A Theoretical Modeling of the Static and Dynamic Polarizability of O^{2-} in Large and Complex Oxides

D. Ray, H. Anton, P. C. Schmidt, and Al. Weiss †

Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstraße 20, D-64287 Darmstadt

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A time-dependent approach is employed in conjunction with a crystal potential model to study the environment-specific optical linear response of the O^{2-} ions in a number of cubic oxides with varying number of constituents, unit-cell dimension and degree of complexity. It is shown that the static polarizability of the anion may vary significantly depending on the position of the anion within the unit-cell. Due to neglect of overlap compression, our method has limited success in predicting the refractive indices of large crystals of complex structures. For small binary oxides the frequency-dependent polarizability of the O^{2-} ion is found to exhibit the first poles close to the ultraviolet absorption edges ascribed to the lowest excitonic transitions in these crystals.

1. Introduction

Theoretical modeling of the electronic polarizability of ions within solids are of interest because these numbers determine optical-response-related macroscopic quantities such as the index of refraction, the high-frequency dielectric constant and many other important properties of solids. The free-cation polarizabilities are changed almost negligibly within crystals, while the free anion polarizabilities are reduced drastically in and highly sensitive to crystalline environments, varying widely with crystals for a particular anion. An useful means for a theoretical modeling of the optical-response-related quantities of ionic solids may be based on the Clausius-Mossotti relation, via a combination of the ionic hypothesis that assumes the existence of discrete polarizable ions within solids and the additivity rule of such individual in-crystal ion polarizabilities within a crystal formula unit.

There are only a few calculations [1 - 5] of the O^{2-}-polarizability taking account of the specific crystalline environments. In some of these calculations the crystal potential on the anion due to the solid matrix is approximated by constructing a suitable Watson sphere [6] centered around the anion taking into consideration the Madelung energy of respective crystals at the ion site in question [3, 4] and then by applying a correction for the short-range effects [4], or by using spherically-averaged sum of pseudopotentials at the anion site [5]. At a somewhat higher level of sophistication, the anion at the local site of full crystal symmetry is considered with or without the surrounding nearest-neighbour cation-cluster embedded in a finite-fragment point-charge representation of the remaining crystal lattice [1, 2]. The static in-crystal response has been the main concern of most of these studies and the frequency (real)-dependent response has not been touched upon so far.

In [7] we have combined a time-dependent procedure with the model crystal potential approach in order to treat the in-crystal dynamic response of halogen anions F^- and Cl^- within alkali halides. It is the purpose of the present study to extend the investigation to the cases of O^{2-}anions in binary, ternary and quaternary crystals of fairly complex structures. In our calculation we have used the Madelung-energy-dependent variable-radius Watson sphere model of the crystal potential mainly because of (i) its efficacy in predicting the static response-associated quantities at a level tolerable for practical purposes, as evident from the earlier calculations [3,4] and (ii) the high numerical tractability of this model irrespective of the crystal structure, that requires no more complications for in-crystal ions than that involved for a free ion. Within this model we have left out the effects of electron correlation and spin-orbit coupling from our consideration, and have worked out at the coupled Hartree-Fock (CHF) level within the framework

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of the time-dependent perturbation-variation theory (TDPVT). Our method of calculation is outlined in Sect. 2; this is followed by a discussion of the results obtained for the systems under consideration in this report.

2. Method

The unperturbed Hamiltonian H_0^C of an in-crystal ion (the superscript 'C' denotes in-crystal entities and the atomic units are adopted throughout, unless specified otherwise) is formally written as

$$H_0^C = H^{Free} + V^C, \tag{1}$$

where the free-ion Hamiltonian H^{Free} contains the usual electronic kinetic energy, electron-nuclear attraction, and the interelectronic repulsion terms. The crystal potential V^C at the probe ion site is generated by considering an uniformly charged hollow sphere of radius R and charge q with the ion at the center such that

$$\begin{aligned} V^C(r) &= q/R \quad \text{for } r \leq R \\ &= q/r \quad \text{for } r > R. \end{aligned} \tag{2}$$

The charge of the sphere is taken to be of equal magnitude and opposite sign of the ion enclosed i. e. $q = -q_{ion}$, and the radius is determined in such a way that the Madelung potential of the crystal lattice is introduced at the probe ion site i.e. the criterion: $V^C = V^{Madelung}$ (for $r < R$) is fulfilled. Thus, the electrostatic point charge model of the crystal lattice and the specific geometry and symmetry of the crystal structure are taken care of in an implicit manner, although the overlap between neighbouring lattice sites, giving rise to the short-range repulsive contribution to the lattice potential, is ignored in this study.

