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# Analysis of high pressure equations of state for solids

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Four equations of state for solids with adjustable parameter $K'_\infty$, the pressure derivative of bulk modulus at infinite pressure have been studied. These equations are the Keane EOS, the Stacey reciprocal $K'$ - EOS, the generalized Rydberg EOS and the Roy-Roy EOS. It is found that the Keane EOS and the Stacey EOS are very similar requiring $K'_\infty$ to be considerably larger than 5/3. The generalized Rydberg EOS yields satisfactory results with a value of $K'_\infty$ = 5/3. For the Roy-Roy EOS, $K'_\infty$ has been found to remain between 5/3 and 2. This has been demonstrated by calculating $P$, $K$ and $K'$ for hcp iron at different compressions.

**Keywords :** Pressure derivative of bulk modulus, Infinite pressure behaviour, hcp iron, Constraints for $K'_\infty$

## 1 Introduction

The extreme compression ($V\to 0$) value of the pressure derivative of bulk modulus, i.e. $K'_\infty$ has been treated as an adjustable parameter in recent studies on high pressure equation of state (EOS) for solids[1-3] . It has been emphasized that $K'_\infty$ is an important EOS parameter. A careful observation of Table 1 given by Stacey in Ref.(3) reveals that there are two types of EOS. In first category are those equations which yield a fixed numerical value for $K'_\infty$. This value of $K'_\infty$ is a characteristic property of the EOS considered[4] , and it is the same for all types of materials for which the EOS is applied. The value of $K'_\infty$ is changed only when one EOS is replaced by the other. Several[5,6] EOS have been formulated such that $K'_\infty$=5/3. There has been a long list of researchers[5-8] who have provided a fundamental support to this value (5/3) of $K'_\infty$ on the basis of the Thomas-Fermi model applicable at extreme compression.

Stacey[1-3] does not agree with the Thomas-Fermi model because solids, even at extreme compression, do not resemble with the Thomas-Fermi electron gas and therefore, $K'_\infty$= 5/3 should be rejected. Stacey developed a new constraint $K'_\infty$>5/3 on the basis of thermodynamics in the limit of infinite pressure. But this is also subject to the criticism recently made by Shanker *et al*[9]. on the basis of the generalized theory of the Grüneisen parameter[8].

The second type of EOS includes those equations which treat $K'_\infty$ as an adjustable parameter. For such equations, $K'_\infty$ is not a characteristic parameter of the EOS, but it depends on the material for which the EOS is applied. Thus, $K'_\infty$ is a property of the given solid in the same sense as the zero pressure parameters $K_0$ and $K'_0$ representing bulk modulus and its pressure derivative, respectively, are the properties. The most striking point for such EOS is that $K'_\infty$, which is an infinite pressure parameter, is directly related to the zero-pressure parameters.

## 2 Method of Analysis

In the present study , we consider four equations of state, viz. (a) the Keane[10] EOS , (b) the Stacey reciprocal[1-3] $K'$-EOS , (c) the generalized Rydberg[3] EOS , and (d) the Roy-Roy[11] EOS . The pressure-volume relationships based on these EOS are, respectively given below:

$$\text{(a)}\quad P=K_0\left[\frac{K'_0}{K'^2_\infty}\left\{\left(\frac{V}{V_0}\right)^{K'_\infty}-1\right\}+\left(\frac{K'_0}{K'_\infty}-1\right)\ln\frac{V}{V_0}\right] \quad \ldots(1)$$

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

$$\text{(c)}\quad P=3K_0X^{K'_\infty}(1-X^{-1/3})\exp[f(1-X^{-1/3})] \quad \ldots(3)$$

where

$$f=(3/2)K'_0-3K'_\infty+\frac{1}{2}=-3K_0K''_0-\frac{3}{4}K'^2_0+\frac{1}{12},$$

and $X=\dfrac{V}{V_0}$

Table 1 — Maximum values of $K_0\ K''_0$ derived from (a) the Stacey reciprocal $K'$-EOS (Eq. 11), (b) the generalized Rydberg EOS (Eq.12) and (c) the Roy-Roy EOS (Eq. 13). *Ab- initio* values of $K_0\ K''_0$ due to Hama and Suito[6] are given in the last column

