Band theory analysis of shock velocity-particle velocity relations for metals

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Abstract. The systematics of the shock constants in shock velocity-particle velocity relations for metals have been examined by energy band theory methods. The causes of non-linearity of this relation at high pressure are discussed in terms of $s \rightleftharpoons d$ electron transfer.

1. Introduction

Measurement of Hugoniot equation of state has become one of the major tasks of shock wave research during the last forty years. The Hugoniot, as is well known, is a pressure-volume relation, which satisfies the shock jump conditions (Rice *et al* 1958). In most experiments to date, the commonly measured variables are shock velocity (U_s) and particle velocity (U_p) and it is very common to represent the Hugoniot of materials by its $U_s - U_p$ plot. This representation is quite attractive, as shock velocity being in essence a differential quantity, $[V_0(p_1 - p_0)/(V_0 - V_1)]^{1/2}$ where p_1 and p_0 are the pressures behind and ahead of the shock front and V_1 and V_0 are the corresponding specific volumes or reciprocals of the corresponding densities, i.e., $V_1 = 1/\rho_1$, $V_0 = 1/\rho_0$, is a very sensitive quantity. Thus changes in the equation of state due to various physical phenomena, barely discernible in pV curves are easily seen in the $U_s - U_p$ plots.

The $U_s - U_p$ curve, in general, can be represented by the relation

$$U_s = a + b\, U_p + c U_p^2 + - -$$

where a, b, c, etc are constants for a particular material. It was found almost thirty years ago that the $U_s - U_p$ relation of many materials was linear (i.e. $c = 0$) over the entire range of available data. Departures from linearity or breaks in $U_s - U_p$ curves which were very few, could usually be traced to porosity, large Hugoniot elastic limit or phase transitions. More recently, the other causes identified for nonlinearity have been the pressure and temperature – (these are simultaneously produced in a shock) induced inter-band transitions or core ionizations. Some schematic $U_s - U_p$ curves are presented in figure 1. The phenomenon responsible for the change in the slope of the $U_s - U_p$ curve in each case is also indicated there. In this paper, we present a band theory analysis of some of these $U_s - U_p$ relations for metals (for a review of the applications of band theory for equations of state theories, we refer to the article by Godwal *et al* 1983).

2. Some detailed band theory results for ρ_0, a and b constants

For the linear $U_s - U_p$ relation, the Hugoniot is completely described by the quantities ρ_0, a and b. These are electronic quantities. The constant a, the intercept of $U_s - U_p$ curve, is the bulk sound velocity and is related to the isothermal bulk modules (Rice et al 1958).

$$B_0 = \rho_0 \, a^2.$$

The slope b has been shown (Alder 1963) to bear a close relationship to the pressure derivative of the bulk modulus.

$$B'_0 = (dB/dp)_{p=0} \simeq 4b - 1.$$

These relationships allow us to examine these by using the $0°K$ density functional theories (Hohenberg and Kohn 1965). Numerous calculations have been done especially for ρ_0 and B_0. Let us first see as to how well these theories predict these quantities. Figures 2 and 3 and table 1 show these values in comparison to the experimental data. The average agreement is 6% for density and about 10% for $\rho_0 a^2$
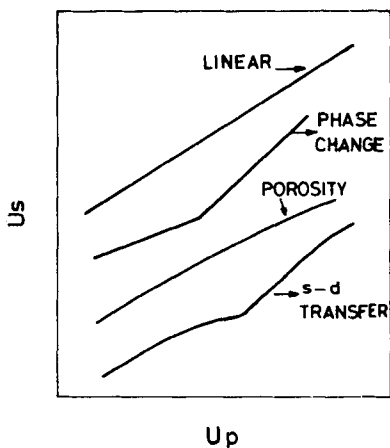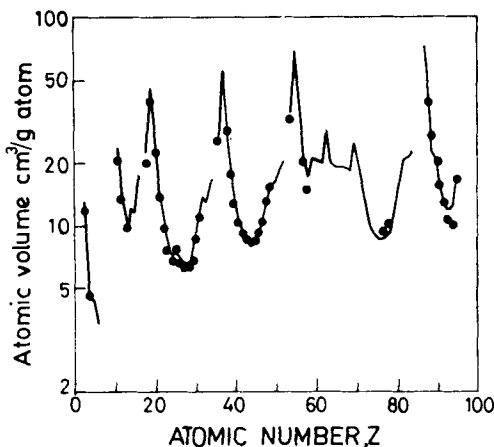

Figure 1.   Schematic $U_s - U_p$ curves.