Now, the single-particle Hartree-Fock-Roothaan equations containing the additional term V^C for crystal-ions are solved self-consistently by the standard method of basis-set expansion in Slater-type orbitals (STO).The one-electron orbitals (η_j^C)with their corresponding energies (ε_j^C) are obtained by optimizing the total (unperturbed ground state) crystal-ion energy E_0^C simultaneously with respect to the expansion coefficients as well as the exponents of the basis functions. The computer program of Pitzer [8] for free ions is suitably modified for this purpose.

Next, we consider the dynamic response of the crystal-ion to an external spin-free harmonic field treated as a time-dependent perturbation and expressed as

$$H'(t) = \sum_l h_l(r) \exp(-i\omega t) + \text{complex conjugate}, \tag{3}$$

where

$$h_l(r) \approx r^l Y_{l0}(\theta, \varphi). \tag{4}$$

In this article we have considered the dipolar perturbation ($l = 1$) that introduces two-component first-order oscillatory admixtures $\delta\eta_j^{C\pm}$ to each unperturbed (ground state) crystal-ion orbital η_j^C. In order to determine these admixtures, first we invoke the following time-dependent variational functional [9 - 11] averaged over the complete cycle of the applied field:

$$J[\Phi^C] = \frac{1}{T}\int_0^T dt\, \langle \Phi^C \left| H^C - i(\partial/\partial t) \right| \Phi^C \rangle \tag{5}$$

which is subject to the optimization condition

$$\delta J[\Phi C] = 0, \tag{6}$$

where Φ^C stands for the normalized total perturbed crystal-ion wavefunction corresponding to the perturbed crystal-ion Hamiltonian $H^C = H_0^C + H'$ and is expressed (up to the first order) in terms of the normalized antisymmetrizer A as

$$\Phi^C(t) = e^{-iE_0^C t} A \prod_j (\eta_j^C + \delta\eta_j^{C-} e^{-i\omega t} + \delta\eta_j^{C+} e^{i\omega t}). \tag{7}$$

In the second step the radial part of the perturbed orbitals are expanded in a linear combination of appropriate Slater-type bases and the coefficients of expansion are obtained through a linear variation procedure. Finally, these first-order admixtures are employed to obtain the dynamic dipole electronic polarizability (only the real part is considered here) of the in-crystal ion as a function of the frequency ω of the external field:

$$\alpha_d(\omega) = \sum_j (\langle \delta\eta_j^{C-} | r\cos\theta | \eta_j^C \rangle + \langle \delta\eta_j^{C+} | r\cos\theta | \eta_j^C \rangle). \tag{8}$$

Table 1. Crystal space-groups and unit-cell parameters.

Crystal	Space group	a/Å
MgO	Cubic Fm3m (O_h^5)	4.208[a]
CaO	Cubic Fm3m (O_h^5)	4.799[a]
SrO	Cubic Fm3m (O_h^5)	5.1396[a]
Li_2O	Cubic Fm3m (O_h^5)	4.6114[b]
Na_2O	Cubic Fm3m (O_h^5)	5.560[b]
K_2O	Cubic Fm3m (O_h^5)	6.436[b]
Na_2CaSiO_4	Cubic $P2_13$ (T^4)	7.48[c]
$LiAl_5O_8$	Cubic $P4_332$ (O^6)	7.908[d]
$MgAl_2O_4$	Cubic Fd3m (O_h^7)	8.090[e]
Mg_2TiO_4	Cubic Fd3m (O_h^7)	8.4376[f]
$K_2Mg_2(SO_4)_3$	Cubic $P2_13$ (T^4)	9.920[g]
Y_2O_3	Cubic Ia3 (T_h^7)	10.604[h]
$Ca_{12}Al_{14}O_{33}$	Cubic $I\bar{4}3d$ (T_d^6)	11.989[i]
$Mg_3Al_2(SiO_4)_3$	Cubic Ia3d (O_h^{10})	11.456[j]
$Ca_{12}Be_{17}O_{29}$	Cubic $F\bar{4}3m$ (T_d^2)	14.023[k]

