Crystal Radii and Effective Ionic Radii of the Rare Earth Ions

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There exist some relationships between the crystal radii of the rare earth ions, the $4f$ electron number, and the coordination number. On the basis of these relationships, two empirical formulas have been proposed to calculate the unknown crystal radii of the rare earth ions from the known crystal radii of the trivalent rare earth ions. The crystal radii and effective ionic radii of all the rare earth ions (trivalent and divalent) with different coordination number ($N = 6$–12) have been evaluated. The calculated results are very satisfactory, and for most of examples the relative error is less than 1.0%. © 1991 Academic Press, Inc.

Introduction

The crystal radius and the effective ionic radius of an ion are important parameters. Some authors have determined the crystal radii and the effective ionic radii of many ions (*1–4*). Shannon and Prewitt have carried out a thorough and systematic research and revision on the ionic radii of all the elements (*2*). Shannon has obtained a set of crystal radii and effective ionic radii of all the ions in consideration of the new structural data, empirical bond strength–bond length relationships, and plots of the radii vs the oxidation state and the radii vs the volume based on oxides and fluorides (*5*). The data of Shannon included the crystal radii and effective ionic radii of some rare earth ions. However, the crystal radii and effective ionic radii of some trivalent rare earth ions with different coordination number as well as of most of the divalent rare earth ions have not been reported due to lack of knowledge of the structure chemistry of the corresponding compounds.

The existence of some rare earth compounds with an unusual oxidation state has been predicted as research on the rare earth compounds progresses. For example, recently, more and more dihalides of rare earths have been synthesized and identified (*6*). The infrared spectra of gaseous molecules of dihalides of some rare earths have been measured and assigned (*7, 8*). Therefore, data on the crystal radii of the rare earth ions with different valence and different coordination number will be very useful to understand or predict the possible structure of new compounds.

We have found that there exist some relationships between the crystal radii, the $4f$ electron number, and the coordination number. Therefore, we can evaluate unknown ionic radii from the known ionic radii based on these relationships. Thus, we have proposed two empirical formulas to calculate the crystal radii of all the trivalent and divalent rare earth ions with different coordination number.

Calculation and Discussion

The radii of rare earth ions and atoms decrease with increasing atomic number or the $4f$ electron number in the ions and atoms due to the lanthanide contraction. We have also found that the ratio of the crystal radius of the trivalent ion to that of the divalent ion for the same rare earth element is related to the $4f$ electron number in the rare earth ion. The ratio can be obtained by the following formula,

$$\frac{R^{3+}}{R^{2+}} = 0.842 + 0.0016\,N_f, \qquad (1)$$

where R^{3+} and R^{2+} are the crytal radii of the trivalent and divalent ions with six coordination, respectively, and N_f is the number of the $4f$ electrons in the trivalent ion.

Zachariasen found that the bond lengths in compounds increased with increasing cation coordination number (9). We have also noted that the crystal radius of a rare earth ion, despite its valence, increases gradually with increasing coordination number, and the relationship can be described approximately as follows,

$$R^c(N) = R^c(N - 1) + \left(\frac{0.00135}{(N - 1)}\right)^{1/3}, \qquad (2)$$

where $R^c(N)$ and $R^c(N - 1)$ are the crystal radii of the rare earth ion with coordination numbers N and $N - 1$, respectively, $(12 \geq N \geq 7)$.

We feel that the crystal radii of the trivalent rare earth ions Shannon obtained on the basis of the oxides and fluorides of rare earths may be a very systematic set of crystal radii of ions, and may be more reliable, although these results may be specifically for use in the oxides and fluorides. So, we can take the crystal radii of all the trivalent rare earth ions with six coordination as a set of primary values in calculations for the crystal radii of all the rare earth ions with different valence and different coordination.

Initially, we can get the crystal radii of all the divalent rare earth ions with six coordination from those of the trivalent ions with six coordination by means of Formula (1). Then, we can calculate the crystal radii of all the trivalent and divalent rare earth ions with different coordination number from the crystal radii of the trivalent and divalent ions with six coordination by using Formula (2). Finally we can evaluate the effective ionic radii of all the trivalent and divalent ions by the definition $R^c = R^e + 0.14$ Å $(2, 5)$. The calculated results are listed in Table I. For comparison, the crystal radii and effective ionic radii of Shannon are also listed in Table I. As the results in Table I show, the calculated results are very close to those of Shannon. For most examples, the relative error is less than 1%.

