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Analysis of high pressure properties of metals using equations of state

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ABSTRACT

We have analysed the study of high pressure properties of metals using various equations of state. The results have been obtained for pressure P, isothermal bulk modulus K, and its derivatives K′ for four metals viz. Zinc (Zn), Lanthanum (La), Vanadium (V) and Niobium (Nb) at different values of compression V/V_0 (0.5 to 1.0). The calculations have been performed using Modified Rydberg EOS (equation of state), Hama Suito EOS, Stacey Reciprocal K-primed EOS, Kushwah logarithmic EOS and Kushwah Exponential EOS. The results for various parameters show the systematic variations with the increase in pressure and compare well with the Stacey EOS.

Keywords: High Pressure, Isothermal bulk modulus, Metals, Equation of State

INTRODUCTION

The equation of state (EOS) of condensed matter is very important in many fields of basic and applied sciences including physics and geophysics.[1-3] An EOS provides useful information about the relationship among thermodynamic variables such as pressure (P), temperature (T) and volume (V) that helps us to understand the behaviour of materials under the effects of high pressure and high temperature.[4-6]

The parameters are determined by using available low-pressure data such as the equilibrium volume V_0, the isothermal bulk modulus K_0 and its pressure derivatives K_0' at zero pressure.[7]

The EOS expressing a relationship between pressure and volume at constant temperature is known as the isothermal EOS. The EOS`s have been derived by many authors based on different physical assumption. Among these EOS's it is very difficult to choose appropriate EOS for calculations under high pressure and high temperature. So, we have chosen the equation of state depend on free volume theory[8]. Equations involving K-prime are more advantageous for determining pressure derivative of bulk modulus than the pressure volume relationship[9-13].

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In the present study we have studied the pressure, bulk modulus and its pressure derivatives for four metals viz. Zn, La, V and Nb at different values of compression V/V_0 (from 0.5 to 1.0). We have used five EOS`s (a) Modified Rydberg EOS, (b) Hama Suito EOS, (c) Stacey reciprocal K-primed EOS, (d) Kushwah logarithmic EOS,(e) Kushwah Exponential EOS.

The results for different metals obtained from these EOS's for various parameters show the behaviour with the variations in pressure and compare well with the Stacey reciprocal K-primed EOS.[6]

EQUATION OF STATE

The equation of state used in the present study are

(a) Modified Rydberg EOS[5,13]

$$P = 3K_0 x^{-K'_\infty}\left(1-x^{1/3}\right)\exp\left[t\left(1-x^{1/3}\right)\right]$$

$$K = 3K_0 x^{-K'_\infty}\exp\left[t\left(1-x^{1/3}\right)\right]$$

$$\left\{K'_\infty\left(1-x^{1/3}\right)+\frac{t}{3}\left[x^{1/3}\left(1-x^{1/3}\right)\right]+\frac{x^{1/3}}{3}\right\}$$

$$K' = K'_\infty + t\frac{x^{1/3}}{3} + \frac{x^{1/3}}{3\left(1-x^{1/3}\right)} - \frac{P}{9K}tx^{1/3}$$

$$+\frac{1}{1-x^{1/3}} + \frac{x^{1/3}}{\left(1-x^{1/3}\right)^2}$$

Where

$$x = V/V_0$$

$$t = \frac{3}{2} K'_0 - 3K'_\infty + \frac{1}{2}$$

$$t = -3K_0 K''_0 - \frac{3}{4} K'^2_0 + \frac{1}{12}$$

Here K_0, K'_0 and K''_0 are respectively zero pressure values of K, K', K'' and K'_∞ is the value of K' at $P \to \infty$.

(b) Hama Suito EOS [6,13]

$$P = 3K_0 x^{-K'_\infty}\left(1-x^{1/3}\right)\exp\left[A\left(1-x^{1/3}\right)+B\left(1-x^{1/3}\right)^2\right]$$

$$K = \frac{P}{3}\left\{3K'_\infty + \frac{x^{1/3}}{1-x^{1/3}}\right\} + x^{1/3}\left\{A + 2B\left(1-x^{1/3}\right)\right\}$$

$$K' = \frac{K}{P} - \frac{1}{3} + \frac{P}{9K}\left\{3K'_\infty + \left(x^{1/3}\right)^2 2B - \frac{1}{\left(1-x^{1/3}\right)^2}\right\}$$

