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APPLICATION OF HYDROSTATIC PRESSURE AND SHOCK WAVE DATA
TO THE THEORY OF COHESION IN METALS

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The parameter $K' = dK/dP$ (where K is isothermal or adiabatic bulk modulus)is useful in analyzing interatomic forces or interactions. A model is presented that is useful in predicting K' values in certain close-packed and other metallic structures. K is assumed to consist of two additive components: K_F, the free-electron Fermi gas component, and K_{SR}, the interatomic short-range repulsive component derived from a Born-Mayer approximation. At infinitely large molar volumes, only K_F is important and K' should approach a value of 5/3. With decreasing molar volume, the K_{SR} contribution of K' increases through the relation: $K'_{SR} = K_{SR}(B+1)/3K_T$, where K_T is isothermal bulk modulus, B is the "hardness" parameter in the Born-Mayer expression for the energy of interatomic repulsion, and the ratio K_{SR}/K_T is assumed to vary with $1/\Omega_0$, where Ω_0 is the initial molar volume. The K' values from the ultrasonic and shock wave data for metals have been selectively used to compare with the above model. It is shown that the data for the close-packed metal structures, h.c.p. and f.c.c., are reasonably consistent with the model, whereas the limited data for b.c.c. transition metals indicate that K' for this group is influenced by electron band structure and other contributions to the elastic moduli.

Introduction

An analysis of the data for the pressure derivatives of bulk modulus, $K' = dK/dP = (\partial K/\partial P)_T$ as $P \to 0$ (K denotes both isothermal and adiabatic modulus), shows that for purely ionic solids the ultrasonic value of this parameter seldom varies from its range of 4 to 6, and that for a given structure the parameter value shows no systematic relationship to unit cell volume (for example, in alkali halides). In oxides and simple silicates, which are partly ionic and partly covalent, K' tends to increase with decreasing density at constant mean atomic weight [1].

The conclusions reached from a Born model treatment of the data for ionic compounds of NaCl-structure type (which include some oxides) are that the variations of dK/dP are primarily a function of the repulsive parameter, n, which is derived from a $1/r^n$ type of interatomic repulsive potential [2] and which is numerically related to the repulsive parameter, B, in the Born-Mayer form of the potential for ion-core interactions.

In contrast to ionic solids, metals show a wider variation in values of dK/dP, ranging approximately from 3 to 7. In addition, the reported dK/dP values for metals appear to increase continuously with decreasing molar volume (see Figure 1). The purpose of this paper is to show that most of the data are indeed consistent with a model for the bulk modulus which contains two components: a free electron Fermi gas component, and a Born-Mayer interatomic repulsive component. This simple treatment shows that the two-component model is a reasonably good physical model for the cohesive forces in f.c.c. and h.c.p. metals, but may not

be valid for the b.c.c. transition metals where the electron band structure energy makes an important contribution to the elastic moduli.

Data

The values of $K'_T = dK_T/dP$ that we have used in this study and which are plotted in Figure 1 were obtained from direct ultrasonic measurements that appear in the literature [3-13] or from recent unpublished measurements as noted in Table 1. In this survey we were somewhat selective and did not include all the unpublished values. Excluded are certain f.c.c. metals (for example, Zn, Cd, and Pb) with very high K' values. These metals have high compressibility, and it is regarded that anomalous properties and experimental errors may have contributed to atypical K' values.

In addition to the ultrasonic data, we have relied to some extent on K'_T values derived from shock wave data using the second order Birch-Murnaghan equation [13]:

$$P = \frac{3}{2K_{T_0}} (\eta^{7/3} - \eta^{5/3}) \left[1 + \frac{3}{4} (K'_T - 4) \right.$$
$$\left. \cdot (\eta^{2/3} - 1) + \ldots \right] \qquad (1)$$

where K_{T_0} is the initial bulk modulus, P is the hydrostatic pressure, and $\eta = V(0)/V(P)$ is the ratio of initial volume at pressure P. Since K_{T_0} is known,

$$K'_T = 4 + \frac{P - \frac{3}{2} K_{T_0} (\eta^{7/3} - \eta^{5/3})}{\frac{9}{8} K_{T_0} (\eta^{7/3} - \eta^{5/3})} \qquad (2)$$

