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Global expression for representing cohesive-energy curves

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The R dependence of the cohesive energy of partially ionic solids is examined with a two-term generalization of the universal energy relationship consisting of a Coulomb term arising from the valence charge transfer, δZ, between the atoms, and a scaled universal energy function, $E^*(a^*)$, which accounts for the partially covalent character of the bond, and for the repulsion between the atomic cores for small R; a^* is a scaled length. Data from NaCl-structure alkali halide crystals are used to test the procedure. We find that this procedure gives a reasonable apportionment of ionic and covalent terms for the alkali halides. Plots of the normalized cohesive-energy curves for Li, Na, K, and Rb halides indicate that they scale within each family and are essentially identical.

I. INTRODUCTION

Recently,[1] we demonstrated that the ground-state energy of partially ionic, partially covalent diatomic molecules may be accurately characterized by a generalization of the universal energy relation of the form

$$E(R)=CE^*(a^*)-(\delta Z)^2/R \equiv \mathcal{E}(a^*,\delta Z)D_e , \qquad (1)$$

where a^* is a suitably defined scaled length, and D_e is the molecular dissociation energy, $E^*(a^*)$ is the universal binding-energy relation, δZ is the charge transfer, and R is the interionic separation. This form has physical appeal, since it allows for the possibility of partially covalent, partially ionic bonds. For $\delta Z=0$ the energy relation reduces to the universal form previously found to describe metallic and covalent bonds in adhesion,[2] chemisorption[3] and cohesion,[4] binding of covalent diatomic molecules,[5] and of nuclear matter.[6] In our previous work[1,7] we used Eq. (1) in conjunction with spectroscopic data to predict charge-transfer values for 62 halide molecules. The charge-transfer values obtained are comparable to the values obtained by other methods.[8,9]

In this paper we use an energy relationship, similar to Eq. (1), to estimate the ionic and covalent contributions to the cohesive energy of partially ionic solids at equilibrium. We then investigate the variation of the cohesive energy as a function of lattice parameter. This generalization conforms to Pauling's description of a partially covalent, partially ionic bond, and thus treats a broader class of bonding than either the Born-Mayer potential,[10] which does not allow for an attractive covalent contribution to binding, or the universal binding-energy relation,[2-5] which does not explicitly include any charge transfer. The generalized form approaches the Born-Mayer potential in the limit of a very weak covalent bond, and it approaches the universal energy relation in the limit of very weak ionic bonding ($\delta Z \approx 0$). The parameters used to generate the cohesive-energy curves are obtained from the equilibrium values of the isothermal bulk modulus, the pressure derivative of the bulk modulus, the equilibrium lattice parameter, and the equilibrium cohesive energy. These input parameters are used to determine the well depth (C) for the covalent term and the charge transfer (δZ) for the ionic term as defined in Eq. (1).

II. PARTIALLY IONIC SOLIDS

Analogous to the case of partially ionic bonding in molecules[1] we write the cohesive energy of partially ionic solids as a function of the nearest-neighbor distance, R, as

$$E(R)=CE^*(a^*)-\alpha(\delta Z)^2/R \equiv \mathcal{E}(a^*,\delta Z)\Delta E , \qquad (2)$$

where the Coulomb term arises from the valence charge transfer, δZ, between the atoms, ΔE is the cohesive energy at equilibrium lattice spacing, and α is the Madelung constant for the lattice. The universal energy function, $E^*(a^*)$, accounts for both the partially covalent character of the bond, as well as for the repulsion between the atomic cores as R approaches zero; the scaled length $a^* \equiv (R-R_e')/l$, where R_e' is the value of R for which $E^*(a^*)$ is a minimum, and the scaling length

$$l \equiv \{\Delta E/[d^2E(R)/dR^2]_{R_e}\}^{1/2} .$$

Since the Coulomb term shifts the minimum of $E(R)$ away from the minimum of $E^*(a^*)$, R_e' is not equal to the equilibrium lattice spacing, R_e. The values of C, R_e', and l are obtained in terms of the experimental values at equilibrium lattice spacing of the bulk modulus, B_0, the pressure derivative of the bulk modulus, B_0', and the cohesive-energy ΔE.