where $x = V/V_0$

$$A = (3/2)\left(K'_0 - 2K'_\infty + 1/3\right)$$

$$B = (3/8)\left(4K_0K''_0 + K'^2_0 + 2K'_0 - 4K'_\infty + 5/9\right)$$

(c) Stacey Reciprocal k-primed EOS [1,13]

$$\ln\frac{V}{V_0} = \frac{K'_0}{K'^2_\infty}\ln\left(1-K'_\infty\frac{P}{K}\right)+\left(\frac{K'_0}{K'_\infty}-1\right)\frac{P}{K}$$

$$K = K_0\left(1-K'_\infty\frac{P}{K}\right)^{-\frac{K'_0}{K'_\infty}}$$

$$\frac{1}{K'} = \frac{1}{K'_0} + \left(1-\frac{K'_\infty}{K'_0}\right)\frac{P}{K}$$

(d) Kushwah Logarithmic EOS [2,13]

$$Px^{K'_\infty} = B_1\ln(2-x)$$

$$B_2\left[\ln(2-x)\right]^2 + B_3\left[\ln(2-x)\right]^3$$

$$K = K'_\infty P + \frac{x^{1-K'_\infty}}{2-x}$$

$$\left[B_1 + 2B_2\ln(2-x) + 3B_3\left\{\ln(2-x)^2\right\}\right]$$

$$K' = 2K'_\infty - \frac{K'^2_\infty P}{K} + \frac{2}{2-x}$$

$$\left[\frac{K'_\infty P}{K} + \frac{x^{2-K'_\infty}}{K(2-x)}\left\{B_2 + 3B_3\ln(2-x)\right\} - 1\right]$$

Where $x = V/V_0$

$$B_1 = K_0$$

$$B_2 = \left(\frac{K_0}{2}\right)\left(K'_0 - 2K'_\infty + 2\right)$$

$$B_3 = \left(\frac{K_0}{6}\right)\left(K_0K''_0 + K'^2_0 + 3K'^2_\infty\right.$$

$$\left.-3K'_0K'_\infty - 12K'_\infty + 6K'_0 + 6\right)$$

(e) Kushwah Exponential EOS [3]

$$P\ (1-x)^{K'_\infty} = B_1\left(1-e^{-x}\right)$$

$$+B_2\left(1-e^{-x}\right)^2 + B_3\left(1-e^{-x}\right)^3$$

$$K = K'_\infty P + \frac{e^{-x}}{(1-x)^{K'_\infty - 1}}$$

$$\left[B_1 + 2B_2\left(1-e^{-x}\right) + 3B_3\left\{\left(1-e^{-x}\right)^2\right\}\right]$$

$$K' = 2K'_\infty + x - 2 - K'_\infty\left(x + K'_\infty - 2\right)\frac{P}{K}$$

$$+ \frac{e^{-2x}}{K(1-x)^{K'_\infty - 2}}\left[2B_2 + 6B_3\left(1-e^{-x}\right)\right]$$

Where

$$x = 1 - \frac{V}{V_0}$$

$$B_1 = K_0$$

$$B_2 = \left(\frac{K_0}{2}\right)\left(K'_0 - 2K'_\infty + 2\right)$$

and $B_3 = (K_0/6)(K_0K''_0 + K'_0(K'_0 - 3K'_\infty + 6) + 3K'_\infty(K'_\infty - 4) + 7)$

We make use of these equations to calculate values of pressure.

RESULTS AND DISCUSSIONS

The five different Equation of state (EOS) (a) Modified Rydberg EOS, (b) Hama Suito EOS, (c) Stacey reciprocal K-primed EOS, (d) Kushwah logarithmic EOS and (e)

Kushwah Exponential EOS have been described for calculation of different properties. The Values of input parameters K_0, K'_0 , K'_∞ and $K^0K''_0$ used in the present calculations are taken from the literature[15,16] and are given in table 1. Using the input parameters and equations, we have calculated pressure P, bulk modulus K and pressure derivative of bulk modulus K' for four metals (Zn, La, V and Nb) at different values of compressions down to $V/V_0 = 0.5$. These are given in Table 2 & 3.

Table 1. Values of input data for different metals at room temperature and zero pressure[15,16].

