Transferable Deformation-Dipole Model for Ionic Materials

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A model for the ionic interactions in polyvalent metal halides was originally built for chloroaluminate clusters using an analysis of data on static and dynamic structure of their molecular monomers [for a review see M. P. Tosi, Phys. Chem. Liquids **43**, 409 (2005)]. Recently, by continuing the deformation-dipole model calculations, the transferability of the halogen parameters was tested through the calculation of the structure of alkali halides and alkaline-earth halides. In this work we test the usefulness of the deformation-dipole model in the study of ionic materials by examining the transferability of the overlap parameters for the halogen ions across families of halide compounds. Following a comparative discussion of alkali and alkaline-earth halide monomers near equilibrium, results on alkaline-earth halides are given. By using the transferable ionic potential model we also calculate the equilibrium structure of the molecular clusters, as well as the vibrational frequencies of ACl_4 compounds (where A = U, Np, Pu, Am and Th).

Key words: Ionic Models; Ionic Clusters; Molten Salts.

1. Introduction

Studies of metal halide melts by neutron and X-ray diffraction have shown that melting usually preserves the type of chemical order which is found in the crystal. The crystal structures of metal halide compounds arise from electronic charge transfer and local compensation of positive and negative ionic charges by formation of chemical order.

Calculations of the structure and physical properties of molten salts, ionic glasses and disordered solids have so far mainly relied on ionic models stemming from the early work of Born and Mayer [1] on cohesion in alkali halide crystals. In extending the early Born-Mayer model to calculations of the potential energy curve of the alkali halide molecular monomers, Rittner [2] recognized the need to allow for the electronic polarization dipoles carried by the ions. Tosi and Doyama [3] supplemented the Rittner model by including the overlap deformation dipole. These ideas have been successfully extended to study a number of polyvalent metal halides in both pure and mixed liquid states. Charged or neutral microclusters are stable in many of these melts near freezing, so that the relationship between molecular states and molten states can be quite direct. A remarkable example has been the development and use of such models to study the stability of molecular clusters in molten chloroaluminates [4]. Important examples of computer simulation work on metal halide systems can be found in the work of Madden and coworkers [5, 6].

In this work, we first present the deformation-dipole model and then discuss the results from the ionic model calculations of our recent work on alkali halides [7]. We then present results on alkaline-earth halides obtained by using transferable halogen parameters. Results on the equilibrium structure of molecular clusters, as well as the vibrational frequencies of ACl_4 compounds (where A = U, Np, Pu, Am and Th) are discussed by analyzing various potential model parameters.

2. Interionic Force Model

The potential energy $U(\{r_{ij}\},\{p_i\})$ of a molecular cluster in an arbitrary configuration is written as a function of the bond vectors r_{ij} and of the electric dipole moments p_i carried by the ions. This is

$$U(\{r_{ij}\},\{p_i\}) =$$

$$\sum_{i<j}\left[\frac{z_i z_j e^2}{r_{ij}}+\Phi_{ij}(r_{ij})-\frac{C_i C_j}{r_{ij}^6}\right] + U_{\mathrm{pol}}^{\mathrm{cl}}(\{r_{ij}\},\{p_i\})+U_{\mathrm{shell}}(\{r_{ij}\},\{p_i\}). \quad (1)$$

Minimization of (1) with respect to the dipoles yields the dipole p_{h} on a halogen as

$$p_{\mathrm{h}}=\alpha_{\mathrm{h}}E_{\mathrm{h}}(\{r_{ij}\},\{p_i\})+\alpha_{\mathrm{s}}\sum_{i_{\mathrm{m}}}\hat{r}_{i\mathrm{h}}\left|\frac{d\Phi_{i\mathrm{h}}(r_{i\mathrm{h}})}{dr_{i\mathrm{h}}}\right|, \quad (2)$$

where E_{h} is the self-consistent electric field on the halogen, α_{h} and α_{s} are its electrical and short-range polarizabilities, and i_{m} denotes a metal ion which is first neighbour of the halogen. Each component of the shell-deformation dipole in (2) lies along a metal-halogen bond and points toward the metal ion: it is thus opposite to the corresponding electrical induction dipole, so that the dipoles saturate as the ions deform in reaching their equilibrium positions. Van der Waals dipole-dipole interactions are included for the halogens in (1). The overlap repulsive energy in (1) is written in the Busing form [8] adopted by Yuen et al. [9] as

$$\Phi_{ij}(r_{ij})=f(\rho_i+\rho_j)\exp[(R_i+R_j-r)/(\rho_i+\rho_j)], \quad (3)$$

where f has the standard value $f=0.05$ e^2/Å^2. The reader is referred to our earlier work [4] for expressions of the classical polarization energy $U_{\mathrm{pol}}^{\mathrm{cl}}$ and of the shell deformation energy U_{shell}.