can be calculated at each (P, η) point along the Hugoniot; the (P, η) points along the Hugoniot are sufficiently close
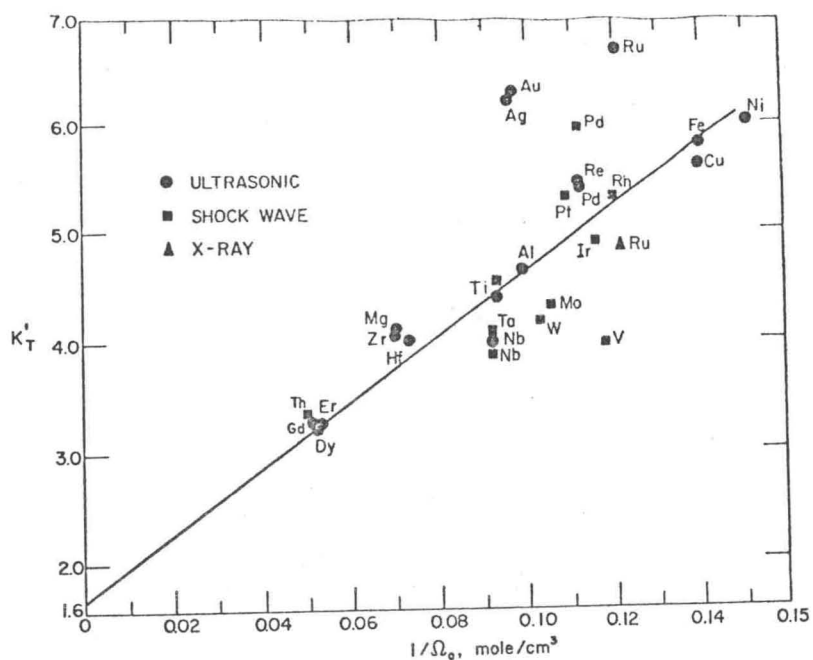
Figure 1. K_T' versus $1/\Omega_o$ for h.c.p., f.c.c., and b.c.c. metals.

Table 1

Values of dK_s/dP and dK_T/dP derived
from the hydrostatic pressure derivatives of the
elastic constants of h.c.p. and f.c.c. metals
(in order of decreasing molar volume)

Metal	Structure	Molar volume, cm^3	dK_s/dP	dK_T/dP	References
Gd	h.c.p.	19.94	3.32	$\sim$3.32	[3]
Dy	h.c.p.	18.99	3.21	3.23	[3]
Er	h.c.p.	18.46	3.30	3.26	[3]
Zr	h.c.p.	14.02	4.08	4.11	[4]
Mg	h.c.p.	14.00	4.06	4.16	[5]
Hf	h.c.p.	13.45	4.03[a]	4.04[a]	
Ti	h.c.p.	10.63	4.31	4.35	[6]
Ag	f.c.c.	10.27	6.18		[7]
Au	f.c.c.	10.22	6.43		[7]
Al	f.c.c.	10.00	5.19	5.31	[5]
Pd	f.c.c.	8.88		5.42	[9]
Re	h.c.p.	8.86		5.43[b]	[8]
Ru	h.c.p.	8.18	6.62[a]	6.66[a,c]	
Fe	b.c.c.	7.09	5.97		[10]
Cu	f.c.c.	7.11	5.84		[11]
Cu	f.c.c.	7.11	5.59		[7]
Ni	f.c.c.	6.59	6.07		[12]

[a]Unpublished.

[b]dK_T/dP value based on x-ray diffraction data is 2.43 ± 1.33 [18].