Figure 2. Zero pressure atomic volumes of elements versus the atomic number. The experimental values lie along the quasi continuous lines. Those calculated by band theory are represented by points.
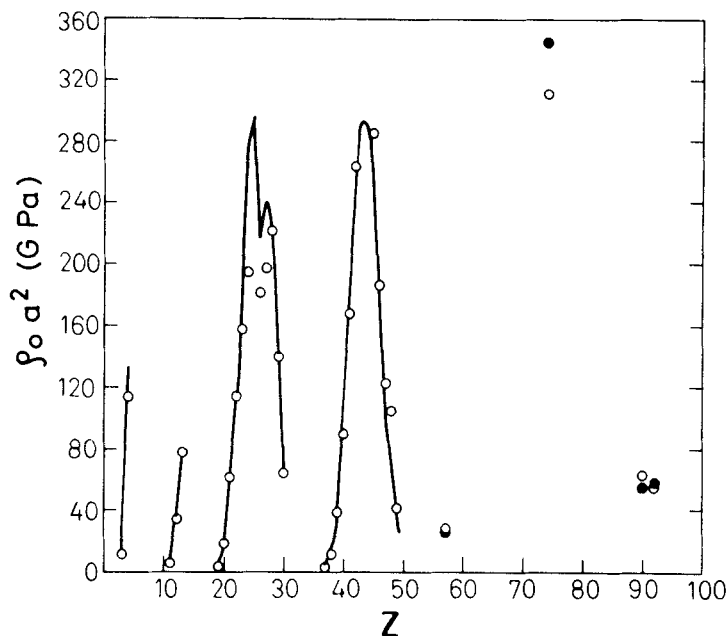
Figure 3. Shock bulk modulus of elements versus *Z*.

Table 1. Observed and calculated values of the *b* parameter*

Element	b_{cal}	b_{obs}
Li	1·07	1·08
Na	1·14	1.25
K	1·15	1·175
Rb	1·18	1·21
Be	1·04	1·13
Mg	1·27	1·26
Ba	1·41	1·08
Al	1·29	1·34
In	1·40	1·53
Tl	1·41	1·38
Sn	1·46	1·58
Pb	1·49	1·528

* see references for experimental values in Sikka and Godwal (1981b).

and *b*. This is quite satisfactory in the framework of local density approximation in theoretical band structure methods.

3. Physics of the *a* parameter

The bulk modulus (and hence the *a* parameter in the present context) in the free electron theory is related to the electron density parameter
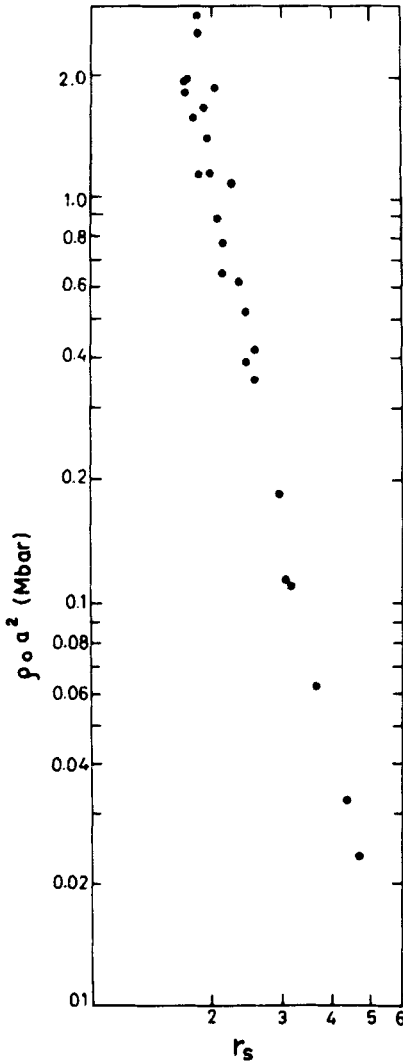
Figure 4. Shock bulk modulus $(\rho_0 a^2)$ versus the electron density parameter r_s for elements.

