Two Universal Equations of State for Solids

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In this paper, two equations of state (EOSs) (Sun Jiu-Xun-Morse with parameters n = 3 and 4, designated by SMS3 and SMS4) with two parameters are proposed to satisfy four merits proposed previously and give improved results for the cohesive energy. By applying ten typical EOSs to fit experimental compression data of 50 materials, it is shown that the SMS4 EOS gives the best results; the Baonza and Morse EOSs give the second best results; the SMS3 and modified generalized Lennard-Jones (mGLJ) EOSs give the third best results. However, the Baonza and mGLJ EOSs cannot give physically reasonable values of cohesive energy and P-V curves in the expansion region; the SMS3 and SMS4 EOS give fairly good results, and have some advantages over the Baonza and mGLJ EOSs in practical applications.

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1. Introduction

The equation of state (EOS) of a system describes the relationships among thermodynamic variables such as pressure, temperature, and volume. It provides numerous information of nonlinear compression of a material at high pressure, and has been widely applied to engineering and other scientific researches. In 1986 Rose et al. [1] proposed that there exist a universal EOS (UEOS) being valid for all types of solids through analyzing the energy-band data. Since then a lot of forms of UEOS have been proposed with different success [2 – 17]. Among these EOSs, the Vinet [2] EOS has been shown having fairly high precision [7]. Baonza et al. [8 – 13] proposed another EOS from a pseudospinodal hypothesis; they claim that the EOS has high precision being equivalent to the Vinet EOS. But the EOS cannot give reasonable values of cohesive energy.

Holzapfel [15, 16] pointed out that the limitation condition of an EOS at high pressure should be the Fermi gas (FG) model. Since most of the existing EOSs cannot satisfy the limitation condition, they modified the Vinet EOS to satisfy the FG limitation (Holzapfel EOS) [15, 16]. However, we proposed two Murnaghan-type EOSs [17], and compared the precision of five EOSs mentioned above by fitting the experimental compression data of 50 solids. The results show that EOSs satisfying the FG limitation give worse results than other EOSs not satisfying it. For practical applications, the FG limitation condition is not important for it only operates if the volume tends to zero. Nowadays, more and more EOSs have been proposed, and people expect finding an ideal UEOS. However, we notice that in fact no criteria or characteristics of an ideal UEOS has been proposed, and correspondingly no EOS has been explicitly claimed or judged being ideal. In a previous paper [18] we proposed that an ideal UEOS should satisfy four merits from practical viewpoint, except the FG limitation condition, and a modified generalized Lennard-Jones (mGLJ) EOS is proposed to satisfy these four merits [18].

Since the FG limitation condition has been shown being not important for practical applications [17], we do not take it as a characteristic of an ideal EOS. We proposed in [18] that, from the practical viewpoint, an ideal universal EOS should have following four merits: The first one is that the energy should be analytic, $U = U(V)$. The second one is that the EOS had better to be both pressure analytic, $P = P(V)$, and volume analytic, $V = V(P)$. The third one is that it should satisfy the spinodal condition [8 – 12],

$$B \propto (P - P_{\mathrm{sp}})^{1/2}, \text{ with } B(P = P_{\mathrm{sp}}) = 0, \qquad (1)$$

have the correct limitation as volume tends infinity,

$P(V \to \infty) = 0$, and can be applied to the expanded materials, including expanded liquids and solids. Here B is the bulk modulus. The fourth one is that it should have enough high precision while simple in form and a small number of parameters, and has the ability to predict the compression curve of materials at high pressure only using the parameters determined from experimental data at low pressure. Here we emphasize that one condition should be amended in the third merit, that is a universal EOS should give reasonable values of cohesive energy U_0. Perdew et al. defined the cohesive energy U_0 of a solid [19, 20], and they derived the expression of U_0 for several EOSs as

$$U_0 = U(V = \infty) - U(V = V_0), \tag{2}$$

V_0 is the volume at zero-pressure condition. U_0 is an important physical property of a material. Shanker and Kushwah [21, 22] (SK) proposed a quadratic EOS, $P = [(V_0/V) - 1][a_1(V_0/V) + a_2]$, and applied it to iron and other materials. Poirier and Tarantola [23] proposed a logarithmic EOS, Stacey et al. [24, 25] extended it to fourth order. And Kushwah et al. [26] further proposed two generalized EOSs based on [21, 25, 27]. Suzuki et al. [28] proposed a relation for the volume as a function of temperature very early, which was extensively used in geophysics and ceramic science [28 – 32]. However, we found that the relation of Suzuki [28] is based on the quadratic EOS $P = [1 - (V/V_0)][b_1(V/V_0) + b_2]$. We think that the EOSs in [21 – 31] cannot be an ideal EOS as compared with the four merits mentioned in the previous paragraph.

In this paper, we have two main goals. The first goal is to propose two EOSs with two parameters by modifying the Morse EOS, which can hold the four merits. The second goal is to apply the new and other typical EOSs in literature to 50 solids to check the applicability of these equations within wide pressure ranges. In Section 2 these two EOSs are proposed and the advantages are discussed and compared with the Baonza EOS. In Section 3 ten EOSs are applied to 50 solids with the experimental compression data available within wide pressure ranges, and the results are discussed. At last, the conclusion is presented in Section 4.

2. Advancement of Equations of State

In a previous paper [18], we have proposed an mGLJ EOS to hold all of the four merits, whereas it cannot give reasonable values of U_0. Considering most of the present EOSs, they cannot hold all of the four merits, even have more or less disadvantages against these merits. So we would propose two EOS instead of the mGLJ and the Baonza EOS by modifying the Morse EOS. The Morse potential is as follows [17, 33, 34]:

$$U = \frac{n^2 B_0 V_0}{2\beta^2}\left[e^{2\beta(1-X)} - 2e^{\beta(1-X)}\right], \tag{3}$$

where

$$X = (V/V_0)^{1/n} \tag{4}$$

and

$$U_0 = U(X = \infty) - U(X = 1) = \frac{n^2 B_0 V_0}{2\beta^2}. \tag{5}$$

V_0 is the volume, B_0 (and B_0') the bulk modulus (and its first-order pressure derivative) at zero pressure, respectively. For ordinary Morse potential, n should take the value $n = 3$. Here in order to obtain an extended EOS, we use an extended form of Morse potential. By using the relationship $P = -\partial U/\partial V$ we derived the EOS

$$P = \frac{nB_0}{\beta X^{n-1}}\left[e^{2\beta(1-X)} - e^{\beta(1-X)}\right], \tag{6}$$

where

$$\beta = \frac{n}{3}(B_0' - 2) + 1. \tag{7}$$

(6) is energy and pressure analytic, but it is not volume analytic.