At the minimum of the cohesive-energy curve, Eq. (2), $a_e^* \equiv (R_e - R_e')/l$,

$$E(R_e) \equiv -\Delta E = [C'E^*(a_e)^* - Z']\Delta E \ , \qquad (3)$$

where the normalized Coulomb energy is $Z' \equiv \alpha(\delta Z)^2/R_e\Delta E$, and the normalized well depth is $C' \equiv C/\Delta E = [Z'-1]/E^*(a_e^*)$.

As in our previous work[1-7] we use the Rydberg potential, $E^*(a^*) = -(1+a^*)\exp(-a^*)$, to represent the universal energy function. In this case, $a_e^* = Z'l'/[(Z'-1)-Z'l']$, where the normalized scaling length $l' \equiv l/R_e$. The second derivative of $\mathcal{E}(a^*,\delta Z)$ at R_e is given by

$$\mathcal{E}''(a_e^*) \equiv 2\gamma(l')^2 = (1-Z') + 2Z'l' - 2Z'(l')^2 \ , \qquad (4)$$

where the parameter γ may be expressed in terms of the zero pressure isothermal bulk modulus B_0 and volume V_0 as $\gamma \equiv 9B_0V_0/2\ \Delta E$. Finally, the pressure derivative of the bulk modulus at zero pressure can be written as

$$B_0' = 1 - Z'/\gamma + [4(\gamma+Z')l' - Z']/6\gamma(l')^2 \ . \qquad (5)$$

These equations may be solved simultaneously for l' and either Z' or B_0'. (One may solve for Z' using the experimental B_0, B_0', ΔE, and V_0 values, or alternatively solve for B_0' for fixed values of γ and Z' generated with the experimental B_0, ΔE, and V_0 values, and theoretical values for Z'.)

III. RESULTS

We now test this procedure on the alkali halides in order to determine its consistency with intuitive expectations that the ionic contributions are large and the covalent small. An extensive database of values of B_0 and B_0' is available from ultrasonic experiments performed by Smith and co-workers[11-15] for the NaCl-structure alkali