The potential energy function in (1) is handled by a computer programme which first searches for zero-force configurations corresponding to extrema in the total energy of the molecule, and then evaluates deformations of each zero-force structure in order to assess its mechanical stability and its vibrational frequencies.

In (1)–(3) z_i are the effective valencies, R_i are the ionic radii, ρ_i are the ionic stiffness parameters and α_{s} is the short-range overlap polarizability. The parameters of the transferable deformation-dipole model parameters for the halogen atoms that we have adopted for the alkali halide molecules [7], using interionic overlap potentials and overlap polarizabilities from the work of Yuen et al. [9] on crystalline properties of these compounds data and from [10], are reported in Table 1 for divalent and tetravalent metal halides. Similar features are shown by results from calculations on trivalent and pentavalent metal halides, to be reported elsewhere.

Table 1. Model parameters for halogen ions[a].

	R_i (Å)	ρ_i (Å)	C_i (e Å$^{5/2}$)	α_i (Å)	α_{s} (Å^3/e)
F	1.32	0.215	2.08	0.64	0.40
Cl	1.71	0.238	5.50	2.96	0.83
Br	1.84	0.258	7.17	4.16	1.2
I	2.02	0.289	10.1	6.43	1.7

[a] The electronic polarizabilities α_i are from [11]. All the other parameters are from [10].

3. Alkali Halides and Alkaline-Earth Halides

In our recent work [7] we have quantitatively tested two important aspects of the usefulness of the deformation-dipole model in the study of ionic materials. Firstly, we have seen that the model parameters can be usefully transferred not only between different states of aggregation of these materials, as already demonstrated in our previous work [4], but also between different families of compounds. Secondly, we have checked the reliability of the model in accounting for strong anharmonicity against a basic quantum mechanical treatment of the potential energy curve of the NaCl monomer [11].

In Table 2 we report the transferable-model results for the alkali halide molecules [7], which are the equilibrium bond length r_0, the equilibrium dipole moment $d(r_0)$, the molecular cohesive energy $U(r_0)$ and the vibrational frequency ω. The corresponding experimental values are reported in parentheses, whenever available, from [3, 12–14]. It is seen from Table 2 that the phenomenological theory reproduces the observed trends and often is in good quantitative agreement with the experimental data. This degree of compatibility is especially remarkable for the molecular dipole moments, which directly reflect the distortions of the electronic charge distribution. There are also correlations between the error in the calculated bond length and the inaccuracies of the theory in the other calculated molecular properties: it is therefore good practice to fit measured bond lengths in dealing with clusters of the halides of polyvalent metals. The results confirm that, given the minimal experimental data needed to determine the parameters that are appropriate to the metal ions across different families of compounds, the model has semiquantitative predictive value.

Electrical deflection experiments of molecular beams of alkaline-earth halides by Klemperer et al. [16, 17] have revealed the presence of a large permanent dipole moment of several of these molecules (CaF_2, SrF_2, $SrCl_2$, BaF_2, $BaCl_2$, $BaBr_2$, and BaI_2). The dipole moment is associated with a bent molec-

Table 2. Properties of the alkali halide molecular monomers [equilibrium bond length r_0, dipole moment $d_0 = d(r_0)$, dissociation energy $U_0 = -U(r_0)$ into separated ions, and vibrational frequency ω] from the deformation dipole model and (in parentheses) from experiment[a].

