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Self-Consistent Local Orbitals for NaCl, NaBr, KCl, and KI[†]

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Using the Adams-Gilbert local-orbitals theory, accurate to first order in interatomic overlap, it has been possible to obtain self-consistent local orbitals for several fcc alkali halide crystals. In this paper, results are reported for NaCl, NaBr, KCl, and KI. In this calculation, nearest neighbors are considered exactly while more distant neighbors are considered in a point-ion model. The method of Roothaan is used to obtain the results. All relativistic effects are neglected in this calculation.

I. INTRODUCTION

Since the introduction of exact localized-orbitals theories by Adams[1] and Gilbert,[2] one has been given a method capable of treating the exact self-consistent Hartree-Fock problem for certain extended systems. The Adams-Gilbert equation is in general rather cumbersome and it is useful to simplify the equation. A pseudopotential method of obtaining such a simple local-orbitals equation has been proposed by Anderson.[3] The author has suggested that one can simplify the Adams-Gilbert equation by expanding it in powers of interatomic overlap, and retaining terms to first order.[4] This seems justified for such systems as the alkali halides where the interatomic overlaps are typically of the order 0.1 or less.[5] Previously we have reported such solutions for the LiX crystals.[6] Here, as previously, we adopt the analytic Hartree-Fock technique of Roothaan[7] in a somewhat modified form. In this present work, the calculations for NaCl and NaBr were performed using the same computer code as were used in the work for the lithium halide crystals. In the case of KCl and KI, a modified version of our previous code was used. The chief effect of the modified code is to produce single-particle energies with the error in the fifth or sixth significant figure rather than in the fourth figure as was the case of the lithium halide crystals. Differences of this sort are not significant for most solid-state problems.

The local orbitals, which the author and others previously obtained for the LiX crystals, and also the current results for NaCl and NaBr have proven useful for band-structure calculations.[8] Calculations of elastic constants, using these local orbitals, seem to improve the agreement between theory and experiment with respect to computing the deviation from the Cauchy relations for the lithium halides.[9]

The general results of band calculations using Hartree-Fock theory and self-consistent local orbitals are in general in poor agreement with previous results for these materials.[8,10] This is especially true for the Slater type of exchange or modification of it. In general, the Hartree-Fock results have valence bands which are substantially broader than previous calculations led one to expect.

The computer codes used in this study were developed by the author for the IBM 360-75 computer at the University of Illinois. In Sec. II, we provide a brief description of the local-orbitals technique and our numerical methods. In Sec. III, numerical results are presented for NaCl, NaBr, KCl, and KI.

II. LOCAL-ORBITAL EQUATIONS

If we have a solid containing filled shells, we may write the Hartree-Fock operator for an electron in this solid in the form

$$F_i = -\nabla_i^2 - 2\sum_A \frac{Z_A}{|\vec{R}_{Ai}|} + 4\int |\vec{r}_i - \vec{r}_j|^{-1}\rho(\vec{r}_j, \vec{r}_j)\, d\vec{r}_j - 2\rho(\vec{r}_i, \vec{r}_j)\, |\vec{r}_i - \vec{r}_j|^{-1} . \qquad (1)$$

In Eq. (1) we represent the Fock operator in rydberg units. Z_A is the atomic number of the nucleus at site A, $\vec{R}_{Ai}$ is the separation of electron i from site A, and $\vec{r}_i$ and $\vec{r}_j$ are the coordinates of the electron. We sum over all nuclear sites in the lattice. The quantity $\rho(\vec{r}, \vec{r}\,')$ is the spin-independent part of the kernel of the density operator and is

$$\rho(\vec{r}, \vec{r}\,') = \sum_{Ai, Bj} |Ai(\vec{r})\rangle\, S^{-1}_{Ai,Bj} \langle B_j(\vec{r}\,')| . \qquad (2)$$

