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Abstract. In a previous paper it was shown that *in-crystal* ion polarizabilities derived from low-frequency precision measurements of the dielectric constants of single-crystal oxides can be given a quantitative interpretation using a quantum mechanically based result for a single, completely filled, electron subshell. In this paper, by exploiting the fact that the radii of related subshells differ only slightly, we propose an equation amended to include the possibility of contributions from incomplete or several subshells. Using the new result, effective electron numbers are derived for all the ions for which experimental polarizabilities have recently been published. It is shown that there is generally a good correspondence between these numbers and the known electronic configurations of the ions concerned. The new calculations show that the concept of a polarizability determined by the contribution of a single electron subshell is certainly valid with ions corresponding to elements of low atomic number, but that in the case of transition and rare earth ions there is probably more than one contributing electron subshell.

1. Introduction

In a previous paper [1] it was shown that, with oxides, when a polarizability is derived from a measured low-frequency dielectric constant, ε_0, the result can be expressed as a sum of electronic *in-crystal* polarizabilities together with a term related to ion displacement. For a rock-salt structure this outcome has the form

$$\frac{3V}{4\pi}\left(\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}\right) = (\alpha_1 + \alpha_2) + \frac{2Z}{F_0}(Z' - Z/2) \tag{1}$$

where

$$F_0 = \frac{\mu w_0^2}{e^2}\frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2}. \tag{2}$$

α_1, α_2 are the *in-crystal* polarizabilities and ε_∞ is the high-frequency dielectric constant, w_0 the transverse optical frequency, μ the reduced mass, Z the ionic charge and Z' the Szigeti charge. In deriving individual ion polarizabilities however, Shannon [2], in effect, took an average over a range of compounds where the second term was sometimes positive and sometimes negative. This was shown in [1] to lead to a set of low-frequency in-crystal ion polarizabilities. For ions with closed-shell electronic configurations the quantum theoretical expression for these polarizabilities reduces to

$$\alpha_D = \tfrac{8}{9}a_0(2l + 1)[a_0\langle r^2\rangle]^2 \tag{3}$$

where the factor $[a_0\langle r^2\rangle]^2$ is a form of mean square radius of the outer orbit (r is the radius in dimensionless atomic units and a_0 the radius of the first Bohr orbit in hydrogen) which

can be related to the square of a traditional measure of ionic size [1] and l is the orbital angular momentum quantum number of the electron subshell concerned.

That equation (3) only holds for ions with closed-shell electronic configurations is evidently restrictive, however, when good experimentally based values of polarizability exist for more than 60 different ions from the periodic table [2]. It is the purpose of this paper to present a more complete theoretical analysis and to derive further results. In particular, we show how the applicability of our method may be broadened to include the transition and rare earth ions where it is clear that there should be a contribution to the polarizability from incomplete or several subshells.

2. Further analysis and new results

Equation (3) as stated is an exact quantum mechanical expression for the contribution to polarizability, to first order, from a complete subshell containing $2(2l + 1)$ electrons and consequently, in our introductory paper [1], was applied only to those ions with closed-shell electronic configurations. The theory may be readily amended, however, to facilitate a wider application by writing

$$\alpha_D = \tfrac{4}{9}a_0 N[a_0\langle r^2\rangle]^2 \tag{4}$$

where N is the effective number of electrons contributing to α_D, provided that the factor $[a_0\langle r^2\rangle]^2$, previously interpreted as the square of a modified crystal radius [1], remains reasonably representative of the subshells involved. As quantum mechanics has shown that, for a given atom or ion, the mean radius of an electronic orbit is largely determined by the principal quantum number, n (see, for example, [3]), the approximation should hold for related subshells. Therefore we have used equation (4) to derive effective electron numbers for each of the ions in table III from [2] noting, once again [1], that each ion polarizability listed there corresponds to an average over a variety of environments dominated by sixfold co-ordination. These new results are summarized in table 1 and compared with the known electronic configurations of the ions concerned.

3. Discussion

The objective of our extended analysis is now sharply focused. We seek a correlation between N, the effective number of electrons contributing to the in-crystal low-frequency ion polarizability of a given ionic species, and its corresponding electronic configuration. For this purpose it should be noted that polarizabilities derived from measured dielectric constants are associated with experimental uncertainties which have been estimated to be typically between 4 and 8% (with smaller ions, the error may be much larger according to Shannon [2]), while many crystal radii may be reliable to better than 2% [4]. Our calculated N values are therefore estimated to be subject to about $\pm 12\%$.