	r_0 (Å)	d_0 (Debye)	U_0 (eV)	ω (cm^{-1})
LiF	1.54 (1.564)	6.76 (6.28)	7.9 (7.80)	860 (867)
NaF	1.84 (1.926)	7.75 (8.12)	6.5 (6.52)	454 (492)
KF	2.11 (2.171)	8.21 (8.56)	5.8 (5.88)	344 (399)
RbF	2.21 (2.270)	8.16 (8.51)	5.6 (5.65)	292 (347)
CsF	2.30 (2.345)	7.48 (7.85)	5.4 (–)	272 (313)
LiCl	2.02 (2.020)	7.14 (7.08)	6.6 (6.53)	718 (569)
NaCl	2.36 (2.361)	8.89 (8.97)	5.5 (5.64)	343 (335)
KCl	2.67 (2.666)	9.99 (10.2)	4.8 (5.01)	247 (248)
RbCl	2.79 (2.786)	10.3 (10.5)	4.6 (4.83)	198 (207)
CsCl	2.91 (2.906)	10.0 (10.4)	4.5 (–)	180 (189)
LiBr	2.17 (2.170)	7.31 (7.23)	6.3 (6.25)	632 (512)
NaBr	2.52 (2.502)	9.29 (9.09)	5.2 (5.41)	282 (277)
KBr	2.83 (2.821)	10.6 (10.6)	4.6 (4.79)	194 (193)
RbBr	2.96 (2.945)	10.9 (–)	4.4 (4.60)	144 (150)
CsBr	3.09 (3.072)	10.8 (–)	4.2 (–)	126 (133)
LiI	2.34 (2.392)	7.12 (7.43)	5.9 (5.92)	568 (433)
NaI	2.72 (2.711)	9.44 (9.21)	4.9 (5.15)	247 (246)
KI	3.05 (3.048)	11.0 (11.0)	4.3 (4.53)	166 (173)
RbI	3.18 (3.177)	11.4 (–)	4.1 (4.36)	119 (125)
CsI	3.31 (3.315)	11.4 (12.1)	4.0 (–)	101 (109)

[a] The sources of the experimental data are as follows: (i) bond lengths, from microwave spectroscopic determinations reported in [12]; (ii) dipole moments, from data reported in [13]; (iii) dissociation energies, from thermochemical data reported in [3]; and (iv) vibrational frequencies, from spectroscopic measurements reviewed in [14]. In the calculations the values of the model parameters that we have adopted for the alkali metals, using data from [15] and [16], are reported in [7].

Table 3. Model parameters for alkaline-earth halides[a].

	R_i (Å)	ρ_i (Å)	α_i (Å^3)	C_i (e Å$^{5/2}$)
Be	0.733	0.0394	0	0
Mg	1.007	0.0538	0.1	0
Ca	1.322	0.0711	1.1	0
Sr	1.449	0.0777	1.6	0
Ba	1.578	0.0850	2.5	0

[a] The electronic polarizabilities are taken from [15], except for Mg [10]. The parameters for Be are taken from [19] and all the other parameters are from [10].

ular configuration, and a full account of the observed trends across the family of compounds has been obtained as arising from the interplay of the electronic polarizability of the cation and of the cation-anion bond length [10]. A broader viewpoint on molecular shapes in alkaline-earth dihalides and in other sp-bound triatomic molecules and clusters has been taken within pseudopotential theories of electronic structure by Andreoni et al. [18].

By using the transferable halogen parameters in Table 1 and the metal parameters in Table 3 we obtained the results given in Table 4 on alkaline-earth halide molecules. Excellent agreement with the experimental data is obtained. Our results are indeed quite similar to those obtained by Galli and Tosi [10].

4. Actinide Chlorides

The physical and chemical properties of molten actinide halides, and especially of chlorides, are important in molten salt technology. Little is known, however, about their liquid structure, justifying an effort to develop interionic-force models that may help in complementing diffraction experiments with simulation studies [20].

In our early work [21] we have described a model for the ionic interactions in the halides of some tetravalent actinide metals from an analysis of their gaseous monomers. The main focus was on the effective valence, the ionic radius and the electric polarizability of these metal ions, for a given input on the overlap and polarization parameters of the halogens. We have demonstrated some simple and reasonable trends in the metal ion parameters, which might be usefully extended to the whole series of transuranic elements. In the halides of U, Np, Pu and Am we found simple regular trends in the model parameters, while some quantitative deviations from these trends appear in the Th halides.