[a] W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, Vol. 2, Pergamon Press 1967; [b] Landolt-Börnstein Tables (New Series), Gr. III, Vol. 7, pt. b1, Springer-Verlag (1975); [c] Strukturber. **2**, 159,557 (1937); [d] Struct. Rep. for 1979, **45A**, 221 (1981); [e] Strukturber. **1**, 350, 417 (1931); [f] Struct.Rep. for 1989, **56A**, 133 (1991); [g] Struct.Rep. for 1957, **21**, 362 (1964); [h] Struct.Rep. for 1965, **30A**, 309 (1975); [i] Struct.Rep. for 1974, **40A**, 301 (1976); [j] Landolt-Börnstein Tables (New Series), Gr. III, vol. 7, pt. d1α, Springer-Verlag (1985); Struct. Rep. for 1965, **30A**, 426 (1975); [k] Struct. Rep. for 1966**31A**, 130 (1975).

3. Results and Discussion

The list of the crystals, their space-groups and the unit-cell parameters investigated here are summarized in Table 1. Due to the limitations of our computer program our choice has mostly been restricted to the optically isotropic crystals composed of 1s-, 2p- and 3p-closed-shell cations. All the crystals are assumed to be predominantly ionic in character.

The dipole polarizability α_d of an np-closed-shell ion ($n \geq 2$) induced by a dipole perturbation (4) constitutes of the following first-order perturbed orbital contributions: 1) the p-type polarization of the s-orbitals, 2) the s-type polarization of the p-orbitals and 3) the d-type polarization of the p-orbitals. Adequate representation of each of these polarization functions for all the ions separately in terms of a large and flexible 15-parameter STO expansion is ensured on the basis of a well-converged set of the static limits of the corresponding orbital polarizabilities.

Table 2. Static limits of the electronic dipole polarizability $\alpha_d(0)$ (in a_0^3; $a_0 = 0.529$Å) of O^{2-} ions in oxides. (Wyckoff position: Number of available (occupied) positions of O^{2-}; E_M: Madelung energy at the O^{2-}-sites in eV; R: Watson sphere radius in a_0).

Crystal	Wyckoff position	E_M [eV]	R [a_0]	$\alpha_d(0)$ This work	$\alpha_d(0)$ Other values
MgO	4 (4) a	–47.841	2.275	14.37	(21.18, 10.96)[a] (16.15, 12.82)[b] 8.7[c], 11.54[d]
CaO	4 (4) a	–41.949	2.595	18.60	(29.12, —)[a] (19.99, 16.88)[b] 11.07[c], 15.43[d]
SrO	4 (4) a	–39.169	2.779	21.45	(34.46, —)[a] (22.46, 20.30)[b] 11.94[c], 17.73[d]
Li_2O	4 (4) a	–47.251	2.304	14.76	(16.46, 14.32)[b]
Na_2O	4 (4) a	–39.189	2.778	21.53	(22.25, 19.11)[b]
K_2O	4 (4) a	–33.855	3.215	29.45	(29.64, 26.43)[b]

[a] [1] (XTAL and CLUS results respectively at the CHF level); [b] [4] (results without and with the correction for short-range compressive effects); [c] [5]; [d] [13] (empirical values).

Table 2 (cont).

Crystal	Wyckoff position		E_M [eV]	R [a_0]	$\alpha_d(0)$
Na_2CaSiO_4	O_I:	4 (4) a	–57.398	1.896	10.32
	O_{II}:	12 (12) b	–49.906	2.181	13.27
$LiAl_5O_8$	O_I:	24 (24) e	**–52.141**	**2.087**	**12.21**
	O_{II}:	8 (8) c	–54.966	1.980	11.22
$MgAl_2O_4$		32 (32) e	–51.279	2.122	12.59
Mg_2TiO_4		32 (32) e	–46.977 to –52.678	2.317 to 2.066	14.91 to 12.07
$K_2Mg_2(SO_4)_3$	O_I:	12 (12) b	–61.858	1.760	9.12
	O_{II}:	12 (12) b	–63.797	1.706	8.69
	O_{III}:	12 (12) b	–63.569	1.712	8.77
	O_{IV}:	12 (12) b	–63.679	1.709	8.72
Y_2O_3		48 (48) e	–43.817	2.484	17.08
$Ca_{12}Al_{14}O_{33}$	O_I:	48 (48) e	–48.923 to –54.268	2.225 to 2.006	13.78 to 11.41
	O_{II}:	16 (16) c	–41.806 to –48.146	2.604 to 2.261	18.77 to 14.21
	O_{III}:	24 (2) d	–17.285	6.297	182
$Mg_3Al_2Si_3O_{12}$		96 (96) h	–54.030	2.015	11.62
$Ca_{12}Be_{17}O_{29}$	O_I:	48 (48) h	–53.490	2.035	11.71
	O_{II}:	48 (48) h	–49.439	2.202	13.51
	O_{III}:	4 (4) c	–67.410	1.615	8.01
	O_{IV}:	16 (16) e	–45.804	2.376	15.62

