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Global expression for representing cohesive-energy curves. II

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In paper I [Phys. Rev. B **44**, 9696 (1991)] we showed that the R dependence of the cohesive energy of partially ionic solids may be characterized by a two-term energy relationship consisting of a Coulomb term arising from the charge transfer, δZ, and a scaled universal energy function, $E^*(a^*)$, which accounts for the partially covalent character of the bond and for repulsion between the atomic cores for small R; a^* is a scaled length. In paper I the normalized cohesive-energy curves of NaCl-structure alkali-halide crystals were generated with this expression. In this paper we generate the cohesive-energy curves of several families of partially ionic solids with different crystal structures and differing degrees of ionicity. These include the CsCl-structure Cs halides, and the Tl and Ag halides, which have weaker ionic bonding than the alkali halides, and which have the CsCl and NaCl structures, respectively. The cohesive-energy-curve parameters are then used to generate theoretical isothermal compression curves for the Li, Na, K, Cs, and Ag halides. We find good agreement with the available experimental compression data.

I. INTRODUCTION

Recently,[1] we demonstrated that the R dependence of the normalized cohesive energy, $\mathcal{E}(a^*,\delta Z,X)\equiv E(R)/\Delta E$, of partially ionic–partially covalent solids may be obtained from,

$$\mathcal{E}(a^*,Z',X)\equiv C'E^*(a^*)-Z'/X \ , \tag{1}$$

where R is the nearest-neighbor distance, ΔE is the equilibrium cohesive energy, and $X\equiv(R/R_e)=(V/V_0)^{1/3}$. In Eq. (1), the normalized Coulomb energy $Z'\equiv\alpha(\delta Z)^2/R_e\Delta E$, the normalized well depth $C'\equiv[Z'-1]/E^*(a_e^*)$, and the universal energy function $E^*(a^*)$ accounts for both the partially covalent character of the bond and for the repulsion between the atomic cores for small R; α is the Madelung constant, δZ is the charge transfer between atoms, R_e is the equilibrium nearest-neighbor distance, the scaled length $a^*\equiv[X-(R_e'/R_e)]/1'$, where R_e' is the value of R for which $E^*(a^*)$ is a minimum,[2] and the normalized scaling length $l'\equiv\{\Delta E/[d^2E(R)/dR^2]_{R_e}\}^{1/2}/R_e$. As previously,[1,3,4] we represent the universal energy function by the Rydberg potential, $E^*(a^*)=-(1+a^*)\exp(-a^*)$. The parameters C', Z', a_e^*, and l' are calculated[1] from experimental values of the zero pressure isothermal bulk modulus, B_0, the pressure derivative of the bulk modulus, B_0', and the cohesive energy, ΔE, measured at R_e. We note that Eq. (1) has physical appeal, since it explicitly allows for both covalent and ionic binding in contrast to the Born-Mayer potential,[5] which includes only ionic attraction and exponential repulsion, and the universal energy relation,[6] which does not include ionic binding.

II. GENERATION OF COMPRESSION CURVES

The isothermal compression curves (pressure-volume relationship) for a given solid may be calculated from the cohesive-energy relationship, since $P(V)\equiv-(dE/dV)=-\Delta E(d\mathcal{E}/dV)$. Thus, the pressure is given in terms of the cohesive-energy parameters by the following expression,

$$P=-[C'a^*e^{-a^*}/l'+Z'/X^2]\Delta E/[\beta X^2R_e^3] \ , \tag{2}$$

where $\beta=12$ for the NaCl structure, and $\beta=16/\sqrt{3}$ for the CsCl structure. As discussed in paper I, generation of the cohesive-energy curves requires a consistent data set of B_0 and B_0' values. Data for NaCl-structure alkali halides was obtained from the ultrasonic experiments of Smith and co-workers,[7–9] and for Cs halides from Chang and Barsch.[10] Experimental B_0' values were not available for Ag halides. Hence, theoretical values[11] of the charge transfer, δZ, were used in conjuction with experimental B_0 values to obtain the cohesive-energy parameters. Our theoretical compression curves are compared with the experimental compression data from Vaidya and Kennedy[12] (0–45 kbar), and from Yagi[13] (0–90 kbar).