| Solids | $K'_0$ [Ref. 6] | Maximum values of $-K_0\ K''_0$ | | | $-K_0\ K''_0$ Hama and Suito[6] |
|---|---|---|---|---|---|
| | | (a) | (b) | (c) | |
| Ne | 7.61 | 45.23 | 16.76 | 20.70 | 18.19 |
| Ar | 7.07 | 38.20 | 14.51 | 16.96 | 15.89 |
| Al | 4.85 | 15.44 | 6.78 | 5.41 | 7.55 |
| Cu | 5.93 | 25.28 | 10.23 | 10.26 | 11.21 |
| LiH | 3.51 | 6.47 | 3.31 | 1.43 | 4.15 |
| MgO | 4.37 | 11.81 | 5.43 | 3.73 | 6.28 |

(d) $$\frac{V}{V_0}=\left[1+aP(1+bP)^{C}\right]^{-1} \quad \ldots(4)$$

where

$$a=\frac{1}{K_0},\ b=\left[\frac{\left(4K_0K_0''-5K_0'^2+6K_0'-1\right)}{[6K_0'(1-K_0')]}\right] \text{ and}$$

$$c=\left[\frac{3(1-K_0')^2}{(4K_0K_0''-5K_0'^2+6K_0'-1)}\right]$$

The Keane EOS and the Stacey EOS both yield the identical relationship[2].

$$K_0K_0''=-K_0'(K_0'-K_\infty') \quad \ldots(5)$$

where $K_0\ K''_0$ is the zero-pressure value of $KK''$ with $K''=\mathrm{d}^2K/\mathrm{d}P^2$. The generalized Rydberg EOS and the Roy-Roy EOS give the following relations[3] respectively

$$K_\infty'=K_0K_0''+\frac{K_0'^2}{4}+\frac{K_0'}{2}+\frac{5}{36} \quad \ldots(6)$$

and

$$K_\infty'=1-\frac{3(K_0'-1)^2}{4K_0K_0''-2K_0'^2+2} \quad \ldots(7)$$

We can present a test of Eqs (5-7) by using two well accepted constraints which have no contradictions. $K_0\ K''_0$ must be negative, i.e. less than zero (Eq.5), and $K'_\infty$must not be less than 5/3 ( Eq.6). The first constraint is based on the fact that $K'$ decreases with the increase in pressure. This is supported theoretically, as well as experimentally[2] . The second constraint is so defined that it neither contradicts the Thomas-Fermi model $K'_\infty$=5/3, nor the Stacey thermodynamic constraint $K'_\infty$>5/3. According to both the models $K'_\infty$ cannot be less than 5/3, it is either 5/3 or greater than 5/3. The following inequalities must hold when $K_0\ K''_0$ is necessarily negative in Eqs(5-7).

$$K_\infty'<K_0' \quad \ldots(8)$$

$$K_\infty'<\frac{K_0'^2}{4}+\frac{K_0'}{2}+\frac{5}{36} \quad \ldots(9)$$

$$K_\infty'<\frac{(5K_0'-1)}{2(K_0'+1)} \quad \ldots(10)$$

Inequalities given in Eqs (8-10) are derived from Eqs (5-7), respectively. Inequalities in Eqs (8 and 9) are satisfied for all the known values of $K'_\infty$ and $K'_\infty$. The most reliable information comes from the analysis of seismic data for lower mantle and the outer core[2] which reveals that $K'_\infty/K'_0$=3/5. However, inequality given in Eq.(10) gives a restricted range for the values of $K'_\infty$. For example, $K'_0$ = 5 when used in Eq. (10) yields $K'_\infty$< 2. This result is not compatible with the value $K'_\infty$=3.0 for the outer core[2] .

The second constraint viz. $K'_\infty$ cannot be less than 5/3 when used in Eqs (5-7) yield the following inequalities, respectively:

