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Hartree-Fock-Roothaan Wave Functions, Electron Density Distribution, Diamagnetic Susceptibility, Dipole Polarizability and Antishielding Factor for Ions in Crystals*

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Using the Hartree-Fock method the wave functions of Li^+, Be^{2+}, O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+}, S^{2-}, Cl^-, K^+, Ca^{2+}, Sc^{3+} and Ti^{4+} have been calculated for the free ion and the ion in a potential well. The main result of these calculations is a contraction of the anion and an expansion of the cation due to the external potential. A comparison of the calculations with an experimental determination of the electron density distribution in NaCl and MgO shows qualitative agreement. The diamagnetic susceptibility χ, the dipole polarizability α_d, and the Sternheimer antishielding factor γ_∞ of the ions given above were also calculated for the free ions and the "spherical potential" ions (SPI). The charged hollow sphere model improves the theoretical values towards the properties determined by experiment.

Unter Verwendung der Hartree-Fock-Methode wurden analytische Wellenfunktionen für die Ionen Li^+, Be^{2+}, O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+}, S^{2-}, Cl^-, K^+, Ca^{2+}, Sc^{3+} und Ti^{4+} berechnet. Es wurden sowohl die freien Ionen als auch Ionen im Potentialtopf untersucht. Es zeigt sich eine durch das äußere Potential hervorgerufene Kontraktion der Anionen und eine Expansion der Kationen. Der Vergleich der Rechnungen mit experimentellen Bestimmungen der Elektronendichteverteilung in NaCl und MgO zeigt qualitative Übereinstimmung zwischen Theorie und Experiment. Ferner wurden die diamagnetische Suszeptibilität χ, die Dipolpolarisierbarkeit α_d und der Antishieldingfaktor γ_∞ (Sternheimerfaktor) sowohl für die freien als auch für die durch ein kugelsymmetrisches Potential gestörten Ionen berechnet. Das hier benutzte Festkörpermodell der geladenen Hohlkugel ergibt Werte, die in guter Übereinstimmung mit dem Experiment sind.

Les fonctions d'onde de Li^+, Be^{2+}, O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+}, S^{2-}, Cl^-, K^+, Ca^{2+}, Sc^{3+} et Ti^{4+} ont été calculées par la méthode de Hartree-Fock pour l'ion libre et pour l'ion dans un puit de potentiel. Le résultat essentiel de ces calculs montre une contraction de l'anion et une expansion du cation sous l'effet du potentiel extérieur. Les densités électroniques calculées et celles obtenues expérimentalement dans NaCl et MgO sont en accord qualitatif. La susceptibilité diamagnétique χ, la polarisabilité dipolaire α_d, et le facteur anti-écran de Sterneimer γ_∞ des ions ci-dessus ont été calculés pour les ions libres et pour les ions à «potentiel sphérique» (SPI). Le modèle de la sphère creuse chargée améliore les valeurs théoriques par rapport aux données expérimentales.

I. Introduction

Many physical properties of ionic crystals, as the distribution of electrons, the diamagnetic susceptibility, the dipole polarizability or the quadrupole polarizability of an ionic crystal can be calculated in a first approximation by summing up the corresponding values calculated for the free ions. Free ion properties are

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* D 17 (E. Paschalis, 1967).

obtained using the Hartree-Fock-SCF method. A critical comparison of the experiment and the calculation on the basis of the free ion model by HF-SCF-procedure is not satisfactory. Therefore it was decided to evaluate a number of physical properties of ionic crystals through HF-SCF solutions for ions in a potential of spherical symmetry (SPI).

The physical model for our calculations is a very simple one. To our knowledge this model was first used by Watson [1] to find analytical HF-SCF wave functions for the O^{2-} ion. L. Sachs [2] has used the model to calculate the diamagnetic susceptibility of LiF and NaF. Somewhat different approaches to the problem "ions in crystals" have been proposed by Yamashita and Kojima [3] and by Kristoffel [4].

The calculations reported here were carried out for the closed shell ions Li^+, Be^{2+}, O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+}, S^{2-}, Cl^-, K^+, Ca^{2+}, Sc^{3+} and Ti^{4+}. The program of C. C. J. Roothaan [5] was modified for our purpose [6], to calculate analytical SCF-HF-Roothaan [7, 8] wave functions for the free ions and the SP-ions of interest.

II. The Hartree-Fock-Equation and the Model for the Crystal Potential

For the free ion problem the Hamiltonian of interest has to be formulated as:

$$\hat{H} = -\sum_{i=1}^{N} \left(\frac{1}{2} \nabla_i^2 + \frac{Z}{r_i} \right) + \frac{1}{2} \sum_{i,j=1}^{N}{}' \frac{1}{r_{ij}}, \tag{1}$$

where Z = nuclear charge, ∇_i = Nabla operator for the i'th electron, r_i and r_{ij} are the distances of the i'th electron from the nucleus and from the j'th electron resp. Hartree atomic units are used throughout this paper.

In the approximation presented, we have choosen a spherical symmetric potential around the ion of interest to simulate the environment of the ions in the crystal. This means that the ion is embedded in a hollow sphere which carries an electric charge of the same magnitude but opposite sign as the ion considered. This very simple model fulfills the following conditions: It preserves the symmetry of the free ion and the electroneutrality of the crystal. Furthermore it can be generalized in order to take into account the actual symmetry of the ions in the crystal. The main disadvantages of the model are the neglection of the overlap terms and the somewhat artificial introduction of a radius r_0 of the counter charge sphere.

The charged sphere around the ion creates a potential of the form:

$$\begin{aligned} V &= n/r_0 \quad \text{for} \quad r \leqq r_0, \\ V &= n/r \quad \text{for} \quad r \geqq r_0. \end{aligned} \tag{2}$$

We have choosen the number n of charges as: $n_{\text{sphere}} = -n_{\text{ion}}$ for all ions. Partial compensation of the ionic charge by the charged sphere was used by Watson [1], for the O^{2-} problem. Fig. 1 shows the physical model stated above. Within the sphere with the radius r_0 the potential of the charged sphere is constant. Out of it, it goes with $1/r$ to zero like the potential of a point charge. The Hamiltonian of the ion in the crystal is then:

$$\hat{H}_{\text{in}} = -\sum_{i=1}^{N}\left(\frac{1}{2}\nabla_i^2 + \frac{Z}{r_i} - \frac{n}{r_{i0}}\right) + \frac{1}{2}\sum_{i,j=1}^{N}{}' \frac{1}{r_{ij}}, \tag{3}$$

$$\hat{H}_{\text{out}} = -\sum_{i=1}^{N}\left(\frac{1}{2}\nabla_i^2 + \frac{Z}{r_i} - \frac{n}{r_i}\right) + \frac{1}{2}\sum_{i,j=1}^{N}{}' \frac{1}{r_{ij}}. \tag{4}$$

In the frame of SCF-Roothaan-theory the one electron functions are:

$$\Phi_{i\lambda\alpha} = \sum_{p} C_{i\lambda p}\chi_{p\lambda\alpha} \tag{5}$$

with

$$\chi_{p\lambda\alpha}(r, \vartheta, \varphi) = R_{\lambda p}(r)\, Y_{\lambda\alpha}(\vartheta, \varphi) \tag{6}$$

and

$$R_{\lambda p}(r) = [(2n_{\lambda p})!]^{-1/2}(2\zeta_{\lambda p})^{n_{\lambda p}+1/2} r^{n_{\lambda p}-1}\exp(-\zeta_{\lambda p} r), \tag{7}$$

$i\lambda$ indicates the shell, $C_{i\lambda p}$ is the expansion coefficient for the p'th basis function, α (magnetic quantum number) represents the subspecies of the symmetry λ;

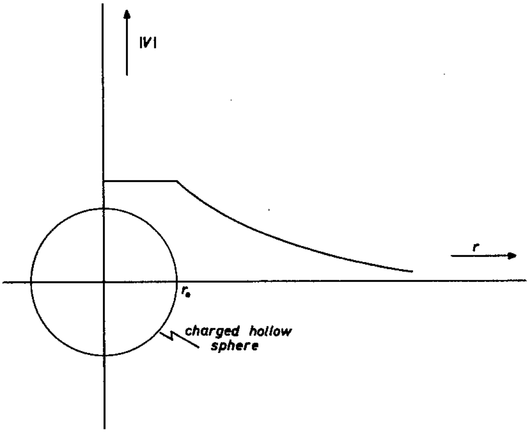

Fig. 1. The potential of a charged hollow sphere with a radius r_0 as a function of r

$R_{\lambda p}(r)$ and $Y_{\lambda\alpha}(\vartheta, \varphi)$ are the radial and the angular part of the basis function resp. The radial basis function is a normalized Slater-type orbital, characterized by the principal quantum number $n_{\lambda p}$ and the orbital exponent $\zeta_{\lambda p}$. $Y_{\lambda\alpha}(\vartheta, \varphi)$ are the normalized spherical harmonics.

First the wave functions for the free ions considered have been refined by $\zeta_{\lambda p}$ and $C_{i\lambda p}$ variation procedure. As a start set the wave functions for the closed shell ions given by Clementi [9] and by Clementi *et al.* [10, 11] have been used. Good agreement with Clementi's coefficients has been found. In some cases slight improvement in energy was reached. Using the optimized free ion basis functions the expansion coefficients have been made self consistent for the ion in the potential. We have also optimized the basis functions for one ion (Be^{2+}) in the potential. This procedure however has not influenced the energy considerably.

The following set of parameters has been choosen for the free ion and for the SP-ion too:

Closed shell $1s^2$: 4 basis functions;

closed shell $1s^2 2s^2 2p^6$: 5 s- and 5 p-basis functions for the anions and 5 s- and 4 p-basis functions for the cations;

closed shell $1s^2 2s^2 2p^6 3s^2 3p^6$: 7 s- and 6 p-basis functions.

The parameter r_0, *i.e.* the radius of the sphere which carries the counter charge of the ion considered, was varied in discrete steps. For six different radii the SP-ion wave functions have been calculated (except for K^+ for which only four radii have been considered).