The static limits $\alpha_d(0)$ of O^{2-}-dipole polarizabilities in oxides are displayed in Table 2. Wherever

Cation	$\alpha_d(0)$ Free	In-Crystal
Li^+	0.1894	0.1903 - 0.1944
Be^{2+}	0.0519	0.0565 - 0.0582
Na^+	0.9477	0.9564 - 0.9598
Mg^{2+}	0.4715	0.4735 - 0.4842
Al^{3+}	0.2662	0.2663 - 0.2667
Si^{4+}	0.1635	0.1635
S^{6+}	0.0728	0.0728
K^+	5.4770	5.6000 - 5.7753
Ca^{2+}	3.2770	3.3114 - 3.5863
Ti^{4+}	1.4926	1.4961

Tab. 3. Static limits of the electronic dipole polarizability $\alpha_d(0)$ (in a_0^3; a_0 = 0.529Å) of the cations.

available we have also given the results of other theoretical studies of the static α_d of these oxides. Our results should be compared with values which are gained by similar methods. These are the data of Fowler and Madden in which the ionic environment is represented by a lattice of point charges (values a in Table 2) and the values "uncorrected for short-range effect" of Pearson et al. [4] (values b in Table 2). Our values are close to the values of Pearson et al. who also used the Watson-sphere model. The values c and d in Table 2 are theoretical values for which both the electrostatic and the overlap contraction caused by covalent contributions to α_d are taken into account. As we have neglected the overlap between the anion and its neighbouring sites, our values should be larger than the experimental or empirical values (values e in Table 2).

In some of the larger systems listed in Table 2 the O^{2-} ion occupies more than one equivalent position, and its polarizability varies within the unit cell of the crystal depending on the Madelung potential at the anion site in question. An extreme example are the 24(2)d sites of $Ca_{12}Al_{14}O_{33}$, where the value of α_d is equal to 182 a_0^3 because of the extremely small Madelung potential at this site.

The static polarizabilities $\alpha_d(0)$ of the O^{2-} ions are found to follow a definite smooth trend with the inverse of the Watson sphere radius R (or equivalently, with the Madelung potentials at the O^{2-} sites). This is shown in Fig. 1 and can be analytically expressed as

$$\frac{\alpha_d(0)}{a_0^3} = 0.1061 \frac{\exp(4.238 a_0/R)}{(a_0/R)^{3.688}} \qquad (9)$$

with a_0 = 0.529Å.

In order to obtain the electronic dipole polarizabilities of the crystal formula units α_m from the additivity principle we have calculated the free and in-crystal

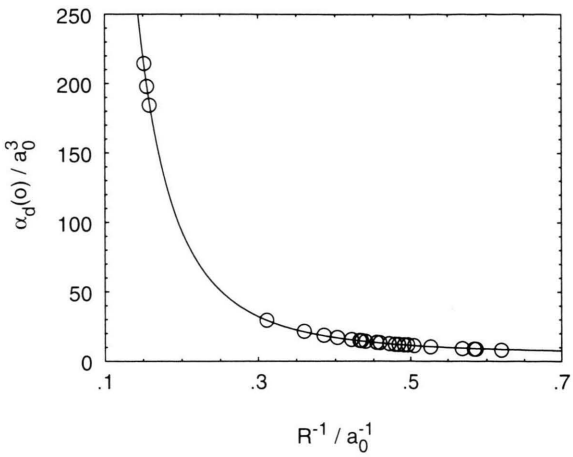

Fig. 1. Static limits [$\alpha_d(0)$] of the O^{2-} dipole polarizability versus the inverse of the Watson sphere radii (R^{-1} of the anion in oxides; a_0 = 0.529 Å.