In this work we repeat the ionic model calculations on the bond lengths and vibrational frequencies for the tetrahedral ACl_4 monomers by using the transferable halogen parameters from Table 1. The actinide metal parameters are taken from [21], since the overall agreement with the available data and estimates for tetrachlorides is very good. Our present results are reported in Table 5, where they are compared with available data and estimates from [22]. We have adjusted the effective valence z_A by fitting to the available experimental data to improve the agreement with the experimental evidence on the bond length (first row) or on the vibrational frequencies (second row). Overall charge neutrality determines $z_A = -3z_{Cl}$. The agreement with the available data is quite good.

5. Concluding Remarks and Future Perspectives

We have tested the deformation-dipole model for ionic materials by invoking the transferability of potential parameters for halogen ions from one material to another. We have seen that the model parameters

	r_0	U_0	ν_1	ν_2	ν_3
BeF_2	1.348 (1.374)*	770 (–)	764 (680)	378.2 (345)	1651 (1555)
MgF_2	1.7 (1.77)	609 (615)	581.3 (550)	155.4 (240)	891 (841.8)
CaF_2	2.065 (2.10)	499 (522)	486.3 (484.8)	57.9 (163.4)	587.6 (555)
SrF_2	2.206 (2.20)	467 (490)	452.5 (441.5)	67.5 (82)	471.6 (443)
BaF_2	2.330 (2.32)	441 (469)	424 (413.2)	87 (64)	433.5 (389.6)
$BeCl_2$	1.775 (1.791)	688 (–)	533.6 (390)	287 (250)	1436.8 (1135)
$MgCl_2$	2.133 (2.18)	544 (543)	407.7 (326.5)	115 (93)	754 (600.8)
$CaCl_2$	2.523 (2.51)	445 (460)	318.7 (243)*	22 (63.6)*	479.8 (402.3)*
$SrCl_2$	2.676 (2.67)	416 (437)	298.8 (269.3)	17 (43.7)	356 (299.5)
$BaCl_2$	2.811 (2.82)	392 (414)	292 (255.2)	37 (61)*	301 (260)
$BeBr_2$	1.89 (–)	663 (–)	331 (230)	263 (220)	1282 (1010)
$MgBr_2$	2.254 (2.34)	526 (524)	255.5 (197.9)	102.6 (81)	653.3 (479.1)
$CaBr_2$	2.65 (2.67)	431 (443)	200.6 (195)$^{\#}$	25.4 (61)*	403.7 (324)*
$SrBr_2$	2.807 (2.82)	403 (417)	184 (184)$^{\#}$	6.4 (–)	280 (–)
$BaBr_2$	2.95 (2.95)	379 (394)	189 (175)$^{\#}$	23 (38)$^{\#}$	222 (–)
BeI_2	2.04 (–)	639 (–)	249.7 (160)	241 (175)	1127 (373)
MgI_2	2.411 (2.52)	507 (500)	188 (147.6)	96.7 (55.8)	579.8 (444.9)
CaI_2	2.818 (2.88)	415 (422)	148 (142)$^{\#}$	28 (50)$^{\#}$	355.5 (299)*
SrI_2	2.979 (3.03)	388 (398)	136 (134)$^{\#}$	12 (–)	240 (200)*
BaI_2	3.13 (3.20)	364 (374)	139 (128)$^{\#}$	15 (10)$^{\#}$	185 (–)

Table 4. Bond length r_0 (Å), binding energy U_0 (kcal/mol) and vibrational frequencies ν (cm^{-1}) of alkaline-earth halides[a].

[a] The experimental values denoted by * are taken from [12], while those marked with $^{\#}$ are estimated gas-phase data taken from [12].

		z_A	ρ_A (Å)	R_A (Å)	α_A (Å^3)	r_{A-Cl}	ν_1	ν_2	ν_3	ν_4
UCl_4	M1	3.093	0.0726	1.35	2.0	2.514	352	73	317	62
	M2	2.96	0.0726	1.35	2.0	2.544	333	61	302	68
	Expt.	–	–	–	–	2.506	327	62	337	72
$NpCl_4$	M1	3.093	0.0720	1.34	2.0	2.502	354	74	317	62
	M2	2.96	0.0720	1.34	2.0	2.532	335	61	303	69
	Expt.	–	–	–	–	(2.49)	(340)	(80)	(330)	(70)
$PuCl_4$	M1	3.093	0.0710	1.32	2.0	2.478	359	76	316	61
	M2	2.96	0.0710	1.32	2.0	2.508	339	71	302	60
	Expt.	–	–	–	–	(2.48)	(340)	(80)	(335)	(70)
$AmCl_4$	M1	3.093	0.0704	1.31	2.0	2.466	362	76	316	61
	M2	2.96	0.0704	1.31	2.0	2.496	342	72	302	60
$ThCl_4$	M1	3.093	0.0742	1.38	2.0	2.550	344	70	316	63
	M2	2.96	0.0742	1.38	2.0	2.580	326	66	301	61
	Expt.	–	–	–	–	2.567	(325)	(60)	335	(70)