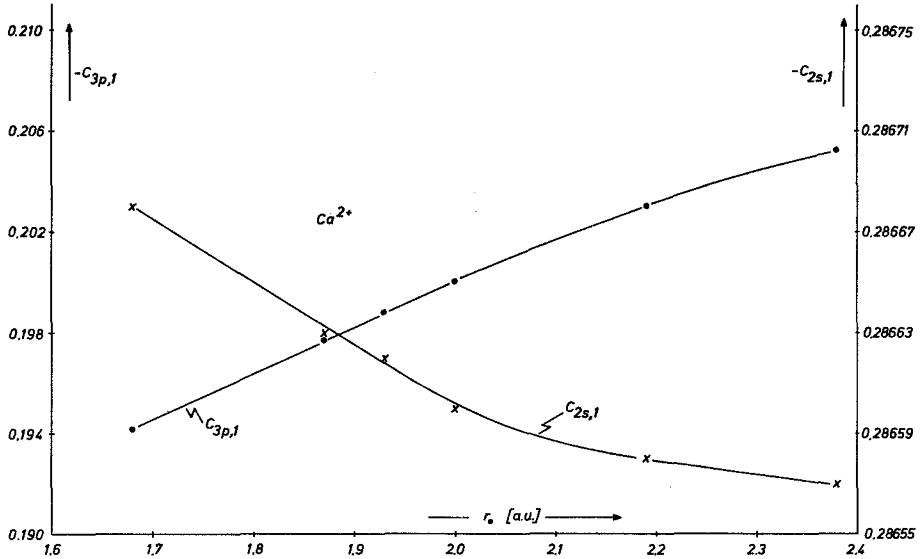

Fig. 2. Expansion coefficients of Ca^{2+} as a function of the hollow sphere radius r_0

Table 1 shows the orbital exponents and the principal quantum numbers of the basis functions. These orbital exponents have been used for the calculation of the expansion coefficients of the SP-ions. The results of these calculations are listed in Table 2 together with the orbital energies and the total energy of the crystal ions. The free ion total energies are given for comparison. In each case one of the radii used is the ion radius, $r_{0,\mathrm{ion}}$ as given by Pauling [12]. It shows up that for all radii lying between $r_{0,\mathrm{min}}$ and $r_{0,\mathrm{max}}$ in the calculations most of the parameters $C_{i\lambda p}$ can be interpolated. In Fig. 2 the change of two $C_{i\lambda p}$ as a function of r_0 is shown graphically. It should be mentioned that in some cases such an interpolation is doubtful. However in these cases these basis functions contribute very little to the energy.

Table 1. *Orbital exponents* $\zeta_{\lambda p}$ *and principal quantum numbers* $n_{\lambda p}$ *of the basis functions*

	Li^+	Be^{2+}	O^{2-} [a]	F^-	Na^+	Mg^{2+}	Al^{3+}	S^{2-}	Cl^-	K^+	Ca^{2+}	Sc^{3+}	Ti^{4+}
1*s*[b]	2.54098	3.32630	7.61690	8.91749	11.22888	10.87648	12.89008	15.76694	17.26298	19.06810	20.08360	20.93470	21.78320
1*s*	3.05814	4.90541	12.22000	14.70270	15.88978	18.77653	19.02694	24.11069	27.33257	27.76203	38.36796	33.10000	34.57420
1*s*	4.45465	7.49012											
1*s*	1.45188	2.19824											
2*s*			2.76150	3.27621	4.39983	4.86040	5.48864	6.71523	15.37845	16.77271	16.66555	18.00780	18.70590
2*s*			7.08980	8.04670	10.44332	11.82459	11.88087	13.92710	6.80846	7.51000	8.45000	8.60000	9.30981
2*s*			1.48610	1.84894	2.83010	3.32310	3.80227						
3*s*								2.61453	5.94375	6.54286	7.42820	7.37980	8.23718
3*s*								1.42984	2.86663	3.55815	3.54404	4.73540	4.83162
3*s*								5.72673	1.67131	2.32541	2.38167	3.20867	3.37930
2*p*			1.55660	2.06361	2.89587	3.39303	3.93395	7.05765	7.64908	8.63410	9.13081	9.58918	10.12014
2*p*			3.43000	3.93632	5.24339	6.03075	6.82608	13.11130	13.92875	15.20120	14.40180	16.47600	16.66123
2*p*			0.43020	1.42784	1.97103	2.47206	2.95071						
2*p*			0.55010	0.97630	11.02211	12.58859	13.85620						
2*p*			8.12680	8.29430									
3*p*								2.57880	5.94114	6.91269	7.59523	7.86514	8.22002
3*p*								0.76380	2.92208	3.18530	3.62548	4.14168	5.06664
3*p*								5.38796	1.85701	1.88513	2.33592	2.83910	3.23640
3*p*								1.82404	1.03740	1.65156	1.95785	2.06791	1.61011

[a] Clementi *et al.* [10]. — [b] The notation 1*s*, 2*s* *etc.* refers to the Slater-type orbital.

Table 2. *Expansion coefficients $C_{i\lambda p}$, orbital energies, and total energy for the free and the crystal ions*

	Li^+	Be^{2+}	O^{2-}		
	C_{1s}	C_{1s}	C_{1s}	C_{2s}	C_{2p}
r_0	∞	∞		∞[a]	
	1.06423	0.83892	0.89703	0.20153	0.59510
	-0.21832	0.16445	0.06383	0.01235	0.29159
	0.15640	0.02622	0.00417	-0.70969	0.51530
	0.01289	-0.01896	0.05143	0.08239	-0.13422
			-0.00059	-0.40236	0.01046
$-\varepsilon_{i\lambda}$	2.79236	5.66714	20.0476	0.6286	-0.1255
$-E_{\mathrm{tot}}$	7.2364137	13.611292		74.48442	
r_0	1.247	0.700		2.646	
	0.86603	0.45234	0.89246	0.18957	0.75442
	-0.05216	0.34886	0.06230	0.01239	0.25982
	0.13366	-0.00582	0.00553	-0.62987	-0.12482
	0.07392	0.23533	0.05795	0.07659	0.18264
			-0.00096	-0.47698	0.01668
$-\varepsilon_{i\lambda}$	2.00321	2.93343	20.16716	0.93979	0.22474
$-E_{\mathrm{tot}}$	5.6451517	8.0544506		81.511375	
r_0	1.134	0.640		2.570	
	0.81315	0.36057	0.89234	0.18680	0.76505
	-0.01638	0.37507	0.06234	0.01394	0.25923
	0.13087	-0.00742	0.00560	-0.63429	-0.09106
	0.09635	0.30792	0.05803	0.07945	0.13776
			-0.00098	-0.47329	0.01686
$-\varepsilon_{i\lambda}$	1.93237	2.73168	20.15721	0.94339	0.22676
$-E_{\mathrm{tot}}$	5.4955386	7.6118464		81.685078	
r_0	1.020	0.590		2.495	
	0.75945	0.27261	0.89212	0.18369	0.77526
	0.01151	0.39362	0.06240	0.01572	0.25909
	0.13111	-0.00694	0.00568	-0.63982	-0.05656
	0.12535	0.38204	0.05812	0.08276	0.09225
			-0.00101	-0.46860	0.01696
$-\varepsilon_{i\lambda}$	1.84975	2.54945	20.14632	0.94702	0.22851
$-E_{\mathrm{tot}}$	5.3174510	7.2025899		81.863175	

[a] Clementi *et al.* [10].

	F^-			Na^+		
	C_{1s}	C_{2s}	C_{2p}	C_{1s}	C_{2s}	C_{2p}
r_0		∞			∞	
	0.89484	-0.20216	-0.49246	0.82735	-0.17405	0.53073
	0.03599	-0.00801	-0.30720	0.06332	-0.03229	0.30998
	0.00396	0.62921	-0.06074	0.00628	0.47480	0.22400
	0.08595	-0.09699	-0.26372	0.13011	-0.13113	0.01344
	-0.00035	0.48245	-0.01704	-0.00116	0.62651	
$-\varepsilon_{i\lambda}$	25.82940	1.07432	0.18076	40.75990	3.07375	1.79720
$-E_{\mathrm{tot}}$		99.459363			161.67689	

Table 2 (continued)

	F^-			Na^+		
	C_{1s}	C_{2s}	C_{2p}	C_{1s}	C_{2s}	C_{2p}
r_0		2.646			1.984	
	0.89456	−0.20080	−0.34476	0.82736	−0.17432	0.52078
	0.03609	−0.00792	−0.32578	0.06332	−0.03216	0.31296
	0.00417	0.61647	−0.42223	0.00626	0.47506	0.23241
	0.08610	−0.09558	0.00458	0.13011	−0.13103	0.01298
	−0.00040	0.49422	−0.01587	−0.00115	0.62625	
$-\varepsilon_{i\lambda}$	26.08143	1.37259	0.48161	40.26465	2.57478	1.29865
$-E_{\text{tot}}$		103.14911			156.64369	
r_0		2.570			1.795	
	0.89454	−0.20035	−0.35136	0.82737	−0.17478	0.51256
	0.03610	−0.00812	−0.32380	0.06332	−0.03188	0.31531
	0.00419	0.61649	−0.42214	0.00624	0.47492	0.23947
	0.08612	−0.09594	0.01133	0.13011	−0.13073	0.01263
	−0.00040	0.49428	−0.01624	−0.00115	0.62633	
$-\varepsilon_{i\lambda}$	26.08020	1.37643	0.48510	40.22002	2.52659	1.25094
$-E_{\text{tot}}$		103.24729			156.12230	
r_0		2.513			1.607	
	0.89451	−0.19995	−0.35793	0.82740	−0.17594	0.49823
	0.03611	−0.00830	−0.32202	0.06330	−0.03117	0.31922
	0.00421	0.61667	−0.41985	0.00620	0.47415	0.25191
	0.08613	−0.09630	0.01553	0.13010	−0.12993	0.01204
	−0.00041	0.49419	−0.01656	−0.00113	0.62688	
$-\varepsilon_{i\lambda}$	26.07882	1.37926	0.48760	40.17097	2.47064	1.19597
$-E_{\text{tot}}$		103.32387			155.48832	