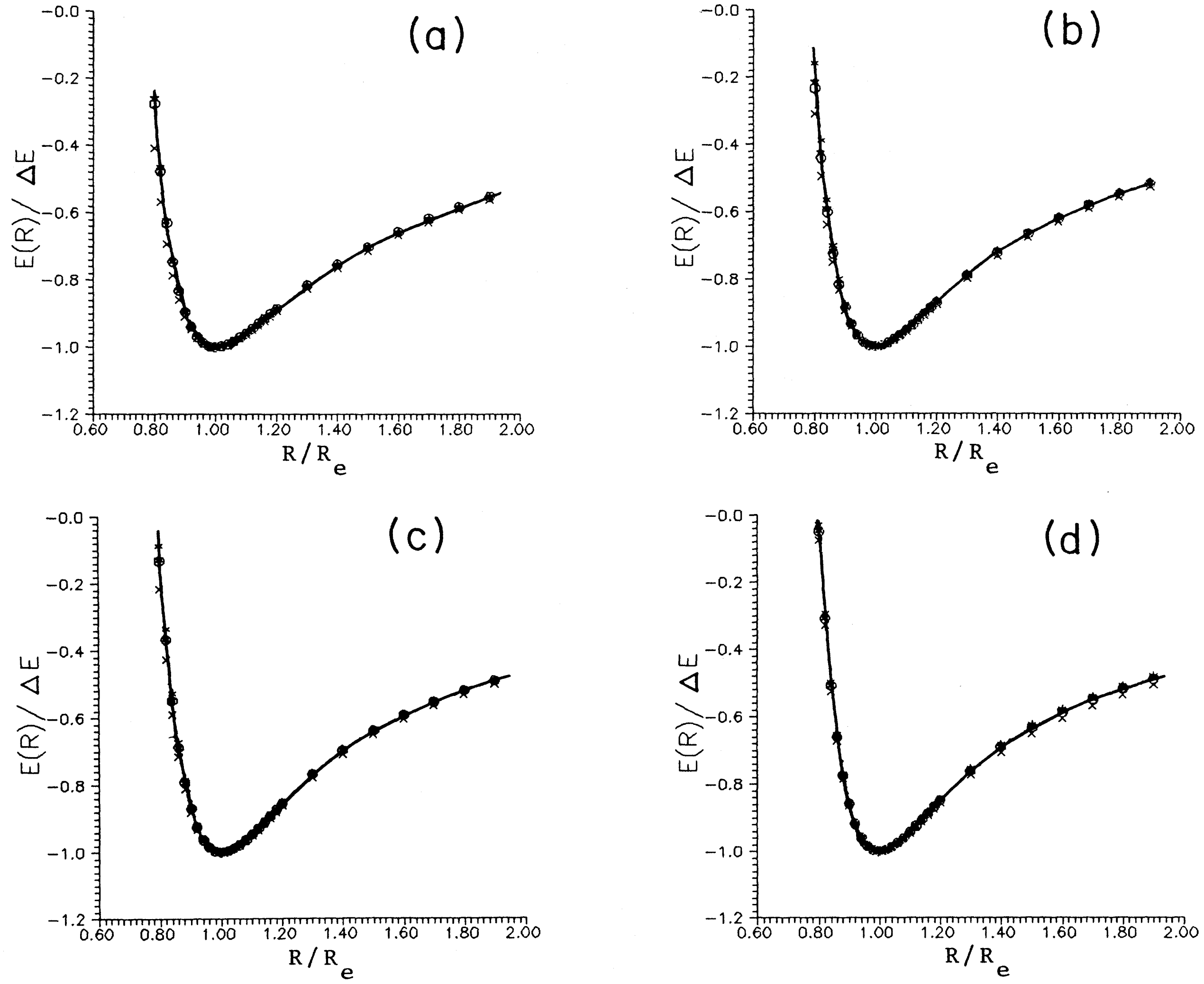

FIG. 1. Normalized-cohesive-energy curves for alkali halides. (a) Li halides: (×) LiF, (○) LiCl, (★) LiBr. (b) Na halides: (×) NaF, (○) NaCl, (★) NaBr, (∗) NaI. (c) K halides: (×) Kf, (○) KCl, (★) KBr, (∗) KI. (d) Rb halides: (×) RbF, (○) RbCl, (★) RbBr, (∗) RbI.

TABLE I. δZ values which fit the ultrasonic B_0 and B_0' values and l', a_e^*, C', and Z' values, which fit the experimental B_0 and B_0' values.

Material	B (GPa)	B' (Expt.)	δZ	l'	a_e^*	C'	Z'
LiF	66.51	5.305	0.9621	0.115 739 6	−2.204 726	0.006 180 163	1.067 513
LiCl	29.68	5.625	0.9752	0.110 167 9	−1.781 425	0.010 942 99	1.050 779
LiBr	23.52	5.677	0.9897	0.108 506 7	−1.817 582	0.010 193 63	1.051 313
NaF	46.48	5.282	0.9405	0.129 969 9	−0.980 460 2	0.049 599 93	0.997 416 5
NaCl	23.68	5.412	0.9483	0.127 800 0	−0.863 252 8	0.061 204 37	0.980 157 0
NaBr	19.47	5.430	0.9498	0.128 157 9	−0.812 717 6	0.067 952 72	0.971 314 5
NaI	14.87	5.565	0.9577	0.123 925 6	−0.821 216 1	0.064 389 70	0.973 729 4
KF	30.22	5.361	0.9320	0.131 841 3	−0.734 961 7	0.082 115 44	0.954 613 9
KCl	17.35	5.480	0.9320	0.129 722 4	−0.654 144 7	0.096 480 64	0.935 816 1
KBr	14.64	5.476	0.9355	0.130 214 7	−0.636 808 3	0.100 687 9	0.930 868 6
KI	11.51	5.564	0.9399	0.127 531 3	−0.637 127 7	0.098 681 9	0.932 283 8
RbF	26.68	5.692	0.9401	0.121 656 5	−0.747 672 9	0.074 001 23	0.960 562 2
RbCl	15.58	5.620	0.9330	0.126 334 1	−0.615 718 4	0.102 748 5	0.926 915 0
RbBr	13.24	5.590	0.9304	0.127 967 0	−0.581 076 1	0.112 767 0	0.915 535 3
RbI	10.49	5.599	0.9311	0.128 074 7	−0.564 226 7	0.117 490 9	0.909 987 0