In order to obtain an EOS being volume analytic, we modify (6) to the following form:

$$P = \frac{nB_0}{\alpha}\left[e^{2\alpha(1-X)} - e^{\alpha(1-X)}\right], \tag{8}$$

where

$$\alpha = \frac{1}{3}(nB_0' + 1). \tag{9}$$

(8) just is the two-parameter EOS we proposed (Sun Jiu-Xun (SJX)-Morse EOS). It can be shown that it holds all four merits mentioned above, and the precision is higher than with several popular EOSs, including the widely used Vinet EOS. We notice that the Vinet EOS merely is energy analytic and pressure analytic, but not volume analytic and doesn't satisfy the

spinodal condition. Our subsequent calculations show that (8) gives fairly good results for compressed curves as n takes the values 3 and 4, so we only consider the two cases (designated by SMS3 and SMS4, respectively). (8) can be integrated to give the analytic expression of energy:

$$U = -\int_{\infty}^{V} P\mathrm{d}V = -nV_0 \int_{\infty}^{X} PX^{n-1}\mathrm{d}X$$
$$= -\frac{n^2 B_0 V_0}{\alpha} \int_{\infty}^{X} \left[\mathrm{e}^{2\alpha(1-X)} - \mathrm{e}^{\alpha(1-X)}\right] X^{n-1}\mathrm{d}X$$

or

$$U = \frac{n^2 B_0 V_0}{\alpha} \left[g_n(2\alpha, X) - g_n(\alpha, X)\right], \tag{10}$$

where

$$g_n(\alpha, X) = -\int_{\infty}^{X} \mathrm{e}^{\alpha(1-X)} X^{n-1}\mathrm{d}X \tag{11}$$

and

$$g_3(\alpha, X) = \alpha^{-3}\mathrm{e}^{\alpha(1-X)}(\alpha^2X^2 + 2\alpha X + 2), \tag{12}$$

$$g_4(\alpha, X) = \alpha^{-4}\mathrm{e}^{\alpha(1-X)}(\alpha^3X^3 + 3\alpha^2X^2 + 6\alpha X + 6). \tag{13}$$

(8) can be easily converted to the volume analytic form

$$\mathrm{e}^{\alpha(1-X)} = \frac{1}{2}\left(1 + \sqrt{1 + \frac{4\alpha P}{nB_0}}\right). \tag{14}$$

The bulk modulus is

$$B = -\frac{X}{n}\frac{\partial P}{\partial X} = B_0 X \left[2\mathrm{e}^{2\alpha(1-X)} - \mathrm{e}^{\alpha(1-X)}\right]. \tag{15}$$

We notice that (8), (14), and (15) are simpler than most EOSs in literature [2 – 17] including Vinet, Baonza, and Kumari and Dass (KD) EOSs etc., this is fairly convenient for practical applications. The disadvantage of the new EOS worthwhile mentioned is that the expression of energy is slightly complicated as compared with the Vinet EOS.

We can verify that (8) satisfies the spinodal condition in (1). The reduced spinodal volume X_{sp} can be determined from the equation $B(X = X_{\mathrm{sp}}) = 0$, the spinodal pressure P_{sp} can be determined by substituting X_{sp} into (8). We have

$$\exp\left[\alpha(1 - X_{\mathrm{sp}})\right] = 1/2, \quad P_{\mathrm{sp}} = -\frac{nB_0}{4\alpha}, \tag{16}$$

$$B = -\frac{X}{n}\frac{\partial P}{\partial X} = \frac{2\alpha X}{n}\left\{\left(-P_{\mathrm{sp}}\right)^{1/2} + \left(P - P_{\mathrm{sp}}\right)^{1/2}\right\}\left(P - P_{\mathrm{sp}}\right)^{1/2}. \tag{17}$$

Thus it has been shown that (8) strictly satisfies the spinodal condition. It is interesting to notice that Hama and Suito [7] divide all EOSs into three types: the derivative form, the volume-integral form, and the pressure-integral form. However, (8) belongs to all of the three types.

The expressions of U_0 can be easily derived. The expression for the SJX-Morse EOS in (8) with $n = 3$ (designated by SMS3) is

$$U_0 = U(X = \infty) - U(X = 1) = \frac{9B_0V_0}{4\alpha^4}\left(2\alpha^2 + 6\alpha + 7\right). \tag{18}$$

The expression for the SJX-Morse EOS in (8) with $n = 4$ (designated by SMS4) is

$$U_0 = U(X = \infty) - U(X = 1) = \frac{2B_0V_0}{\alpha^5}\left(4\alpha^3 + 18\alpha^2 + 42\alpha + 45\right). \tag{19}$$

3. Results and Discussion

In this section, we apply ten EOSs to 50 materials to check their applicability. The ten EOS including mGLJ [18], augmented stabilized jellium (designated by ASJ) [19, 20], Vinet (designated by VN) [2], Holzapfel (designated by HP) [15, 16], Baonza (designated by BN) [8 – 13], Kumari and Dass (designated by KD) [4, 5], two-parameter Murnaghan-type EOS (SMnh) proposed by us (designated by SM) [17], Morse EOS with $n = 3$ (designated by MRS3), SJX-Morse EOS in (8) with $n = 3$ (SMS3) and $n = 4$ (SMS4). Only the KD EOS is a three-parameter equation, the other EOSs are two-parameter equations. All experimental data for $V(P, T_0)/V(0, T_0)$ are taken from Kennedy and Keeler (1972) [35], except for n-H_2 [36 – 38], W [39], and NaCl [40]. The average fitting errors for pressure ($P = f(V)$) have been listed in Table 1. The atomic numbers, experimental data of V_0, and the fitted parameters B_0, B_0' for the MRS3, SMS3, and SMS4 EOSs have been listed in Table 2. The values of B_0 and B_0' for KD EOS refer to [4], and for other EOSs refer to [21]. It should be pointed out that in [41], Loubeyre et al. developed an analytic EOS for

Table 1. Average fitting errors for pressure (Δ_p) by using ten universal equations of state. Vinet (designated by VN) [2], Holzapfel (designated by HP) [15, 16], mGLJ [18], ASJ [19, 20], Baonza (designated by BN) [8 – 13], KD [4, 5], two-parameter Murnaghan-type EOS proposed by us (designated by SMnh) [17], Morse EOS with $n = 3$ (designated by MRS3), and SJX-Morse EOS of (11) with $n = 3$ (designated by SMS3) and $n = 4$ (designated by SMS4).