Metals	Zn	La	V	Nb
K_0	61.46	24.62	162.00	168.80
K'_0	3.26	2.86	3.50	3.30
K'_∞	1.96	1.716	2.10	1.98
$K_0K''_0$	-4.25	-3.27	-4.90	-4.36

Table 2. Values of pressure for the different metals calculated from (a) Modified Rydberg EOS, (b) Hama Suito EOS, (c) Stacey reciprocal K-primed EOS, (d) Kushwah logarithmic EOS, (e) Kushwah Exponential EOS

Metals	V/V_0	P				
		(a)	(b)	(c)	(d)	(e)
	1.00	0.00	0.00	0.00	0.00	0.00
	0.95	3.43	3.43	3.43	3.43	3.42
	0.90	7.69	7.67	7.67	7.67	7.66
	0.85	13.03	12.93	12.95	12.95	12.90
	0.80	19.76	19.49	19.54	19.55	19.42
Zn	0.75	28.33	27.70	27.85	27.86	27.58
	0.70	39.36	38.06	38.40	38.43	37.88
	0.65	53.73	51.22	51.97	52.02	51.04
	0.60	72.75	68.14	69.65	69.77	68.07
	0.55	98.39	90.17	93.08	93.32	90.50
	0.50	133.7	119.3	124.8	125.3	120.7
	1.00	0.00	0.00	0.00	0.00	0.00
	0.95	1.36	1.36	1.36	1.36	1.36
	0.90	3.01	3.01	3.01	3.01	3.01
	0.85	5.05	5.02	5.03	5.03	5.01
	0.80	7.57	7.49	7.50	7.50	7.45
La	0.75	10.71	10.53	10.56	10.55	10.45
	0.70	14.67	14.29	14.38	14.36	14.15
	0.65	19.72	19.01	19.20	19.16	18.79
	0.60	26.27	24.98	25.35	25.28	24.65
	0.55	34.89	32.62	33.34	33.22	32.19
	0.50	46.49	42.59	43.91	43.71	42.07
	1.00	0.00	0.00	0.00	0.00	0.00
	0.95	9.09	9.08	9.07	9.08	9.08
	0.90	20.53	20.46	20.47	20.47	20.43
	0.85	35.02	34.72	34.76	34.70	34.65
	0.80	53.51	52.67	52.83	52.88	52.53
V	0.75	77.32	75.36	75.84	75.92	75.17
	0.70	108.30	104.23	105.37	105.56	104.10
	0.65	149.21	141.26	143.77	144.17	141.50
	0.60	204.10	189.28	197.44	195.19	190.50
	0.55	279.01	252.38	262.31	263.87	256.01
	0.50	383.70	336.68	355.46	358.36	345.50
	1.00	0.00	0.00	0.00	0.00	0.00
	0.95	9.42	9.42	9.43	9.42	9.41
	0.90	21.17	21.10	21.11	21.11	21.07
	0.85	35.90	35.63	35.69	35.67	35.54
	0.80	54.52	53.76	53.89	53.92	53.57
Nb	0.75	78.26	76.49	76.88	76.94	76.17
	0.70	108.90	105.20	106.17	106.27	104.00
	0.65	148.90	142.75	143.87	144.08	141.40
	0.60	201.90	188.80	193.08	193.53	188.00
	0.55	273.50	250.17	258.46	259.33	251.50
	0.50	372.50	331.54	347.10	348.77	336.00

Table 3. Values of bulk modulus K and pressure derivative of bulk modulus K' for the different metals calculated from (a) Modified Rydberg EOS, (b) Hama Suito EOS, (c) Stacey reciprocal K- primed EOS, (d) Kushwah logarithmic EOS, (e) Kushwah Exponential EOS.

Metals	V/V_0	K				
		(a)	(b)	(c)	(d)	(e)
	1.00	61.46	61.46	61.46	61.46	61.46
	0.95	72.42	72.27	72.28	72.28	72.19
	0.90	85.59	84.86	84.96	84.96	84.60
	0.85	101.53	99.63	99.99	100.01	99.11
	0.80	121.03	117.07	118.01	118.06	116.32
Zn	0.75	145.14	137.84	139.87	140.00	137.01
	0.70	175.33	162.79	166.73	167.02	162.25
	0.65	213.67	193.12	200.23	200.80	193.56
	0.60	263.17	230.46	242.69	243.74	233.09
	0.55	328.34	277.14	297.57	299.41	284.03
	0.50	416.14	336.60	370.12	373.25	351.26
	1.00	24.62	24.62	24.63	24.62	24.62
	0.95	28.44	28.39	28.40	28.40	28.36