We must point out that Formula (1) may be valid only for the ions which possess similar electronic configurations; that is, there is no $5d$ electron in the divalent ion and the only difference between the electronic configurations of the trivalent and divalent ions is in the number of $4f$ electrons. So, we cannot be sure whether the calculated crystal radius and effective ionic radius of the divalent ions of La, Gd, and Lu is correct. However, the calculated results for the divalent ions of other rare earth elements are reasonable.

The crystal radii and effective ionic radii Shannon obtained on the basis of the oxides and fluorides may be more suitable for the oxides and halides. In this case, the results here may also be more suitable for the oxides and halides of the rare earths.

From the results in Table I, the effect of the lanthanide contraction on the crystal radii, in spite of the valence and coordination number, can also be observed. We have noted that Formula (1) can imply a slightly larger lanthanide contraction for the divalent rare earth ions than for the trivalent rare earth ions.

TABLE I

The Crystal Radii and Effective Ionic Radii of the Trivalent and Divalent Rare Earth Ions with Different Coordination Number (Å)

Ln		Coordination number						
		N = 6	N = 7	N = 8	N = 9	N = 10	N = 11	N = 12
La³⁺	R^c	1.172(*)	1.23(1.24)	1.29(1.30)	1.35(1.35)	1.40(1.40)	1.45	1.50(1.50)
	R^e	1.03	1.09(1.1)	1.15(1.16)	1.21(1.216)	1.26(1.27)	1.31	1.36(1.36)
La²⁺	R^c	1.39	1.45	1.51	1.57	1.62	1.67	1.72
	R^e	1.25	1.31	1.37	1.43	1.48	1.53	1.58
Ce³⁺	R^c	1.15(*)	1.21(1.21)	1.27(1.283)	1.32(1.336)	1.38(1.39)	1.43	1.48(1.48)
	R^e	1.01	1.07(1.07)	1.13(1.143)	1.18(1.196)	1.24(1.25)	1.29	1.34(1.34)
Ce²⁺	R^c	1.36	1.42	1.48	1.54	1.59	1.64	1.69
	R^e	1.22	1.28	1.34	1.40	1.45	1.50	1.55
Pr³⁺	R^c	1.13(*)	1.19	1.25(1.268)	1.30(1.319)	1.36	1.41	1.46
	R^e	0.99	1.05	1.11(1.126)	1.16(1.179)	1.22	1.27	1.32
Pr²⁺	R^c	1.34	1.40	1.46	1.51	1.56	1.62	1.67
	R^e	1.20	1.26	1.32	1.37	1.42	1.48	1.53
Nd³⁺	R^c	1.123(*)	1.18	1.24	1.30	1.35	1.40	1.45
	R^e	0.98	1.04	1.10(1.09)	1.16(1.163)	1.21	1.26	1.31(1.27)
Nd²⁺	R^c	1.33	1.39	1.45	1.50	1.55	1.60	1.65
	R^e	1.19	1.25	1.31(1.29)	1.36(1.35)	1.41	1.46	1.51
Pm³⁺	R^c	1.11(*)	1.17	1.23(1.233)	1.28(1.284)	1.34	1.39	1.44
	R^c	0.97	1.03	1.09(1.093)	1.14(1.144)	1.20	1.25	1.30
Pm²⁺	R^c	1.31	1.37	1.43	1.48	1.54	1.59	1.64
	R^e	1.17	1.23	1.29	1.34	1.40	1.45	1.50
Sm³⁺	R^c	1.098(*)	1.16(1.16)	1.22(1.219)	1.27	1.33	1.38	1.43(1.38)
	R^e	0.958	1.02(1.02)	1.08(1.079)	1.13(1.132)	1.19	1.24	1.28(1.24)
Sm²⁺	R^c	1.29(1.36)	1.35	1.41(1.41)	1.47(1.46)	1.52	1.57	1.62
	R^e	1.15	1.21(1.22)	1.27(1.27)	1.33(1.32)	1.38	1.43	1.48
Eu³⁺	R^c	1.087(*)	1.15(1.15)	1.21(1.206)	1.26(1.26)	1.31	1.37	1.42