No	Solids	Pressure GPa	VN Δ_p	HP Δ_p	ASJ Δ_p	BN Δ_p	KD Δ_p	SMnh Δ_p	mGLJ Δ_p	MRS3 Δ_p	SMS3 Δ_p	SMS4 Δ_p
1	n-H_2	0-590	2.675	4.663	8.844	6.059	29.1	1.992	14.26	1.159	2.564	1.668
2	Cu	0-450	1.050	0.743	0.745	0.501	0.90	0.664	0.603	0.764	0.871	0.719
3	Mo	0-350	1.468	1.510	0.933	1.013	1.44	1.220	1.039	1.025	0.984	0.917
4	W	0-270	0.239	0.406	0.213	0.304	0.26	0.318	0.248	0.203	0.249	0.198
5	Zn	0-250	1.147	0.937	1.595	0.623	0.68	0.398	0.323	0.875	0.984	0.728
6	Ag	0-200	0.821	0.660	1.048	0.441	0.79	0.503	0.409	0.660	0.728	0.624
7	Pt	0-200	1.046	1.003	0.787	0.720	1.00	0.872	0.704	0.757	0.769	0.750
8	Ti	0-200	0.590	1.001	0.744	0.732	0.82	1.091	0.811	0.418	0.381	0.422
9	Ta	0-180	0.932	0.972	0.667	0.684	0.81	0.918	0.718	0.687	0.610	0.614
10	Au	0-180	0.938	0.890	0.725	0.626	0.98	0.949	0.648	0.711	0.737	0.702
11	Pd	0-160	1.059	1.057	0.777	0.726	1.14	0.896	0.723	0.764	0.806	0.758
12	Zr	0-140	0.689	1.314	0.536	0.623	0.62	0.869	0.653	0.470	0.514	0.468
13	Cr	0-120	1.586	1.645	0.998	0.985	1.62	1.650	1.108	1.036	1.027	1.065
14	Co	0-120	0.951	1.107	0.638	0.679	0.95	0.968	0.757	0.641	0.649	0.670
15	Ni	0-120	0.870	0.867	0.642	0.601	0.95	0.854	0.603	0.645	0.656	0.636
16	$A1_2O_3$	0-120	1.132	1.153	0.775	0.793	1.15	1.173	0.778	0.747	0.743	0.746
17	Nb	0-100	2.885	2.808	2.139	2.128	2.73	2.925	1.849	1.836	1.867	1.745
18	Cd	0-100	0.824	0.630	1.189	0.405	0.33	0.291	0.265	0.642	0.707	0.544
19	Al	0-100	0.787	0.886	0.907	1.059	0.64	1.207	1.118	0.804	0.745	0.842
20	Th	0-100	0.383	0.894	0.376	0.450	0.62	0.728	0.535	0.316	0.394	0.296
21	V	0-100	0.811	0.721	0.573	0.558	0.79	0.687	0.564	0.625	0.656	0.617
22	In	0-90	1.020	0.771	1.031	0.727	0.97	0.806	0.675	0.819	0.869	0.739
23	MgO	0-90	0.481	0.482	0.481	0.403	0.58	0.553	0.416	0.389	0.389	0.382
24	*Brass	0-85	0.601	0.518	0.462	0.417	0.57	0.582	0.417	0.465	0.481	0.459
25	Be	0-80	0.629	0.655	0.450	0.449	0.66	0.582	0.454	0.409	0.425	0.410
26	LiF	0-80	0.571	0.482	0.387	0.304	0.45	0.350	0.337	0.413	0.475	0.378
27	Pb	0-75	0.559	0.340	0.592	0.292	0.53	0.397	0.332	0.461	0.515	0.406
28	Sn	0-60	0.637	0.492	0.779	0.329	0.33	0.339	0.307	0.558	0.606	0.497
29	Mg	0-55	0.258	0.349	0.327	0.331	0.40	0.579	0.432	0.243	0.287	0.237
30	CsBr	0-55	0.442	0.920	0.434	0.356	0.50	0.756	0.591	0.303	0.456	0.277
31	Ca	0-36	0.481	2.593	0.432	0.863	0.37	1.325	0.924	0.497	0.282	0.403
32	Tl	0-34	0.501	0.321	0.565	0.291	0.50	0.342	0.285	0.376	0.401	0.349
33	NaCl	0-31	0.296	0.124	0.231	0.108	0.22	0.292	0.238	0.205	0.277	0.145
34	LiI	0-28	0.378	1.085	0.326	0.427	0.38	0.572	0.428	0.324	0.299	0.320
35	LiBr	0-24	0.340	0.316	0.280	0.292	0.39	0.354	0.324	0.306	0.319	0.282
36	NaBr	0-24	0.372	0.416	0.315	0.345	0.35	0.427	0.375	0.302	0.325	0.295
37	NaI	0-24	0.219	0.624	0.348	0.337	0.27	0.565	0.393	0.203	0.217	0.209
38	KF	0-24	1.276	1.175	1.514	0.887	0.53	0.775	0.585	1.047	1.083	0.961
39	RbF	0-24	0.347	0.229	0.207	0.219	0.24	0.333	0.294	0.257	0.327	0.224
40	LiCl	0-22	0.478	0.388	0.348	0.323	0.52	0.307	0.307	0.430	0.463	0.419
41	Li	0-20	0.386	0.412	0.417	0.358	0.35	0.650	0.46	0.29	0.375	0.287
42	Na	0-20	0.356	0.830	0.451	0.301	0.40	0.850	0.628	0.255	0.447	0.266
43	KI	0-18	0.489	0.355	0.298	0.272	0.36	0.363	0.345	0.369	0.467	0.335
44	RbI	0-18	0.389	0.397	0.207	0.194	0.19	0.423	0.36	0.290	0.372	0.264
45	RbBr	0-16	0.682	0.327	0.536	0.310	0.33	0.314	0.33	0.555	0.645	0.463
46	K	0-14	0.228	1.714	0.715	0.367	0.50	1.099	0.838	0.166	0.398	0.163
47	Rb	0-14	0.299	2.467	0.831	0.293	0.86	1.181	1.015	0.182	0.504	0.166
48	NaF	0-14	0.604	0.576	0.497	0.505	0.61	0.547	0.501	0.480	0.474	0.480
49	RbCl	0-12	0.493	0.338	0.682	0.318	0.23	0.242	0.249	0.404	0.442	0.349
50	Nd	0-10	1.493	1.544	1.221	1.226	1.23	1.584	1.206	1.196	1.209	1.202
Total average error			0.764	0.942	0.824	0.661	1.243	0.773	0.855	0.560	0.629	0.542
Average error for 2 – 50			0.725	0.866	0.661	0.541	0.661	0.733	0.581	0.536	0.578	0.509

Table 2. The experimental data of V_0 and fitted parameters B_0 (GPa) and B_0' for BN, ASJ, MRS3, SMS3, and SMS4 EOSs. The values of fitted parameters for KD EOS refer to [40], for other EOSs refer to [18].