halide crystals. We utilized these experimental values in conjunction with the experimental values of ΔE (Ref. 16), and V_0 to generate the cohesive-energy curves for these materials with Eq. (2). In Table I we list the δZ values that fit the ultrasonic B_0 and B_0' values. In addition, we list the l', a_e^*, C', and Z' values that fit the experimental B_0 and B_0' values, and from which the cohesive-energy curves may be generated. First, we note that the values obtained for δZ are reasonable (i.e., >0.9 for the alkali halides). Next we note that C', the normalized well depth, which represents the fractional covalent contribution to the binding energy at equilibrium, is small but not negligible in most cases. It is difficult to generalize about trends in the parameters, since the experimental error in B_0' is approximately ±10% (Ref. 18), and we have found that δZ is proportional to B_0' in this range. For comparison, we reverse the procedure and in Table II present estimates of B_0' for the charge-transfer values given by Phillips and Van Vechten[8] and Nagasaka and Kojima.[16] Except for the lithium compounds, the agreement is within the experimental error.

In Figs. 1(a)–1(d) we have plotted the normalized cohesive-energy curves versus R/R_e for the Li, Na, K, and Rb halides, respectively. In Fig. 2 we have plotted the normalized cohesive energy versus R/R_e for the eight K and Rb halides. The solid lines in each figure are plots of Eq. (2) utilizing average parameter values for the data within each family. Note that to a very good approximation the normalized cohesive-energy curves

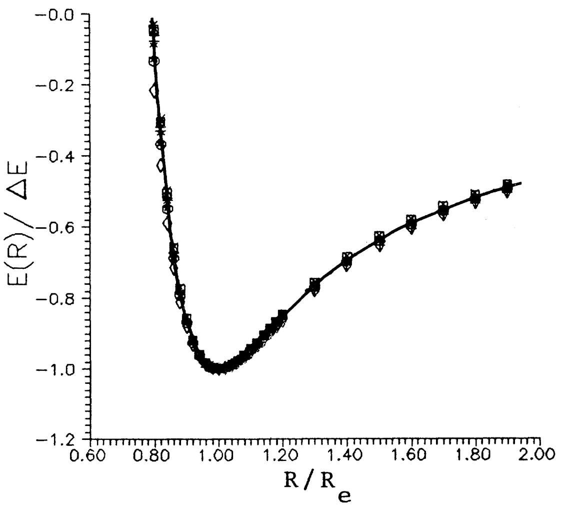

FIG. 2. Normalized-cohesive-energy curves for K and Rb halides: (◇) KF, (○) KCl, (★) KBr, (∗) KI, (+) RbF, (△) RbCl, (□) RbBr, (×) RbI.