cation polarizabilities. The results are given in Table 3. The cation polarizabilities are much less sensitive to crystalline environments. A small expansion of the cation in the lattice potential causes a small increase of its polarizability. The variation of α_d(cation) in different crystals, and in a particular crystal in different cation positions is indicated by giving the ranges of the cation polarizabilities. In Table 4 we present the refractive indices of the oxides derived from their formula unit polarizabilities using the Clausius-Mossotti formula

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \frac{\alpha_m}{V_m}, \qquad (10)$$

where $\epsilon = n^2$ is the dielectric constant, n the high-frequency index of refraction, V_m the volume per crystal formula unit and α_m the sum of the polarizabilities of the ions which compose a formula unit. Since the damping of the anionic charge-cloud and the polarizability by short-range repulsive forces has not been incorporated in this study, a trend of overestimation in the theoretical in-crystal anion size, polarizability and the crystal refractive index may be expected in general; and this is observed in comparison to the experimental values in most cases. However, we also note that our calculated refractive indices are unable to follow the trend in the experimental values even for the MgO series. We conclude that to analyze the trend of the refractive index in various oxides one has to consider in detail the covalent contribution to

Table 4. Refractive indices of the oxides.

Crystal	This work	Other theoretical values	Experiment
MgO	1.983	(2.178,1.845)[a]	1.735[b]
CaO	1.979	(2.070,1.836)[a]	1.837[b]
SrO*	1.979	(2.079,1.955)[a]	1.870[b]
Li_2O	1.692	(1.790,1.662)[a]	1.644[b]
Na_2O	1.592	(1.629,1.532)[a]	
K_2O	1.681	(1.693,1.624)[a]	
Na_2CaSiO_4	1.576		1.594[c]
$LiAl_5O_8$	1.965		1.735[d]
$MgAl_2O_4$	1.930		1.719[d]
Mg_2TiO_4	1.902		1.972[e]
$K_2Mg_2(SO_4)_3$	1.514		1.538[f]
$Ca_{12}Al_{14}O_{33}$	1.905		1.643[g]
$Mg_3Al_2(SiO_4)_3$	1.909		1.705[c]
$Ca_{12}Be_{17}O_{29}$	1.668		1.638[d]

* Sr^{2+}-polarizability used for SrO has been extrapolated from the values given in P. C. Schmidt, Al. Weiss and T. P. Das, Phys. Rev. B**19**, 5525 (1979); [a] [4] (value unmodified by short-range effects and that corrected for nearest and second-nearest-neighbour interactionsrespectively); [b] Landolt-Börnstein Tables (New Series), Gr. III, Vol. 7, pt. b1, Springer-Verlag (1975), (values correspond to the sodium-D line); [c] Landolt-Börnstein Tables (New Series), Gr. III, Vol. 7, pt. d1α, Springer-Verlag(1985); [d] Landolt-Börnstein Tables (New Series), Gr. III, Vol.7, pt.d2, Springer-Verlag(1980); [e] Landolt-Börnstein Tables (New Series), Gr. III, Vol. 7, pt. e, Springer-Verlag(1976); [f] Landolt-Börnstein Tables (New Series), Gr. III, Vol. 7, pt. b3, Springer-Verlag(1982); [g] Crystal Data Determinative Tables (3rd. ed.), Vol. II, NBS-NSRDS-JCPDS, U. S. A.

the chemical bond and it seems to be that this contribution can not be described within a simple model. It is found by Fowler and Madden that the overlap contraction is quite different in MgO and CaO.

Besides the static dipole polarizability of O^{2-} ions in a steady external field we have studied the frequency-dependence of the O^{2-}-dipole polarizability in a number of crystals in which these ions occupy unique positions characterized by a single value of the Madelung energy at all O^{2-} sites within the unit cell of the respective crystals.

The variation of the total polarizability α_d with the frequency υ of the external driving field is shown for CaO and $MgAl_2O_4$ in Figure 2. As can be seen from these representative graphs, the total polarizability initially remains almost constant at the zero-frequency value over a wide range of frequencies and exhibits a small monotonic increase followed by a singularity. We notice that this pole is a consequence of the predominating steep rise of the p→s orbital contribution, which is understood in terms of the divergence

Table 5. Comparison of the in-crystal pole positions of dynamic dipolepolarizability $\alpha_d(\upsilon)$ of O^{2-} ions against the experimental ultravioletabsorption edges of the oxides.