$S^{-1}_{Ai,Bj}$ is the Ai, Bjth element of the inverse of the overlap matrix for the solid and may be obtained using the familiar Löwdin expansion

$$S^{-1}_{Ai,Bj} = \delta_{Ai,Bj} - (S_{Ai,Bj} - \delta_{Ai,Bj}) + \sum_{Ck} (1-\delta_{CA})(1-\delta_{CB}) S_{Ai,Ck} S_{Ck,Bj} + \cdots , \qquad (3)$$

where

$$S_{Ai,Bj} = \langle Ai \,|\, Bj \rangle .$$

In the above formulas, we allow for the general case in which the Fock orbitals are nonorthogonal. In this case Gilbert[2] has shown that one may replace the orthogonality constraint with an arbitrary constraint such that the Fock equation has the form

$$(F_i - \rho U_A' \rho)\phi_{Ai} = \epsilon_{Ai}\, \phi_{Ai} , \qquad (4)$$

where U_A' is an arbitrary Hermitian operator, chosen to produce local solutions to Eq. (4). We divide the Fock operator into two parts:

$$F_i = F_A + U_A , \qquad (5)$$

$$F_A = -\nabla_i^2 - 2Z_A/|\vec{R}_{Ai}| + 4\int |\vec{r}_i - \vec{r}_j|^{-1} \sum_k \phi_{Ak}^2(\vec{r}_j)\, d\vec{r}_j - 2\sum_k \phi_{Ak}(r_i)\phi_{Ak}^\dagger(\vec{r}_j)\, |\vec{r}_i - \vec{r}_j|^{-1} . \qquad (6)$$

In order to obtain solution to Eq. (4) we proceed as follows: We choose $U_A = U_A'$ and we obtain $\rho U_A \rho$ and U_A by expanding the pertinent expressions in powers of interatomic overlap retaining terms linear in $S_{Ai,Bj}$. When this is done one must solve the equation[4]

$$\Big[-\nabla_1^2 - 2Z_A/|\vec{R}_{A1}| + 4\sum_j \int \phi_{Aj}^2(\vec{r}_2)\, |\vec{r}_1 - \vec{r}_2|^{-1} d\vec{r}_2 - \sum_B{}' 2Z_B/|\vec{R}_{B1}| + 4\sum_B{}' \sum_j \int \phi_{Bj}^2(\vec{r}_2)\, |\vec{r}_1 - \vec{r}_2|^{-1} d\vec{r}_2 - \epsilon_{Ai}\Big]\phi_{Ai}(\vec{r}_1) - 2\sum_j \phi_{Aj}(\vec{r}_1) \int \phi_{Aj}^*(\vec{r}_2)\phi_{Ai}(\vec{r}_2)\, |(\vec{r}_1 - \vec{r}_2|^{-1} d\vec{r}_2$$

$$= \sum_k \phi_{Ak}(\vec{r}_1) \int \phi_{Ak}^*(\vec{r}_1)\phi_{Ai}(\vec{r}_1) \Big[-\sum_B{}' 2Z_B/|\vec{R}_{B1}| + 4\sum_B{}' \sum_j \int \phi_{Bj}^2(\vec{r}_2)\, |\vec{r}_1 - \vec{r}_2|^{-1}\Big] d\vec{r}_1 d\vec{r}_2 . \qquad (7)$$

This equation is solved iteratively for both a halogen and an alkali site in the lattice utilizing the symmetry of the crystal.

We solve Eq. (7) by the method of Roothaan.[6,7] We assume the one-electron solutions (dropping the lattice-site subscript) to be of the form

$$\phi_n(\vec{r}) = R_{nl}(r) Y_l^m(\theta, \phi) X(s) . \qquad (8)$$

In Eq. (8) the Y_l^m are the usual spherical harmonics and the X are the spin functions. We then assume

$$rR_{nl}(r) = \sum_j C_{jnl} N_{lj}\, r^{l+1+A_{lj}} e^{-Z_{lj} r} ,$$

$$N_{lj} = [(2Z_{lj})^{2l+2A_{lj}+3}/(2l + 2A_{lj} + 2)!]^{1/2} , \qquad (9)$$

where A_{lj} and Z_{lj} are either chosen by the variational technique or otherwise. The C_{jnl} are chosen by a variational technique. In general, we use A and Z determined by prior calculations.