With the s^2 ions there is no difficulty in making the desired connection, as only two electrons in a single shell can be involved. Inspection of table 1 shows that Be^{2+} provides excellent agreement with theoretical expectations, while the experimental values of polarizability for Li^+ and B^{3+} are evidently, respectively, too high and too low. This accords with our previous conclusions.

The polarizabilities of the p^6 ions O^{2-}, F^-, Na^+ down to Al^{3+} yield N values acceptably close to the expected number, six. The N values from higher-valence ions with the p^6 configuration, however, are clearly anomalous. There is thus a confirmation of our previous analysis which led to the conclusion that it is probably significant that oxide

Table 1. Ion polarizability data—effective number of electrons.

Ion	Modified crystal radius r (Å)	r^2 (Å^2)	Pol. α_D (Å^3)	Effective number of electrons	Electronic configuration
Li^+	0.96	0.922	1.20	5.53	$1s^2$
Be^{2+}	0.65	0.423	0.19	1.91	$1s^2$
B^{3+}	0.47	0.221	0.05	0.96	$1s^2$
O^{2-}	1.20	1.440	2.01	5.93	$2s^2 2p^6$
F^-	1.13	1.277	1.62	5.39	$2s^2 2p^6$
Na^+	1.22	1.488	1.80	5.14	$2s^2 2p^6$
Mg^{2+}	0.920	0.846	1.32	6.63	$2s^2 2p^6$
Al^{3+}	0.735	0.540	0.79	6.22	$2s^2 2p^6$
Si^{4+}	0.600	0.360	0.87	10.28	$2s^2 2p^6$
P^{5+}	0.58	0.336	1.22	15.44	$2s^2 2p^6$
K^+	1.58	2.496	3.83	6.52	$3s^2 3p^6$
Ca^{2+}	1.20	1.440	3.16	9.33	$3s^2 3p^6$
Sc^{3+}	0.945	0.893	2.81	13.38	$3s^2 3p^6$
Ti^{4+}	0.805	0.648	2.93	19.23	$3s^2 3p^6$
V^{5+}	0.74	0.548	2.92	22.66	$3s^2 3p^6$
Cr^{3+}	0.815	0.664	1.45	9.28	$3s^2 3p^6 3d^3$
Mn^{2+}	1.030	1.061	2.64	10.58	$3s^2 3p^6 3d^5$
Fe^{3+}	0.845	0.714	2.29	13.64	$3s^2 3p^6 3d^5$
Fe^{2+}	0.980	0.960	2.23	9.88	$3s^2 3p^6 3d^6$
Co^{2+}	0.945	0.893	1.65	7.86	$3s^2 3p^6 3d^7$
Ni^{2+}	0.890	0.792	1.23	6.60	$3s^2 3p^6 3d^8$
Cu^{2+}	0.93	0.865	2.11	10.37	$3s^2 3p^6 3d^9$
Zn^{2+}	0.940	0.884	2.04	9.81	$3s^2 3p^6 3d^{10}$
Ga^{3+}	0.820	0.672	1.50	9.49	$3s^2 3p^6 3d^{10}$
Ga^{4+}	0.730	0.533	1.63	13.00	$3s^2 3p^6 3d^{10}$
As^{5+}	0.66	0.436	1.72	16.77	$3s^2 3p^6 3d^{10}$
Rb^+	1.72	2.958	5.29	7.60	$3d^{10} 4s^2 4p^6$
Sr^{2+}	1.38	1.904	4.24	9.47	$3d^{10} 4s^2 4p^6$
Y^{3+}	1.100	1.210	3.81	13.39	$3d^{10} 4s^2 4p^6$
Zr^{4+}	0.92	0.846	3.25	16.33	$3d^{10} 4s^2 4p^6$
Nb^{5+}	0.84	0.706	3.97	23.91	$3d^{10} 4s^2 4p^6$
Cd^{2+}	1.15	1.323	3.40	10.93	$4s^2 4p^6 4d^{10}$
In^{3+}	1.000	1.000	2.62	11.14	$4s^2 4p^6 4d^{10}$
Sn^{4+}	0.890	0.792	2.83	15.19	$4s^2 4p^6 4d^{10}$
Sb^{3+}	0.96	0.922	4.27	19.69	$4d^{10} 5s^2$
Te^{4+}	1.17	1.369	5.23	16.24	$4d^{10} 5s^2$
Cs^+	1.87	3.497	7.43	9.03	$4d^{10} 5s^2 5p^6$
Ba^{2+}	1.55	2.403	6.40	11.32	$4d^{10} 5s^2 5p^6$
La^{3+}	1.232	1.518	6.07	17.00	$4d^{10} 5s^2 5p^6$
Ce^{4+}	1.07	1.145	3.94	14.63	$4d^{10} 5s^2 5p^6$
Ce^{3+}	1.21	1.464	6.15	17.86	$4f^1 5s^2 5p^6$
Pr^{3+}	1.19	1.416	5.32	15.97	$4f^2 5s^2 5p^6$
Nd^{3+}	1.183	1.399	5.01	15.23	$4f^3 5s^2 5p^6$
Sm^{3+}	1.158	1.341	4.74	15.03	$4f^5 5s^2 5p^6$
Eu^{3+}	1.147	1.316	4.53	14.64	$4f^6 5s^2 5p^6$
Eu^{2+}	1.37	1.877	4.83	10.94	$4f^7 5s^2 5p^6$