	Mg^{2+}			Al^{3+}		
	C_{1s}	C_{2s}	C_{2p}	C_{1s}	C_{2s}	C_{2p}
r_0		∞			∞	
	1.03536	−0.22276	0.54565	0.88794	−0.22236	0.55606
	0.03700	−0.02673	0.28809	0.05135	−0.01824	0.26195
	0.00714	0.42858	0.22063	0.00584	0.39526	0.22887
	−0.08025	−0.08939	0.01024	0.07365	−0.12443	0.00876
	−0.00189	0.66506		−0.00118	0.71084	
$-\varepsilon_{i\lambda}$	49.76833	4.48278	3.00594	59.79106	6.15103	4.47222
$-E_{\text{tot}}$		198.83071			240.00032	
r_0		1.361			1.039	
	1.03546	−0.22746	0.48001	0.88827	−0.24195	0.37463
	0.03698	−0.02450	0.30525	0.05124	−0.00624	0.30749
	0.00699	0.42399	0.27656	0.00541	0.36318	0.38246
	−0.08029	−0.08516	0.00780	0.07354	−0.10570	0.00236
	−0.00182	0.66871		−0.00097	0.73550	
$-\varepsilon_{i\lambda}$	48.36374	3.05047	1.57820	57.11067	3.38767	1.72422
$-E_{\text{tot}}$		184.21409			211.46081	

Table 2 (continued)

	Mg^{2+}			Al^{3+}		
	C_{1s}	C_{2s}	C_{2p}	C_{1s}	C_{2s}	C_{2p}
r_0		1.228			0.945	
	1.03558	−0.23224	0.43803	0.88857	−0.25504	0.28687
	0.03695	−0.02217	0.31523	0.05112	0.00192	0.32682
	0.00687	0.41789	0.31309	0.00514	0.33884	0.45858
	−0.08035	−0.08062	0.00640	0.07341	−0.09264	−0.00027
	−0.00176	0.67368		−0.00085	0.75444	
$-\varepsilon_{i\lambda}$	48.25657	2.92190	1.45341	56.95461	3.18394	1.52961
$-E_{tot}$		182.70312			208.86374	
r_0		1.096			0.850	
	1.03583	−0.24114	0.37433	0.88910	−0.27530	0.16532
	0.03687	−0.01777	0.32920	0.05091	0.01470	0.35107
	0.00666	0.40539	0.36932	0.00472	0.29827	0.56555
	−0.08048	−0.07198	0.00448	0.07317	−0.07184	−0.00350
	−0.00166	0.68394		−0.00065	0.78612	
$-\varepsilon_{i\lambda}$	48.15185	2.78118	1.31917	56.81129	2.97040	1.32943
$-E_{tot}$		180.90620			205.82916	

	S^{2-}				
	C_{1s}	C_{2s}	C_{3s}	C_{2p}	C_{3p}
r_0			∞		
	0.92660	−0.26494	0.07909	0.65868	−0.14170
	0.03566	−0.00506	−0.00141	0.03797	−0.00678
	0.00435	0.79698	−0.22967	0.00953	0.18654
	0.04736	−0.13060	0.03285	0.00003	0.49526
	0.00016	0.00806	0.68777	0.37200	−0.08085
	−0.00008	−0.00106	0.46587	−0.00124	0.51661
	−0.00108	0.35034	−0.18650		
$-\varepsilon_{i\lambda}$	91.46614	8.46134	0.36254	6.14172	−0.12956
$-E_{tot}$			397.34251		
r_0			3.817		
	0.92650	−0.26480	0.07739	0.65813	−0.17159
	0.03570	−0.00503	−0.00204	0.03798	−0.00107
	0.00439	0.79567	−0.21868	0.01002	−0.05031
	0.04742	−0.13032	0.03013	−0.00001	0.22339
	0.00016	0.00900	0.63721	0.37235	−0.03683
	−0.00008	−0.00114	0.51239	−0.00118	0.91773
	−0.00110	0.35106	−0.18024		
$-\varepsilon_{i\lambda}$	91.67192	8.68204	0.68230	6.36385	0.19884
$-E_{tot}$			406.43538		

Table 2 (continued)

	S^{2-}				
	C_{1s}	C_{2s}	C_{3s}	C_{2p}	C_{3p}
r_0			3.477		
	0.92647	−0.26477	0.08064	0.65787	−0.17488
	0.03571	−0.00501	−0.00364	0.03798	−0.00112
	0.00440	0.79528	−0.21355	0.01052	−0.06559
	0.04744	−0.13023	0.02662	0.00001	0.17327
	0.00016	0.00935	0.65244	0.37244	−0.03695
	−0.00008	−0.00121	0.50011	−0.00135	0.96504
	−0.00110	0.35125	−0.18962		
$-\varepsilon_{i\lambda}$	91.64421	8.66118	0.68811	6.34261	0.20318
$-E_{\text{tot}}$			407.23991		
r_0			3.137		
	0.92644	−0.26473	0.08623	0.65745	−0.17685
	0.03573	−0.00499	−0.00622	0.03798	−0.00209
	0.00442	0.79468	−0.20626	0.01141	−0.05656
	0.04746	−0.13008	0.02111	0.00004	0.12328
	0.00016	0.00991	0.68362	0.37257	−0.04412
	−0.00008	−0.00133	0.47414	−0.00169	0.99172
	−0.00111	0.35152	−0.20603		
$-\varepsilon_{i\lambda}$	91.60249	8.63036	0.69235	6.31096	0.20312
$-E_{\text{tot}}$			408.17367		

	Cl^{-}				
	C_{1s}	C_{2s}	C_{3s}	C_{2p}	C_{3p}
r_0			∞		
	0.91476	−0.25536	0.07479	0.65426	−0.16262
	0.01841	−0.00573	0.00192	0.03730	−0.00938
	0.08149	−0.13944	0.04489	0.37184	−0.11307
	0.00335	0.89295	−0.28811	0.01282	0.32551
	−0.00083	0.23869	−0.15134	−0.00270	0.50974
	0.00007	0.00633	0.69647	0.00053	0.31979
	−0.00004	−0.00040	0.45171		
$-\varepsilon_{i\lambda}$	104.50479	10.22848	0.73263	7.69489	0.14968
$-E_{\text{tot}}$			459.57669		
r_0			3.761		
	0.91474	−0.25531	0.07471	0.65412	−0.17116
	0.01842	−0.00573	0.00169	0.03731	−0.00741
	0.08151	−0.13940	0.04408	0.37192	−0.09907
	0.00336	0.89265	−0.28524	0.01295	0.26880
	−0.00083	0.23886	−0.15124	−0.00269	0.63124
	0.00007	0.00656	0.68726	0.00052	0.22401
	−0.00004	−0.00043	0.46040		
$-\varepsilon_{i\lambda}$	104.69533	10.42347	0.95238	7.89008	0.37041
$-E_{\text{tot}}$			464.29694		

Table 2 (continued)

	Cl$^-$				
	C_{1s}	C_{2s}	C_{3s}	C_{2p}	C_{3p}
r_0			3.420		
	0.91472	−0.25529	0.07533	0.65402	−0.17357
	0.01843	−0.00573	0.00134	0.03731	−0.00706
	0.08151	−0.13937	0.04320	0.37196	−0.09651
	0.00336	0.89249	−0.28343	0.01308	0.25542
	−0.00084	0.23896	−0.15365	−0.00272	0.66782
	0.00007	0.00669	0.68933	0.00052	0.19115
	−0.00004	−0.00046	0.45903		
$-\varepsilon_{i\lambda}$	104.68797	10.41896	0.95975	7.88549	0.37698
$-E_{\text{tot}}$			464.73356		
r_0			3.080		
	0.91471	−0.25526	0.07671	0.65387	−0.17583
	0.01843	−0.00573	0.00067	0.03731	−0.00698
	0.08152	−0.13932	0.04159	0.37202	−0.09593
	0.00337	0.89223	−0.28056	0.01334	0.24663
	−0.00084	0.23910	−0.15899	−0.00280	0.70423
	0.00006	0.00691	0.69738	0.00053	0.15378
	−0.00004	−0.00051	0.45273		
$-\varepsilon_{i\lambda}$	104.67193	10.40772	0.96564	7.87400	0.38081
$-E_{\text{tot}}$			465.24467		

	K$^+$				
	C_{1s}	C_{2s}	C_{3s}	C_{2p}	C_{3p}
r_0			∞		
	0.91901	−0.27132	0.08650	0.66806	−0.21089
	0.02922	−0.00423	0.00308	0.04231	−0.01112
	0.06493	−0.14232	0.05466	0.34668	−0.12165
	0.00125	0.98566	−0.36384	0.01418	0.61218
	0.00022	0.14813	−0.15659	−0.01345	0.55384
	−0.00033	0.00596	0.65939	0.00898	−0.05885
	0.00012	−0.00008	0.50599		
$-\varepsilon_{i\lambda}$	133.75322	14.70886	1.96383	11.73901	1.17049
$-E_{\text{tot}}$			599.01722		
r_0			2.513		
	0.91902	−0.27134	0.08605	0.66812	−0.20862
	0.02922	−0.00423	0.00336	0.04231	−0.01167
	0.06493	−0.14233	0.05520	0.34664	−0.12497
	0.00125	0.98574	−0.36493	0.01412	0.62887
	0.00023	0.14809	−0.15515	−0.01344	0.43476
	−0.00033	0.00589	0.65832	0.00898	0.05204
	0.00012	−0.00006	0.50654		
$-\varepsilon_{i\lambda}$	133.37484	14.32851	1.57670	11.35874	0.78413
$-E_{\text{tot}}$			591.86598		

Table 2 (continued)

	K^+				
	C_{1s}	C_{2s}	C_{3s}	C_{2p}	C_{3p}
r_0			2.450		
	0.91902	−0.27135	0.08595	0.66813	−0.20837
	0.02922	−0.00423	0.00342	0.04231	−0.01171
	0.06493	−0.14233	0.05531	0.34664	−0.12521
	0.00125	0.98575	−0.36514	0.01411	0.63042
	0.00022	0.14808	−0.15480	−0.01342	0.42097
	−0.00033	0.00587	0.65790	0.00897	0.06523
	0.00012	−0.00006	0.50681		
$-\varepsilon_{i\lambda}$	133.36851	14.32178	1.56878	11.35204	0.77638
$-E_{\text{tot}}$			591.69448		
r_0			2.050		
	0.91904	−0.27138	0.08444	0.66826	−0.20630
	0.02921	−0.00423	0.00427	0.04230	−0.01187
	0.06492	−0.14236	0.05685	0.34656	−0.12615
	0.00124	0.98597	−0.36788	0.01391	0.64023
	0.00023	0.14797	−0.14960	−0.01321	0.29956
	−0.00033	0.00568	0.65037	0.00883	0.18467
	0.00012	−0.00000	0.51208		
$-\varepsilon_{i\lambda}$	133.33036	14.27849	1.51114	11.30909	0.72130
$-E_{\text{tot}}$			590.32027		