In this method we use the local-orbitals equation in integral form. Using the notation of Hartree,[11] one finds for the np shell of Cl^- as an example

$$\epsilon_{np} = K_{np} + 2F^0(np, 1s) + 2F^0(np, 2s) + 2F^0(np, 3s) + 6F^0(np, 2p) + 6F^0(np, 3p) - \tfrac{1}{3}G^1(np, 1s) - \tfrac{1}{3}G^1(np, 2s) - \tfrac{1}{3}G^1(np, 3s) - G^0(np, 2p) - G^0(np, 3p) - 0.4G^2(np, 2p) - 0.4G^2(np, 3p) . \qquad (10)$$

III. RESULTS

Although all the one-center integrals could be evaluated analytically, we have evaluated some integrals by numerical techniques, using previously developed and tested codes. The multicenter integrals are computed by numerical techniques. Sufficient accuracy is maintained so that the total energies of the free ions are accurate to about five significant figures in the case of KCl and KI. This was determined by comparison of results obtained from these codes with previous calculations by other authors.[12–14]

We require that, in order to be self-consistent, the wave functions from the Nth iteration differ by no more than one part in one thousand from the wave functions from the $(N-1)$st iteration. This produces single-particle eigenvalues consistent to better than one part in ten thousand.

In all cases, the values for A and Z were chosen from previous calculations. The choices for Cl^- were given in Refs. 6 and 13, for Br^- the values of Ref. 14 are used, for I^- the values of Ref. 6 are used, for Na^+ the values of Ref. 12 are used, and finally, for K^+ the values of Ref. 13 are used.

TABLE I. Atomic parameters for Na^+ in the notation of Ref. 13. Energy parameters defined as $\epsilon_{nn'} = \langle n | F_A + U_A | n' \rangle$ (in rydbergs).

	Basis members A_{lj} and Z_{lj} from Ref. 12			
	$l=0$		$l=1$	
j	A_{0j}	Z_{0j}	A_{1j}	Z_{1j}
1	0	15.949	0	12.048
2	0	9.439	0	5.703
3	2	11.624	0	3.336
4	1	4.384	0	2.146
5	1	2.811		
	Free-atom results			
	$\epsilon_{1s,1s} = -81.66$	$\epsilon_{2s,2s} = -6.13$	$\epsilon_{2p,2p} = -3.59$	
j	C_{10j}	C_{20j}	C_{21j}	
1	0.213 934	0.014 920	0.012 262	
2	0.976 288	0.334 173	0.360 720	
3	−0.011 265	0.054 471	0.713 569	
4	−0.027 044	−0.601 795	0.600 458	
5	0.015 336	−0.723 174		
	NaCl results for Na^+			
	$\epsilon_{1s,1s} = -81.05$	$\epsilon_{1s,2s} = 1339 \times 10^{-7}$		
	$\epsilon_{2s,2s} = -5.514$	$\epsilon_{2p,2p} = -2.972$		
1	0.213 942	0.014 878	0.012 036	
2	0.976 286	0.334 195	0.362 580	
3	−0.011 261	0.054 231	0.708 270	
4	−0.027 065	−0.600 998	0.605 595	
5	0.015 345	−0.723 846		
	NaBr results for Na^+			
	$\epsilon_{1s,1s} = -81.06$	$\epsilon_{1s,2s} = 1197 \times 10^{-7}$		
	$\epsilon_{2s,2s} = -5.539$	$\epsilon_{2p,2p} = -2.997$		
1	0.213 930	0.014 886	0.012 045	
2	0.976 289	0.334 190	0.362 503	
3	−0.011 272	0.054 260	0.708 541	
4	−0.027 057	−0.601 092	0.605 322	
5	0.015 342	−0.723 768		

TABLE II. Atomic parameters for K^+ in the notation of Ref. 13. Energy parameters defined as $\epsilon_{nn'} = \langle n | F + U_A | n' \rangle$ (in rydbergs).