No	Solid	V_0	BN		ASJ		MRS3		SMS3		SMS4	
		cm^3/mol	B_0	B_0'	B_0	B_0'	B_0	B_0'	B_0	B_0'	B_0	B_0'
1	n-H_2	22.90	0.1579	7.0012	0.1384	11.440	0.1696	7.0567	0.1548	7.4095	0.1755	6.7984
2	Cu	7.115	141.05	4.7335	138.17	5.1113	138.34	5.059	137.53	5.1459	138.8	4.9951
3	Mo	9.387	268.74	3.8003	268.93	3.8846	269.23	4.0024	266.6	4.0766	266.86	4.0332
4	W	9.550	313.28	3.7393	313.86	3.7942	312.54	3.951	312.1	3.9973	312.67	3.9367
5	Zn	9.166	59.979	5.6113	57.699	6.6241	59.21	5.9849	58.976	6.0452	59.351	5.9115
6	Ag	10.27	105.46	5.5640	103.63	6.2258	104.28	5.9254	104.72	5.889	104.49	5.8236
7	Pt	9.098	280.54	5.0364	280.06	5.2913	280.19	5.2392	279.77	5.2756	280.28	5.1957
8	Ti	12.01	99.271	3.3311	99.678	3.3394	98.62	3.5498	97.677	3.6699	98.5	3.5514
9	Ta	10.80	198.98	3.5772	198.82	3.6301	198.88	3.7537	197.05	3.8506	197.75	3.7863
10	Au	10.22	185.01	4.9556	183.02	5.3487	184.09	5.221	183.94	5.2566	184.51	5.1732
11	Pd	8.896	195.96	5.0195	194.33	5.3745	194.25	5.3156	194.79	5.2743	194.03	5.2775
12	Zr	14.02	95.956	2.5662	95.430	2.6691	95.138	2.7573	94.53	2.8591	94.917	2.7909
13	Cr	7.231	191.83	4.7310	189.88	5.0195	191.27	4.9033	189.22	5.0634	188.93	5.0181
14	Co	6.689	197.87	4.1208	196.95	4.2577	196.08	4.3533	195.25	4.4473	196.66	4.3411
15	Ni	6.592	188.81	4.6331	187.94	4.8479	187.4	4.8811	187.2	4.9224	187.46	4.8637
16	$A1_2O_3$	26.62	250.58	3.8488	250.12	3.9334	250.85	3.9807	249.96	4.0516	250.77	3.9791
17	Nb	10.83	167.89	3.9064	166.79	3.9742	167.95	3.986	170.86	3.8241	169.11	3.9201
18	Cd	13.00	50.176	5.6205	48.653	6.5357	49.388	6.0152	49.233	6.066	49.594	5.927
19	Al	10.00	76.992	4.3887	76.443	4.6054	76.488	4.6395	76.542	4.6673	76.538	4.6155
20	Th	19.79	52.635	3.8763	52.841	3.9398	52.128	4.1686	51.863	4.2559	52.153	4.1432
21	V	8.365	159.88	3.5864	159.64	3.6386	157.99	3.8222	158.5	3.8208	158.51	3.7918
22	In	15.73	39.558	5.1765	38.848	5.7787	39.107	5.5442	39.357	5.5381	39.391	5.4362
23	MgO	8.465	148.26	5.6334	147.05	6.1389	147.49	5.8863	147.24	5.9298	147.3	5.8813
24	*Brass	37.82	118.02	4.5616	116.98	4.8343	116.54	4.8759	116.55	4.91	117.02	4.8163
25	Be	4.890	120.91	3.3618	120.38	3.4404	120.06	3.5593	120.06	3.602	120.21	3.5445
26	LiF	9.789	63.133	4.6020	62.539	4.9109	62.498	4.9101	62.043	5.0049	62.608	4.8697
27	Pb	18.27	44.268	5.0536	43.446	5.5903	43.765	5.404	43.65	5.4485	43.93	5.3266
28	Sn	16.32	43.601	5.2630	42.884	5.8627	43.163	5.5978	42.999	5.6618	43.294	5.5385
29	Mg	14.00	34.946	3.7676	34.901	3.8520	34.499	4.068	34.308	4.1583	34.557	4.0404
30	CsBr	47.93	22.262	3.7354	22.229	3.8135	21.89	4.0814	21.687	4.1912	21.905	4.0533
31	Ca	26.13	19.738	2.2804	19.565	2.4614	19.568	2.4704	19.398	2.6078	19.49	2.5187
32	Tl	17.23	35.550	5.4186	35.042	6.0310	35.196	5.7517	35.176	5.7859	35.276	5.6888
33	NaCl	27.00	23.828	4.7561	23.489	5.1437	23.528	5.0863	23.487	5.1328	23.569	5.0391
34	LiI	32.80	33.256	2.2688	32.991	2.4206	33.017	2.419	32.931	2.5044	33.016	2.4498
35	LiBr	25.07	22.236	4.2894	21.992	4.5288	21.954	4.5944	21.871	4.6622	21.903	4.5888
36	NaBr	32.15	21.107	4.0674	21.010	4.2161	20.801	4.3812	20.717	4.4534	20.812	4.3591
37	NaI	40.84	20.099	3.6160	20.036	3.7022	19.882	3.8773	19.787	3.9635	19.902	3.8588
38	KF	23.43	11.824	5.6176	11.454	6.5204	11.661	5.9797	11.611	6.0556	11.78	5.872
39	RbF	37.44	15.179	4.5036	14.954	4.8264	14.905	4.8695	14.845	4.9394	14.966	4.807
40	LiCl	20.60	32.930	3.8965	32.828	3.9946	32.67	4.1239	32.624	4.1689	32.692	4.104
41	Li	13.02	10.791	3.3080	10.797	3.3452	10.595	3.6187	10.513	3.7291	10.577	3.6223
42	Na	23.71	6.1114	3.6461	6.1307	3.6862	5.918	4.0548	5.8507	4.1761	5.9467	4.0141
43	KI	53.29	9.5170	4.2852	9.4017	4.5328	9.2874	4.6779	9.2627	4.7381	9.3119	4.6233
44	RbI	59.82	9.5753	4.2899	9.4858	4.5226	9.3695	4.6714	9.3458	4.7283	9.428	4.6009
45	RbBr	49.36	7.6948	4.7221	7.5592	5.1445	7.5848	5.0767	7.4357	5.2328	7.584	5.035
46	K	45.62	3.1277	3.3612	3.1734	3.3341	3.0158	3.7659	2.9475	3.9426	3.0175	3.7514
47	Rb	56.08	2.0832	3.5430	2.1324	3.4939	1.9848	4.0094	1.9123	4.2291	1.9898	3.9782
48	NaF	15.10	46.841	3.7838	46.706	3.8558	46.463	3.9869	46.516	3.9965	46.501	3.9678
49	RbCl	43.81	5.8188	5.4550	5.4678	6.5771	5.6901	5.8801	5.6528	5.9551	5.725	5.7856
50	Nd	20.60	31.932	4.4115	31.519	4.7003	31.578	4.6967	31.5473	4.7475	31.79	4.5397

the n-H2. However, Loubeyre et al. just used the experimental compression data up to 120 Gpa, and they have not given the original data. So we do not use their results in our calculations.