$$r_s \left(V = \frac{4\pi}{3} z r_s^3 \right).$$

The band theory results of Moruzzi *et al* (1978) have shown that this relationship has more general validity, if the electron density is taken to be the one in the interstitial region of an atomic sphere (e.g. the volume excluding the muffintin spheres). In figure 4, we have plotted $\rho_0 a^2$ against these r_s values. $\rho_0 a^2$ varies as $r_s^{-4.7}$, instead of r_s^{-5} as predicted by the free electron theory.

4. Nature of the b parameter

Regarding the nature of the b parameter, there have been many speculations. Alder (1963) pointed out that b is related to the repulsive potential in a solid. This was

confirmed by Sikka and Godwal (1981a) who showed that b is related to the repulsive parameter B in the empirical total energy expression formula (see figure 5).

$$E_c = A\eta^{2/3} \exp\left(-B\eta^{-1/3}\right) - c\eta^{1/3},$$

where $\eta = V_0/v$. Al'tshuler (1965) noted that b for a material was dependent upon the type of conduction electrons. This is evident from the values of b for materials having the same number but different types of conduction electrons (e.g. see figure 6 for $Z = 3$). In general, b values are systematically lower for materials containing d electrons.
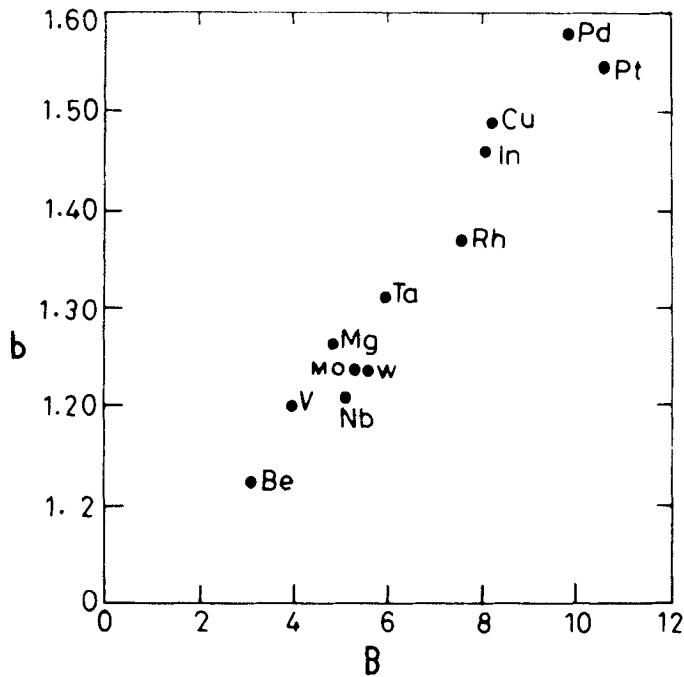

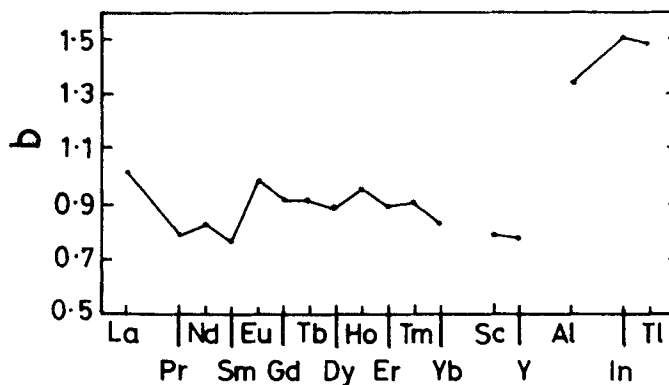**Figure 5.** b versus the repulsive parameter B.