III. RESULTS

A. Cohesive energy

In Figs. 1(a) to 1(c) we have plotted the normalized cohesive-energy curves for the Cs, Ag, and Tl halides, respectively. The solid lines in each figure are plots of Eq. (1) using average values for the parameters within each family. Note, that to a very good approximation the normalized cohesive-energy curves within each family with common cation are essentially identical.[1] Hence, we may conclude that the normalized cohesive-energy curves are accurately described by the generalized universal form [Eq. (1)]. the calculated cohesive-energy parameter values for the Cs, Ag, and Tl halides are tabulated in Table I. The δZ and Z' values for the Ag and Tl halides are much smaller and the C' values are much larger than those for the Cs halides, since the Ag and Tl halides are more covalently bonded than Cs halides. Note that as expected, δZ is approximately equal to 1 for the Cs halides

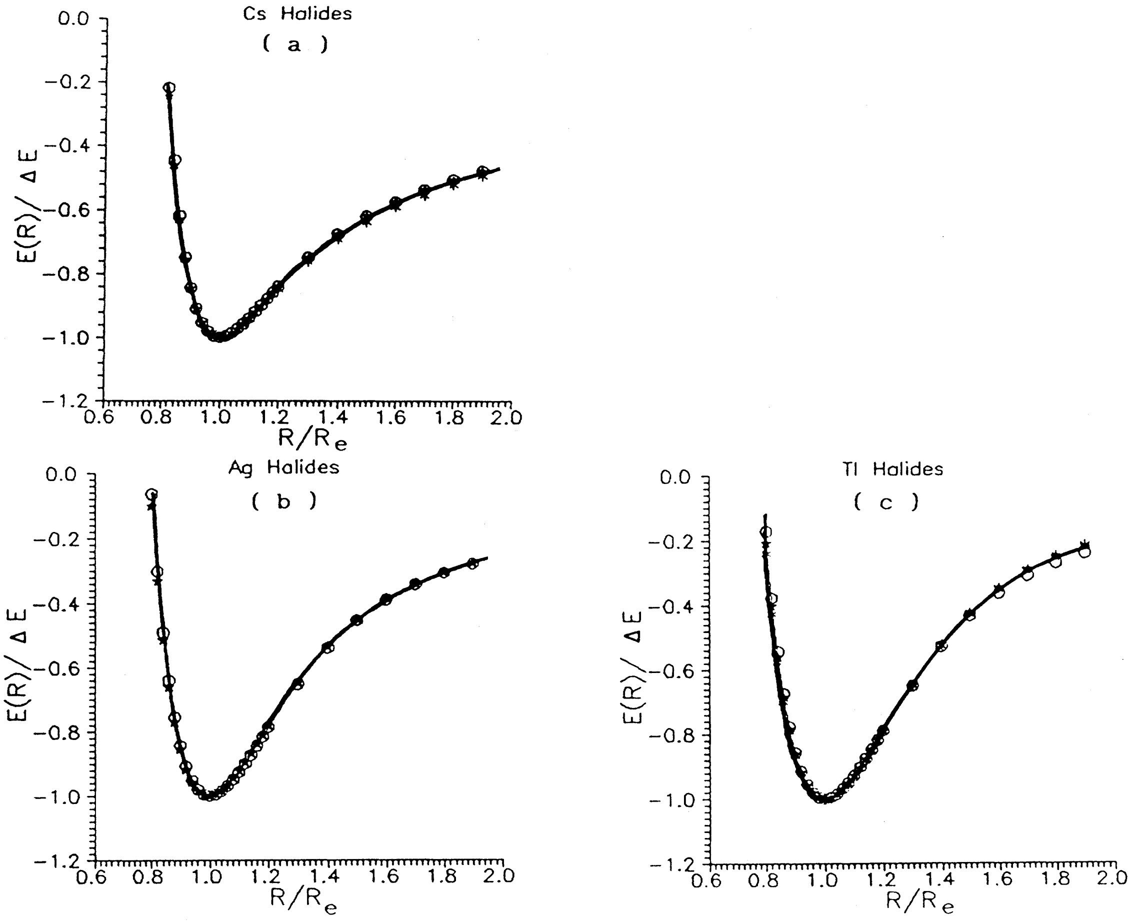

FIG. 1. Normalized cohesive energy curves. (a) Cs halides: (○) CsCl, (star) CsBr, (∗) CsI. (b) Ag halides: (○) AgCl, (star) AgBr. (c) Tl halides: (○) TlCl, (star) TlBr, (∗) TlI.

and substantially smaller for the Ag and Tl halides. Hence, this procedure predicts the expected general trends.