	0.90	32.96	32.74	32.77	32.76	32.62
	0.85	38.34	37.78	37.87	37.85	37.50
	0.80	44.82	43.66	43.90	43.84	43.17
La	0.75	52.68	50.58	51.10	50.98	49.84
	0.70	62.35	58.80	59.79	59.59	57.80
	0.65	74.38	68.66	70.43	70.11	67.45
	0.60	89.61	80.66	83.66	83.19	79.35
	0.55	109.21	95.47	100.41	99.73	94.30
	0.50	135.01	114.09	122.07	121.10	113.51
	1.00	162.00	162.00	162.00	162.00	162.00
	0.95	193.17	192.69	192.70	192.73	192.51
	0.90	230.96	228.72	229.07	229.09	228.11
	0.85	277.17	271.26	272.45	272.63	270.22
	0.80	334.26	321.84	342.96	325.43	320.72
V	0.75	405.59	382.48	389.31	390.32	382.17
	0.70	495.88	455.85	469.17	471.18	458.09
	0.65	611.88	545.62	569.85	573.55	553.49
	0.60	763.51	656.90	699.07	705.44	675.62
	0.55	965.76	797.05	867.88	878.85	835.30
	0.50	1242.1	976.89	1094.3	1112.4	1049.25
	1.00	168.80	168.00	168.80	168.80	168.80
	0.95	199.30	198.86	198.93	198.89	198.80
	0.90	235.99	233.94	234.22	234.24	233.23
	0.85	280.50	275.12	276.21	276.22	273.76
	0.80	335.02	323.81	326.47	326.70	321.90
Nb	0.75	402.55	381.85	387.62	388.15	379.88
	0.70	487.25	451.68	462.92	463.99	450.79
	0.65	595.04	536.63	556.97	558.99	538.93
	0.60	734.50	641.35	676.41	680.04	650.48
	0.55	918.50	772.43	831.12	837.34	794.59
	0.50	1166.9	939.61	1036.1	1046.5	985.25

Metals	V/V_0			K'		
		(a)	(b)	(c)	(d)	(e)
	1.00	3.26	3.26	3.26	3.26	3.26
	0.95	3.14	3.06	3.07	3.07	3.03
	0.90	3.04	2.89	2.92	2.92	2.85
	0.85	2.94	2.73	2.79	2.79	2.70
	0.80	2.86	2.59	2.68	2.69	2.59
Zn	0.75	2.78	2.47	2.59	2.60	2.49
	0.70	2.70	2.36	2.51	2.52	2.41
	0.65	2.64	2.26	2.44	2.45	2.35
	0.60	2.57	2.16	2.37	2.39	2.30
	0.55	2.51	2.08	2.32	2.34	2.25
	0.50	2.46	2.00	2.26	2.29	2.21
	1.00	2.86	2.86	2.86	2.86	2.86
	0.95	2.77	2.71	2.71	2.71	2.67
	0.90	2.69	2.57	2.59	2.58	2.51
	0.85	2.61	2.44	2.48	2.47	2.38
	0.80	2.54	2.33	2.39	2.38	2.27
La	0.75	2.47	2.23	2.31	2.30	2.19
	0.70	2.41	2.14	2.24	2.23	2.11
	0.65	2.35	2.05	2.18	2.17	2.05
	0.60	2.30	1.97	2.12	2.11	2.01
	0.55	2.25	1.90	2.07	2.06	1.96
	0.50	2.20	1.84	2.03	2.02	1.93
	1.00	3.50	3.50	3.50	3.50	3.50
	0.95	3.37	3.27	3.28	3.28	3.24
	0.90	3.25	3.07	3.12	3.12	3.04
	0.85	3.14	2.90	2.98	2.98	2.98
	0.80	3.04	2.75	2.87	2.87	2.77
V	0.75	2.95	2.61	2.77	2.77	2.67
	0.70	2.85	2.48	2.69	2.69	2.59
	0.65	2.80	2.37	2.62	2.62	2.52
	0.60	2.73	2.27	2.56	2.56	2.46
	0.55	2.67	2.18	2.50	2.50	2.41
	0.50	2.61	2.09	2.45	2.45	2.37
	1.00	3.30	3.30	3.30	3.30	3.30
	0.95	3.18	3.10	3.11	3.11	3.06
	0.90	3.07	2.92	2.95	2.95	2.88
	0.85	2.98	2.76	2.82	2.82	2.73
	0.80	2.89	2.62	2.72	2.72	2.62
Nb	0.75	2.80	2.49	2.63	2.63	2.52
	0.70	2.73	2.38	2.55	2.55	2.44
	0.65	2.66	2.28	2.48	2.48	2.38
	0.60	2.60	2.18	2.42	2.42	2.32
	0.55	2.55	2.10	2.37	2.37	2.28
	0.50	2.49	2.02	2.32	2.32	2.24

