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High-pressure equation of state for partially ionic solids

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Recently, we showed that the cohesive energy of partially ionic solids may be characterized by a two-term 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. Normalized cohesive-energy curves of alkali halide crystals and of Tl and Ag halide crystals were obtained, and the cohesive-energy-curve parameters were used to generate theoretical equation-of-state (EOS) curves for the Li, Na, K, Cs, and Ag halides. Good agreement was obtained with the experimental isothermal compression curves over a wide pressure range (0–90 kbar). In this paper we verify that the cohesive-energy relationship is valid for divalent partially ionic solids; physically reasonable charge-transfer values ($1.80 < \delta Z < 2.0$) are obtained for MgO, CaO, and CaS. Next, EOS curves for LiF, NaF, NaI, CsCl, CsI, MgO, CaO, and CaS are generated in terms of the cohesive-energy parameters. These EOS's yield excellent fits to experimental isothermal-compression data and to shock-wave data to very high pressures ($P_{\max} = 250$–1350 kbar).

I. INTRODUCTION

The R dependence of the normalized cohesive energy, $\mathcal{E}(a^*,\delta Z,X) \equiv E(R)/\Delta E$, of a partially ionic, partially covalent solid may be obtained from[1,2]

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

where R is the nearest-neighbor distance, ΔE is the cohesive energy measured at equilibrium nearest-neighbor distance R_e, 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 $C' \equiv C/\Delta E = [Z'-1]/E^*(a_e^*)$, 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 valance charge transfer between atoms, the scaled length $a^* \equiv [X-(R_e'/R_e)]/l'$, where R_e' is the value of R for which $E^*(a^*)$ is a minimum,[3] and the normalized scaling length $l' \equiv \{\Delta E/[d^2E(R)/dR^2]_{R_e}\}^{1/2}/R_e$. As previously,[1,2] 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[1,2] from experimental values of ΔE, R_e, the zero pressure isothermal bulk modulus, B_0, and the pressure derivative of the bulk modulus, B_0'.

An isothermal equation of state (EOS)[2] is obtained by differentiating Eq. (1) with respect to volume

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

since $P(V) \equiv -(dE/dV) = -(d\mathcal{E}/dV)\Delta E$; in Eq. (2), $\beta = 12$ for the NaCl structure and $\beta = 16/\sqrt{3}$ for the CsCl structure. We found[2] that Eq. (2) yields P-V curves which are in good agreement with the experimental compression curves for the alkali halides[4,5] over a wide pressure range (0–90 kbar).

The solids studied in our previous work[1,2] are monovalent. In this paper, we investigate the applicability of Eq. (1) to the calculation of the cohesive energy of divalent partially ionic solids. We find physically reasonable values for the charge transfer, δZ, for MgO, CaO, and CaS; namely, $1.80 < \delta Z < 2.0$. This verifies the applicability of Eq. (1) to divalent solids.

Next, we generate EOS for LiF, NaF, NaI, CsCl, MgO, CaO, and CaS from the cohesive-energy parameters to much higher pressures ($P_{\max} = 250$–1350 kbar) than previously.[2] Of particular interest is the comparison with the raw (unsmoothed) experimental compression data of Drickhamer and co-workers[6,7] for several alkali halides and for MgO, CaO, and CaS. We find that in all cases Eq. (2) yields an excellent fit with a *single* set of parameters to their unsmoothed data over essentially the entire pressure range.

II. GENERATION OF EOS

The ability to test the use of Eq. (1) in generating the cohesive-energy curves over a wide range of lattice spacing is limited since there is no experimental data and the few available first-principles calculations in the literature only cover a small range of separations. Previously,[2] the cohesive-energy expression was tested in the alkali and Ag halides by first generating the cohesive-energy curve parameters from the experimental values[8–12] of B_0, B_0', and ΔE measured at R_e, and then substituting these parameters in Eq. (2) to obtain a theoretical EOS which was compared with experimental compression data. Good fits were obtained to the experimental P-V data over the entire pressure range, $P \leq 45$–90 kbar. In this paper we use the cohesive-energy parameters to obtain theoretical EOS which fit the experimental P-V curves of LiF, NaF,