	Ca^{2+}				
	C_{1s}	C_{2s}	C_{3s}	C_{2p}	C_{3p}
r_0			∞		
	0.95228	−0.28656	0.09678	0.62610	−0.20971
	0.00704	0.00195	0.00013	0.07016	−0.02174
	0.05358	−0.16025	0.06630	0.35384	−0.14293
	−0.00114	0.90810	−0.35630	0.02539	0.54121
	0.00103	0.25745	−0.17676	−0.02129	0.54720
	−0.00039	0.01037	0.85851	0.01160	0.01796
	0.00015	−0.00252	0.28137		
$-\varepsilon_{i\lambda}$	149.91566	17.36958	2.77785	14.17891	1.87676
$-E_{\text{tot}}$			676.15367		
r_0			2.000		
	0.95229	−0.28660	0.09561	0.62633	−0.20008
	0.00703	0.00195	0.00054	0.07015	−0.02463
	0.05357	−0.16032	0.06877	0.35371	−0.15484
	−0.00116	0.90846	−0.36140	0.02510	0.60002
	0.00104	0.25727	−0.16818	−0.02116	0.28065
	−0.00039	0.01004	0.84309	0.01157	0.24792
	0.00015	−0.00240	0.29420		
$-\varepsilon_{i\lambda}$	148.99001	16.43441	1.81683	13.24453	0.92065
$-E_{\text{tot}}$			658.24623		

Table 2 (continued)

	Ca^{2+}				
	C_{1s}	C_{2s}	C_{3s}	C_{2p}	C_{3p}
r_0			1.871		
	0.95230	−0.28663	0.09499	0.62645	−0.19775
	0.00703	0.00195	0.00074	0.07015	−0.02503
	0.05357	−0.16037	0.06996	0.35366	−0.15657
	−0.00116	0.90866	−0.36375	0.02491	0.61326
	0.00105	0.25716	−0.16375	−0.02101	0.20020
	−0.00039	0.00986	0.83423	0.01149	0.32097
	0.00015	−0.00233	0.30167		
$-\varepsilon_{i\lambda}$	148.95713	16.39631	1.76638	13.20690	0.87307
$-E_{\text{tot}}$			657.05292		
r_0			1.680		
	0.95232	−0.28668	0.09355	0.62674	−0.19419
	0.00703	0.00195	0.00117	0.07013	−0.02517
	0.05355	−0.16047	0.07252	0.35353	−0.15731
	−0.00118	0.90915	−0.36866	0.02443	0.63027
	0.00106	0.25690	−0.15365	−0.02059	0.06072
	−0.00039	0.00945	0.81261	0.01128	0.45236
	0.00015	−0.00216	0.32007		
$-\varepsilon_{i\lambda}$	148.91991	16.34659	1.69009	13.15833	0.80372
$-E_{\text{tot}}$			655.03063		

	Sc^{3+}				
	C_{1s}	C_{2s}	C_{3s}	C_{2p}	C_{3p}
r_0			∞		
	0.94343	−0.28510	0.10095	0.68501	−0.24184
	0.01951	−0.00139	0.00114	0.04663	−0.01518
	0.04734	−0.15627	0.06352	0.31870	−0.14806
	0.00184	0.98632	−0.39260	0.01302	0.43061
	−0.00048	0.17459	−0.22860	−0.00416	0.62868
	0.00004	−0.00519	0.40831	0.00106	0.05548
	−0.00004	0.00439	0.80216		
$-\varepsilon_{i\lambda}$	167.09071	20.29577	3.71329	16.88289	2.70359
$-E_{\text{tot}}$			758.21453		
r_0			1.720		
	0.94348	−0.28525	0.09753	0.68541	−0.22749
	0.01949	−0.00136	0.00285	0.04662	−0.01838
	0.04731	−0.15631	0.06850	0.31851	−0.16954
	0.00182	0.98688	−0.40249	0.01245	0.53408
	−0.00046	0.17450	−0.20732	−0.00392	0.36128
	0.00004	−0.00594	0.38149	0.00101	0.25748
	−0.00004	0.00456	0.81688		
$-\varepsilon_{i\lambda}$	165.48650	18.67108	2.04261	15.25981	1.04396
$-E_{\text{tot}}$			727.02658		

Table 2 (continued)

	Sc^{3+}				
	C_{1s}	C_{2s}	C_{3s}	C_{2p}	C_{3p}
r_0			1.531		
	0.94353	−0.28539	0.09348	0.68581	−0.22101
	0.01948	−0.00134	0.00476	0.04662	−0.01882
	0.04728	−0.15638	0.07400	0.31835	−0.17321
	0.00179	0.98748	−0.41299	0.01176	0.57037
	−0.00044	0.17438	−0.18104	−0.00355	0.22408
	0.00003	−0.00671	0.34418	0.00092	0.37350
	−0.00004	0.00474	0.83834		
$-\varepsilon_{i\lambda}$	165.40306	18.56637	1.89814	15.15698	0.91163
$-E_{\mathrm{tot}}$			723.39318		
r_0			1.380		
	0.94359	−0.28556	0.08786	0.68635	−0.21522
	0.01945	−0.00133	0.00730	0.04662	−0.01840
	0.04724	−0.15648	0.08126	0.31816	−0.17108
	0.00175	0.98829	−0.42642	0.01074	0.58888
	−0.00042	0.17422	−0.14370	−0.00294	0.10200
	0.00002	−0.00774	0.28771	0.00073	0.48662
	−0.00003	0.00501	0.87149		
$-\varepsilon_{i\lambda}$	165.36321	18.49758	1.78454	15.09095	0.81457
$-E_{\mathrm{tot}}$			719.98088		

	Ti^{4+}				
	C_{1s}	C_{2s}	C_{3s}	C_{2p}	C_{3p}
r_0			∞		
	0.94983	−0.29145	0.11160	0.68807	−0.24715
	0.02169	−0.00104	−0.00155	0.04941	−0.01944
	0.03613	−0.15898	0.05779	0.32149	−0.18992
	0.00388	0.93886	−0.36507	−0.00687	0.31024
	−0.00188	0.22675	−0.26991	0.00699	0.82384
	0.00062	0.00379	0.52203	−0.00149	0.01242
	−0.00028	0.00186	0.68864		
$-\varepsilon_{i\lambda}$	185.27865	23.48742	4.76832	19.85129	3.65101
$-E_{\mathrm{tot}}$			845.18984		
r_0			1.410		
	0.94995	−0.29175	0.10026	0.68895	−0.23079
	0.02165	−0.00102	0.00377	0.04944	−0.02078
	0.03606	−0.15921	0.07425	0.32137	−0.20116
	0.00381	0.94040	−0.39604	−0.00840	0.36005
	−0.00183	0.22638	−0.20890	0.00735	0.67616
	0.00061	0.00183	0.43069	−0.00155	0.17489
	−0.00028	0.00246	0.74889		
$-\varepsilon_{i\lambda}$	182.80470	20.95442	2.12685	17.32392	1.03866
$-E_{\mathrm{tot}}$			794.77290		

Table 2 (continued)

	Ti^{4+}				
	C_{1s}	C_{2s}	C_{3s}	C_{2p}	C_{3p}
r_0			1.285		
	0.95002	−0.29192	0.09363	0.68950	−0.22797
	0.02163	−0.00102	0.00672	0.04946	−0.01894
	0.03601	−0.15937	0.08331	0.32130	−0.18987
	0.00377	0.94136	−0.41255	−0.00937	0.34944
	−0.00180	0.22612	−0.17209	0.00761	0.63792
	0.00061	0.00068	0.37030	−0.00157	0.23252
	−0.00028	0.00283	0.78946		
$-\varepsilon_{i\lambda}$	182.75140	20.86506	1.98589	17.23824	0.91599
$-E_{\text{tot}}$			790.53165		
r_0			1.090		
	0.95020	−0.29229	0.07687	0.69098	−0.22387
	0.02157	−0.00103	0.01362	0.04950	−0.01264
	0.03590	−0.15988	0.10416	0.32112	−0.14681
	0.00366	0.94402	−0.44862	−0.01213	0.28305
	−0.00172	0.22527	−0.07621	0.00853	0.58883
	0.00059	−0.00227	0.19633	−0.00171	0.34088
	−0.00027	0.00386	0.90807		
$-\varepsilon_{i\lambda}$	182.72684	20.74330	1.77983	17.12721	0.75793
$-E_{\text{tot}}$			782.08809		

III. Diamagnetic Susceptibility, Dipole Polarizability and Antishielding Factor

As shown by Van Vleck [13] the diamagnetic susceptibility, χ, may be calculated by perturbation methods. For closed shell ions with N electrons χ results as:

$$\chi = -\frac{e^2}{6mc^2} \sum_{p=1}^{N} \overline{r_p^2} \tag{8}$$

where e is the electron charge, m the electron mass, c the velocity of light and r_p the radial coordinate of the electron p. Eq. (8) shows that the diamagnetic susceptibility of an ion is a sensitive measure for the mean diameter of the orbitals. Both χ-values for the free ion and for the ion in the potential have been calculated. The matrix elements:

$$\overline{r_p^2} = \langle \Phi_{i\lambda\alpha} | r_p^2 | \Phi_{i\lambda\alpha} \rangle$$

are easily obtained from the analytical wave functions. Crystal ion susceptibilities have been calculated by SCF methods first by L. Sachs for Na^+ and F^- [2].

From the different multipole polarizabilities we have calculated only the dipole polarizability α_d. During the last years a number of calculations of α_d of closed shell ions have been published and the literature about these calculations is extensively covered by Langhoff and Hurst [14].

We have used perturbation theory in calculating the dipole polarizabilities for the free ions and the ions in the crystals. The energy created by the external field F within the polarizable ions is proportional to F:

$$\Delta E = -\frac{1}{2}\alpha_d F^2 .$$

The proportionality factor α_d is called the dipole polarizability. From Buckingham's theory [15] the polarizability follows in the form:

$$\alpha_d = \frac{4}{9} \sum_{\varrho} (\overline{R_e^2})^2 \qquad [\mathrm{a.u.}] \,. \tag{9}$$

The summation over ϱ has to consider all occupied states. Eq. (9) takes the fact into consideration that the polarization of the electrons depends on the quantum level ϱ they occupy.