Crystal	In-crystal pole position [eV]	Ultraviolet absorption edge [eV]
MgO	8.0	7.6[a]
CaO	6.7	6.8[b]
SrO	6.0	5.7[c]
Li_2O	7.9	
Na_2O	6.1	
K_2O	4.8	
$MgAl_2O_4$	8.8	7.8[d]
Y_2O_3	7.1	6.0[a]
$Mg_3Al_2(SiO_4)_3$	9.3	

[a] E. D. Palik (Ed.), Handbook of Optical Constants of Solids, Vol. II, Academic Press, Inc. 1991; [b] R. C. Whited and W. C. Walker, Phys. Rev. **188**, 1380 (1969); [c] G. P. Summers, Phys. Rev. B**20**, 5275 (1979); A. S. Rao and R. J. Kearney, Phys.Stat.Sol.(b) **95**, 243 (1979); [d] G. P. Summers, G. S. White, K. H. Lee, and J. H. Crawford, Jr., Phys. Rev. B**21**, 2578 (1980).

of the corresponding first-order perturbed amplitude at resonance in absence of any phenomenological damping in the theory.

In the vicinity of a discontinuity we have performed finer scanning to pinpoint the pole and have listed the pole-positions (in eV) of O^{2-} in-crystal dynamic polarizability in Table 5. Also tabulated in the same Table are the experimental ultraviolet (uv) absorption edges of these crystals for comparison purposes. The onset of uv absorption in these crystals is usually attributed to the lowest $n = 1$ (in the hydrogenic model) non-conducting excitonic transition below the conduction band, and the first pole positions should

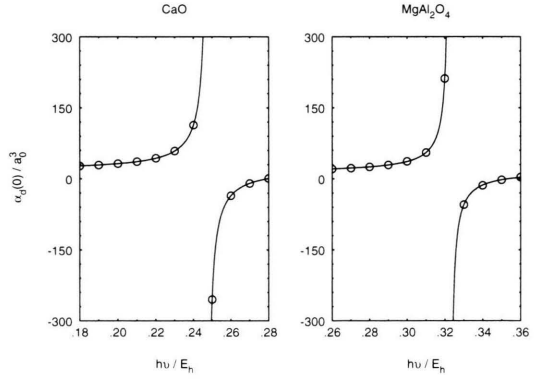

Fig. 2. Frequency (υ)-dependence of the dipole polarizability (α_d) of O^{2-} in CaO and $MgAl_2O_4$; $a_0 = 0.529$ Å, $E_h = 27.21$ eV.

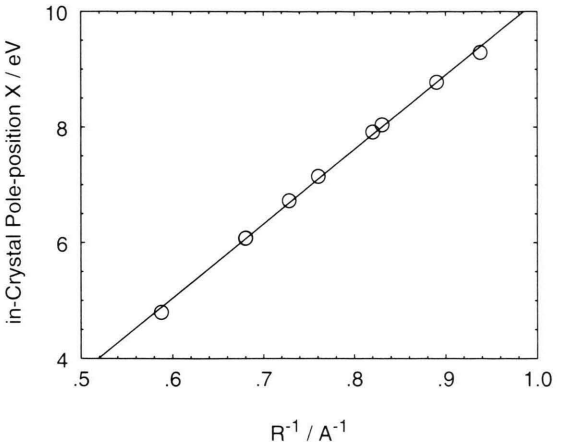

Fig. 3. Variation of the in-crystal pole-positions (X) of O^{2-} with the inverse of the Watson sphere radii (R^{-1}) of the anion in oxides; $a_0 = 0.529$ Å, $E_h = 27.21$ eV.

correspond to them. Figure 3 shows that the in-crystal pole-positions are found to depend linearly on the Madelung potentials at the O

$$X/\text{eV} = -2.678 + 12.86\text{Å}/R, \qquad (11)$$

where X represents the theoretical pole-positions as a function of the inverse of the Watson sphere radius R.

4. Conclusion

We have used the Madelung-energy-dependent Watson sphere model in order to study the optical characteristics of O^{2-} ions in solids. The model shows that the dipole polarizability of O^{2-} in an ionic crystal can be distinctly different at non-equivalent sites. Although the difference between the calculated and experimental refractive index is less than 15 %, the pure ionic model cannot verify the experimental trend in n in various oxides, whereas the trend in the excitonic transitions can be described satisfactorily using the simple Watson sphere model.

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