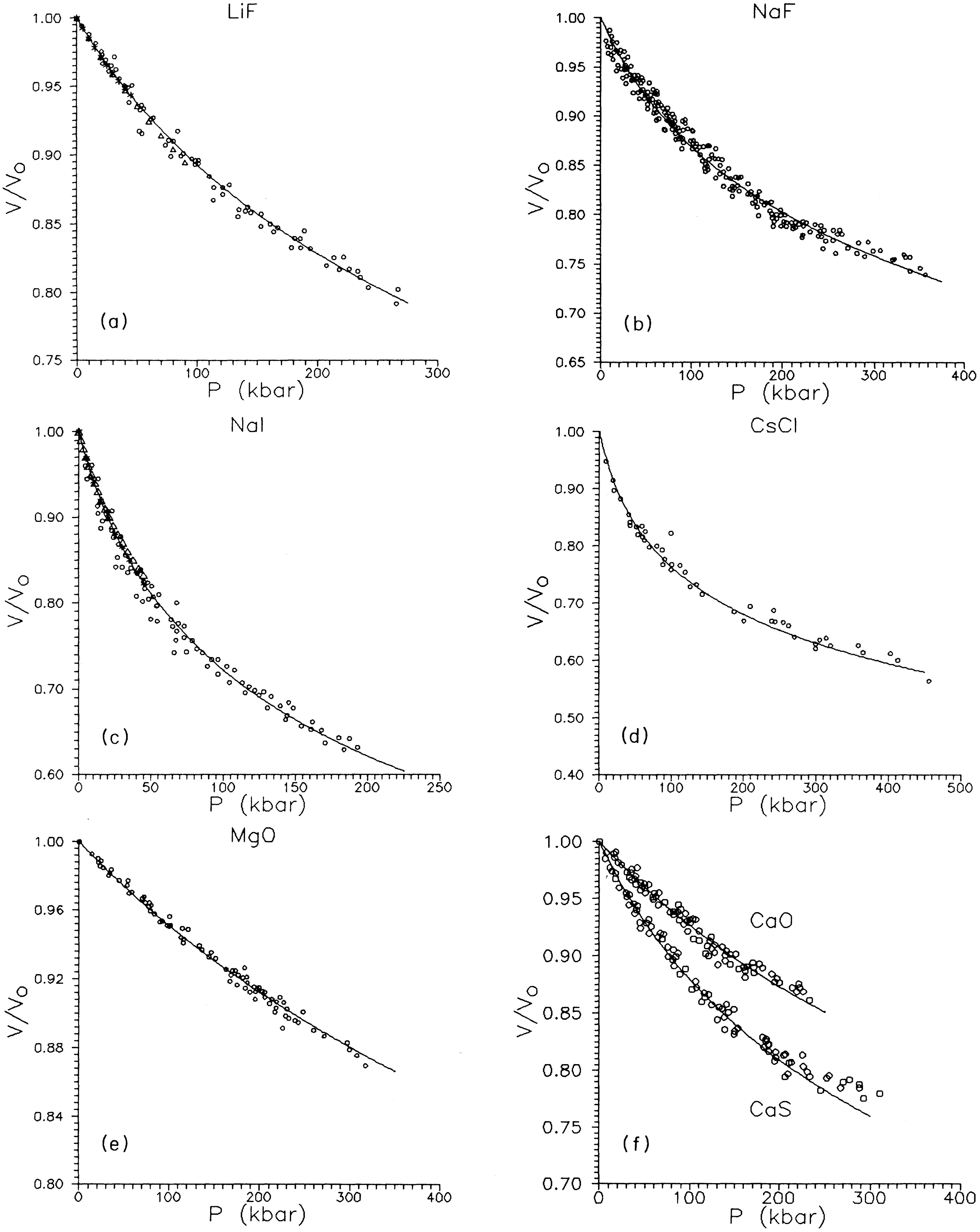

FIG. 1. Isothermal-compression curves. (a) LiF: (∗) expt., Ref. 4; (△) expt., Ref. 5; (○) expt., Ref. 7; (—) theory. (b) NaF: (○) expt., Ref. 7; (—) theory. (c) NaI: (∗) expt., Ref. 4; (△) expt., Ref. 5; (○) expt., Ref. 7; (—) theory. (d) CsCl: (○) expt., Ref. 6; (—) theory. (e) MgO: (○) expt., Ref. 6; (—) theory. (f) CaO: (○) expt., Ref. 6; (—) theory, CaS: (○) expt., Ref. 6; (—) theory.