	R^e	0.947	1.01(1.01)	1.07(1.066)	1.12(1.12)	1.17	1.23	1.28
Eu²⁺	R^c	1.28	1.34(1.34)	1.40(1.39)	1.45(1.44)	1.50(1.49)	1.55	1.60
	R^e	1.14(1.17)	1.20(1.2)	1.26(1.25)	1.31(1.3)	1.36(1.35)	1.41	1.46
Gd³⁺	R^c	1.078(*)	1.14(1.14)	1.20(1.193)	1.25(1.247)	1.31	1.36	1.41
	R^e	0.938	1.00(1.0)	1.06(1.053)	1.11(1.107)	1.17	1.22	1.27
Gd²⁺	R^c	1.26	1.32	1.38	1.44	1.49	1.54	1.59
	R^e	1.12	1.18	1.24	1.30	1.35	1.40	1.45
Tb³⁺	R^c	1.063(*)	1.12(1.12)	1.18(1.182)	1.24(1.235)	1.29	1.34	1.39
	R^e	0.923	0.98(0.98)	1.04(1.04)	1.10(1.095)	1.15	1.20	1.25
Tb²⁺	R^c	1.24	1.31	1.36	1.42	1.47	1.52	1.57
	R^e	1.10	1.17	1.22	1.28	1.33	1.38	1.43
Dy³⁺	R^c	1.052(*)	1.11(1.11)	1.17(1.167)	1.23(1.223)	1.28	1.33	1.38
	R^e	0.912	0.97(0.97)	1.03(1.027)	1.09(1.083)	1.14	1.19	1.24
Dy²⁺	R^c	1.23(1.21)	1.29(1.27)	1.35(1.33)	1.40	1.46	1.51	1.56
	R^e	1.09(1.07)	1.15(1.13)	1.21(1.19)	1.26	1.32	1.37	1.42
Ho³⁺	R^c	1.041(*)	1.10	1.16(1.155)	1.22(1.212)	1.27(1.26)	1.32	1.37
	R^e	0.901	0.96	1.02(1.015)	1.08(1.072)	1.13(1.12)	1.18	1.23
Ho²⁺	R^c	1.21	1.27	1.33	1.39	1.44	1.49	1.54
	R^e	1.07	1.13	1.19	1.25	1.30	1.35	1.40
Er³⁺	R^c	1.03(*)	1.09(1.085)	1.15(1.144)	1.20(1.202)	1.26	1.31	1.36
	R^e	0.89	0.95(0.945)	1.01(1.004)	1.06(1.062)	1.12	1.17	1.22
Er²⁺	R^c	1.20	1.27	1.32	1.37	1.43	1.48	1.53
	R^e	1.06	1.12	1.18	1.23	1.29	1.34	1.39
Tm³⁺	R^c	1.02(*)	1.08	1.14(1.134)	1.19(1.192)	1.25	1.30	1.35
	R^e	0.88	0.94	1.00(0.994)	1.05(1.052)	1.11	1.16	1.21
Tm²⁺	R^c	1.18(1.17)	1.25(1.23)	1.30	1.36	1.41	1.46	1.51
	R^e	1.04(1.03)	1.11(1.09)	1.16	1.22	1.27	1.32	1.37
Yb³⁺	R^c	1.008(*)	1.07(1.065)	1.13(1.125)	1.18(1.182)	1.24	1.29	1.34
	R^e	0.868	0.93(0.925)	0.99(0.985)	1.04(1.042)	1.10	1.15	1.20
Yb²⁺	R^c	1.17(1.16)	1.23(1.22)	1.29(1.28)	1.34	1.40	1.45	1.50
	R^e	1.03(1.02)	1.09(1.08)	1.15(1.14)	1.20	1.26	1.31	1.36
Lu³⁺	R^c	1.001(*)	1.06	1.12(1.117)	1.17(1.172)	1.23	1.28	1.33
	R^e	0.86	0.92	0.98(0.977)	1.04(1.032)	1.09	1.14	1.19
Lu²⁺	R^c	1.16	1.22	1.28	1.33	1.39	1.44	1.49
	R^e	1.02	1.08	1.14	1.19	1.25	1.30	1.35

Note. R^c, crystal radius; R^e, effective ionic radius. The values of R^c marked (*) were taken as the primary values in the calculation. The values of R^c marked (*) and the values in parentheses are from Ref. (5).

Conclusion

Based on some relationships between the crystal radii, the $4f$ electron number, and the coordination number of the rare earth ions, two empirical formulas have been proposed to calculate the unknown crystal radii of trivalent and divalent rare earth ions with different coordination number $(6-12)$. The calculated results are in good agreement with those of Shannon and the relative error for most of examples is less than 1%.

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