In our calculations, it is found that the parameters of Baonza EOS are sensitive to the fitting approach. In order to find the optimized parameter values, we improved our fitting procedure as follows: For a two-

Table 3. The parameters B_0 (GPa) and B_0' for VN, BN, MRS3, SMS3, and SMS4 EOSs and for 37 matters, respectively, determined by fitting experimental compression data in the low-pressure ranges.

No	Solid	Pressure	VN		BN		MRS3		SMS3		SMS4	
		GPa	B_0	B_0'	B_0	B_0'	B_0	B_0'	B_0	B_0'	B_0	B_0'
1	n-H_2	0-4.06	0.1700	7.162	0.1738	6.601	0.1717	7.000	0.1711	7.049	0.1719	6.912
2	Cu	0-34	140.95	4.798	141.46	4.572	141.47	4.691	141.47	4.711	141.38	4.722
3	Mo	0-60	269.51	3.857	270.55	3.742	267.24	4.077	267.82	4.039	267.32	4.027
4	W	0-70	314.99	3.802	313.00	3.833	312.82	3.954	312.40	3.993	312.73	3.949
5	Zn	0-16	60.204	5.680	60.615	5.475	60.237	5.715	60.252	5.712	60.298	5.679
6	Ag	0-28	105.50	5.564	105.65	5.537	105.32	5.742	105.61	5.695	105.39	5.692
7	Pt	0-70	281.42	4.879	282.09	4.954	281.27	5.115	281.18	5.132	281.36	5.100
8	Ti	0-22	97.788	3.842	98.005	3.582	97.766	3.680	97.868	3.716	97.806	3.705
9	Ta	0-48	197.60	4.012	197.75	3.706	197.68	3.810	197.64	3.809	197.20	3.842
10	Au	0-46	184.07	5.029	184.64	4.983	184.74	5.118	184.30	5.165	184.49	5.125
11	Pd	0-70	193.37	5.565	196.03	5.016	195.18	5.227	194.94	5.250	195.25	5.209
12	Zr	0-20	95.913	2.339	95.614	2.527	95.254	2.691	95.285	2.719	95.173	2.740
13	Cr	0-46	190.63	4.586	190.49	4.851	191.54	4.858	190.49	4.979	191.22	4.887
14	Co	0-46	196.40	4.145	196.75	4.175	195.97	4.359	196.27	4.359	195.86	4.352
15	Ni	0-46	188.32	4.614	188.94	4.610	188.59	4.752	188.35	4.803	188.72	4.730
16	$A1_2O_3$	0-50	249.53	3.766	249.92	3.970	249.70	4.073	249.78	4.089	249.56	4.075
17	Nb	0-38	167.28	3.447	169.99	3.704	168.00	4.093	168.31	4.142	167.90	4.104
18	Cd	0-14	50.959	4.704	50.798	5.423	50.767	5.554	50.704	5.592	50.726	5.553
19	Al	0-18	74.762	5.036	75.802	4.766	75.416	4.945	75.406	4.956	75.516	4.902
20	Th	0-12	52.062	3.920	52.181	4.067	52.112	4.171	52.054	4.215	52.124	4.164
21	V	0-36	159.80	3.449	159.99	3.510	159.66	3.626	159.50	3.670	159.82	3.614
22	In	0-1	40.064	5.017	40.228	4.913	39.727	5.347	39.946	5.280	39.830	5.289
23	MgO	0-38	147.11	6.055	148.09	5.671	147.47	5.887	147.35	5.918	147.63	5.845
24	*Brass	0-28	117.21	4.668	117.92	4.564	117.82	4.703	117.76	4.727	117.69	4.711
25	Be	0-26	119.97	3.434	120.42	3.429	120.25	3.530	120.16	3.555	120.24	3.520
26	LiF	0-12	63.488	4.496	63.418	4.514	63.347	4.623	63.345	4.634	63.362	4.605
27	Pb	0-12	44.026	4.996	44.223	5.066	44.005	5.277	44.066	5.256	44.117	5.217
28	Sn	0-12	43.636	5.338	43.957	5.114	43.841	5.283	43.826	5.296	43.847	5.266
29	Mg	0-8	34.527	4.049	34.669	3.834	34.614	3.9626	34.586	3.998	34.612	3.957
30	CsBr	0-5	22.065	4.022	22.056	3.861	22.042	3.932	21.984	4.025	21.957	4.006
31	Ca	0-4	19.480	2.532	19.397	2.478	19.336	2.579	19.299	2.632	19.336	2.585
32	Tl	0-18	35.268	5.551	35.570	5.404	35.362	5.663	35.336	5.697	35.434	5.613
33	NaCl	0-5.62	23.603	5.030	23.709	4.840	23.643	5.006	23.634	5.026	23.646	4.992
34	LiI	0-7	32.916	2.473	33.012	2.393	32.956	2.480	32.852	2.559	32.937	2.500
35	LiBr	0-5	21.849	4.509	22.012	4.332	22.000	4.520	21.945	4.580	21.932	4.566
36	NaBr	0-5	20.828	4.157	21.063	4.060	20.849	4.321	20.871	4.318	20.891	4.280
37	NaI	0-4.5	19.809	3.989	19.833	3.829	19.842	3.911	19.851	3.924	19.820	3.923

parameter EOS we suppose $P = P(B_0, B_0', V)$ and introduce the aim function

$$f(B_0, B_0') = \sum_{i=1}^{N} \left[P(B_0, B_0', V_i) - P_{ei}\right]^m. \qquad (20)$$

In a previous paper [18], the power m has been fixed as constant 2, the fitting parameters of Baonza EOS gives a total average error of 0.676% for the 50 materials. However, in the calculations of the present paper, we found that the fitting error and the values of the parameters are sensitive to m. For values of m larger than 2, the convergence of the fitting procedure becomes better. We fix $m = 8$ after some calculations because this value gives stable and optimized values of the parameters; the corresponding total average error of Baonza EOS for the 49 materials [18] except the solid n-H_2 decreases from 0.681% to 0.541%. The optimized parameters for several typical EOS have been given in Table 2.