B. Compression curves

The ability to test the procedure for generating the cohesive-energy curves over a wide range of separations is limited, since there is no experimental data and the few available first-principles calculations cover a small range of separations near equilibrium. However, extensive experimental data exists for the pressure dependence of the volume. Therefore, we test our cohesive-energy expression by comparing the predicted P-V curve from Eq. (2) with experimental data. The theoretical compression curves (solid line) for the Li, Na, K, Cs, and Ag halides are plotted in Fig. 2 and compared with the experiments of Vaidya and Kennedy.[12] For the K halides, phase changes occur in the vicinity of 17 kbar. Hence, for the K halides P vs V is plotted to the compression values at which the phase change occurs experimentally. For the remaining halides in Fig. 2 no phase transitions were detected to 45 kbar.[12] Note that in each family with common cation the order of the relative compressibility is iodides > bromides > chlorides > fluorides. In Fig. 3 we have plotted the compression curves for LiF, NaF, KF, and CsCl. In each case, the asterisks denote the experimental data of Vaidya and Kennedy, the circles denote the Yagi data,[13] and the solid lines are the theoret-

TABLE I. δZ, l', a_e^*, C' and Z' values that fit the experimental B_0 and B_0' values. Crystal structure: (a) CsCl (b) NaCl.

Material		B (GPa)	B' (expt)	δZ	l'	a_e^*	C'	Z'
CsCl	(a)	16.2	5.89	0.9618	0.119 136 6	−0.644 171 3	0.091 118 06	0.938 255
CsBr	(a)	14.2	5.72	0.9482	0.124 960 6	−0.547 120 9	0.119 765 3	0.906 260
CsI	(a)	11.4	5.79	0.9533	0.122 991 1	−0.548 107 6	0.117 766 6	0.907 344
AgCl	(b)	42.5	5.19	0.847	0.149 855 0	−0.256 318	0.315 345 7	0.696 966
AgBr	(b)	40.0	5.33	0.860	0.145 201 9	−0.239 926	0.326 095 2	0.684 936
TlCl	(a)	23.1	4.25	0.5973	0.200 961 3	−0.98 144 49	0.652 063 0	0.351 291
TlBr	(a)	20.7	4.32	0.6303	0.196 221 3	−0.109 166 9	0.619 536 8	0.384 435
TlI	(a)	17.1	4.43	0.6805	0.189 035 0	−0.129 214 1	0.565 378 5	0.439 768

ical predictions. Particularly note in the case of KF that the theoretical results agree very well with Yagi's experimental compression data and that the data of Vaidya and Kennedy is in disagreement. Thus, our results are in agreement with Yagi who pointed out that the KF results of Vaidya and Kennedy are suspect. In addition, we note that the bulk modulus calculated from the KF data of Vaidya and Kennedy is approximately half that found in ultrasonic experiments.

Experimental compression data were also available for the Ag halides.[12] However, in this case B_0 values but no B_0' values were available from independent experiments. Hence, cohesive-energy parameters were generated by nonlinear curve fitting to the experimental compression curves. We find that the following values give good agreement with the experimental compression curves,