Table 1. (Continued)

| Ion	Modified crystal radius r (Å)	r^2 (Å^2)	Pol. α_D (Å^3)	Effective number of electrons	Electronic configuration
Gd^{3+}	1.138	1.295	4.37	14.35	$4f^7 5s^2 5p^6$
Tb^{3+}	1.123	1.261	4.25	14.33	$4f^8 5s^2 5p^6$
Dy^{3+}	1.112	1.237	4.07	13.99	$4f^9 5s^2 5p^6$
Ho^{3+}	1.101	1.212	3.97	13.93	$4f^{10} 5s^2 5p^6$
Er^{3+}	1.090	1.188	3.81	13.64	$4f^{11} 5s^2 5p^6$
Tm^{3+}	1.080	1.166	3.82	13.93	$4f^{12} 5s^2 5p^6$
Yb^{3+}	1.068	1.141	3.58	13.34	$4f^{13} 5s^2 5p^6$
Lu^{3+}	1.061	1.126	3.64	13.74	$4f^{14} 5s^2 5p^6$
Ta^{5+}	0.84	0.706	4.73	28.49	$4f^{14} 5s^2 5p^6$
Tl^+	1.70	2.89	7.28	10.71	$5d^{10} 6s^2$
Pb^{2+}	1.39	1.932	6.58	14.48	$5d^{10} 6s^2$
Bi^{3+}	1.23	1.513	6.12	17.20	$5d^{10} 6s^2$
Th^{4+}	1.14	1.300	4.92	16.09	$5d^{10} 6s^2 6p^6$
U^{4+}	1.09	1.188	4.45	15.93	$5f^2 6s^2 6p^6$

structures formed with these ions tend to have local environments with other than sixfold co-ordination [1].

The N values for the higher-atomic-number alkali metals are generally considered acceptable. An N of 6.52 for K^+, for example, is well within experimental error of its expected value. Rb^+ has the higher value $N = 7.60$, but this would agree very well with the estimate by Fowler *et al* [5] of eight effective electrons ($4s^2 4p^6$) for this ion, although their conclusion was derived through a different theoretical route. On the same basis, it seems possible that $N = 9.03$ for Cs^+ also corresponds to eight effective electrons.

With the first-transition-series ions there are some difficulties because, *a priori*, it is not clear how many electron subshells might contribute. Here we suggest that the ions of elements either side of the transition series may be used as a guide. The polarizability of Ca^{2+} seems likely to correspond to $3s^2 3p^6$, i.e. to $N = 8$ electrons, while with Zn^{2+} perhaps only the $3d^{10}$ outermost electrons are effective. In the absence of any other information, it seems reasonable to suggest a linear interpolation between the points associated with these ions. It may be significant therefore that, as shown in figure 1, the N values derived for the first-transition-series ions from the latest experimental data are scattered quite evenly about the trend line. Most of these transition series ions have the valency 2+ but Fe^{3+}, one of the two 3+ ions, has an N value which is clearly erroneous. As pointed out previously [1], it is probable that this deviation arises from the inclusion of measurements taken from ferrites which are anti-ferroelectric [6, 7].

The variation of polarizability within the rare earth series of ions poses difficulties similar to those presented by the experimental results from transition ions but in a more subtle form. In this case, inspection of table 1 shows that as the number of 4f electrons increases from zero (the configurational situation in La^{3+}) to 14 (in Lu^{3+}), there is a monotonic decline in the deduced polarizability. How is this apparent conflict to be reconciled?