Table 4. Average relative errors (Δ%) of B_0 and B_0' between the values obtained by fitting all experimental data available (high-pressure ranges), and those obtained by fitting the experimental data at low-pressure ranges, for VN, BN, MRS3, SMS3, and SMS4 EOSs, respectively.

Δ%	VN	BN	MRS3	SMS3	SMS4
B_0	1.065	0.889	0.724	1.107	0.670
B_0'	5.679	2.811	2.737	3.167	2.397

Table 1 shows that the SMS4 EOS gives the best results with average error 0.542%, the MRS3 and SMS3

Table 5. Cohesive energies U_0 (kJ/mol) from various equations of state.

Solid	Exp.	MRS3	SMS3	SMS4	VN	Birch	mGLJ	HP	SJ	ASJ
Li	157.3	90.52	72.82	97.01	75.38	203.4	1195.4	216.5	414.2	196.6
Na	107.7	67.66	56.40	75.99	57.17	169.5	547.47	189.7	205.3	
K	90.50	80.93	62.65	88.46	66.73	172.9	1378.5	∞	433.8	
Rb	82.31	55.31	42.33	61.55	46.22	118.4	751.38	∞	272.3	
Mg	143.9	230.9	197.3	256.4	207.9	525.4	1258.0	339.3	325.4	
Be	320.4	403.3	339.2	438.4	398.9	802.1	3683.7	740.5	1482	
Al	325.3	259.8	239.7	288.7	186.9	618.0	869.34	202.5	−2083	401.3
In	243.6	134.1	130.3	155.4	157.6	296.1	385.22	201.8	−4891	
Pb	195.1	185.8	174.3	211.7	201.1	341.0	510.28	225.4	−5680	
Tl	183.4	120.9	115.4	136.4	115.5	167.7	290.04	133.9	−5518	
Sn	299.9	149.9	140.4	169.3	149.5	196.2	387.74	170.5	−5866	
Mo	667.4	1262	1077	1334	1240	2855	5692.5	3143	1311	1222
Average errors		38	38	36	41	100	472.4	–	–	–

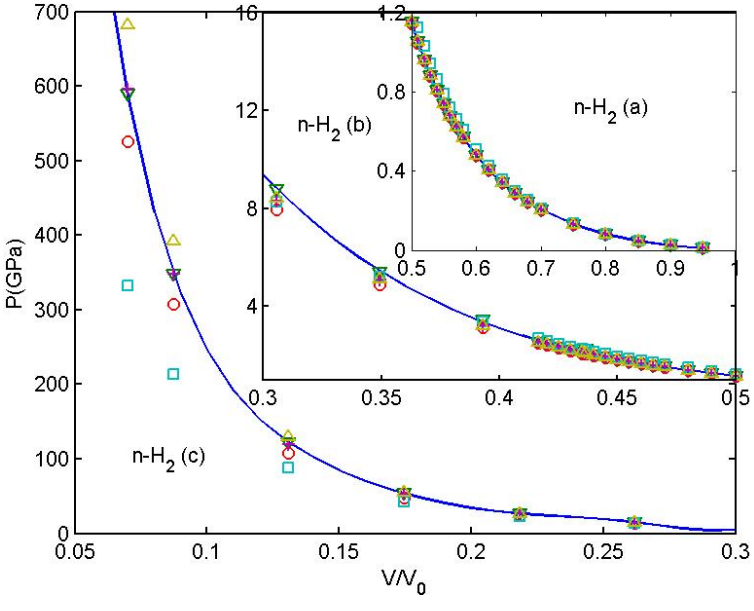
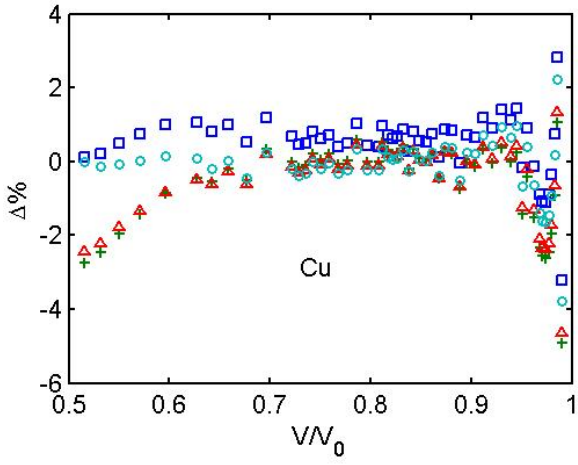
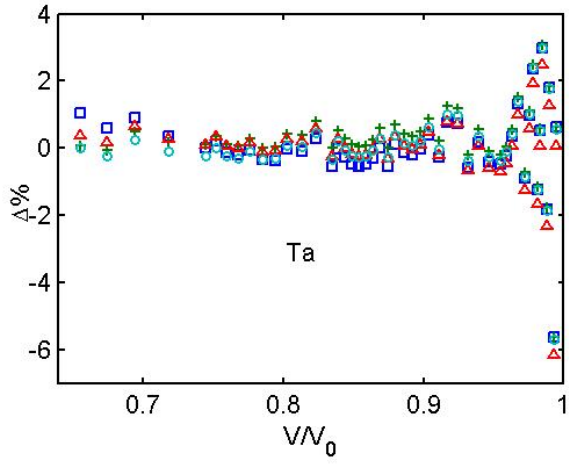


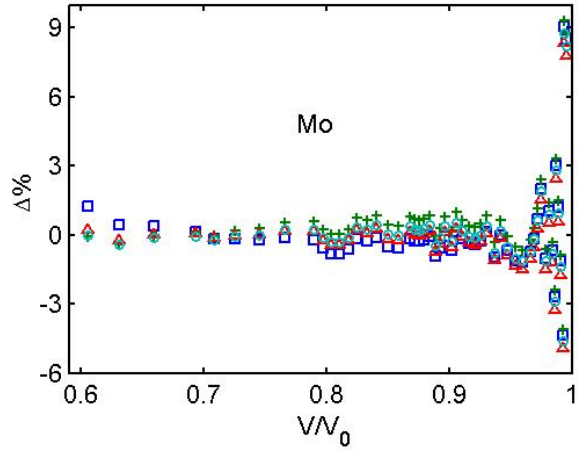
Fig. 1. Comparison of the P-V curves of several EOSs with the experimental data for n-H_2: (a) $0.5 \leq (V/V_0) \leq 1$, (b) $0.3 \leq (V/V_0) \leq 0.5$, (c) $0.07 \leq (V/V_0) \leq 0.3$. Line with ○: experiment; □: Baonza; +: MRS3; Δ: SMS4. The parameters of the EOSs are determined by using the values of B_0, B_0', and B_0'' listed in Table 2.