The above calculations for pressure P, bulk modulus K and pressure derivative of bulk modulus K' have been calculated using various EOS's at different relative compression volume (V/V_0) ranging from 1.0 to 0.5 for metals Zn (Figure1-3), La (Figure4-6), V (Figure7-9) and Nb (Figure10-12) and also have been shown by the various graphs.

In Figure 1, Figure 4, Figure 7 and Figure 10, the plotted graphs show comparison between calculated pressure (P) versus relative compression volume (V/V_0). From these graphs, one can see that Pressure increases continuously with decrease in relative volume compression for all metals. It also shows that all EOS have good agreement with Stacey reciprocal k-primed EOS and coincides at similar points.

In Figure 2, Figure 5, Figure 8 and Figure 11, the plotted graphs reflects comparison between calculated Bulk modulus (K) versus relative compression volume (V/V_0). From these graphs, we conclude that Bulk modulus also increases continuously with decrease in relative volume compression for all metals. It also shows that all EOS have close agreement with Stacey reciprocal k-primed EOS except Modified Rydberg EOS. It deviates slightly after compression range 0.65 in the same direction.

In Figure 3, Figure 6, Figure 9 and Figure 12, the plotted graphs show comparison between calculated Pressure derivative of bulk modulus (K') versus relative compression volume (V/V_0). From these graphs, one can see that Pressure derivative of bulk modulus decreases continuously with decrease in relative volume compression for all metals. It also shows that there is close agreement between Kushwah logarithmic EOS with Stacey reciprocal k-primed EOS . In case of Hama Suito EOS and Kushwah exponential EOS, there is a crossover between the calculated values for derivative of bulk modulus (K') at relative volume compression 0.75 for Zn metal shown in Figure 3. Similarly, In Figure 6 there is crossover between the calculated values for derivative of bulk modulus (K') at relative volume compression 0.65 for La metal. There is a deviation in between the calculated values for derivative of bulk modulus (K') at relative volume compression 0.8 for V metal shown in Figure 9, but there is crossover between the calculated values for derivative of bulk modulus (K') at relative volume compression 0.8 for Nb metal shown in Figure 12. The calculated values by Modified Rydberg EOS deviates and does not show good agreement with all other EOS's.

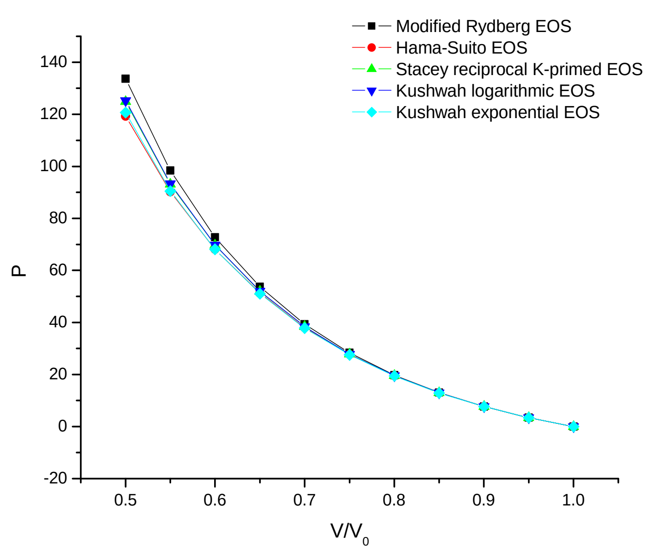

Figure 1. Pressure P (GPa) versus relative volume (V/V_0) for Zn.