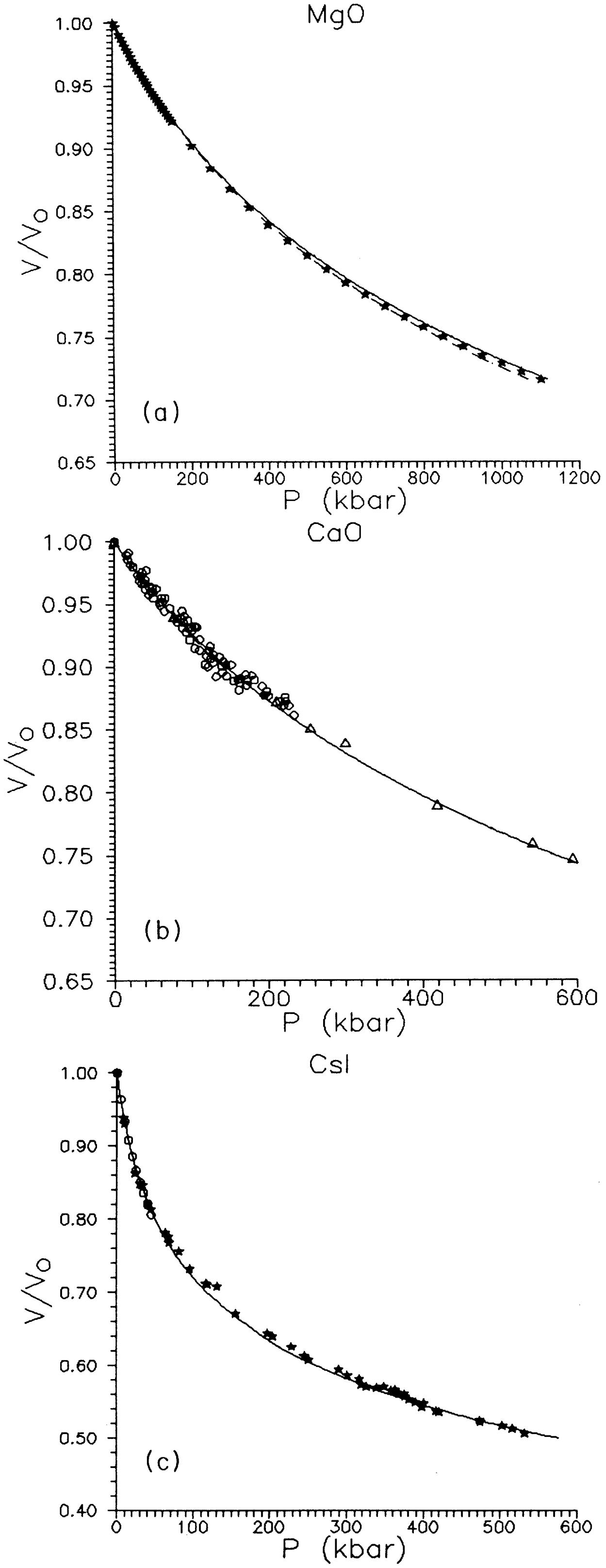

FIG. 2. Higher-pressure *P*-*V* curves. (a) MgO: (star) expt., Ref. 14; (—) theory. (b) CaO: (△) expt., Ref. 15; (○) expt. Ref. 6; (—) theory. (c) CsI: (star) expt., Ref. 16; (○) expt., Ref. 5; (—) theory.

NaI, CsCl, CsI, MgO, CaO, and CaS crystals over a much higher pressure range.[4–7] $P \leq 250-1350$ kbar, than in our earlier work.[2]

The procedure we use to obtain theoretical EOS from Eq. (2) is to generate sets of cohesive-energy parameters C', Z', a_e^*, and l' for fixed values of R_e, ΔE, and B_0 from ultrasonic data,[9,10] and with variable B_0'; B_0' is varied until the best fit to the experimental EOS data is obtained over the entire pressure range ($P \leq 250-1350$ kbar). Note that B_0' is used as a fitting parameter since the ultrasonic B_0' values, used previously,[2] do not yield the best fit to the higher-pressure EOS curves.[6,7] The rationale for varying B_0' while keeping B_0 fixed is that the experimental B_0' values are not accurate to better than about ±10% and also vary with the model used to reduce the low-pressure experimental data,[13] while the B_0 values are much more accurate and are much less model dependent. In general the best fit values for B_0' were within the range of experimental error of the ultrasonic data. For MgO, CaO, and CaS, independent ultrasonic values of B_0' were not available.

III. RESULTS

The cohesive-energy parameters that fit the experimental *P*-*V* curves for the halides and for MgO, CaO, and CaS are given in Table I. Note that there are two listings for MgO. This is a consequence of the large difference between the experimental B_0 values for the isothermal compression data and for the shock wave data; the difference in B_0 between the data sets is much greater than the error in the experimental values of B_0 in each data set. Also note that the parameters for the alkali halides, listed in Table I, are somewhat different from those given in Refs. 1 and 2 since the B_0' values used to generate them are different from the ultrasonic values used previously.