As a third parameter we have calculated with the aid of "crystal ion" wave functions also the antishielding factor γ_∞ (Sternheimer factor); unfortunately this factor is not directly accesible to the experiment. On the other side the interpretation of quadrupole coupling constant, in view of the nuclear quadrupole moment or the crystal field, depends heavely on the antishielding factor used. Beside the basic work by Sternheimer [16] numerous calculations of this factor have been performed [17]. The method, Sternheimer has used, is the numerical integration of the differential equations obtained by perturbation theory. Another method is the use of the variational procedure first discussed by Das and Bersohn [18]. In this paper the method given by Das and Bersohn in its simplest form is applied.

Per definitionem the antishielding factor γ_∞ is defined by the equation

$$V_{ZZ} = V_{ZZ}^0 (1 - \gamma_\infty) \,. \tag{10}$$

V_{ZZ}^0 is the electric field gradient created by all electric charges outside the ion considered at the site of its nucleus. This external gradient is amplified by the polarized core and therefore an effective gradient V_{ZZ} interacts with the nuclear quadrupole moment. For most ions this amplification factor is bigger than one (antishielding). Symmetry considerations show that the s-orbitals contribute to the quadrupole shielding only through the angular excitations $ns \rightarrow d$. The p-orbitals undergo not only an angular but also a radial excitation namely $np \rightarrow f$ and $np \rightarrow p$ respectively [18].

During the last years the calculation of the antishielding factor for free ions have been considerably improved by the coupled Hartree-Fock approximation, see Dalgarno [17]. Burns and Wikner [19] using crystal ion wave functions, as those of Watson for O^{2-} [1], of Yamashita and Kojima for F^- [3], *etc.*, have calculated the antishielding factor for a few crystal ions. The differences between the γ_∞-values obtained using the "contracted" wave functions and the free ion wave functions are very considerable.

IV. Discussion

1. The Electron Density Distribution

From Table 2 it follows that the total energy of the ions in the crystal changes appreciably compared with the free ions values. This change seems to be a steady one as a function of the radius r_0 of the potential well. In Fig. 3 the difference of the total energy of the free ion K^+ and the SP-ion is shown as a function of r_0 (charged sphere radius). For the radius $r_0 \rightarrow 0$, the energy approaches the total energy of the free value of the rare gas atom next to the ion considered.

The radial electron distribution of the ions can easily be calculated from the functions given in Eqs. (5—7) and from the coefficients given in Tables 1 and 2. The radial electron density is given by

$$P^2(r) = \sum_{i\lambda} \sum_{pq} C_{i\lambda p} C_{i\lambda q} r^2 R_{\lambda p}(r) R_{\lambda q}(r) \cdot N_\lambda \tag{11}$$

with N_λ = the occupation number of the shell $i\lambda$ (with the symmetry λ). In Fig. 4 $P^2(r)$ of Cl^- and Ca^{2+} are given for the free ion and the SP-ion with a radius of the potential well $r_0 = 3.420$ and 1.871 resp. One recognizes that the perturbation due to the potential generates a contraction of the anions and an expansion for the

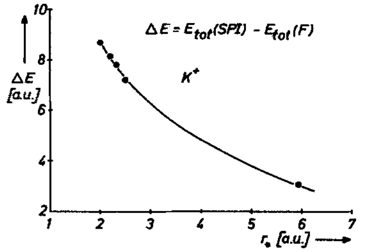

Fig. 3. The difference of the total energies of the potassium ion within the potential well, $E_{\mathrm{tot}}(\mathrm{SPI})$, and the free ion, $E_{\mathrm{tot}}(\mathrm{F})$, as a function of r_0

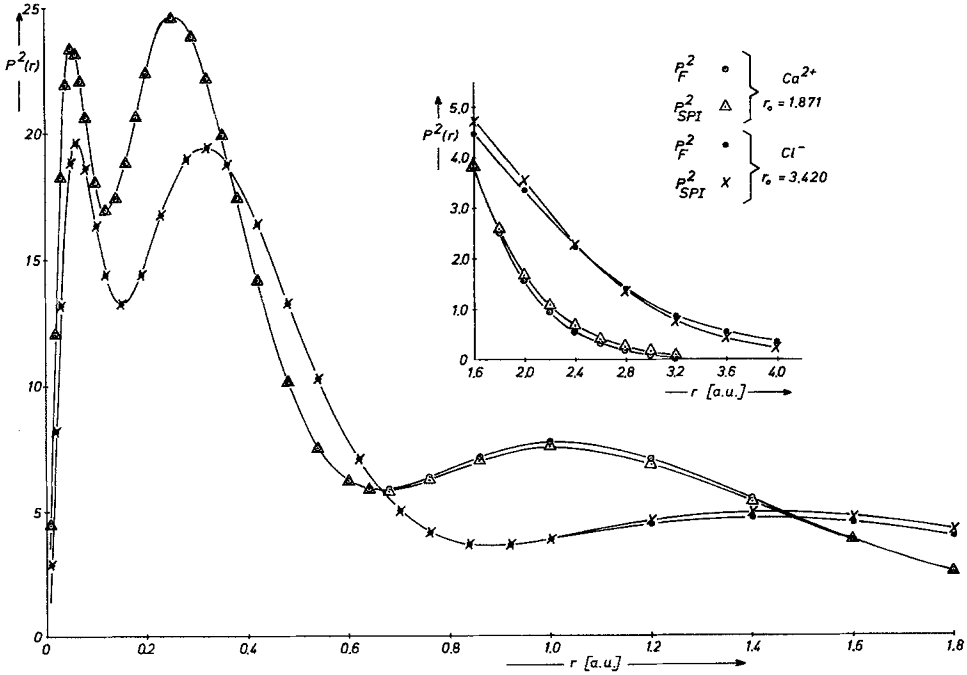

Fig. 4. The radial electron density distribution of Cl^- and Ca^{2+} for the free ions, F, and the SP-ions, SPI.

P^2_{F} ⊙ } Ca^{2+} P^2_{F} ● } Cl^-
P^2_{SPI} △ } $r_0 = 1.871$ P^2_{SPI} × } $r_0 = 3.420$

cations. This is an expected result, since the charged hollow sphere reduces or raises the total Hartree-Fock potential for the cations and anions resp. This perturbation of the radial electron density as a function of the radius of the hollow sphere is given in Fig. 5. These curves show the same behaviour as those of the energy (see Fig. 3); the bigger the radius the smaller the deviation from the free ion value. Given the difference $\Delta P^2(r)$ defined as:

$$\Delta P^2(r) = P^2_{\mathrm{SPI}}(r) - P^2_{\mathrm{F}}(r) \tag{12}$$

where $P^2_{\mathrm{SPI}}(r)$ and $P^2_{\mathrm{F}}(r)$ is the radial electron density of the SP- and the free ion resp., one recognizes the expansion or contraction of the ions by considering the sign of $\Delta P^2(r)$.

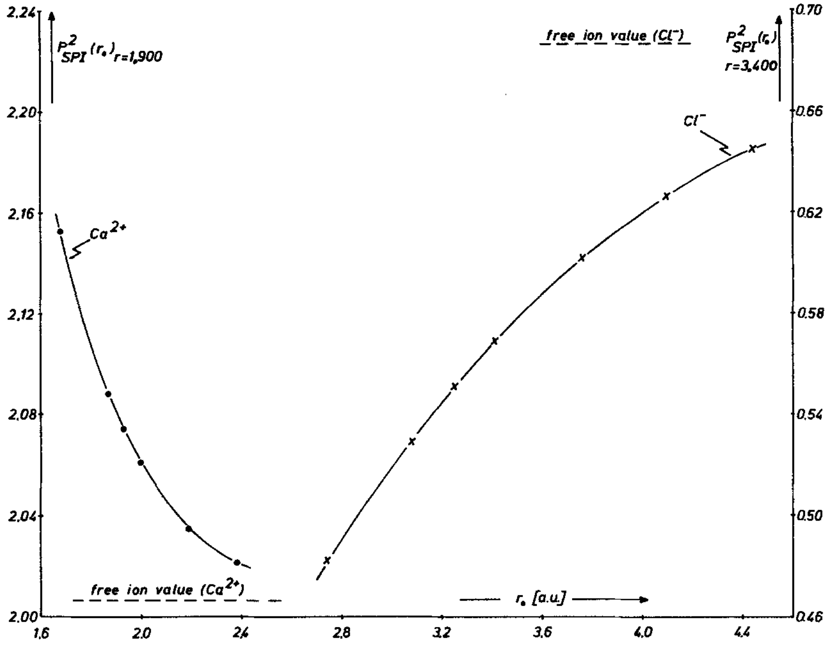

Fig. 5. The radial electron density $P^2_{\mathrm{SPI}}(r)$ of Ca^{2+} and Cl^- at $r = 1.900$ and $r = 3.400$ resp., as a function of the hollow sphere radius r_0. ● Ca^{2+}; × Cl^-

For comparison with the experimental evidence we consider the results of Burley's investigation of the electron density distribution in MgO-crystals [20]. The electron density distribution for Mg^{2+} in this compound obtained by Fourier transformation of the scattering factor for the free ion and the ion in MgO demonstrates qualitative agreement with our results, see Fig. 6. Although the theoretical curve has to have two maxima, the first one is very sharp and cannot be resolved by the Fourier transformation. The difference $\Delta P^2(r)$ defined by:

$$\Delta P^2(r) = P^2_{\mathrm{EXP}}(r) - P^2_{\mathrm{SCF}}(r) \tag{13}$$

where $P^2_{\mathrm{EXP}}(r)$ is the experimental electron density and $P^2_{\mathrm{SCF}}(r)$ is the free ion

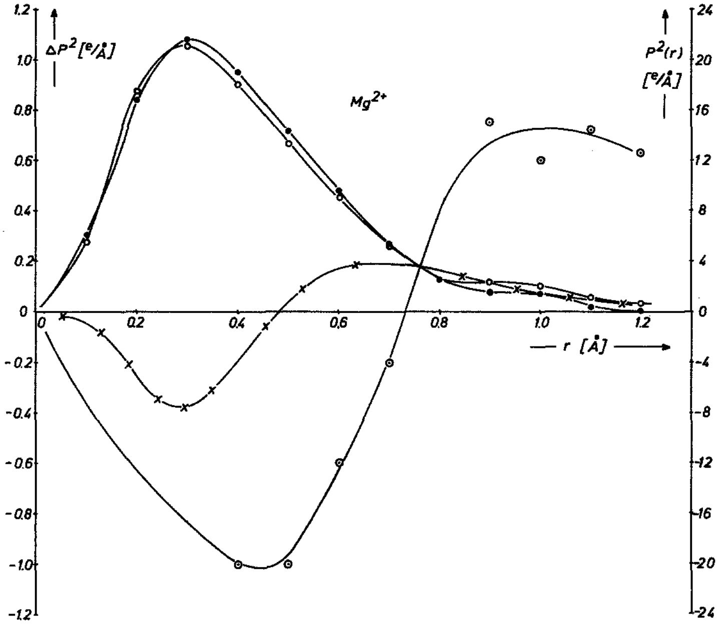

Fig. 6. The radial electron density distribution for Mg^{2+} obtained as Fourier transform of the atomic scattering factor by Burley [20] and the differences $\Delta P^2(r)$ defined by Eqs. (12) and (13).