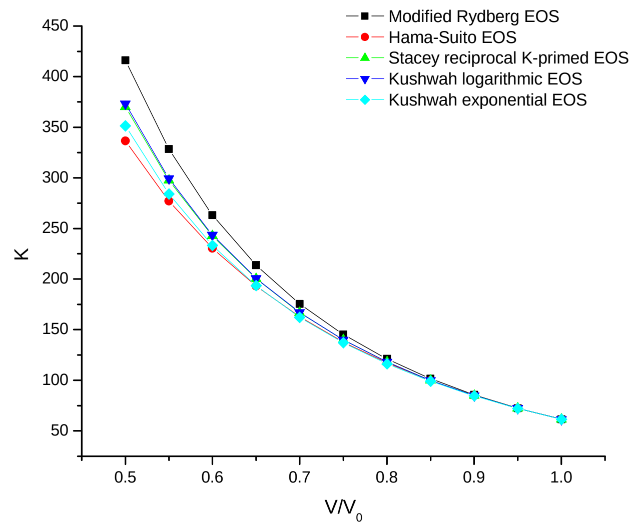

Figure 2. Bulk modulus K versus relative volume (V/V_0) for Zn.

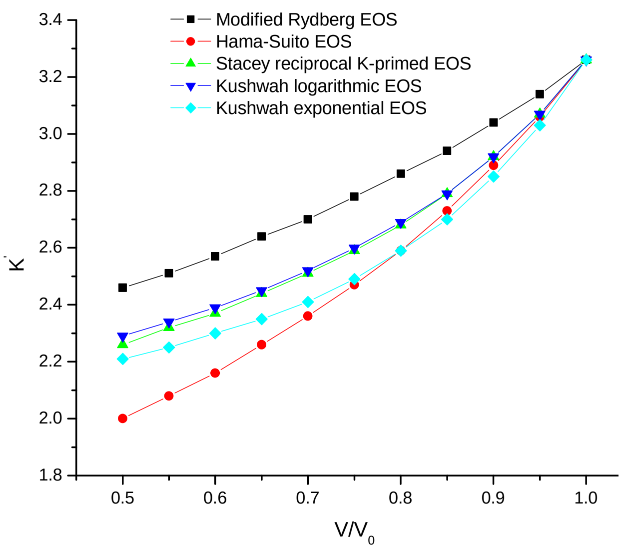

Figure 3. Pressure Derivative of Bulk modulus K versus relative volume (V/V_0) for Zn.

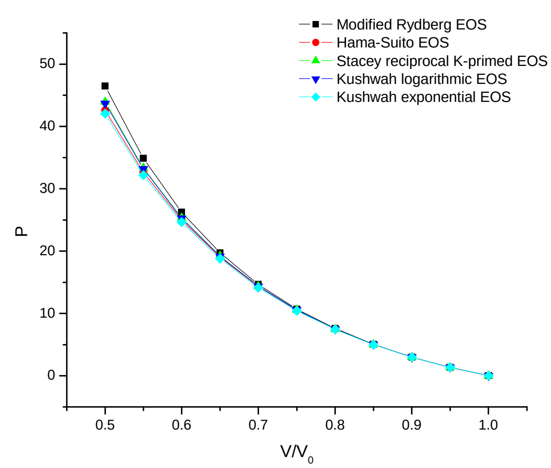

Figure 4. Pressure P (GPa) versus relative volume (V/V_0) for La.

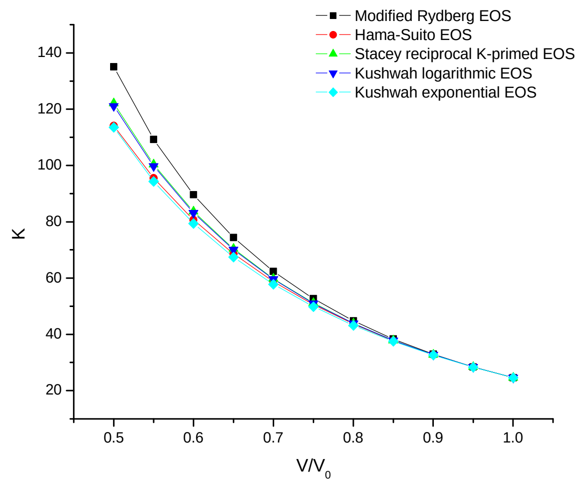

Figure 5. Bulk modulus K versus relative volume (V/V_0) for La.