EOSs give the slightly inferior results with average error 0.560% and 0.629%, the Vinet, SMnh, ASJ, and mGLJ EOSs give the subsequently inferior results with average error 0.764%, 0.773%, 0.824%, and 0.855%, respectively. Although the HP EOS strictly satisfy the limitation condition at high pressure, it gives fairly bad results with average fitting error 0.942%. The three-parameter KD EOS gives the worst results with average error 1.243%. For n-H_2, the pressure range is widest, the highest pressure reaches 590 GPa, and the highest compression ratio $V_{\min}/V_0$ reaches 0.0699. Although for Cu the highest pressure reaches 450 GPa, the value of $V_{\min}/V_0$ only is 0.516, and for all other materials, the value of $V_{\min}/V_0$ is larger than 0.51. For these materials, the corresponding pressure ranges belong to low and middle compression; the limitation condition obviously does not operate. The applicability of these EOSs to n-H_2 can be seen as a check of the limitation condition. From first line of Table 1, we know that although the HP EOS strictly satisfies the FG limitation condition at high pressure, it gives a fairly bad result for n-H_2 with average error 4.663%. Although the MRS3 and SMS4 EOSs do not satisfy the FG limitation, the MRS3 EOS gives the best results with average error 1.159%, and the SMS4 gives a slightly inferior result with average error 1.668%. Such results can be seen as a further verification of the conclusion in [21], where we concluded that for practical applications, the FG limitation condition is not important for it only operates if the volume tends to zero.

It is meaningful to analyze the errors ignoring n-H_2. In the last line of Table 2, we listed the total average







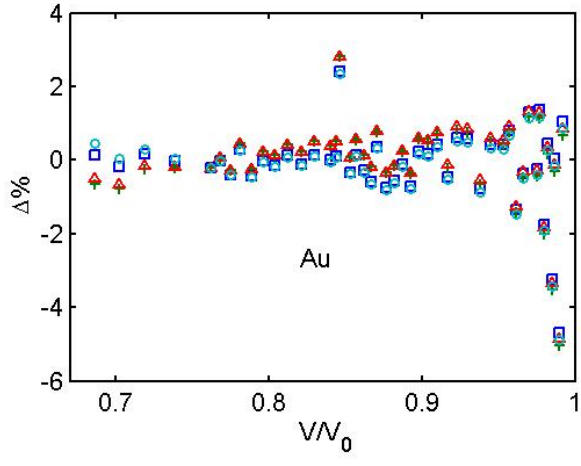


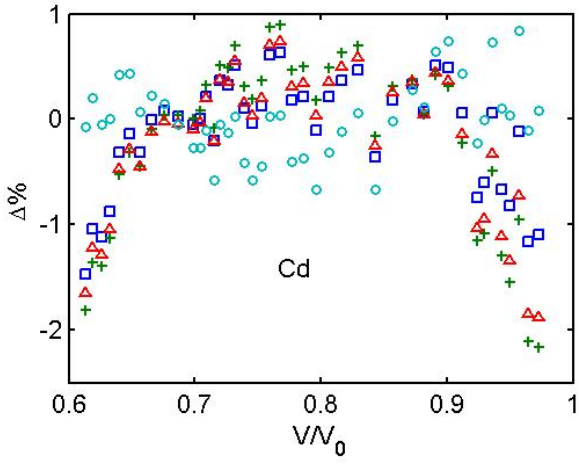
Fig. 2. Relative error ($\Delta\% = (P_{\rm cal} - P_{\rm exp})/P_{\rm exp} \times 100\%$) comparison of several EOSs for Cu and Mo: □: Baonza; +: MRS3; Δ: SMS4. The parameters of the EOSs are determined by using the values of B_0, B_0', and B_0'' listed in Table 2.

Fig. 3. As for Fig. 2, but for Ta and Au.

errors for the other 49 materials. It can be seen that the SMS4 EOS also gives the best results, the average error only is 0.509%. The MRS3, SMS3, and mGLJ EOSs give inferior results with average errors of 0.536%, 0.578%, and 0.581%. The Baonza, KD, SJ, Vinet, and SMnh EOSs give average errors of 0.541%, 0.661%, 0.661%, 0.725%, and 0.733%, respectively. The HP EOS gives the worst results with an average error of 0.866%.

In Figure 1, we compared the P-V curves of Baonza, MRS3, and SMS4 EOSs with the experimental data for n-H_2. And in Figures 2 – 6, we give the fitting error comparison of the four EOSs for ten typical materials, Cu, Mo, Ta, Au, Cd, Al, Tl, Li, Na, and NaCl. The parameters used for these EOSs are determined by using the values of B_0 and B_0' listed in Table 2, which are on their part determined by fitting the compression data. Figure 1 shows that the Morse EOS gives the best results for n-H2, the other figures show that the four EOSs equivalently give the same good results for the ten materials. The tendency is in agreement with the average errors listed in Table 1.

The lack of numerical stability of some "universal" EOSs published to date is well known . In order to compare the numerical stability of these EOSs in fitting P-V results, we further apply five typical EOSs (including Vinet, Baonza, MRS3, SMS3, and SMS4 EOSs) to 37 solids among the 50 materials at low-pressure ranges. These materials have been chosen because they have enough experimental data points.