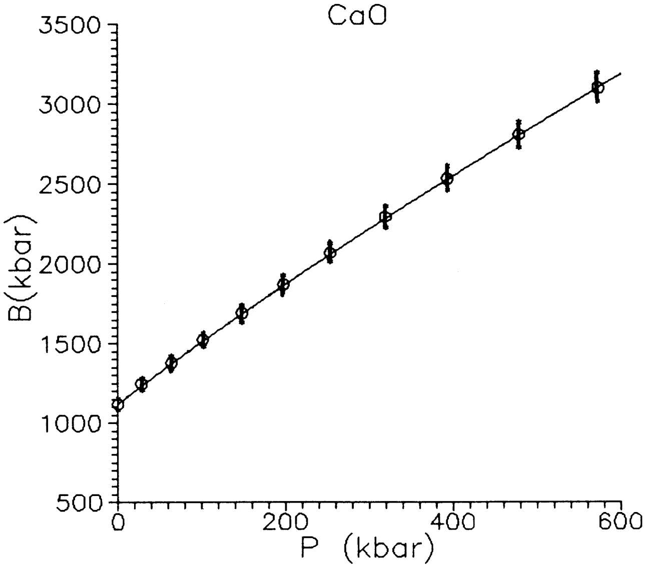

FIG. 3. Bulk modulus vs pressure curves for CaO. (○) expt., Ref. 15; (—) theory.

TABLE I. $\delta Z, l', a_e^*, C'$, and Z' values that fit the experimental P-V curves.

Material	B_0 (GPa)	B'_0	δZ	l'	a_e^*	C'	Z'
LiF	66.51	5.00	0.949 2	0.133 811	−1.390 340	0.024 897 593	1.039 036
NaF	46.48	6.10	0.970 5	0.093 320 9	−2.678 261	0.002 541 797	1.062 109
NaI	14.87	4.60	0.843 7	0.172 363 5	−0.347 880 6	0.264 447 01	0.755 798 6
CsCl	16.2	6.20	0.980 5	0.107 927 0	−0.810 965 0	0.057 696 16	0.975 459 9
MgO	178	4.50	1.887 2	0.156 846 5	−1.438 938	0.027 152 01	1.050 249
CaO	112	4.10	1.813 9	0.189 643 0	−0.761 039 0	0.109 874 05	0.943 800
CaS	57	4.80	1.996 8	0.126 357 2	−3.248 530	0.001 655 234	1.095 843
MgO[a]	159.7	4.50	1.933 4	0.140 130 0	−2.990 039	0.002 599 098	1.102 859
CsI[b]	11.4	6.00	0.968 21	0.115 929 3	−0.626 898	0.092 419 17	0.935 457 2

[a] Shock-wave data.

[b] High-pressure compression data.

The theoretical EOS curves [—] for LiF, NaF, NaI, CsCl, MgO, CaO, and CaS are plotted in Fig. 1 and compared with the unsmoothed experimental data [○] of Drickhamer and co-workers[6,7] and with the lower pressure Vaidya and Kennedy[4] [$*$] data and the Yagi[5] [Δ] data. In Fig. 2 the calculated EOS [—] is compared with the MgO (Ref. 14) [star] shock-wave data, and with high-pressure compression data for CaO (Ref. 15) [Δ] and CsI (Ref. 16) [star]. Lower-pressure data [○] for CsI and CaO are also plotted in Fig. 2. Two theoretical EOS curves which bracket the experimental shock-wave data for MgO are plotted in Fig. 2; the dashed line corresponds to $B'_0 = 4.25$, while $B'_0 = 4.5$ for the solid line.

Of particular interest is the comparison with the raw (unsmoothed) experimental data of Drickhamer and co-workers[6,7] for LiF, NaF, NaI, CsCl, MgO, CaO, and CaS several halides to high pressure (200–450 kbar). We find that Eq. (2) yields an excellent fit to their unsmoothed data with a *single* set of parameters over the entire experimental pressure range. This is particularly striking in the case of NaF and CaS; Drickhamer and co-workers reported that four different fits were required to cover the experimental pressure range for NaF, whereas Eq. (2) yields an excellent fit over essentially the entire pressure range with a single set of parameters. They were unable to fit their experimental data for CaS, while Eq. (2) yields an excellent fit over most of the experimental pressure range (i.e., out to ≅230 kbar.)

Finally, in Fig. 3 we compare the pressure dependence of the bulk modulus for the $B1$ phase of CaO calculated from our EOS with the data reported in Ref. 16. Note the excellent agreement.[17]

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. The parameters in this expression are obtained from the equilibrium values of B_0, B'_0, the cohesive energy ΔE, and R_e. Previously, we used the cohesive-energy parameters, calculated from low-pressure data for the alkali and Ag halides, to generate theoretical EOS curves which were compared with experimental compression curves out to $P_{\max} = 90$ Kbar. In this paper we show that the cohesive-energy expression is applicable to divalent partially ionic solids such as MgO, CaO, and CaS and yields reasonable charge-transfer values in the range $(1.80 \leq \delta Z \leq 2.00)$. Using the cohesive-energy parameters, we obtain theoretical EOS which yield excellent fits to isothermal-compression and shock-wave experiments to very high pressures, $P \leq 250$–1350 kbar.

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