P^2_{SCF} ●
P^2_{EXP} ○ } Burley [20]; × ΔP^2, this paper
ΔP^2 ⊙

Hartree-Fock density both obtained by Burley, is also drawn in Fig. 6 together with the difference $\Delta P^2(r)$ defined by Eq. (12). The two curves are in qualitative agreement. We have however smoothed somewhat the experimental results. Burley finds additionally a sharp maximum of $\Delta P^2(r)$ for $r \cong 0.2$ Å. Another experimental investigation also shows the expansion of the cations and the contraction of the anions. Schoknecht [21] has compared from his X-ray investigations of the electron density distribution in NaCl $P^2_{EXP}(r)$ and $P^2_{SCF}(r)$ (free ion) for the anion and the cation. In Fig. 7 the difference between SCF calculations and the experimental values of $P^2(r)$, Eq. (13), is compared with $\Delta P^2(r)$ from our calculations, Eq. (12). Again a qualitative agreement is found.

There is another possibility to indicate the contraction and the expansion of the anions and the cations resp. One can compare the integral over the atomic scattering factor with the mean reciprocal radius of the ion using the Obata-Silverman rule [22]. Such a comparison was made by Ruffa [23] who used the experimental results of Burley [20]. He concludes an expansion of Mg^{2+} in MgO.

2. The Diamagnetic Susceptibility

The diamagnetic susceptibility can be calculated for free ions and for ions in crystals. The experiment on the other side gives only the total susceptibility of the crystal, that is:

$$\sum_{i,j} [\chi_i\,(\text{cation}) + \chi_j(\text{anion})]\,.$$

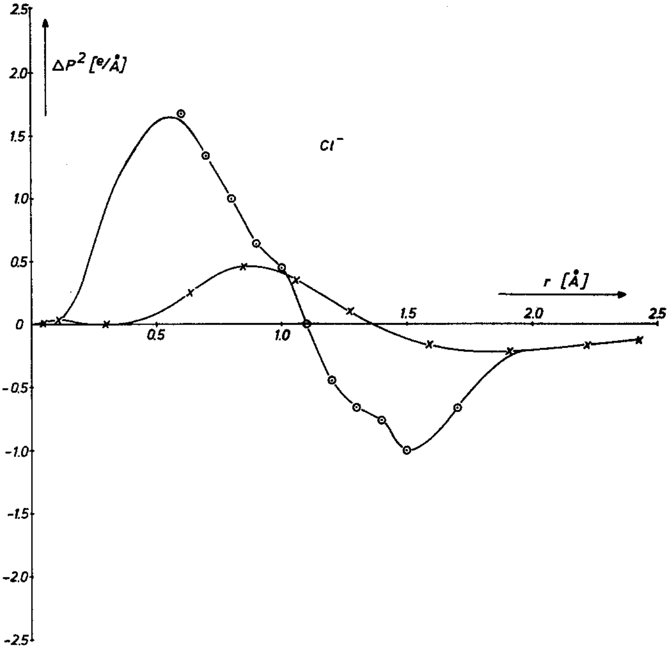

Fig. 7. Comparison between the radial deformation of Cl^- calculated here and the experiment. ⊙ Schoknecht [21], × this paper

To obtain the individual ionic susceptibilities from the crystal susceptibility measured, an empirical partition of the sum into a cation and an anion part has to be made. Different approaches of extracting the ionic susceptibility from experimental values have been used. A critical review of the methods is given by Myers [24]. Today the ion susceptibility set of Brindley and Hoare [25] is generally accepted in the literature. These authors have used the calculated susceptibilities for the free Li^+ ion (χ_{Li^+}(calcul.) $= -0.7 \times 10^{-6}$ [cm^3/Mol]) as standard. With the assumption that the influence of the crystal field on $\chi(Li^+)$ is negligible, the χ-values for the halogen ions are extracted from the measurements on crystalline lithium halides. Then with $\chi(F^-)$, $\chi(Cl^-)$ *etc.*, the susceptibilities of the remaining alkali and alkaline earth ions can be calculated. Another method was used by Klemm [26] to obtain the ionic susceptibilities. Klemm has fixed the χ-values of the halogen ions and alkali ions under the assumption that the relation:

$$\chi_{\text{theor.}}(Cl^-)/\chi_{\text{theor.}}(A) = \chi_{\text{exp.}}(Cl^-)/\chi_{\text{exp.}}(A)$$

is valid. In view of the observation of the expansion of the cations and the contraction of the anions in the lattice, compared with the free ions, this method seems to be questionable. Table 3 gives the free ion and the SPI χ-values calculated from the corresponding wave functions given in Tables 1 and 2. Furthermore χ(Brindley-Hoare) and χ(Klemm) are listed in this table, too[1].

A semi-theoretical method for the evaluation of the individual ion susceptibilities from the susceptibilities measured was done by Trew and Husain [27]. These

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[1] The diamagnetic susceptibility is given in units of -10^{-6} [cm^3/Mol].

Table 3. *The diamagnetic susceptibility of the free ions and the spherical potential ions calculated with the wave functions of Table 1 and 2. For comparison the values of Brindley and Hoare* [25] (Br.-Ho.) *and of Klemm* [26] (Kl.) *are given. The radii r_0 of the potential well for each ion are chosen equal to the ionic radii of Pauling* [12]. *χ is given in units of* -10^{-6} [cm^3/Mol]

Ion	χ_{free}	χ_{r_0}	χ (Br.-Ho.)	χ (Kl.)
Li^+	0.706	0.741	0.7	0.6
Be^{2+}	0.367	0.473	—	0.4
O^{2-}	–	15.750	—	12
F^-	12.635[b]	10.895[b]	9.4	11.0
Na^+	5.082[b]	5.122[b]	6.1	4.6
Mg^{2+}	3.737	3.881	4.3	3.0
Al^{3+}	2.880	3.139	—	2
S^{2-}	55.486	35.177	—	(38)[a]
Cl^-	30.300	27.239	24.2	26.0
K^+	15.488	15.717	14.6	12.9
Ca^{2+}	12.230	12.916	10.7	8.3
Sc^{3+}	9.969	11.115	—	—
Ti^{4+}	8.335	10.334	—	5

[a] Estimated. — [b] Sachs [2] has calculated the following values for χ: F^-: χ (free) = 12.665, χ (r_{0i} = 2.57 a.u.) = 11.784; Na^+: χ (free) = 5.0816, χ (r_{0i} = 1.795 a.u.) = 5.1539.

authors measured the susceptibility of KCl (and other salts). Then from SCF free ion electron distributions, χ was calculated for K^+ and Cl^-. The ion radii of K^+ and Cl^- have been used as cut off radii. From the ratio:

$$\chi_{\text{exp.}}(Cl^-) = \chi_{\text{exp.}}(KCl)\left[\sum_p \int_0^{r'} r_p^2 P_{Cl^-}^2\, dr_p\right] \Big/ \left[\sum_p \int_0^{r'} r_p^2 P_{Cl^-}^2\, dr_p + \sum_p \int_0^{r''} r_p^2 P_{K^+}^2\, dr_p\right]$$

where r' and r'' are the ionic radii of Cl^- and K^+ resp. and $P_X^2(r)$ the radial electron density of the ion X, the ion susceptibilities have been evaluated. This method however has some disadvantages. A considerable amount of the susceptibility of an ion is given by the electrons outside of the ionic radius. In Table 4 some of the susceptibility values calculated here are divided up into the part within the radius r_0, χ_{in}, and the part outside of the radius, χ_{out}. The results of Table 4 show quite clearly, that Watson's [1] proposal, to neglect the out-part of the wave functions, is not meaningful in calculations of physical properties, which depend on $\overline{r^n}$ of high power n. An improvement of the semi-empirical method of Trew and Husain [27] would be a renormalization of the Hartree-Fock wave functions in a similar way

Table 4. *Contribution to the diamagnetic susceptibility from electrons in- and outside a hollow sphere with the radius r_0 for the free ions and* SP-*ions. χ is given in units of* -10^{-6} [cm^3/Mol]

	Ion	Li^+	Na^+	K^+	F^-	S^{2-}	Cl^-
	r_0	1.134	1.795	2.513	2.570	3.477	3.420
χ_{in}	Free	0.47858	4.35533	12.95877	8.75418	23.26569	21.98042
	SPI	0.47802	4.36478	12.93945	8.85258	25.72380	22.04688
χ_{out}	Free	0.22708	0.72714	2.52941	3.88054	32.22034	8.31980
	SPI	0.26309	0.75754	2.77794	2.04229	9.45273	5.19251

as done by Hartmann and Kohlmaier [28] in their calculation of polarizabilities of ions. But since through the renormalization the self consistency is lost, the wave functions and the physical properties computed using such a method are not strictly comparable with the SCF-values.

As already discussed, the radial electron density of the spherical potential ions depends strongly on the radius r_0 of the charged hollow sphere and consequently the diamagnetic susceptibility χ is also a function of r_0. Fig. 8 gives an example for a cation (Ca^{2+}) and an anion (Cl^-).