[c]dK_T/dP value calculated from x-ray diffraction data [19] is 4.7 ± 2.2.

to the isotherm for our purpose. In order to derive the most reproducible values of K_T' pressure versus η values were obtained from shock wave velocity U_s and particle velocity U_p data [14-15] at pressures above 100 kbar using the relations,

$$P = \rho_0 U_p U_s \tag{3a}$$

$$\eta = \frac{V(0)}{V(P)} = \frac{U_s}{U_s - U_p} \tag{3b}$$

The general procedure involved calculating K_T' as a function of pressure for a given element and selecting only those data where the values of K_T' did not vary by more than 10 per cent over those calculated from at least six consecutive (P,η) points. The occurrence of pressure-induced phase transition at relatively intermediate pressures is well established [15-17] for the metals Ti, Zr, and Hf. McQueen et al. [15] estimate that the phase transition pressure for the three metals is 175, 260, and 400 kbar respectively. The phenomenon is revealed in Table 2, where the computed K_T' values are given for Ti. The first two higher measurements at P = 190 kbar when combined with the values at lower pressures give a simple average $K_T' = 4.58$, whereas the third 190 kbar measurement when combined with all the measurements at higher pressures gives $K_T' = 3.34$. The lower-pressure value (4.58), plotted in Figure 1, is presumed to be that for the h.c.p. α phase, whereas the higher-pressure value (3.34) evidently corresponds to the ω phase.

It may be noted that no K_T' value is given in Table 3 for Zr as evaluated from the shock wave data [14-15]. Only those metals for which the computed K_T' values were reasonably consistent over a wide range of pressures well below the known phase transitions are included. In this respect, the Zr data were too widely scattered to be useful. The $\alpha \rightarrow \omega$ transition in Zr is now considered to occur at much lower pressures, at $\sim$30 kbar [17]. A comparison of ultrasonic and shock wave K' values for Hf, Ti, Ag, Au, Re, Pd, and Cu (Table 3) shows that agreement is fairly good between the two considering the uncertainties and errors involved in evaluating the shock wave data.

Table 3

Average values of dK_T/dP for f.c.c. and h.c.p. metals derived from shock wave data [14-15], as fitted to Birch-Murnaghan equation of state

Metal	Molar volume, cm^3	dK_T/dP (shock wave)	dK_S/dP (ultrasonic)	dK_T/dP (ultrasonic)
Th	19.79	3.31		
Hf[a]	13.45	4.13	4.03	4.04
Ti[b]	10.63	4.58	4.31	4.35
Ag	10.27	6.78	6.18	
Au	10.25	6.39	5.19	5.31
Al	10.00	4.98		
Pt	9.10	5.31		
Pd	8.88	5.94		5.42
Re	8.86	4.96		5.43
Ir	8.55	4.90		
Rh	8.30	5.30		
Cu	7.11	5.53	5.59	

[a] from data below 460 kbar

[b] from data below 190 kbar

Table 2

Computed values of K_T' as a function of pressure for the metal Ti using shock wave data [14-15]

P, kbar	K_T'	
130	4.34	
140	4.97	h.c.p. α phase
150	5.25	average value of
160	4.14	$K_T' \sim 4.58$
190	4.45	
190	4.38	
190	3.23	
200	3.43	
270	3.18	
320	3.32	
370	3.39	
370	3.21	ω phase
440	3.43	average value of
460	3.38	$K_T' \sim 3.34$
500	3.48	
520	3.43	
700	3.36	
730	3.45	
880	3.27	
1010	3.38	
1170	3.38	

Table 4 gives the values of K_T' for the b.c.c. transition metals, as evaluated from the shock wave data [14-15] in the manner discussed above. Our recently determined value of $K_T' = 4.03$ from ultrasonic measurements for Nb provides further confidence in the reliability of the models used and the derived K_T' values shown in Table 4 as well as in Figure 1.

Discussion of Results

Figure 1 is a plot of K_T' versus $1/\Omega_o$ (where Ω_o is the initial molar volume) for the metals listed in Tables 1, 3, and 4. Wherever K_T' values were not available, the K_s' values were used (no serious error is involved in this since $K_T' \sim K_s'$). The

Table 4

Average values of K_T' for b.c.c. transition
metals as derived from equation (1)
using the shock wave data [14-15]

Metals	Molar volume, cm^3	K_T'
Ta	10.8	4.10
Nb	10.8	3.90
W	9.6	4.18
Mo	9.4	4.32
V	8.4	4.00

general trend is for K_T' to increase with
decreasing Ω_o. The data points of most of
the f.c.c. and h.c.p. metals fall within
$\pm$ 10 per cent of the straight line shown
in Figure 1. Exceptions are Ag and Au,
which are discussed later, and Ru. Recent
work at the University of Hawaii indicates
that the ultrasonic value of K_T' is subject
to reexamination. Our analysis of the Ru
high pressure x-ray data [9] gives $K_T' =$
4.7 ± 2.2, which is more consistent with
the other data, but is still poorly deter-
mined.