	Basis members A_{lj} and A_{lj} from Ref. 12			
j	A_{0j}	Z_{0j}	A_{1j}	A_{1j}
1	0	21.536	0	17.000
2	1	15.255	0	8.890
3	2	17.000	0	5.450
4	2	11.085	2	8.800
5	1	6.687	1	3.253
6	2	3.502	2	2.412
7	2	2.338	1	1.650

	K^+ free-ion results				
	$\epsilon_{1s,1s} = -267.9$			$\epsilon_{2p,2p} = -23.47$	
	$\epsilon_{2s,2s} = -29.45$			$\epsilon_{3p,3p} = -2.342$	
	$\epsilon_{3s,3s} = -3.932$				
j	C_{10j}	C_{20j}	C_{30j}	C_{21j}	C_{31j}
1	0.891 298	0.235 030	0.079 651	0.025 204	0.004 552
2	0.415 108	0.226 946	0.103 541	0.876 021	0.244 525
3	−0.182 045	−0.094 549	−0.031 265	0.447 807	0.114 531
4	−0.009 571	−0.163 896	0.014 555	0.177 247	0.073 560
5	0.006 169	−0.925 935	−0.519 943	0.001 731	−0.841 927
6	−0.001 281	−0.009 806	0.662 880	0.001 088	−0.435 357
7	0.000 586	0.001 451	0.521 531	−0.000 674	−0.152 584
	K^+ results in KI				
$\epsilon_{1s,1s} = -267.4$		$\epsilon_{1s,2s} = 200 \times 10^{-7}$		$\epsilon_{2p,2p} = -22.98$	
$\epsilon_{2s,2s} = -28.95$		$\epsilon_{1s,3s} = 50 \times 10^{-7}$		$\epsilon_{3p,3p} = -1.842$	
$\epsilon_{3s,3s} = -3.421$		$\epsilon_{2s,3s} = 2846 \times 10^{-7}$		$\epsilon_{2p,3p} = 2738 \times 10^{-7}$	
1	0.891 279	0.235 038	0.079 740	0.025 182	0.005 607
2	0.415 134	0.226 960	0.103 358	0.876 356	0.230 982
3	−0.182 085	−0.094 571	−0.031 061	0.446 985	0.146 568
4	−0.009 539	−0.163 935	0.013 309	0.177 667	0.057 727
5	0.006 146	−0.925 922	−0.518 867	0.001 816	−0.851 732
6	−0.001 276	−0.009 735	0.662 037	0.000 960	−0.400 054
7	0.000 584	0.001 432	0.523 737	−0.000 584	−0.190 553
	K^+ results in KCl				
$\epsilon_{1s,1s} = -267.0$		$\epsilon_{1s,2s} = -50 \times 10^{-7}$		$\epsilon_{2p,2p} = -27.92$	
$\epsilon_{2s,2s} = -28.86$		$\epsilon_{1s,3s} = -28 \times 10^{-7}$		$\epsilon_{3p,3p} = -1.781$	
$\epsilon_{3s,3s} = -3.366$		$\epsilon_{2s,3s} = 2835 \times 10^{-7}$		$\epsilon_{2p,3p} = 2743 \times 10^{-7}$	
1	0.884 212	0.233 274	0.079 450	0.024 979	0.005 665
2	0.425 348	0.229 836	0.104 514	0.879 652	0.230 760
3	−0.192 995	−0.097 500	−0.032 018	0.438 702	0.147 269
4	−0.001 006	−0.158 612	0.014 574	0.181 976	0.057 586
5	−0.000 195	−0.926 287	−0.519 804	0.003 520	−0.852 634
6	0.000 112	−0.009 211	0.660 415	−0.000 950	−0.395 962
7	−0.000 096	0.001 152	0.524 579	0.000 620	−0.194 787

Past experience for LiCl indicated that a basis satisfactory for atomic calculation also sufficed for these solids.

In the solid-state calculation, the detailed part of U_A was evaluated exactly for only nearest neighbors and more distant shells are included in a point-ion approximation. This approximation seems consistent with the restriction to terms linear in S in obtaining the equations.

In Table I, we specify the basis used for the Na^+ in NaCl and NaBr. In Table II, we specify the basis used for the K^+ ion and also give the one-electron orbitals and eigenvalues for the free K^+ ion and for K^+ in KCl and KI.