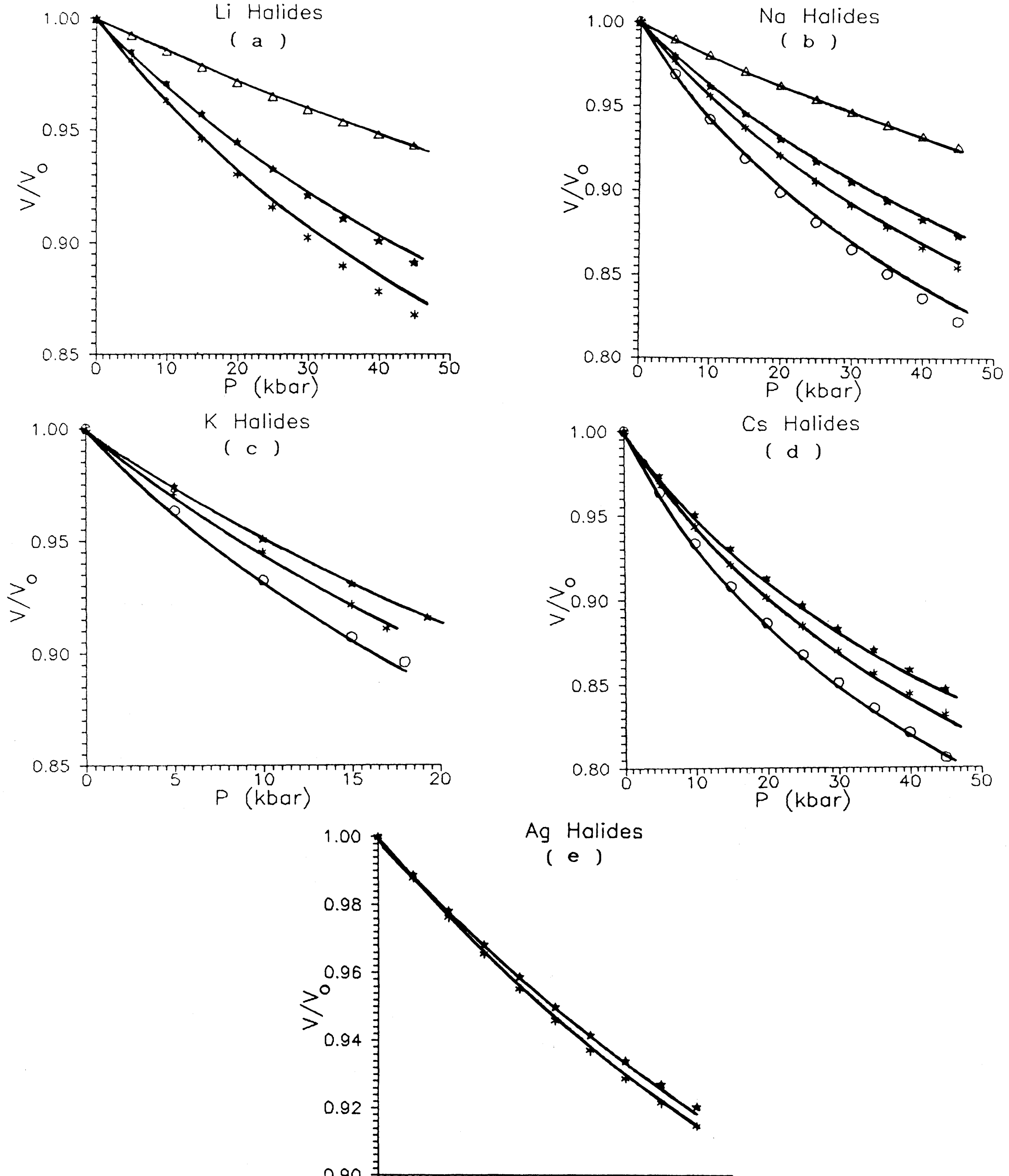

FIG. 2. Isothermal compression curves (experimental data from Ref. 12). (a) Li halides: (△) LiF, (star) LiCl, (∗) LiBr, (—) theory. (b) Na halides: (△) NaF, (star) NaCl, (∗) NaBr, (O) NaI, (—) theory. (c) K halides: (star) KCl, (∗) KBr, (O) KI, (—) theory. (d) Cs halides: (star) CsCl, (∗) CsBr, (O) CsI, (—) theory. (e) Ag halides: (star) AgCl, (∗) AgBr, (—) theory.