The general relation between K_T' and
Ω_o shown in Figure 1 can be understood
from a relatively simple model originally
proposed by Mott and Jones [20] for the
bulk modulus of metals. This model con-
siders two contributions to K_T:

$$K_T = K_F + K_{SR} \qquad (4)$$

where K_F is due to the volume dependence
of the Fermi energy of the free electrons,
and K_{SR} represents a short-range repulsive
interaction between ion cores.

We assume a free electron gas model
for the Fermi contribution. The bulk
modulus of the electron gas is

$$K_F = \frac{2}{3} \frac{E_F}{\Omega_o} Z^* \qquad (5)$$

where Z^* is the effective number of free
electrons per atom, and E_F is the Fermi
energy which is proportional to $\Omega_o^{-2/3}$.
Differentiating (5) with respect to
pressure we get

$$K_F' = \frac{dK_F}{dP} = \frac{5K_F}{3K_T} \qquad (6)$$

The short-range repulsive energy is
assumed to be given by a Born-Mayer poten-
tial of the form

$$W(r) = A \exp[-B(r/r_0 - 1)] \qquad (7)$$

where A and B are material parameters
and r is the interatomic separation.
Fuchs [21] considered a central force
model for the f.c.c. structure and found
the short-range contribution to K to be

$$K_{SR} = \frac{2r^2}{3\Omega_o} \frac{d^2W(r)}{dr^2} \qquad (8)$$

when only nearest neighbor interactions
are taken into account. Since an atom
has twelve nearest neighbors in both
h.c.p. and f.c.c. structures, (8) should
be a reasonable approximation for the
h.c.p. metals also. Now (7) and (8) can
be combined to give

$$K_{SR} = \frac{2B^2A}{3\Omega_o} \qquad (9)$$

and further differentiation with respect
to pressure yields

$$K_{SR}' = \frac{dK_{SR}}{dP} = \frac{K_{SR}}{3K_T} (B+1) \qquad (10)$$

Using (4), (6), (10), and the pres-
sure derivative of (4) we find

$$K_T' = \frac{5}{3} + \frac{K_{SR}}{K_T} \left(\frac{B-4}{3}\right) . \qquad (11)$$

Equation (11) predicts that for very large
Ω_o (when $K_{SR} \sim 0$), $K_T' \rightarrow 5/3$. The straight
line in Figure 1 was in fact obtained by
fixing the intercept at 5/3 and using the
well defined cluster of rare earths (Gd,
Dy, and Er) to determine the slope. The
good agreement over the large range of Ω_o
values indicates that K_T is linear in
Ω_o^{-1} and hence, from (11), and assuming
B is roughly constant (a reasonable
assumption), K_{SR}/K_T is approximately pro-
portional to Ω_o^{-1}. At higher Ω_o^{-1},
$K_{SR} \sim K_T$, and we might expect K_T' to level
off and become less dependent on Ω_o. It
may be noted here that a linear $K_T' - \Omega_o^{-1}$
relationship is probably the simplest
that is consistent with the data for
close-packed metals, and it does not seem
that a more sophisticated formula would
be justified.

In case of Au and Ag, the anisotropy
in the Fermi surface may affect the K_F
term and thus produce a deviation from
the first term (5/3) in equation (11).
Such a conclusion is consistent with the
calculation of Hsieh and Bolsaitis [22].

Referring again to Figure 1, we find
that the b.c.c. transition metals Ta, Nb,
W, Mo, and V fall in a cluster of points
below the straight line. The relatively
small variation among the K_T' values
(3.90-4.32) is in contrast to the large
range in the K_T' values (3.23-6.66) for
the close-packed structures. This is not
unexpected in view of the relatively
greater influence of the electronic band
structure on the elastic moduli for the
b.c.c. metals [23]. Note also that the
short range contribution must be

significantly different from the close-packed case because of the difference in nearest neighbors.