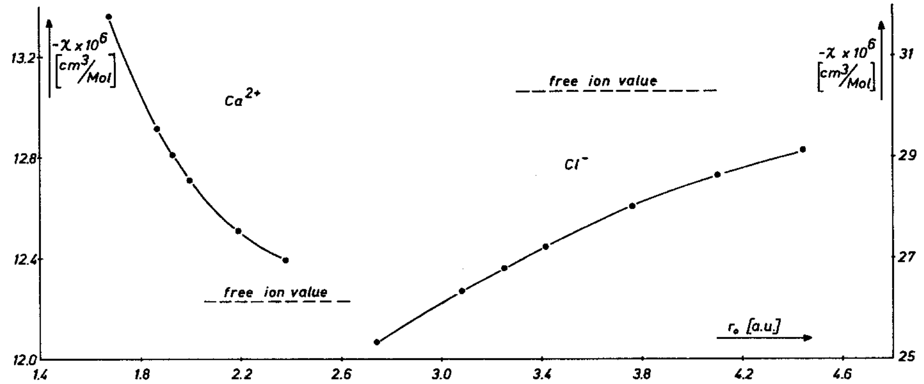

Fig. 8. The diamagnetic susceptibility of Ca^{2+} and Cl^- as a function of the hollow sphere radius r_0. The free ion values of Ca^{2+} and Cl^- are -12.23×10^{-6} [cm³/Mol] and -30.30×10^{-6} [cm³/Mol] respectively

3. *The Dipole Polarizability*

For the dipole polarizability the same problem arises as for χ in dividing up the measured value in an anionic and cationic part. To our knowledge the best attempt made is that of Tessman, Kahn and Shockley [29], which consists in making a least squares fit for the experimental refraction data and assuming an initial value for the Li^+ ion for the dipole polarizability. This method is comparable with Brindley and Hoare's procedure for the calculation of diamagnetic susceptibilities of individual ions. The additivity rule for α_d, which is here of the same importance as in the discussion of χ, is proved by considering the Lorentz factor L. For non overlapping ions L is equal $4\pi/3$. Tessman *et al.* [29] found for the alkali halides that the best fitting of α_d results in taking L equal $4\pi/3$. Of course for some other salts they found deviations for L from $4\pi/3$, indicating strong overlapping. Nevertheless they assume additivity of the individual ion polarizabilities.

The experimental values of Tessman *et al.* [29] are given in Table 5 along with the computed polarizabilities, using the free ion wave functions and the SPI wave functions, the values of Hartmann and Kohlmaier [28] and of Langhoff and Hurst [14]. The SPI polarizabilities are in substantial agreement with those of Tessman *et al.* They also agree with the values of Hartmann and Kohlmaier. A comparison of our values and the polarizabilities calculated by Hartmann and Kohlmaier indicates that for almost all the ions the values of Hartmann and

Table 5. *Dipole polarizabilities.* TKS: *Tessman et al.* [29]; HK: *Hartmann and Kohlmaier* [28]; LH: *Langhoff and Hurst* [14]; F: *free ions (this paper)*; SPI: *spherical potential ions (this paper). The α_d's are given in units of* Å^3

Ion	TKS	HK	LH	F	SPI
Li^+	0.03	0.02	0.0304	0.02612	0.02881
Be^{2+}	—	0.01	0.00815	0.00708	0.01172
O^{2-}	2.1[a]	1.4–1.9	65.9 134.3	—	1.743
F^-	0.76	0.78	1.89	1.310	0.8290
Na^+	0.26	0.18	0.165	0.1517	0.1556
Mg^{2+}	—	0.08	0.0812	0.07638	0.08590
Al^{3+}	—	0.04	0.0453	0.04325	0.05570
S^{2-}	5.1[b]	3.9–4.9	—	30.80	7.798
Cl^-	2.97	2.6	6.61	6.717	4.753
K^+	1.20	0.83	1.14	1.323	1.392
Ca^{2+}	1.1	0.41	0.652	0.7684	0.9178
Sc^{3+}	—	0.22	0.411	0.4867	0.7025
Ti^{4+}	—	—	0.276	0.3243	0.6558

[a] Arithmetical mean of the dipole polarizability of O^{2-} in Li_2O, CaO, SrO, BaO and ZnO.

[b] Arithmetical mean of the dipole polarizability of S^{2-} in CaS, SrS, BaS and ZnS.

Kohlmaier are smaller than ours. We think that this is due to the overestimation of the lattice effects by their model. In the fifth column of Table 5 the free ion values are given, which are to be compared with the polarizabilities of Langhoff and Hurst. The differences which occur are not significant.

The polarizability of Li^+ and Be^{2+} calculated by Cohen and Roothaan [30, 31] (not given in Table 5) is 0.0280 Å^3 and 0.00765 Å^3 resp. They obtained them by solving the Hartree-Fock equation which involves the perturbing electric field. This very accurate calculation yields results lying closely to the free ion values in Table 5. Of special interest are the free ion values for α_d for O^{2-} and S^{2-}, which are 65.9 Å^3 and 30.80 Å^3 resp. These very high polarizabilities result from the diffuse distribution of the *p*-electrons indicated in the positive *p*-orbital energies. This is so much the more the *p*-orbital contribution to the polarizability amounts over 99% of the total value. The superposed potential reduces this effect and a

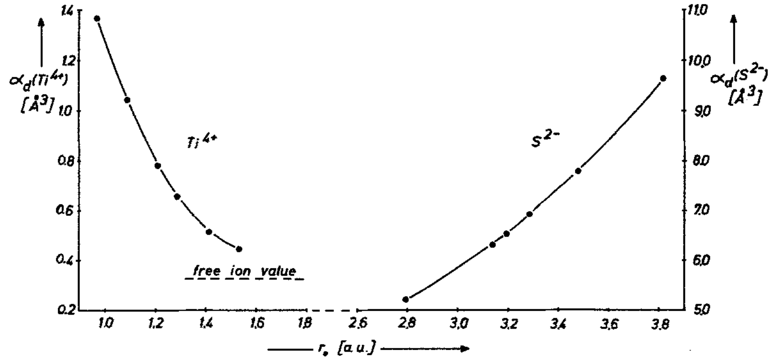

Fig. 9. The dipole polarizability of Ti^{4+} and S^{2-} as a function of the charged hollow sphere radius r_0. The free ion values are 0.3243 Å^3 and 30.799 Å^3 respectively

"bounding" of the p-electron results. The polarizability decreases to 7.798 Å^3 for S^{2-}, quite a reasonable value in comparison with the experiment.

In Fig. 9 the dependence of α_d of the SPI is shown as a function of the charged hollow sphere radius r_0 for Ti^{4+} and S^{2-}.

4. The Antishielding Factor

The experimental evidence shows that generally the γ_∞-values for the free cations agree with the estimations from the experiments fairly well. However for the anions agreement between γ_∞ (calculated) and γ_∞ ("measured") is rather unsatisfying. This problem is discussed extensively by Burns and Wikner [19] and newer results on experimental determinations of coupling constants may be found in the review article of Weiss [32]. Burns and Wikner therefore explored the influence of the condensation of the ions into the lattice on γ_∞. The authors investigated the ions O^{2-}, F^- and Cl^- using for the calculation of γ_∞ (crystal ion) the wave functions of Watson [1], Yamashita and Kojima [3] and Yamashita [33]. For Cl^- Burns and Wikner scaled the free ion wave functions of Hartree and Hartree (for reference see [19]). The Brindley and Hoare susceptibility of Cl^- was used for scaling the $3p$-orbital of the free ion. Extensive calculations of γ_∞ for many free ions are found in [14] showing the importance of the quality of wave functions for these calculations.

In Table 6 the antishielding factors of Langhoff and Hurst [14] are given together with the results of Burns and Wikner [19]. The effect of the wave functions on γ_∞

Table 6. *The antishielding factor* γ_∞. LH: *Langhoff and Hurst* [14]; F: *free ions (this paper)*; BW: *Burns and Wikner* [19]; SPI: *spherical potential ions (this paper)*

Ion	LH	F	BW	SPI
Li^+	0.2570	0.2591		0.2711
	0.2567			
Be^{2+}	0.1857	0.1836		0.1899
O^{2-}	−429.4		− 28.22	− 9.056
	−950.5		− 25.30	
			− 33.90	
F^-	− 23.03	− 21.96	− 66.86	−10.62
	− 22.15		− 23.22	
	− 22.12		− 25.71	
	− 22.00		− 21.11	
Na^+	− 4.514	− 4.580		− 4.747
	− 4.505			
	− 4.497			
Mg^{2+}	− 3.038	− 3.078		− 3.628
Al^{3+}	− 2.236	− 2.282		− 3.217
S^{2-}		−197.1		−37.64
Cl^-	− 66.56	− 57.80	−158.5	−37.90
	− 53.91		− 50.07	
			− 27.04	
K^+	− 12.17	− 21.43		−22.83
Ca^{2+}	− 12.12	− 16.94		−20.58
Sc^{3+}	− 9.461	− 14.21		−20.34
Ti^{4+}	− 7.721	− 12.50		−25.51

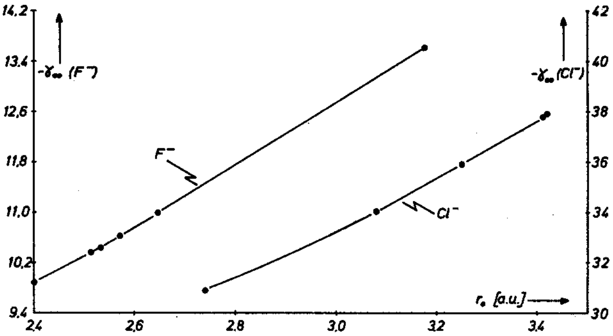

Fig. 10. The dependence of the antishielding factor of F^- and Cl^- upon the charged hollow sphere radius r_0. The free ion values are -21.96 and -57.80 respectively

is shown by the different values of γ_∞ for the same ion. In column 3 and 5 indicated by F and SPI, the γ_∞-values for our free ion wave functions and the spherical potential ions resp., are given. As expected, the influence of the crystal field on the antishielding factor is considerably due to the radial deformation of the electron distribution. This solid state effect on γ_∞ amounts for the small ions a few percent increasing with the number of electrons.

For Al^{3+} one determines a change of about 40% from the free ion value. The change of the free ion γ_∞ of the anions is quite high. For the oxygen ion O^{2-} the free ion antishielding factor calculated by Langhoff and Hurst [14] is -429.4 and -950.5, the first value obtained using the wave functions of McLean (for reference see [14]) and the second those of Clementi and McLean (for reference see [14]). These very extreme values of γ_∞ result from the difficulty in getting meaningful Hartree-Fock wave functions. For the free O^{2-} ion the SCF calculation yields very diffuse p-orbitals since this ion is unstable in the free state. Only the consideration of the stabilizing lattice potential yields reasonable wave functions and consequently meaningful calculations of χ, α_d and γ_∞.