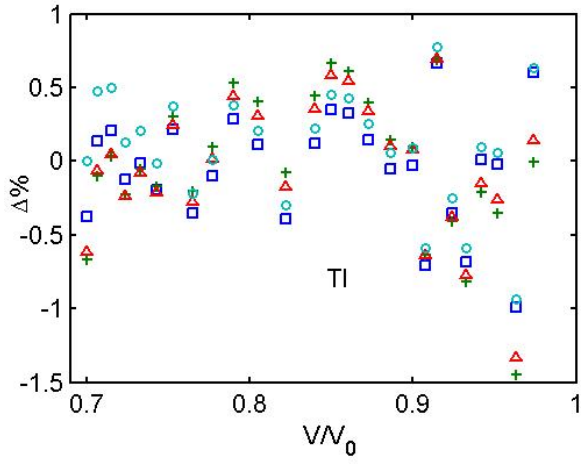
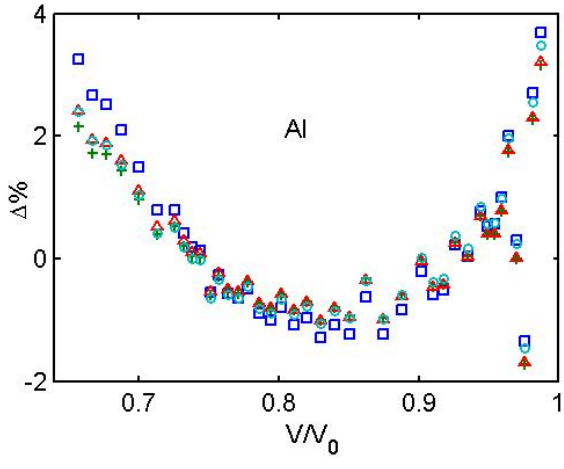


Fig. 4. As for Fig. 2, but for Cd and Al.



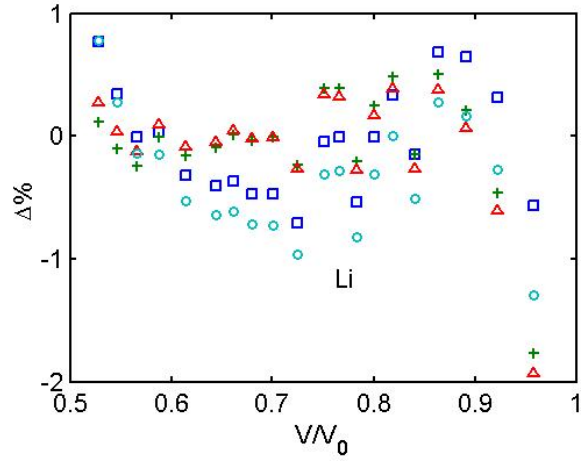


Fig. 5. As for Fig. 2, but for Tl and Li.

The pressure ranges and the values of B_0 and B_0' fitted from low-pressure ranges have been listed in Table 3. It is obvious that the important characteristic of an ideal UEOS should be the consistency of the values of B_0 and B_0' fitted from high-pressure and low-pressure ranges, respectively. The consistency can be scaled by the average relative errors. We also think that the relative errors of B_0 and B_0' are reflecting the numerical stability of an EOS in the fitting P-V data. The smaller the average relative error is, the better the EOS is.

In Table 4, we listed the average relative errors ($\Delta\%$) of B_0 and B_0' between the values obtained by fitting all experimental data available (high-pressure ranges), and that obtained by fitting the experimental data at low-pressure ranges. Table 4 shows that the SMS4 EOS gives the best results. For the errors $\Delta\%$ of B_0 and B_0', the SMS4 EOS gives the best results with errors of 0.670% and 2.397%; the Morse EOS gives slightly inferior results with errors of 0.724% and 2.737%; the VN EOS gives the largest errors 1.065% and 5.679%. By comparing with Table 1, we think that the errors $\Delta\%$ of B_0 and B_0' are in agreement with the average fitting errors of the P-V data. The smaller the fitting errors of the P-V data are, the smaller the errors $\Delta\%$ of B_0 and B_0' are.

In Table 5, we compared the predicted results of the cohesive energy by using nine EOS. In the previous section, it has been pointed out that the Murnaghan EOS and modified equations, including KD [4, 5], Baonza [8 – 13], and SMnh EOSs [17], couldn't give physically reasonable values of cohesive energy [19, 20]. Table 3 shows that Morse, SMS3, SMS3, and Vinet EOS can give reasonable results, these EOSs

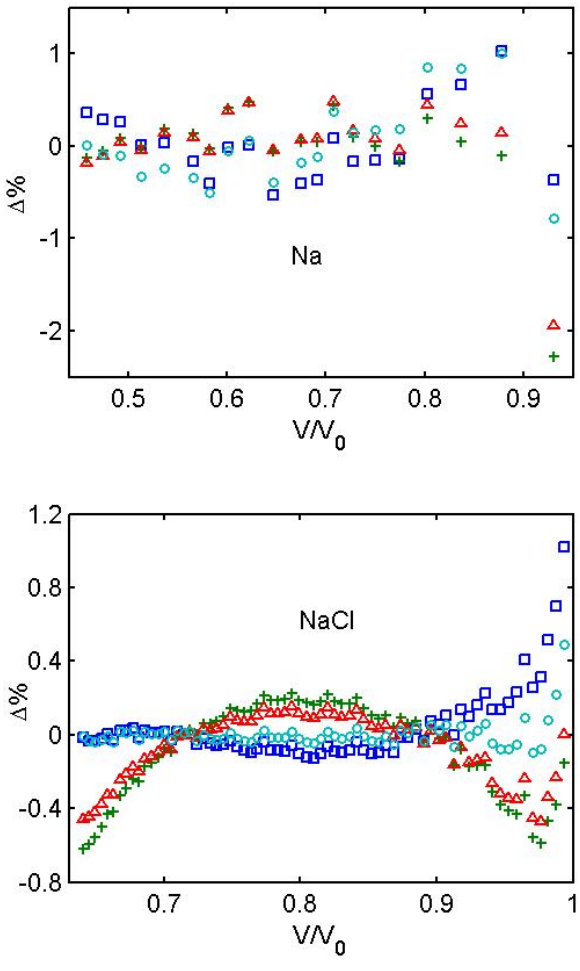


Fig. 6. As for Fig. 2, but for Na and NaCl.

have good applicability to the expanded materials. Other EOSs cannot give reasonable results, such as mGLJ, HP, ASJ, MASJ, and Birch EOS, or even cannot give physically meaningful results, such as KD, Baonza, and SMnh EOSs. These EOSs are inapplicable to the expanded materials, or even cannot be used to research the energy properties of solids.

4. Conclusion

It has been proposed that an ideal universal EOS should satisfy four merits. Considering the mGLJ EOS previously proposed gives bad results for the cohesive energy, two modified Morse-type EOS, the SMS3 and the SMS4 EOSs, have been proposed to satisfy the four merits and give improved results for the cohesive energy. By applying ten EOS to 50 solids, it is shown that SMS4 EOS gives the best results. The Morse and Baonza EOS subsequently give good results. For the cohesive energy, Morse, SMS3, SMS4, and Vinet EOS can give reasonable results; these EOSs have good applicability to the expanded materials and can be applied to the description of energy property of solids. Other EOSs including the Baonza EOS cannot give reasonable or even physically meaningful results; these EOSs are inapplicable to the expanded materials and cannot be applied for the description of energy property of solids.

Acknowledgement

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