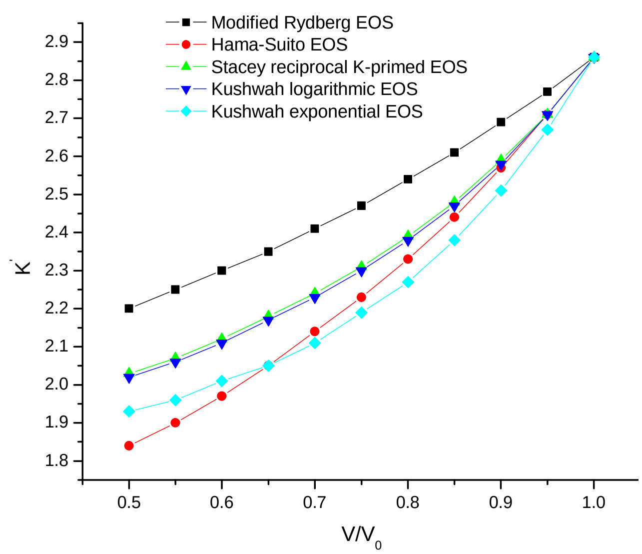

Figure 6. Pressure Derivative of Bulk modulus K versus relative volume (V/V_0) for La.

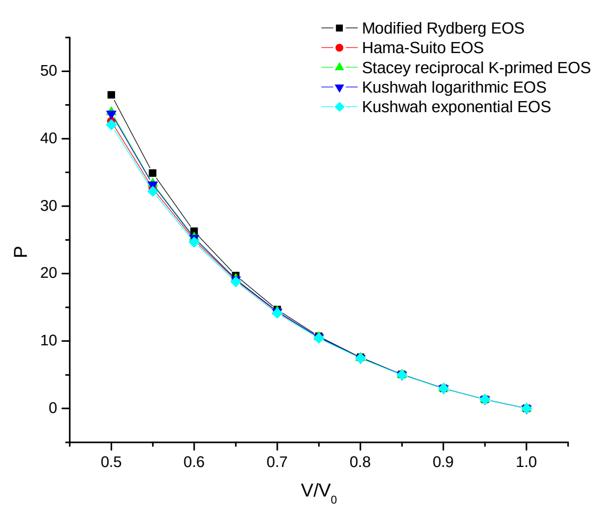

Figure 7. Pressure P (GPa) versus relative volume (V/V_0) for V.

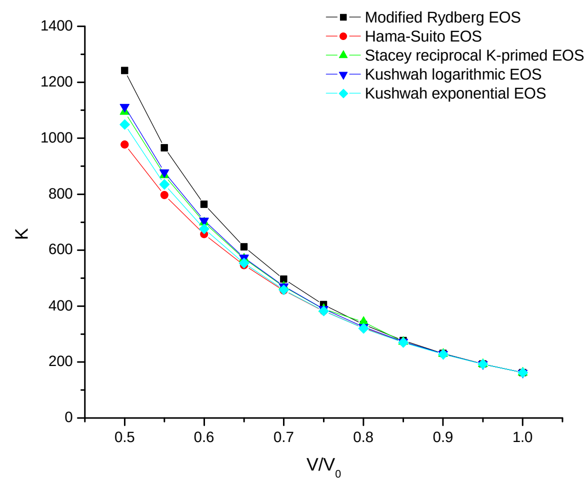

Figure 8. Bulk modulus K versus relative volume (V/V_0) for V.

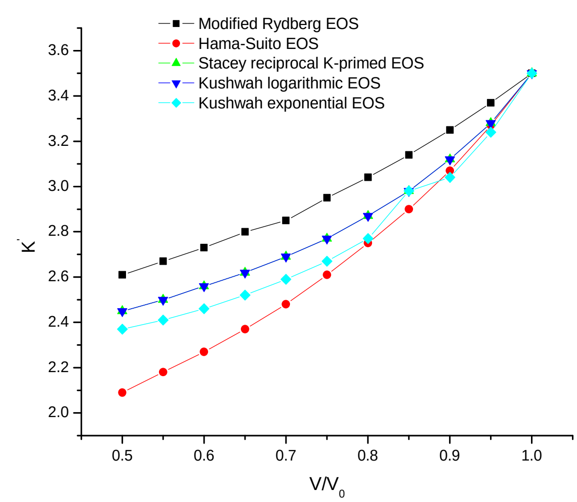

Figure 9. Pressure Derivative of Bulk modulus K versus relative volume (V/V_0) for V.