Conclusions

The main conclusion based on the above study of ultrasonic and shock wave data on metals is that the simple two-component model predicts K_T' values for certain metals quite well. The principal contribution to the theory of interatomic repulsion is that K_{SR}/K_T seems to be a well behaved function of $\Omega_o{}^{-1}$ (i.e., $K_{SR}/K_T \sim \Omega_o{}^{-1}$) in close-packed (h.c.p. and f.c.c.) metals. There may be, however, a critical interatomic spacing below which this relation would not hold. In the case of Au and Ag, the contribution of the anisotropy of the Fermi surface to the K_F term may be involved and thus produce a deviation from the first term (5/3) in equation (11).

On the basis of the limited data, the K_{SR}/K_T versus $\Omega_o{}^{-1}$ relation may not be valid for the b.c.c. transition metals, where the electron band structure energy makes an important contribution to the elastic moduli.

Further experimental verification of the K' values and other theoretical research on the close-packed and b.c.c. transition metals would prove to be valuable in understanding the partitioning of K_F' and K_{SR}' among the exceptional cases in the close-packed structures and in clearer understanding of the cohesive forces in the b.c.c. metals.

Acknowledgments

References

[1] Anderson, O.L., E. Schreiber, R.C. Liebermann and N. Soga, Rev. Geophys. 6, 491 (1968).

[2] Fisher, E.S., phy. stat. sol. (b), 58, 655 (1973).

[3] Fisher, E.S., M.H. Manghnani, and R. Kikuta, J. Phys. Chem. Solids 34, 687, 1973.

[4] Fisher, E.S., M.H. Manghnani, and T.J. Sokolowski, J. Appl. Phys. 41, 2991 (1970).

[5] Schmunk, R.E. and C.S. Smith, J. Phys. Chem. Solids 9, 100 (1959).

[6] Fisher, E.S. and M.H. Manghnani, J. Phys. Chem. Solids 32, 657 (1971).

[7] Daniels, W. B. and C.S. Smith, Phys. Rev. 111, 713 (1958).

[8] Manghnani, M.H., K. Katahara, and E.S. Fisher, Phys. Rev. B 9, (4) 1421 (1974).

[9] Weinmann, C. and S. Steinemann, Solid State Comm. (in press).

[10] Rotter, C.A. and C.S. Smith, J. Phys. Chem. Solids 27, 267 (1966).

[11] Chiarodo, R., J. Green, I.L Spain and P. Bolsaitis, J. Phys. Chem. Solids 33, 1905 (1972).

[12] Sarma, V. and P. Reddy, Phil. Mag. 27 (4) 769 (1973).

[13] Birch, F., J. Geophys. Res. 57, 227 (1952).

[14] McQueen, R.G. and S.P. Marsh, J. Appl. Phys. 31, 1253 (1960).

[15] McQueen, R.G., S.P. Marsh, J.W. Taylor, J.N. Fritz, and W.J. Carter, in High Velocity Impact Phenomena, edited by R. Kinslow (Academic Press, New York, 1970) p. 293.

[16] Jamieson, J.C., Science, 140 (3562), 72 (1963).

[17] Olinger, B. and J.C. Jamieson, High Temperatures-High Pressures, 5, 123 (1973).

[18] Liu, L., T. Takahashi, and W.A. Bassett, J. Phys. Chem. Solids 31, 1345 (1970).

[19] Clendenen, R.L. and H.G. Drickamer, J. Phys. Chem. Solids 25, 865 (1964).

[20] Mott, N.F. and H. Jones, Theory of Properties of Metals and Alloys, Oxford Press, 1936.

[21] Fuchs, K., Proc. Roy. Soc. A 153, 622 (1936); Proc. Roy. Soc. A 157, 444 (1936).

[22] Hsieh, K. and P. Bolsaitis, J. Phys. Chem. Solids 33, 1838 (1972).

[23] Fisher E.S. and D. Dever, Acta Met. 18, 265 (1970).