Again we appeal to the principle previously described, that is, we consider the electronic configurations of the ions at the limits of the 4f series. On this basis, if N values of 18 (La^{3+} has the outer configuration $4d^{10} 5s^2 5p^6$) and 14 (Lu^{3+} has the outer configuration $4f^{14} 5s^2 5p^6$)
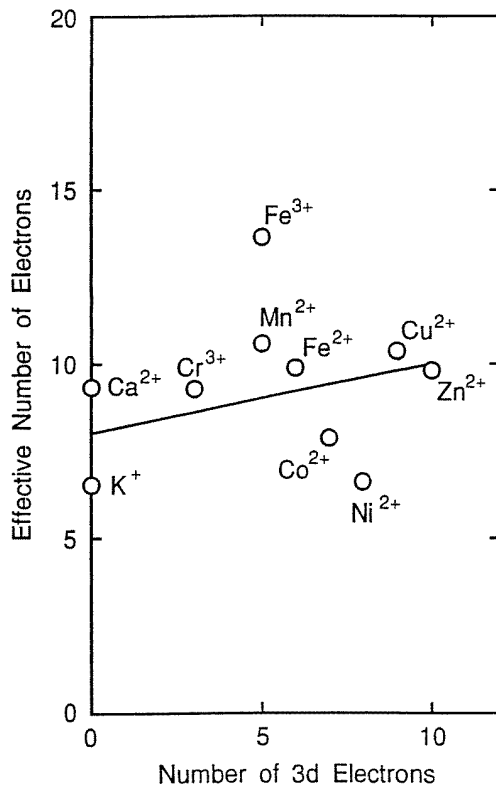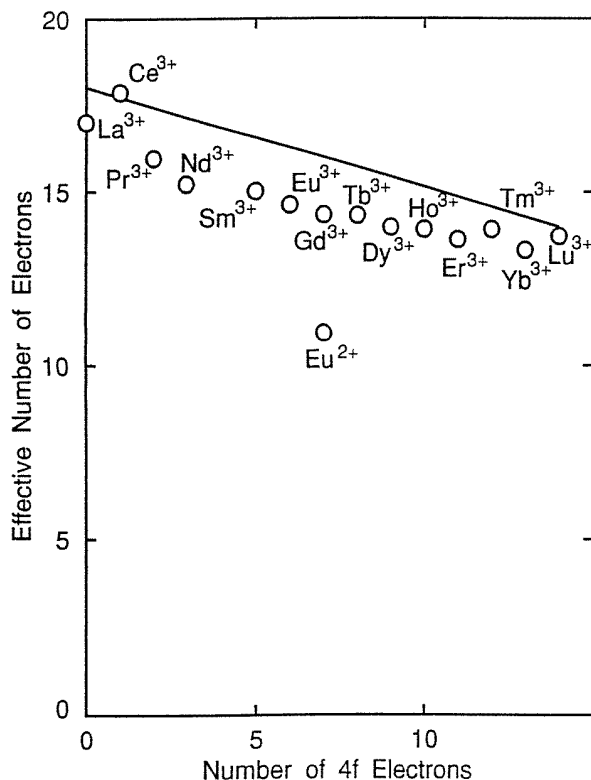
Figure 1. Effective number of electrons—first-transition-series ions—for the significance of the linear interpolation, see the text.

respectively are assumed and if, once more, a linear interpolation can be applied, the data from the rare earth ions can be given an interpretation. Evidently the contribution from the f subshell grows to overwhelm the contributions of the outermost s and p subshells. This is illustrated in figure 2. However, the scatter of the experimental data is persistently below the trend line in this case, indicating the presence of a systematic error. We interpret this effect as a consequence of the tacit assumption that the chosen measure of ion size is also reasonably representative of the radius of a 4d or 4f subshell. The latter would be expected to be smaller, however, and if a correction had been made for this, the N values would have been larger and the data more evenly distributed about the trend line in figure 2.

Finally, it is worth noting that the N values corresponding to the polarizabilities of Tl^+ and Pb^{2+} are consistent with 12 effective electrons and therefore with their known electronic configurations, but the polarizability of Bi^{3+} appears to be too high.

4. Summary and conclusions

In our introductory paper we showed that in-crystal ion polarizabilities derived from low-frequency precision measurements of the dielectric constants of single-crystal oxides can be given a quantitative interpretation using a quantum mechanically based result for a single, completely filled, electron subshell. Noting that the radii of related electronic subshells

Figure 2. Effective number of electrons—rare earth ions—for the significance of the linear interpolation, see the text.

should differ only slightly, this result has now been modified to include the possibility of contributions from incomplete or several subshells.

Using the new result, effective electron numbers have been derived for all the ions for which polarizabilities have recently been published [2]. It has been shown that there is generally a good correspondence between these numbers and the known electronic configurations of the ions concerned.

The new calculations show that the concept of an in-crystal polarizability determined by the contribution of a single electron subshell is certainly valid for ions corresponding to elements of low atomic number, but that in the case of first-transition and rare earth ions there is generally more than one contributing electron subshell.

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