Figure 6. Experimental b values for trivalent elements.

Recently, Sikka and Godwal (1981b) have interpreted this parameter through the pseudopotential theory for *sp* metals

$$R_{sh} \equiv R_a/(b/b-1)^{1/3} = (Z/Z_E)^{1/2} R_c,$$
$$3Z_E = 0.6 Z + 1.37 \alpha Z^{1/3}.$$

Here Z is the valence charge; R_c the core radius; R_a the atomic sphere radius and α is the exchange constant. This relation is displayed in figure 7. In this form b defines a 'hard core' radius, R_{sh} at which the bottom of the conduction band becomes repulsive. It gives the minimum volume the *sp* conduction electrons occupy, consistent with core-orthogonality requirements and the repulsion due to conduction electron-conduction electron interactions (Note the increase in R_{sh}/R_c with Z. It is due to conduction electron interactions as R_a/R_c is almost constant).

For transition metals and other *d* containing materials, a simple analysis of the *b* parameter can be done from the *l*-dependent pressure expression of Pettifor (1977) and Mackintosh and Anderson (1980).

$$P = \sum_l P_l = n_{sp}\, \overline{P}_{sp} + n_d\, \overline{P}_d.$$

Here n_{sp} denotes the number of *sp* electrons, n_d the number of *d* electrons and $\overline{P}_{sp}$ and $\overline{P}_d$ are the corresponding average pressure per electron respectively. Using the expressions for bulk modulus and its pressure derivatives in terms of pressure derivatives (see Vohra *et al* 1983 for more details) it can be shown that

$$B_0' = (4b - 1) \simeq B_R' + \frac{2X}{n_{sp}}$$

where

$$X = -\mathrm{d}n_{sp}/\mathrm{d}\ln v = \mathrm{d}\,n_d/\mathrm{d}\ln v \text{ is } s \rightleftharpoons \mathrm{d}$$

electron transfer parameter. A negative value of X corresponds to electron transfer from $s \rightarrow d$ bands and a positive value indicates the reverse transfer. B_R^1 is the value for the case when $X = 0$ i.e. no electron transfer. From the experimental measurements of
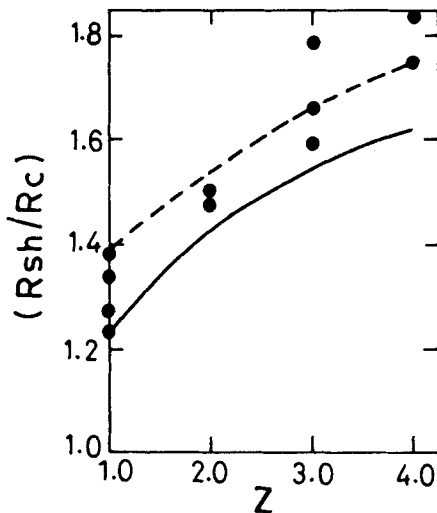

Figure 7. (R_{sh}/R_c) versus Z. The two theoretical curves are: —— with Slater exchange and - - - - with Kohn-Sham exchange.

various physical properties under pressure, and using a model description of the band structure, Svechkarev and Panfilov (1974) obtained X-values for $5d$ transition series. In figure 8, we plot these X-values. This figure can be compared with the experimental curve for b values (figure 9). It can be seen that the variation in b follows approximately the same trend as the X-parameter. In the beginning of the series, X is large and is negative and consequently b values are low. The X parameter decreases towards the middle of the series and changes sign and becomes positive near the end of the series. This is seen as the hardening in b values towards the noble metal end of the series. It may be added here that X is also related to the ratio R_c/R_a (Johansson and Rosengren 1975). Thus, the dependence of b on the core-radius holds both for sp and d containing metals.
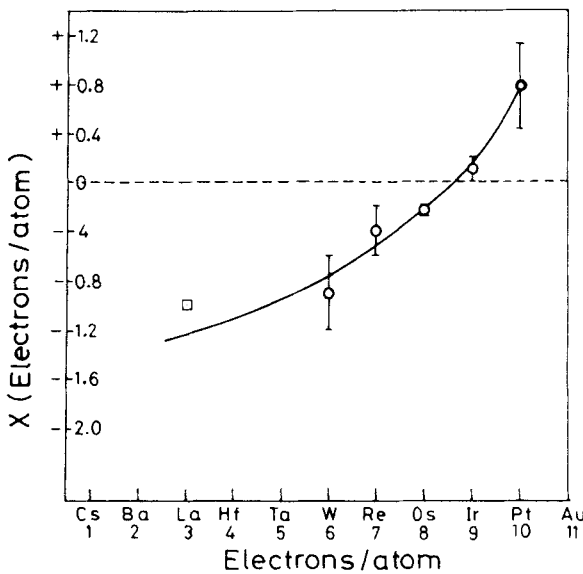