The Cl^- basis is given in Table III along with the one-electron eigenvalues and eigenfunctions for Cl^- in KCl and NaCl. The Br^- basis is given Table IV along with the one-electron eigenvalues and eigenfunctions for Br^- in NaBr. Finally, in Table V, we

TABLE III. Atomic parameters for Cl$^-$ in the notation of Ref. 13. Energy parameters defined as $\epsilon_{nn'} = \langle n | F + U_A | n' \rangle$ (in rydbergs).

Basis members A_{lj} and Z_{lj} from Refs. 6 and 13

j	A_{0j}	Z_{0j}	A_{1j}	Z_{1j}
1	0	18.9832	0	13.7900
2	0	14.7941	0	8.8355
3	1	14.7181	0	5.3987
4	1	9.6220	1	4.0186
5	1	6.7665	1	2.4367
6	2	6.2190	1	1.6382
7	2	3.2450	1	0.8219
8	2	2.1679	1	0.4120
9	2	1.3550		

Cl$^-$ in KCl

$\epsilon_{1s,1s} = -209.7$ $\epsilon_{1s,2s} = 240 \times 10^{-7}$ $\epsilon_{2p,2p} = -16.08$
$\epsilon_{2s,2s} = -21.15$ $\epsilon_{1s,3s} = 64 \times 10^{-7}$ $\epsilon_{3p,3p} = -0.9513$
$\epsilon_{3s,3s} = -2.124$ $\epsilon_{2s,3s} = 73 \times 10^{-7}$ $\epsilon_{2p,3p} = 233 \times 10^{-7}$

j	C_{10j}	C_{20j}	C_{30j}	C_{21j}	C_{31j}
1	0.669 778	0.139 805	0.071 205	0.035 885	0.011 660
2	0.735 753	0.185 610	0.021 104	0.341 238	0.073 760
3	0.055 290	0.168 549	0.087 676	0.938 990	0.294 120
4	−0.060 189	−0.123 583	−0.117 269	−0.003 222	−0.073 687
5	0.054 439	−0.892 704	−0.204 580	0.020 966	−0.692 749
6	−0.019 94	−0.324 178	−0.284 880	−0.010 432	−0.469 828
7	0.003 998	−0.017 044	0.526 615	0.002 767	−0.444 862
8	−0.002 328	0.004 184	0.727 979	−0.000 815	0.062 818
9	0.000 597	−0.001 293	0.206 781		

Cl$^-$ in NaCl

$\epsilon_{1s,1s} = -209.9$ $\epsilon_{1s,2s} = 6 \times 10^{-7}$ $\epsilon_{2p,2p} = -16.06$
$\epsilon_{2s,2s} = -21.15$ $\epsilon_{1s,3s} = -43 \times 10^{-7}$ $\epsilon_{3p,3p} = -0.9689$
$\epsilon_{3s,3s} = -2.138$ $\epsilon_{2s,3s} = -4 \times 10^{-7}$ $\epsilon_{2p,3p} = -26 \times 10^{-7}$

1	0.839 156	0.273 972	0.085 814	0.035 859	0.015 226
2	0.017 518	0.002 839	−0.000 188	0.341 278	0.059 636
3	0.322 597	0.282 125	0.098 834	0.938 990	0.326 528
4	−0.313 230	−0.249 242	−0.126 646	−0.002 829	−0.125 450
5	0.282 344	−0.797 500	−0.196 723	0.020 594	−0.591 599
6	−0.122 521	−0.383 622	−0.284 218	−0.010 095	−0.617 191
7	0.026 217	−0.002 114	0.519 177	0.002 630	−0.369 542
8	−0.015 657	−0.005 896	0.729 958	−0.000 774	0.079 862
9	0.004 179	0.001 632	0.212 052		

give the basis used for I$^-$ along with the one-electron eigenvalues and eigenfunctions for I$^-$ in KI.

In presenting the data in Tables I–V, we use the following conventions:

$$\sum_{j=1}^{m} C_{nlj}^2 = 1 \qquad (11)$$

TABLE IV. Atomic parameters for Br$^-$ in the notation of Ref. 13. Energy parameters defined as $\epsilon_{nn'} = \langle n | F + U_A | n' \rangle$ (in rydbergs).