$$-3K_0K_0''\le 3K_0'^2-5K_0' \quad \ldots(11)$$

$$-36K_0K_0''\le 9K_0'^2+18K_0'-55 \quad \ldots(12)$$

$$-8K_0K_0''\le 5K_0'^2-18K_0'+13 \quad \ldots(13)$$

## 3 Results and Discussion

The results based on inequalities given in Eqs (11-13) are present in Table 1 and compared with the *ab-initio* values of $K_0\ K''_0$ for different solids reported by Hama and Suito[6]. The zero pressure values of $K_0$, $K'_0$ and $K''_0$ have been obtained[6] using the augumented plane wave (APW) method, and they are not based on any EOS or interatomic potential functions. The maximum value of $-K_0\ K''_0$ predicted from the Stacey reciprocal $K'$-EOS (Eq.11) for each solid is considerably higher than the corresponding values predicted from the other two EOS (Eqs 12 and 13). The comparison reveals that the Stacey EOS can be fitted with the help of values of $K'_\infty$ which are considerably larger than 5/3. This has also been evident from the work of Stacey and Davis[2] based on the seismological data which yield $K'_\infty$= 2.4 for the lower mantle and $K'_\infty$ = 3.0 for the core of earth. It has also been found that there is a limited admissible range for $K'_\infty$ satisfying the Keane rule[10]:

$$\frac{K'_0}{2} < K'_\infty < K'_0 - 1 \qquad \ldots(14)$$

Keane's rule given above is well satisfied by the Keane EOS and the Stacey EOS, but the other two equations, the generalized Rydberg EOS and the Roy-Roy EOS do not satisfy (Eq. 14). The values of $K'_\infty$ corresponding to different EOS determined from Eqs (5-7) using the APW values[6] for $K'_0$ and $K_0 K''_0$ are presented in Table 2. The values of $K'_\infty$ for the Stacey EOS or the Keane EOS are found to be substantially larger than the corresponding values of $K'_\infty$ for the generalized Rydberg EOS and the Roy-Roy EOS (Table 2). Such a comparison has been presented here for the first time.

Thus, $K'_\infty$ even for a given material, is not the same for all the EOS under study. We present a direct and confirmatory test by selecting hcp iron which is essentially the core material for the Earth[2,12]. We take $K_0$ = 170 GPa and $K'_0$ = 4.98, the most reliable input parameters[2] derived from the seismic data. To make a direct comparison more sensible, we have used the same input parameters $K_0$ and $K'_0$ in the four EOS. But we take $K'_\infty$= 3.0 for the Keane EOS and the Stacey EOS and $K'_\infty$ = 5/3 for the generalized Rydberg EOS and the Roy-Roy EOS. The results have been obtained for $P$, $K$ and $K'$ in case of hcp iron down to a compression $V/V_0$ = 0.50 (Figs 1-3).

It is found in the present study that the Keane EOS and the Stacey EOS with $K'_\infty$ = 3.0 yield the results which are fairly close to those obtained from the generalized Rydberg EOS with $K'_\infty$ = 5/3. On the other hand, the Roy-Roy EOS with $K'_\infty$= 5/3 yields results which are substantially different. It is pertinent to mention here that the constraint given by Eq. (10) based on the Roy-Roy EOS gives an upper limit $K'_\infty$= 2 for $K'_0$ = 5. When $K'_\infty$ = 2 is used in the Roy-Roy

Table 2 — Values of $K'_\infty$ derived from (a) the Stacey reciprocal $K'$-EOS (Eq. 5), (b) the generalized Rydberg EOS (Eq. 6) and (c) the Roy-Roy EOS (Eq. 7) using the values of $K'_0$ and $K_0 K''_0$ from Hama and Suito[6] given in Table 1

| Solids | $K'_\infty$ | | |
|---|---|---|---|
| | (a) | (b) | (c) |
| Ne | 5.22 | 0.239 | 1.70 |
| Ar | 4.82 | 0.279 | 1.68 |
| Al | 3.29 | 0.895 | 1.59 |
| Cu | 4.04 | 0.684 | 1.65 |
| LiH | 2.33 | 0.824 | 1.48 |
| MgO | 2.93 | 0.849 | 1.56 |