Figure 8. The available experimental values of $s \rightleftharpoons d$ electron transfer parameter for the $5d$ transition series (Svechkarev and Panfilov 1974).
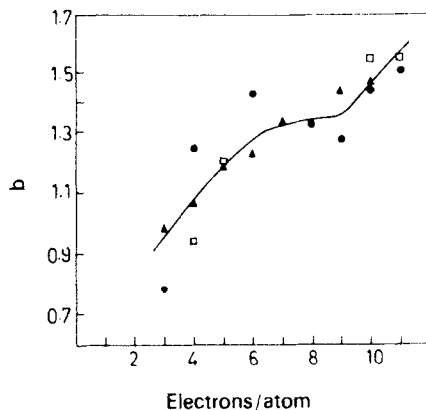

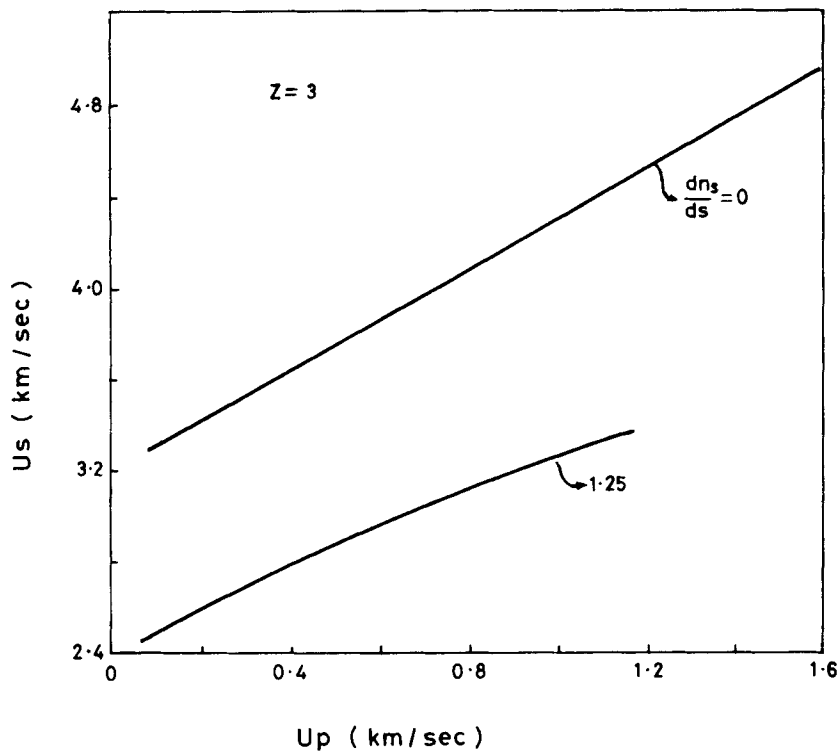**Figure 9.** b values for the three transition metal series.