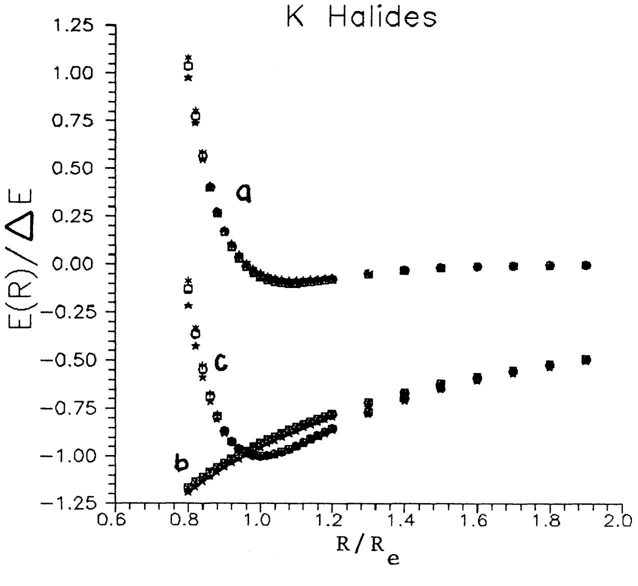

FIG. 3. Components of normalized-cohesive-energy curves for K halides. (a) Rydberg component $\equiv C'E^*(a^*)$: (★) KF, (○) KCl, (□) KBr, (∗) KI. (b) Coulomb component $\equiv Z'/(R/R_e)$: same as Fig. 3(a). (c) Total normalized cohesive energy: same as Fig. 3(a).

TABLE II. Estimates of B'_0 for the charge-transfer values given by Phillips and Van Vechten (Ref. 8) and Nagasaka and Kojima (Ref. 16).

Material	B' (expt.)	δZ	B' (Phillips and Van Vechten)	δZ	B' (Nagasaka and Kojima)	δZ (Nagasaka and Kojima)
LiF	5.305	0.9621	4.555	0.915	5.696	0.971
LiCl	5.625	0.9752	4.612	0.903	4.780	0.923
LiBr	5.677	0.9897	4.518	0.899	4.537	0.902
NaF	5.282	0.9405	5.380	0.946	5.012	0.921
NaCl	5.412	0.9483	5.224	0.935	5.164	0.930
NaBr	5.430	0.9498	5.220	0.934	5.080	0.921
NaI	5.565	0.9577	5.172	0.927	5.145	0.923
KF	5.361	0.9320	5.754	0.946	5.949	0.963
KCl	5.480	0.9320	5.809	0.953	5.625	0.941
KBr	5.476	0.9355	5.716	0.952	5.342	0.924
KI	5.564	0.9399	5.708	0.950	5.304	0.917
RbF	5.692	0.9401	6.092	0.960	6.092	0.960
RbCl	5.620	0.9330	5.972	0.955	5.620	0.933
RbBr	5.590	0.9304	6.000	0.957	5.526	0.925
RbI	5.599	0.9311	5.879	0.951	5.462	0.919

within each family are essentially identical for $R > R_e$. This is expected from our numerical results, since the covalent term decays exponentially and is small in magnitude compared to the binding energy ($\sim 10\%\ \Delta E$). In addition, since there is only a small variation in Z' within a family (Table I) the distance dependence scales with R_e. In the compressive region ($R < R_e$) the deviation is also not large. We find that within a family, C', l' and R'_e/R_e have a relatively small variation, which again leads to R/R_e scaling. This is physically reasonable, since the overlap terms begin to predominate for $R < R_e$, and the halide ionic radii are all approximately equal[17] to within 10% except for F^-. In Fig. 3 we plot a breakdown of the covalent and ionic components of the energy for the potassium halides. It is apparent that there is a nonnegligible contribution to the bonding from the covalent component.

In conclusion, we have tested a generalization of the universal binding-energy relation, which includes an ionic term in order to describe the binding of partially ionic, partially covalent solids. Experimental input at equilibrium is used to determine the relative contributions of these components. We found that this approach gives reasonable behavior for the charge transfer and strength of the covalent contribution for the alkali halides, i.e., a large ionic contribution and small covalent contribution at equilibrium. Thus, we conclude that it is consistent with the input data. A comparison with solids with smaller expected charge transfer and larger covalent contributions is in progress in order to check the generality of our procedure. Also, these results indicate that an approximate R/R_e scaling of the binding-energy curves is present for these compounds. It would be of interest to test Eq. (2) by first-principles calculations, over a wide range of distances and charge transfers, in order to verify that our extrapolation from experimental data at equilibrium is indeed an accurate global representation of cohesive-energy–distance curves.

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