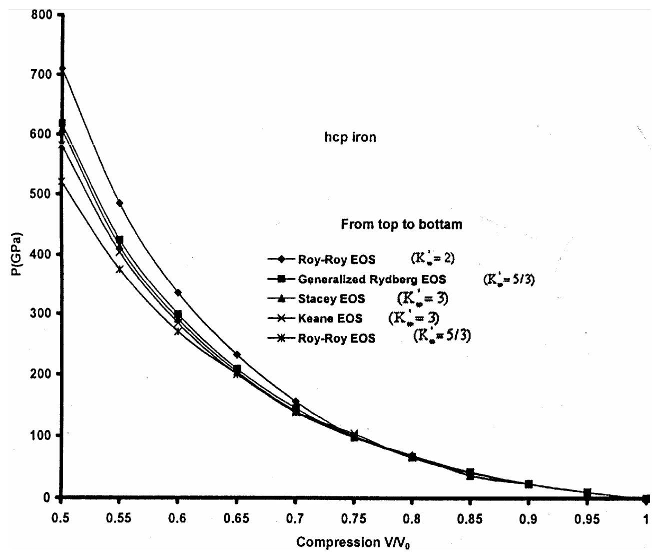


Fig. 1 — Pressure $P$(GPa) versus compression $V/V_0$ for hcp iron

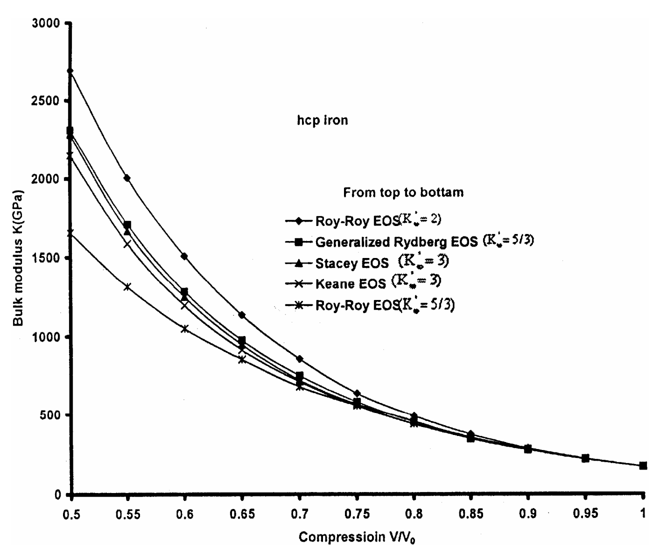


Fig. 2 — Bulk modulus $K$(GPa) versus compression $V/V_0$ for hcp iron

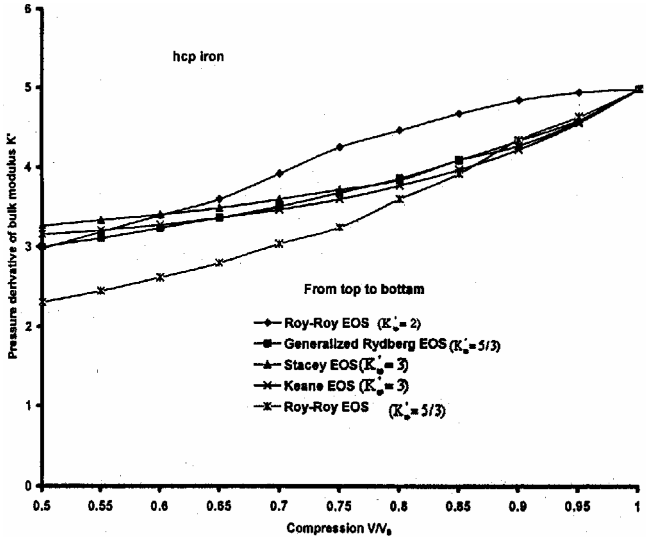


Fig. 3 — Pressure derivative of bulk modulus $K' = dK/dP$ versus compression $V/V_0$ for hcp iron

EOS, the results are significantly modified. It is interesting to note that the results based on the Stacey reciprocal $K'$-EOS remain between the two sets of values estimated from the Roy-Roy EOS taking $K'_\infty$=5/3 and $K'_\infty$=2 (Figs 1-3).Thus, it is concluded that $K'_\infty$, when treated as an adjustable parameter, depends not only on the material considered but also on the equation of state used.

Finally, it should be emphasized that the Stacey constraint $K'_\infty$>5/3 with adjustable values of $K'_\infty$ is a consequence of thermodynamic analysis and the fitting of seismic data. The physical consequence of this constraint is that the thermal expansivity of solids becomes negligibly small in the limit of infinite pressure[1-3]. The Thomas-Fermi model gives $K'_\infty$= 5/3, which is a constant universally for all the materials in the limit of extreme compression. The generalized Rydberg EOS and the Roy-Roy EOS, on the basis of the results obtained in the present study, are found to satisfy closely the Thomas-Fermi model.

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