Table 5. Metal ion parameters, bond lengths (Å) and vibrational frequencies (cm^{-1}) of tetrahedral ACl_4 molecules[a].

[a] For each molecule the first and second line gives our results. In the first line the effective valence z_A is adjusted to the measured values of the A-Cl bond length. In the second line the value of z_A is adjusted to the frequency of the ν_1 mode. The third line reports the data from [22], estimated values being shown in parentheses.

can be usefully transferred not only between different states of aggregation of these materials, as already demonstrated in our previous work [7], but also between different families of compounds.

With regard to future applications of the present results, it is appropriate to remember that electronic distortions of the outer electron shells of the ions have a rather modest role to play in the theory of the liquid structure of alkali halides near freezing at standard pressure [23]. However, these effects will certainly come to the fore even in these systems, as the liquid density is lowered: specifically, in determining their liquid-gas coexistence curve and their critical behaviour, and in quantitatively describing the transition in the bond character that must take place across the liquid-gas interface in going from a dissociated ionic liquid to a molecular gas. The latter topic is of considerable fundamental and practical interest at present.

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[1] M. Born and J. E. Mayer, Z. Phys. **75**, 1 (1932).
[2] E. S. Rittner, J. Chem. Phys. **19**, 1030 (1951).
[3] M. P. Tosi and M. Doyama, Phys. Rev. **160**, 716 (1967).
[4] Z. Akdeniz and M. P. Tosi, Z. Naturforsch. **54a**, 180 (1999).
[5] M. Wilson and P. A. Madden, Phys. Rev. Lett. **80**, 532 (1998).
[6] D. A. Keen, S. Hull, A. C. Barnes, P. Berastegui, W. A. Crichton, P. A. Madden, M. G. Tucker, and M. Wilson, Phys. Rev. B **68**, 014117 (2003).
[7] A. Karaman, Z. Akdeniz, and M. P. Tosi, Phys. Chem. Liq. **44**, 353 (2006).
[8] W. R. Busing, Trans. Am. Crystallogr. Assoc. **6**, 57 (1970).
[9] P. S. Yuen, R. M. Murfitt, and R. L. Collin, J. Chem. Phys. **61**, 2383 (1974).
[10] G. Galli and M. P. Tosi, N. Cimento D **4**, 413 (1984).
[11] W. Andreoni, G. Galli, and M. P. Tosi, unpublished results (1986).
[12] M. Hargittai, Chem. Rev. **100**, 2233 (2000).
[13] P. Brumer and M. Karplus, J. Chem. Phys. **58**, 3903 (1973).
[14] M. H. Brooker and G. N. Papatheodorou, in: Advances in Molten Salt Chemistry, Vol. 5 (Ed. G. Mamantov), Elsevier, Amsterdam 1983, p. 26.
[15] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).
[16] A. Büchler, J. L. Stauffer, and W. Klemperer, J. Am. Chem. Soc. **86**, 4544 (1964).
[17] L. Wharton, R. A. Berg, and W. Klemperer, J. Chem. Phys. **39**, 2023 (1963).
[18] W. Andreoni, G. Galli, and M. P. Tosi, Phys. Rev. Lett. **55**, 1734 (1985).
[19] W. Li and M. P. Tosi, N. Cimento D **10**, 1497 (1988).
[20] Y. Okamoto, F. Kobayashi, and T. Ogawa, J. Alloys Comp. **271 – 273**, 355 (1998).
[21] Z. Akdeniz, A. Karaman, and M. P. Tosi, Z. Naturforsch **56a**, 376 (2001).
[22] R. J. M. Konings and D. L. Hildebrand, J. Alloys Comp. **271 – 273**, 583 (1998).
[23] M. Rovere and M. P. Tosi, Rep. Progr. Phys. **49**, 1001 (1986).