Figure 10. Model $U_s - U_p$ curves for $Z = 3$ from canonical band theory.
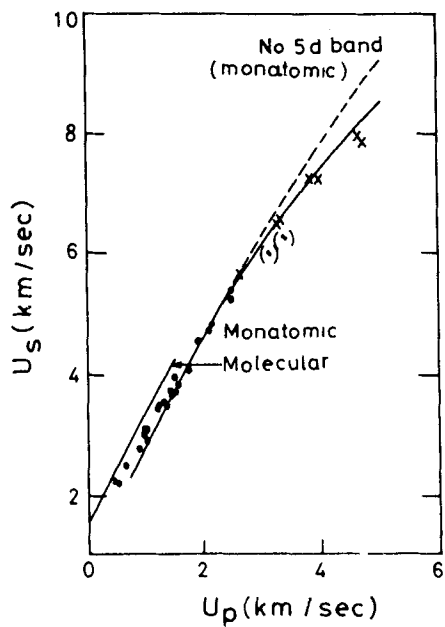

Figure 11. $U_s - U_p$ curve for iodine (McMahan *et al* 1977).

5. Nonlinearity of $U_s - U_p$ curve for $s \rightleftharpoons d$ transitions

Representative curves for $Z = 3$, evaluated from canonical band theory expressions are shown in figure 10 for the two cases when $X = 0$ and when X is large. It is evident that $U_s - U_p$ curve is nonlinear for large X with downward curvature. This is in qualitative agreement with the APW calculations on metallic iodine by McMahan *et al* (1977) as can be seen in figure 11. Similar trends are also noticeable in other materials, notably Sc and
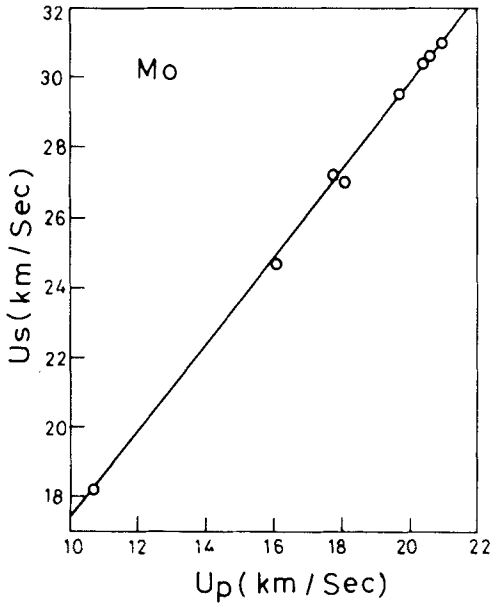
Figure 12. $U_s - U_p$ data for Mo. The solid line is from the fit to the lower pressure region. The experimental points are from Ragan (1982).
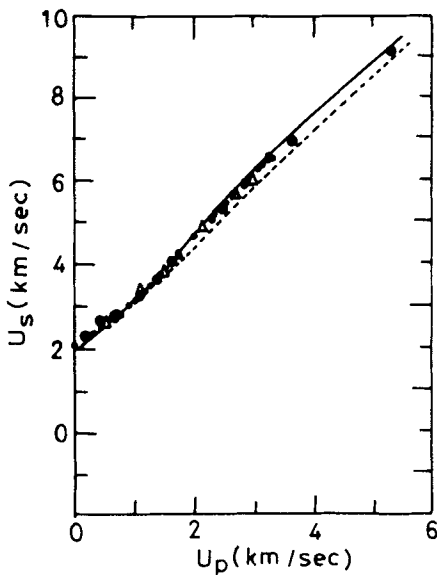
Figure 13. $U_s - U_p$ curve for La (McMahan *et al* 1981). The solid curves for temperature dependent Slater γ and the dotted one is for temperature independent linear γ.

Zr. The $U_s - U_p$ curve for Mo is linear right up to 6.0 TPa pressure (figure 12). This can also be understood from the results of Pettifor (1977) on 4d transition metals which show that for Mo, the respective s and d electron populations do not vary drastically in this pressure region. In La, the $U_s - U_p$ curve stiffens as pressure increases (figure 13). McMahan *et al* attribute this to the termination of the $6s - 5d$ transition due to the movement of 6s bands above the Fermi level. As La now contains only d electrons, the equation of state stiffens due to the loss of $s \rightarrow d$ softening mechanism.

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