb^+	5.6516	6.5810	6.889	7.342	
$4s^24p^6$	(22-886)	(6-289)	(8-480)	(6-218)	
Cs^+	6.014				
$5s^25p^6$	(15-759)				

as follows:

$$\left.\begin{aligned}\Delta(3d) &= 26 \times \frac{a_2 - a_1}{8} + (a_1 - a_3)\\ \Delta(4d) &= 18 \times \frac{a_2 - a_1}{8} + (a_3 - a_4)\\ \Delta(4f + 5d) &= 32 \times \frac{a_2 - a_1}{8} + (a_4 - a_5)\end{aligned}\right\} . \tag{3}$$

By use of Eq. (3), the contractions $\Delta(3d)$, $\Delta(4d)$, and $\Delta(4f + 5d)$ were evaluated and listed in Table III using only the observed data (open circles in Figs. 4 and 5). Each contraction in Table III shows a wide divergence as follows:

$$\left.\begin{aligned}&\Delta(3d) = 0.718 \sim 2.142\ (\text{Å}/3d\ \text{series})\\ &\Delta(4d) = 0.686 \sim 2.005\ (\text{Å}/4d\ \text{series})\\ &\Delta(4f + 5d) =\\ &\quad 1.648 \sim 3.387\ (\text{Å}/4f\text{-plus-}5d\ \text{series})\end{aligned}\right\} . \tag{4}$$

TABLE II

LATTICE PARAMETERS IN Å OF DIVALENT ROCK-SALT-TYPE COMPOUNDS TOGETHER WITH THE FILE NUMBER OF JCPDS POWDER DIFFRACTION DATA, SWARTHMORE (1991)

	$2s^22p^6$	$3s^23p^6$	$4s^24p^6$	$5s^25p^6$	$6s^26p^6$
	O^{2-}	S^{2-}	Se^{2-}	Te^{2-}	Po^{2-}
Mg^{2+}	4.213	5.200	5.462		
$2s^22p^6$	(4-829)	(35-730)	(18-777)		
Ca^{2+}	4.81059	5.6948	5.924	6.3642	6.514
$3s^23p^6$	(37-1497)	(8-464)	(18-304)	(39-1494)	(16-107)
Sr^{2+}	5.160	6.020	6.246	6.660	6.796
$4s^24p^6$	(6-520)	(8-489)	(10-182)	(15-851)	(16-29)
Ba^{2+}	5.5393	6.386	6.600	7.0012	7.119
$5s^25p^6$	(22-1056)	(8-454)	(18-191)	(39-1475)	(16-81)
Ra^{2+}		6.575	6.80		
$6s^26p^6$		(27-495)	(27-493)		

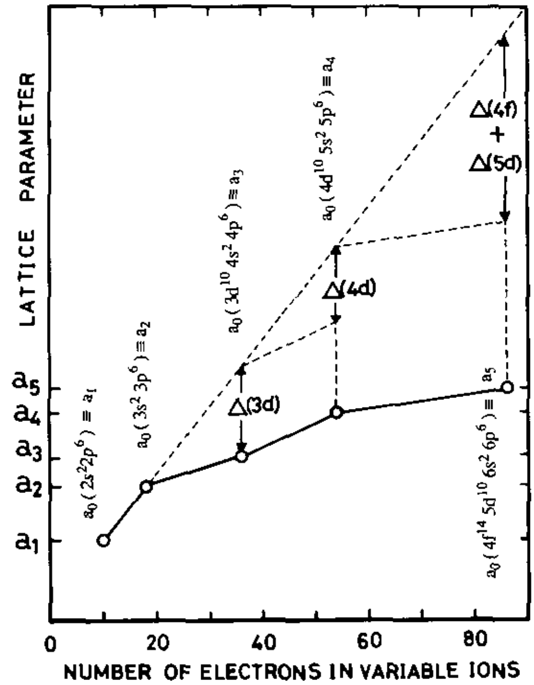

FIG. 6. Depiction of the residual contractions $\Delta(3d)$, $\Delta(4d)$, and $\Delta(4f + 5d) = \Delta(4f) + \Delta(5d)$, where the method of their calculation on the geometrical basis is suggested.

This wide range of divergence mainly comes from the character of the slope in Eq. (1); that is, the factor $(a_2 - a_1)/8$ in Eq. (3). (See Fig. 6.)