Basis members A_j and Z_j from Ref. 14

j	A_{0j}	Z_{0j}	A_{1j}	C_{1j}	A_{2j}	C_{2j}
1	0	37.3537	0	23.3102	0	16.0578
2	1	33.1430	0	15.6532	0	10.0855
3	1	17.2808	1	14.8256	0	7.2889
4	2	16.3407	1	9.5909	0	4.7416
5	2	8.4198	1	6.1399	0	2.9679
6	2	6.6235	2	5.3085		
7	3	6.6182	2	2.8150		
8	3	3.4739	2	1.6374		
9	3	2.1970	2	1.1277		
10	3	1.4859				

Br$^-$ in NaBr

$\epsilon_{1s,1s} = -980.9$ $\epsilon_{1s,4s} = 2 \times 10^{-7}$ $\epsilon_{4p,4p} = -0.9112$
$\epsilon_{2s,2s} = -130.4$ $\epsilon_{2s,3s} = -1 \times 10^{-7}$ $\epsilon_{2p,3p} = -1 \times 10^{-7}$
$\epsilon_{3s,3s} = -19.71$ $\epsilon_{2s,4s} = -3 \times 10^{-7}$ $\epsilon_{2p,4p} = -1 \times 10^{-7}$
$\epsilon_{4s,4s} = -2.005$ $\epsilon_{3s,4s} = 48 \times 10^{-7}$ $\epsilon_{3p,4p} = -27 \times 10^{-7}$
$\epsilon_{1s,2s} = 6 \times 10^{-7}$ $\epsilon_{2p,2p} = -117.0$ $\epsilon_{3d,3d} = -6.403$
$\epsilon_{1s,3s} = 1 \times 10^{-7}$ $\epsilon_{3p,3p} = -14.92$

j	C_{10j}	C_{20j}	C_{30j}	C_{40j}
1	0.988 320	0.318 673	0.129 551	0.041 564
2	0.144 865	0.196 59	0.076 029	0.023 638
3	−0.015 696	−0.729 875	−0.292 041	−0.090 983
4	0.012 828	−0.555 448	−0.430 691	−0.145 691
5	−0.023 306	−0.107 770	0.463 690	0.215 380
6	0.032 710	0.087 670	0.661 950	0.196 048
7	−0.014 545	−0.027 669	0.228 957	0.139 643
8	0.001 031	−0.000 723	0.029 638	−0.687 148
9	−0.000 570	0.000 767	−0.012 168	−0.606 511
10	0.000 199	−0.000 308	0.004 452	−0.145 448

j	C_{21j}	C_{31j}	C_{41j}	C_{32j}
1	0.155 471	0.055 336	0.014 064	0.051 797
2	0.963 835	0.315 906	0.095 743	0.308 490
3	0.211 122	0.181 064	0.049 119	0.542 042
4	0.046 856	−0.345 677	−0.096 732	0.766 897
5	−0.008 477	−0.858 743	−0.319 643	0.142 165
6	0.003 400	−0.083 717	0.037 767	
7	−0.000 555	−0.018 078	0.733 829	
8	0.000 302	0.008 686	0.503 758	
9	−0.000 128	−0.003 813	0.288 080	

and also

$$\epsilon_{nl,n'l'} = \delta_{ll'} \langle Anl \mid F \mid An'l' \rangle \ . \qquad (12)$$

Equation (12) is evaluated to first order in $S_{Ai,Bj}$. We note that, except for the inner orbitals, there is no physical meaning to the diagonal elements

TABLE V. Atomic parameters for I$^-$ in the notation of Ref. 13. Energy parameters defined as $\epsilon_{nn'} = \langle n | F + U_A | n' \rangle$ (in rydbergs).