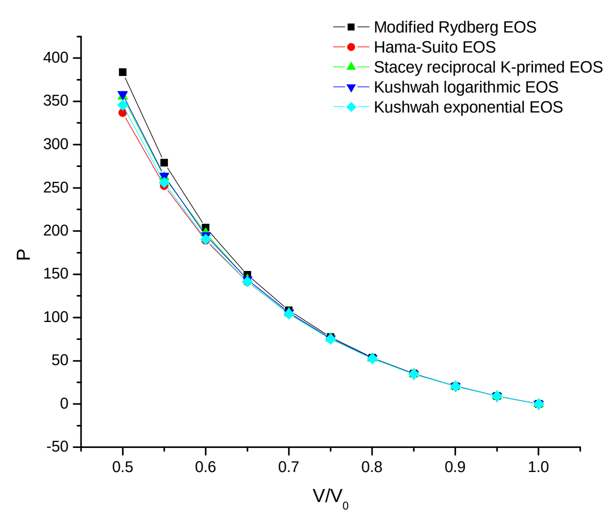

Figure 10. Pressure P (GPa) versus relative volume (V/V_0) for Nb.

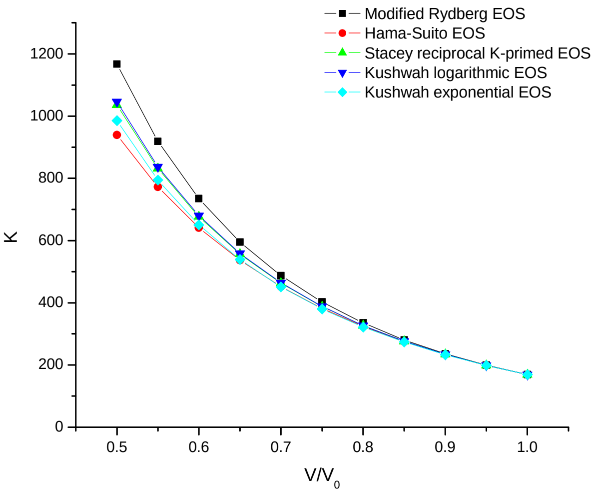

Figure 11. Bulk modulus K versus relative volume (V/V_0) for Nb.

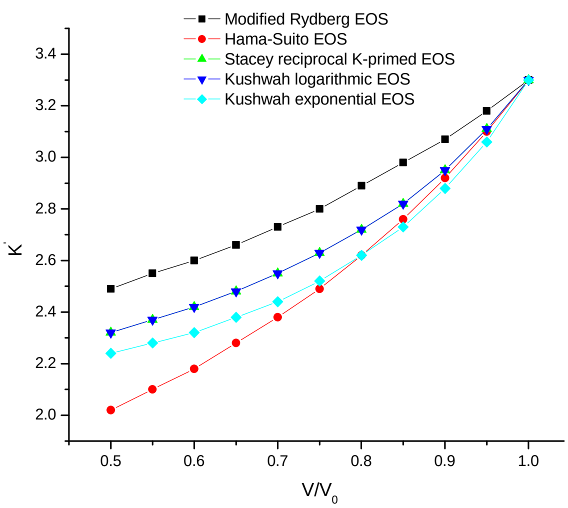

Figure 12. Pressure Derivative of Bulk modulus K versus relative volume (V/V_0) for Nb.

Conclusion

In conclusion, the results obtained for four metals (Zn, La, V and Nb) using the input data (table1) obtained from different equations of state considered in the present study are compared and reported in tables (2&3) for pressure, bulk modulus and its pressure derivatives at different values of V/V_0 (from 0.5 -1.0) and also shown by graphs in Figure(1-3) for Zn, Figure(4-6) for La, Figure(7-9) for V and Figure(10-12) for Nb. Kushwah logarithmic EOS, Hama Suito EOS and Kushwah exponential EOS yields good agreement with the results based on Stacey reciprocal K-primed EOS. Whereas Modified Rydberg EOS deviates after (V/V_0 = 0.65) compression range. Equation which gives satisfactory results for Pressure P and bulk modulus K are used further to calculate Pressure derivative of bulk modulus K'. The results for K' are presented in Figure (3,6,9,12). Again there is a good agreement between the values based on Stacey EOS, Kushwah logarithmic EOS and Hama Suito EOS. The results by equations Modified Rydberg EOS and Kushwah exponential EOS deviates from the other equations of state after ($V/V_0 = 0.85$) compression range.

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