The value of the factor $(a_2 - a_1)/8$ ranges from 0.058 to 0.139 with the average value of 0.096.

Thus, if we a priori fix the value of this factor as

$$\text{slope} = \frac{a_2 - a_1}{8} \equiv 0.1000, \tag{5}$$

Eq. (3) is simplified as

$$\left.\begin{aligned} \Delta(3d) &= 1.8 + a_2 - a_3 \\ \Delta(4d) &= 1.8 + a_3 - a_4 \\ \Delta(4f + 5d) &= 3.2 + a_4 - a_5 \end{aligned}\right\}, \tag{6}$$

and each contraction converges as follows:

$$\left.\begin{aligned} &\Delta(3d) = 1.438 \sim 1.586\,(\text{Å}/3d\,\text{series}) \\ &\Delta(4d) = 1.301 \sim 1.446\,(\text{Å}/4d\,\text{series}) \\ &\Delta(4f + 5d) = \\ &\quad 3.00 \sim 3.08\,(\text{Å}/4f\text{-plus-}5d\,\text{series}) \end{aligned}\right\}. \tag{7}$$

The values of estimated contractions from Eq. (6) are also listed in Table III.

Figure 7 shows the nearest-neighbor atomic distance *(18)* versus atomic number relations for the alkali–metal elements (Li, Na, K, Rb, Cs) with the *bcc* structure, for the inert-gas elements (Ne, Ar, Kr, Xe) with the *fcc* structure, and for the IVb elements (C, Si, Ge, α-Sn) with the diamond structure, together with the relation between the lattice parameter and the number of electrons in variable ions A^+ or X^- for ionic series crystals $AF(A$ = Li, Na, K, Rb, Cs) and $KX(X$ = F, Cl, Br, I) with the rock-salt structure.

Here, the nearest neighbor atomic distance r in the element crystals is equal to the individual atomic diameter d in a spherical atom approximation. Meanwhile, the lattice parameter a_0 of the rock-salt-type ionic crystals is equal to the sum of the diameters of cation and anion; that is,

$$a_0 = d_c + d_a. \tag{8}$$

Since either the cation or the anion in the mentioned rock-salt-series compounds is fixed as a common ion in Figs. 4 and 5, the estimated residual contractions $\Delta(3d)$ and $\Delta(4d)$ from Eqs. (3) and (6) are characteristic of either the anion or the cation via Eq. (8). Therefore, one can mutually compare the absolute values of the residual contractions $\Delta(3d)$ and $\Delta(4d)$, estimated from Eqs. (3) and (6), for the three element series crystals and for the rock-salt-series compounds in Fig. 7, and also in Figs. 4 and 5.

It is very interesting to note in Fig. 7 that the quite similar residual contractions $\Delta(3d)$ and $\Delta(4d)$ as demonstrated in the rock-salt-series compounds are seen in the atomic diameters d of the alkali–metal series crystals cohered with the typical metallic bond, in those of the inert-gas-series crystals held

TABLE III

RESIDUAL CONTRACTIONS IN Å OBTAINED FROM EQS. (3) AND (6) FOR ROCK-SALT-TYPE COMPOUNDS AX AND MZ

	$\Delta(3d)$		$\Delta(4d)$		$\Delta(4f+5d)$	
	Eq. (3)	Eq. (6)	Eq. (3)	Eq. (6)	Eq. (3)	Eq. (6)
Common cation						
Monovalent anion X^- (= F^-, Cl^-, Br^-, I^-) as a variable for AX						
Li^+	2.142	1.438	2.005	1.301		
Na^+	1.932	1.467	1.766	1.301		
K^+	1.815	1.491	1.659	1.335		
Rb^+	1.783	1.492	1.638	1.347		
Divalent anion Z^{2-} (= O^{2-}, S^{2-}, Se^{2-}, Te^{2-}, Po^{2-}) as a variable for MZ						
Ca^{2+}	1.760	1.571	1.549	1.360	3.387	3.050
Sr^{2+}	1.709	1.574	1.521	1.386	3.304	3.064
Ba^{2+}	1.691	1.586	1.504	1.399	3.269	3.082
Common anion						
Monovalent cation A^+ (= Na^+, K^+, Rb^+, Cs^+) as a variable for AX						
F^-	1.303	1.496	1.245	1.438		
Cl^-	1.177	1.511				
Br^-	1.122	1.512				
I^-	1.058	1.524				
Divalent cation M^{2+} (= Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+}) as a variable for MZ						
O^{2-}	0.995	1.451	0.965	1.421		
S^{2-}	0.788	1.475	0.747	1.434	1.790	3.011
Se^{2-}	0.718	1.478	0.686	1.446	1.648	3.00

together with the Van der Waals forces, and also in those of the IV*b*-element series crystals cohered with the typical covalent bond.