Basis members A_{lj} and Z_{lj} from Ref. 6

j	A_{0j}	Z_{0j}	A_{1j}	Z_{1j}	A_{2j}	Z_{2j}
1	0	56.5239	0	26.0738	0	19.7943
2	1	26.1681	1	19.6079	0	11.0375
3	2	24.7445	1	9.2975	0	7.1802
4	2	12.7500	2	8.0386	1	6.9183
5	3	10.0218	2	4.2627	1	4.4943
6	3	5.2591	2	2.4794	1	3.0322
7	3	3.3269	3	2.4549	1	2.2934
8	4	3.0142	3	1.6713		
9	4	2.2501	3	1.0150		
10	4	1.4859	3	0.5075		
11	4	1.1889				

TABLE V. (*continued*)

Γ^- in KI

$\epsilon_{1s,1s} = -2353.0$
$\epsilon_{2s,2s} = -359.51$
$\epsilon_{3s,3s} = -75.637$
$\epsilon_{4s,4s} = -14.437$
$\epsilon_{5s,5s} = -1.6881$
$\epsilon_{1s,2s} = 14 \times 10^{-7}$
$\epsilon_{1s,3s} = 5 \times 10^{-7}$
$\epsilon_{1s,4s} = -23 \times 10^{-7}$
$\epsilon_{1s,5s} = -147 \times 10^{-7}$

$\epsilon_{2s,3s} = 20 \times 10^{-7}$
$\epsilon_{2s,4s} = -62 \times 10^{-7}$
$\epsilon_{2s,5s} = -401 \times 10^{-7}$
$\epsilon_{3s,4s} = -28 \times 10^{-7}$
$\epsilon_{3s,5s} = -183 \times 10^{-7}$
$\epsilon_{4s,5s} = 956 \times 10^{-7}$
$\epsilon_{2p,2p} = -340.28$
$\epsilon_{3p,3p} = -66.057$
$\epsilon_{4p,4p} = -10.961$

$\epsilon_{5p,5p} = -0.83972$
$\epsilon_{2p,3p} = 8 \times 10^{-7}$
$\epsilon_{2p,4p} = 1 \times 10^{-7}$
$\epsilon_{2p,5p} = 15 \times 10^{-7}$
$\epsilon_{3p,4p} = -13 \times 10^{-7}$
$\epsilon_{3p,5p} = 228 \times 10^{-1}$
$\epsilon_{4p,5p} = -323 \times 10^{-7}$
$\epsilon_{3d,3d} = -48.889$
$\epsilon_{4d,4d} = -4.8520$
$\epsilon_{3d,4d} = 4 \times 10^{-7}$

j	C_{10j}	C_{20j}	C_{30j}	C_{40j}	C_{50j}
1	0.906 825	0.256 215	0.095 943	0.025 332	0.013 542
2	0.220 254	−0.231 215	−0.076 048	−0.015 407	−0.007 833
3	−0.207 122	−0.704 548	−0.470 326	−0.157 325	−0.087 376
4	0.110 424	0.196 861	0.849 449	0.338 181	0.192 935
5	−0.086 345	−0.171 095	0.045 505	−0.082 235	−0.052 519
6	0.092 839	0.197 584	0.063 822	−0.603 005	−0.477 263
7	−0.153 172	−0.332 260	−0.115 622	0.465 880	0.631 190
8	0.158 307	0.347 000	0.126 119	−0.449 492	−0.020 0371
9	−0.086 164	−0.190 846	−0.072 393	0.235 157	0.521 326
10	0.041 491	0.092 722	0.036 437	−0.113 243	−0.075 096
11	−0.017 913	−0.040 157	−0.015 983	0.049 160	0.091 589

j	C_{21j}	C_{31j}	C_{41j}	C_{51j}	C_{32j}	C_{42j}
1	0.976 374	0.210 464	0.107 477	0.055 264	0.193 196	0.097 616
2	0.200 405	−0.018 428	0.011 830	0.009 063	0.907 198	0.488 432
3	−0.043 739	−0.722 620	−0.599 834	−0.336 532	−0.269 424	−0.193 844
4	0.033 489	0.341 557	0.658 980	0.406 354	0.239 233	−0.391 921
5	−0.022 603	−0.211 644	0.364 099	0.243 454	−0.083 719	−0.744 009
6	0.040 778	0.387 334	−0.199 333	−0.666 255	0.049 820	−0.073 313
7	−0.035 370	−0.338 680	0.146 259	−0.120 011	−0.018 824	−0.042 474
8	0.008 264	0.080 768	−0.023 158	−0.354 850		
9	−0.002 151	−0.021 338	0.004 870	−0.271 601		
10	0.000 453	0.004 529	−0.000 921	0.035 112		