As already expected from the results of our model calculations on χ and α_d the values of γ_∞ (SPI) depend on the radius r_0 of the spherical potential well. In Figs. 10 and 11 this dependence is shown for Cl^- and F^- and Al^{3+} and Na^+ respectively. Again the difficulty in chosing an appropriate value for r_0 can be seen.

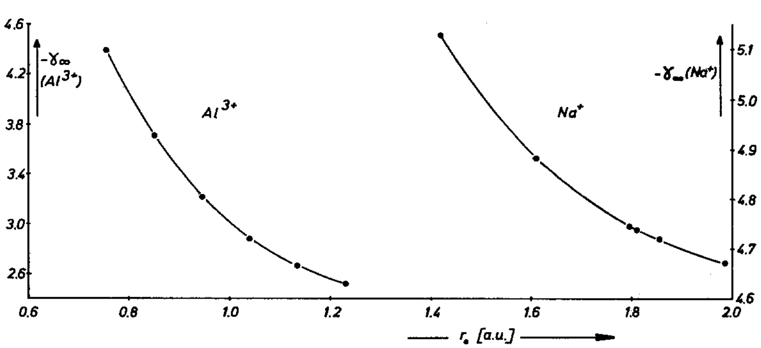

Fig. 11. The dependence of the antishielding factor of Al^{3+} and Na^+ upon the hollow sphere radius r_0. The free ion values are -2.282 and -4.580 respectively

5. The Choice of the Hollow Sphere Radius

Since the SP-model is an electrostatic one, the choice of the radii should be supported by considering the potential in the crystal. We have calculated the electrostatic potential at the site of a Na$^+$-vacancy and a Cl$^-$-vacancy in the NaCl-lattice. The sodium vacancy has a surrounding of 6 Cl$^-$-ions placed at the corners of a regular octahedron; the distance between the center of the vacancy and the next Cl$^-$-ions is $a_0/2$ (a_0 = lattice constant of NaCl = 5.64 Å = 10.66 a.u.). For the Cl$^-$-vacancy the same geometrical arrangement is valid.

Consider the potential around a Hartree-Fock ion. In Fig. 12 this potential is shown for the free Cl$^-$-ion, the free Na$^+$-ion and SP-ions with different SP-radii r_0. The potential of an atom at the distance r from the nucleus is given by

$$V(r) = \frac{Z}{r} - \frac{1}{r}\int_0^r P^2(r')\,dr' - \int_r^\infty \frac{P^2(r')\,dr'}{r'}. \tag{14}$$

From Fig. 12 it can be seen that the potential of the ions Na$^+$ and Cl$^-$ is largely a pure $1/r$-potential for $r \geqq 5$ a.u. Therefore the electrostatic potential at the center of an ion vacancy in the NaCl-lattice can be calculated from the point charge model (Madelung's model). In NaCl the Madelung potential is

$$V_{\mathrm{M}} = \pm\frac{e\alpha}{a_0/2} = \pm 0.328\ \text{a.u.}$$

where α is Madelung's constant.

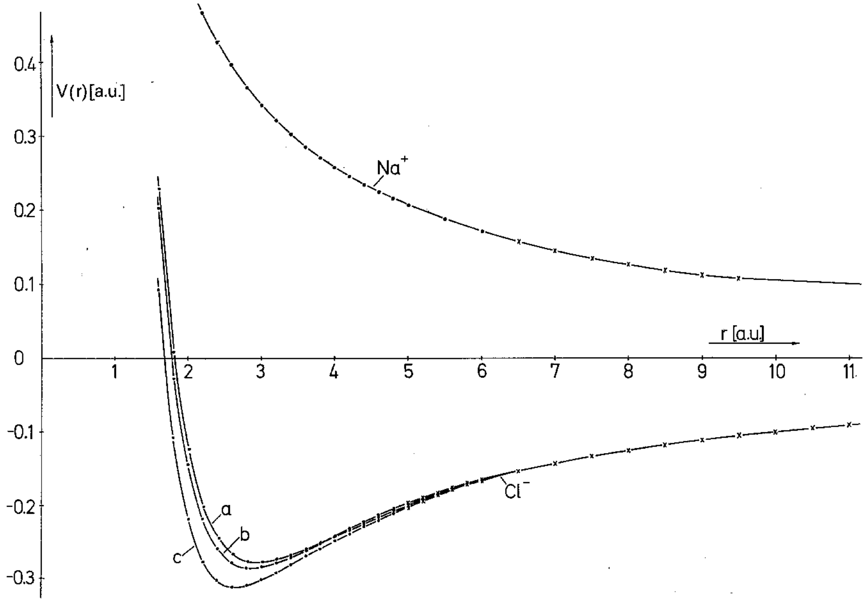

Fig. 12. Electrostatic potential of the Na$^+$- and Cl$^-$-ion. For Cl$^-$ the free ion potential (a), and the SP-ions with $r_0 = 4.441$ a.u. (b), and $r_0 = 2.740$ a.u. (c), are shown. The values of V calculated from Eq. (14) are marked by points (...), the crosses (× × ×) are calculated from $V = 1/r$ and $V = -1/r$ respectively

The electrostatic potential $V_{\mathrm{latt.}}$ along the vector Cl$^-$-vacancy — Cl$^-$ and Na$^+$-vacancy — Na$^+$ (along [100]) was calculated by summing up the contributions of the six ions at the corners of the octahedron. The potential of the rest of the infinite lattice was taken into account by a sphere with a radius of about 6.4 a.u., centered at the vacancy, and carrying a charge of $\pm 5e$. The results of this calculations are shown in Fig. 13. Determinations of the potential along the [110] direction do not alter the results remarkably. It is interesting to note that within the next nearest neighbors octahedron a large volume of constant potential exists.

From Fig. 13 a potential $|V|$ of 0.328 a.u. follows for both ions, Na$^+$ and Cl$^-$, in the NaCl-lattice. For the SP-ions Na$^+$ and Cl$^-$ therefore a radius of 3.05 a.u. has to be choosen for the sphere charged with $\pm e$. This would be a first approximation to r_0. It can be seen immediately, that this radius r_0 changes from substance to substance. For KCl for instance a radius of 3.39 a.u. is calculated from the Madelung model, corresponding to an increase of 11% in the SP-radius r_0 of Cl$^-$. However the influence of such a change in r_0 on χ and α_d is fairly small (Fig. 8) and probably within the experimental uncertainty. Since the consideration of the Hartree-Fock charge distribution has altered the shape of the potential curves compared with the Madelung potential[2], the hollow sphere radius of the SP-ions should be choosen from these calculations.

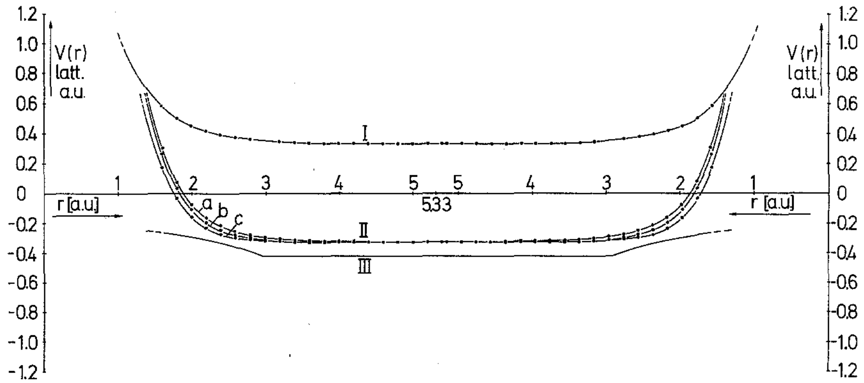

Fig. 13. The potential trough in the NaCl-lattice along [100]. I. The potential around the Cl$^-$-vacancy. II. The potential around the Na$^+$-vacancy; a) free Cl$^-$-ions as next nearest neighbors; b) SP-ions, $r_0 = 4.441$ a.u.; c) SP-ions, $r_0 = 2.740$ a.u. III. The potential function used for the calculation of the SP-ion wave function, $r_0 = 2.362$ a.u.

The potential within the 6 Cl$^-$-octahedron is practically constant within a sphere with a radius of 2.5 a.u. (Fig. 13). Using this radius in our SP-model a potential of 0.400 a.u. within the well results. Pauling's radius for the Na$^+$-ion is about 30% smaller than this radius. The discrepancy to the radius given by Tosi [34] and by Witte and Wölfel [35] is about 10%. The radius of the sphere of constant potential at the site of the Cl$^-$-vacancy is about 2.7 a.u. from which a

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[2] The use of SP-wave functions has flattened the potential curve around the Na$^+$-vacancy. Considering the Cl$^-$-vacancy, no noticeable change in the potential trough due to the use of SP-wave functions was observed.

potential of 0.370 within the SP-well follows. The ionic radii given by Pauling and by Witte and Wölfel deviate 25% and 15% resp. from this value.

It should be remarked that neither the radii r_0 choosen for the potential well coincide necessarily with the ion radii nor coincides the sum of the ion radii with the sum of the potential well radii. In the one case one deals with potential well radii, in the other with radii determined by the electron density distribution. The SP-model for the ions in the lattice changes the wave functions in such a manner that the physical properties χ, α_d and γ_∞ calculated for the SP-ions approach the experimental values fairly well. The choice of potential well radii which are larger than the classical ionic radii of the cations and smaller than the ionic radii of the anions is supported by simple electrostatic arguments and by calculating the physical properties discussed in this paper. The disadvantages of our model are a) the fairly bad approximation of the actual potential outside the hollow sphere and b) the use of equal potential functions (besides the sign) for both the anions and the cations. A further investigation of the actual potential in other crystals than NaCl (change of the ions and the lattice type) would probably be of interest.

V. Conclusions

The application of a simple "crystal model" shows that physical properties of ions which depend on the radial distribution of electron may be calculated from this model with reasonable good success. The agreement between theory and experiment is considerably improved by introducing a spherical potential well. Particularly the difficulties in calculating χ, α_d and γ_∞ for X^{2-} ions (O^{2-} and S^{2-}) are removed by the model. The well-founded fact that the cations expand and the anions contract owing to the lattice potential is reproduced by the model used.

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