Evaluation of the residual contractions, $\Delta(3d)$ and $\Delta(4d)$, for the three element series in Fig. 7 gives the following values.

Alkali-metal series:
$\Delta(3d) = 1.637$ Å via Eq. (3)
1.488 Å via Eq. (6),
$\Delta(4d) = 1.551$ Å via Eq. (3)
1.402 Å via Eq. (6).

Inert-gas series:
$\Delta(3d) = 1.11$ Å via Eq. (3)
1.56 Å via Eq. (6)
$\Delta(4d) = 1.01$ Å via Eq. (3)
1.46 Å via Eq. (6).

IV*b*-element series:
$\Delta(3d) = 1.72$ Å via Eq. (3)
1.70 Å via Eq. (6)
$\Delta(4d) = 1.46$ Å via Eq. (3)
1.44 Å via Eq. (6).

These values, $\Delta(3d)$ and $\Delta(4d)$, for the three element series resemble those for the rock-salt-series compounds summarized in Eqs. (4) and (7).

Consequently, the residual *d*- and *f*-contractions, $\Delta(3d)$, $\Delta(4d)$, and $\Delta(4f + 5d)$, deduced from the known lattice parameters of the rock-salt type compounds, are not caused by a chemical interaction between the cation and anion, such as an increase in

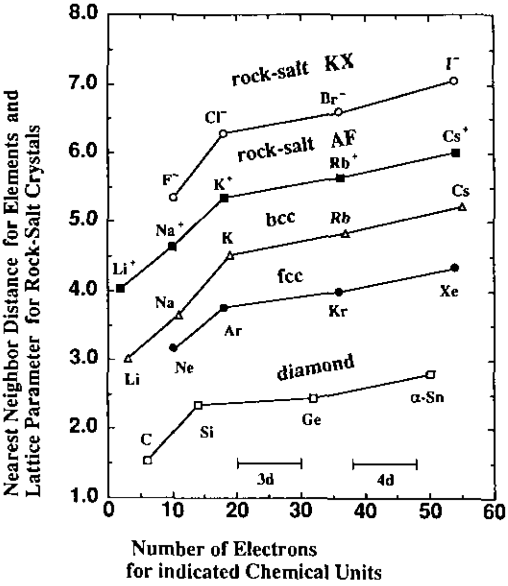

FIG. 7. Nearest neighbor distance versus atomic number for covalent IV$_b$-element series with diamond structure, inert-gas series for *fcc* structure (at 4 K), and alkali-metal series with *bcc* structure (at 5 K), together with the lattice parameter versus number of electrons n_c for *AF* and n_a for *KX*.

covalency with increasing atomic number in the ionic bonding, but come from the contractions in atomic, radical, or ionic cores themselves.

Conclusion

Based on the lattice parameter versus total number of electrons on the relevant series of ions, the presence of residual contractions, $\Delta(3d)$, $\Delta(4d)$, and $\Delta(4f + 5d)$, coming from an imperfect shielding of the nuclear charge has been demonstrated in the series cations and anions with the $2s^2 2p^6$, $3s^2 3p^6$, $3d^{10} 4s^2 4p^6$, $4d^{10} 5s^2 5p^6$, and $4f^{14} 5d^{10} 6s^2 6p^6$ closed shells over the rock-salt-type compounds.

The contractions, $\Delta(3d)$, $\Delta(4d)$, and $\Delta(4f + 5d)$, have been defined and evaluated according to the method shown in Fig. 6.

Since similar contractions are present in the monatomic crystals of inert gas series, of metallic bonding series, and of covalent bonding series, the contractions $\Delta(3d)$, $\Delta(4d)$, and $\Delta(4f + 5d)$ are concluded to exist in the atomic or ionic cores.

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