$\epsilon_{nl,n'l'}$ since we have not included the full effects of crystal symmetry in producing the energy parameters. Thus if a one-electron spectrum is needed, one must use these local orbitals to produce a full band calculation. Such calculations have been performed for LiCl, LiBr, NaCl, and NaBr.[8]

In conclusion, it has proven possible to obtain self-consistent solutions to the local-orbital Hartree-Fock for NaCl, NaBr, KCl, and KI. Previously we presented such results for LiX crystals.[6] Here, however, the Na^+ and K^+ ions are much larger than the Li^+ ion and thus the number of iterations need to obtain self-consistency is increased. The principal effects of going into a crystal environment is to produce changes in the outer orbitals. Thus it appears that the principal effects of the rotation in the Fock manifold in Eq. (4) is to produce intraband mixing rather than interband mixing. This is seen from the smallness of the $\epsilon_{nl,n'l'}$ parameters for $n \neq n'$ in Tables I–V.

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Electric Dipole Interactions Among Polar Defects in Alkali Halides*

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The influence of electric dipole interactions among substitutional polar molecules and atoms in the alkali halides is studied in the systems KCl : Li, KCl : OH, RbCl : OH, NaBr : F, and KCl : CN. A maximum is observed in the dc dielectric constant at a temperature $T_{\max}$ which is shown to be proportional to the average interaction energy. It is also shown that this is not a relaxation effect. A remanent polarization is observed at low temperatures, which is caused by parallel-aligned pairs of dipoles experiencing a reorientation barrier. Specific-heat and thermal-conductivity measurements are also analyzed for the influence of interactions. Owing to the finite zero-field tunnel splitting of the impurity states, there is a threshold concentration, below which interaction effects are vanishingly small. The experimental results are compared to recent theoretical investigations and to results obtained on dilute magnetic alloys. In KCl : OH, the specific heat at high OH^- concentrations N is proportional to $N^{-1/2}T^{3/2}$. An unsuccessful search for direct evidence of polarization waves analogous to spin waves is reported and they are presumed heavily damped. It is conjectured that the above specific-heat result may be due to these modes.

I. INTRODUCTION

Certain atomic and molecular substitutional impurities in alkali halides are known to tunnel among equivalent potential wells within the lattice vacancy they occupy. The tunneling states associated with this motion are well understood.[1] Some of these ions have large electric dipole moments. These ions resemble a dilute gas of polar molecules and therefore allow the study of the dielectric properties of such a gas without the complications of condensation at low temperatures.[2] A particularly attractive question is that of the electric dipole-dipole interaction and the possibility of observing an ordered state.

Electric dipole interactions among such impurities were first reported by Känzig, Hart, and Roberts, who observed a maximum in the ac dielectric constant in KCl : OH at low temperatures.[3] This work led to a number of theoretical investigations of this subject.[4–8]

Analogous magnetic systems, namely, transition-metal impurities in noble metals, have numerous properties resembling the systems studied here.[9,10] Perhaps the most fundamental one is that only local order can exist at moderate concentrations. Anderson has discussed this peculiarity in the magnetic case.[11] Other effects are the appearance of a magnetic remanence that decays in time, a specific heat linear in temperature, and a maximum in the susceptibility occurring at a temperature which is proportional to concentration.

The advantage one finds in the dipolar systems is the basically simple nature of the electric dipole interaction. Consequently, one might hope to observe cooperative phenomena over a wide range of concentration and explain the results in a straightforward manner. It is also possible that a study of dipolar systems will contribute to the understanding of the magnetic alloys.

In this paper we report a detailed study of the dielectric constant of a variety of dipolar impurities and the observation of a hysteresis and remanent polarization, which we explain through electric dipole interactions. These effects are dependent upon temperature, concentration, and time (or frequency). This interaction has also been studied through specific-heat measurements and appears to be noticed in the thermal conductivity. The experimental results will be compared with the published theoretical results and new calculations, presented in Sec. II.

A particularly interesting manifestation of an electrically ordered state would be the existence of the electric analog of spin waves. We shall describe an unsuccessful search for dipolar waves.