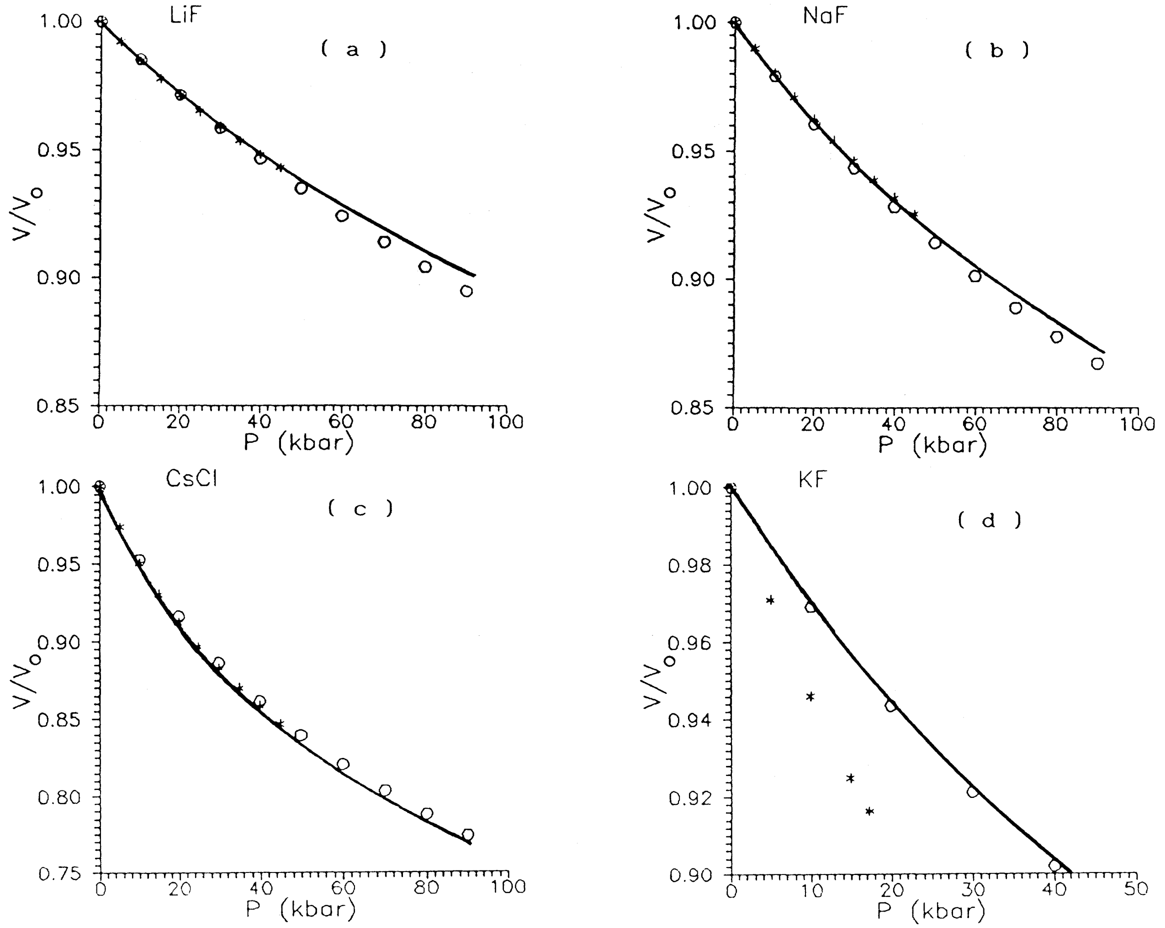

FIG. 3. Isothermal compression curves. (a) LiF: (*) (Ref. 12), (O) Expt. (Ref. 13), (—) Theory. (b) NaF: (*) Expt. (Ref. 12), (O) Expt. (Ref. 13), (—) Theory. (c) CsCl: (*) Expt. (Ref. 12), (O) Expt. (Ref. 13), (—) Theory. (d) KF: (*) Expt. (Ref. 12), (O) Expt. (Ref. 13), (—) Theory.

$B_0=425$ kbar and $B'_0=5.19$ for AgCl, and $B_0=400$ kbar and $B'_0=5.33$ for AgBr. The results obtained with Eq. (2) are plotted in Fig. 2(e).

In conclusion, we have proposed a functional form for the global representation of cohesive-energy curves, which includes both partially covalent and partially ionic bonding contributions. For all solids tested, with the exception of the Ag halides, the cohesive-energy parameters were generated from ΔE, R_e, and from B_0 and B'_0 values obtained from experiments independent of compression data; the parameters were then used to generate *P*-*V* curves which were compared with experimental equation of state curves. For the Ag halides cohesive-energy parameters were obtained by a nonlinear fit to the experimental compression curves. In all cases, when the *P*-*V* values obtained with Eq. (2) were compared with the experimental compression data for the Li, Na, K, Cs, and Ag halides, good agreement was obtained with experiment. A maximum rms deviation of 0.5% was obtained for any of the data sets.

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