EQUATION OF STATE OF SOLIDS[*][†]

F.E. Prieto and G.S. de Oyarzábal

Instituto de Física, Universidad Nacional de México

(Recibido: 30 de Abril 1963)

ABSTRACT

The available experimental data on shock wave compression of the noble metals and sodium chloride is used to examine the validity of some of the equations of state proposed for these solids. The Koehler and Duvall equation gives excellent results for silver and copper, but to fit the Born-Bradburn equation to the available data for silver it is necessary to modify this equation in a suitable form. Some preliminary results for sodium chloride using for the lattice energy expressions containing an attractive Coulomb term, and a repulsive term of power and exponential forms, as well as the Born-Mayer equation of state, are also reported.

I. INTRODUCCION

The purpose of this paper is to report on the work that has been done in the University of Mexico on the subject of the equation of state of solids from the theoretical viewpoint, using the experimental information on the shock wave compression of solids in the high pressure range.

We have limited our work to the noble metals and sodium chloride, mainly because it seems to us that these are some of the more thoroughly studied materials, so that there is abundant theoretical and experimental work to compare with our results.

We have applied the Koehler and Duvall equation to silver and copper; silver has also been studied using the Born-Bradburn equation of state, and also using a modified form of this equation. As regards sodium chloride, we have used for the lattice energy expressions containing an attractive Coulomb term, and a repulsive term of power and exponential forms. Some results have also been obtained using the Born-Mayer equation of state for sodium chloride.

2. GENERAL PROCEDURE

The experimental information[1] is given the form of pairs of values for the shock and particle velocities $(U_s; U_p)$; these data are transformed into the Hugoniot equation of state by means of the Rankine-Hugoniot shock equations[2], and the Hugoniot pressures are finally reduced to the cold $(0°K)$ isotherm $P_c(V)$ using the Mie-Gruneisen equation[3]. One can also use the available data on extrapolations to zero temperature of the cohesive energy, bulk modulus and Grüneisen ratio. For the noble metals we used the experimental data reported by McQueen and Marsh[4] and for sodium chloride the data reported by Al'tshuler, Kuleshova and Pavlovski[5] were used.

To fit an equation of state to these data we assume first an expression for the free energy as a function of the volume V and some arbitrary parameters a_i:

$$W = W(V, a_i) \tag{1}$$

the equation for the cold isotherm and bulk modulus may then be obtained from the relations

$$P_c = -\frac{\partial W}{\partial V} \tag{2}$$

$$B_c = -V\frac{\partial P_c}{\partial V} \tag{3}$$

The volume dependence of the Grüneisen ratio is obtained using either the the Slater[6] formula

$$\Gamma_S = -\frac{2}{3} - \frac{V}{2}\frac{\partial^2 P_c/\partial V^2}{\partial P_c/\partial V} \tag{4}$$

or the Dugdale-MacDonald[7] formula

$$\Gamma_D = -\frac{1}{3} - \frac{V}{2}\frac{\partial^2 (P_c V^{2/3})/\partial V}{\partial(P_c V^{2/3})/\partial V} \tag{5}$$

and the Mie Grüneisen equation[3]

$$P_H - P_c = \frac{\Gamma}{V}(E_H - E_c) \tag{6}$$

is used to obtain the volume dependence of the Hugoniot.

These equations can be used to adjust the values of the arbitrary constants a_i to fit part of the data, and the remaining data are finally used to test the equations.

45

3. SILVER AND COPPER USING THE KOEHLER AND DUVALL EQUATION

Koehler and Duval[8] have recently proposed an expression of the form

$$W(V) = A \frac{V_o}{V} + B\left(\frac{V_o}{V}\right)^{2/3} - C\left(\frac{V_o}{V}\right)^{1/3} + He^{a\left[1 - \left(\frac{V}{V_o}\right)^{1/3}\right]} \qquad (7)$$

for the energy of the noble metals as a function of volume. In this expression $W(V)$ is the energy per atom, V is the atomic volume at zero pressure, V the atomic volume under pressure, A, B, C, H and a are arbitrary constants. The values of the five constants were adjusted by Koehler and Duvall to fit the value $W(V_o)$ of the energy per atom at zero pressure, zero temperature, and four points on the cold isotherm including the origin. Koehler and Duvall remarked also that in the transformation of shock wave date into Hugoniots by means of the Rankins-Hugonoit equations, metals are supposed to behave like perfect fluids, and no allowance is made for shearing stresses. In real materials, which possess in general some rigidity, the Rankine-Hugoniot equations still hold for a shock wave travelling in the positive X-direction, if one replaces P by $-\sigma_x$, and this is what is obtained from the shock equations; the actual pressure P is smaller by an amount which can be estimated to be two-thirds of the yield stress if this is assumed to be a constant independent of pressure.

Calculations using the Koehler and Duvall energy equation have been carried out for silver[9] using the coefficient reported by these authors assuming a perfect fluid behaviour, and also assuming a constant 7 kilobars yield stress independent of pressure. In both cases, with and without yield stress, the results for the cold isotherm and bulk modulus are in very good agreement with the shock wave data reported by McQueen and Marsh[4]. For the Grüneiser ratio the results are found to differ greatly among themselves and also from the values reported by Mc-Qeen and Marsh; however, due to the fact that the Hugoniot obtained from the Mie-Grüneisen equation is not very sensitive to differences in the Grüneisen ratio[7], the four Hugoniots obtained are in very good agreement among themselves and with the

Hugoniot reported by McQueen and Marsh.

These results show that the Koehler and Duvall equation is adequate for the thermodynamic description of high pressure states of silver, and support also the assumption that metals under shock behave like perfect fluids.

Copper has been treated along the same lines[10], with some minor changes in the procedure: instead of four points on the cold isotherm we used only three points, and included the zero pressure value of the bulk modulus in the fitting. A perfect fluid behaviour was assumed and the results are in very good agreement with the available experimental data.

4. SILVER USING THE BORN AND BRADBURN EQUATION

Following Born's ideas on the thermodynamics of crystal lattices[11] Bradburn[12] suceeded in deriving the equation of state for a face-cenured cubic lattice consisting of identical atoms, under the assumption that the mutual potencial energy of a pair of neighbouring atoms is of the form

$$\varphi(r) = D \left\{ \frac{1}{n} \left(\frac{r_o}{r}\right)^n - \frac{1}{m} \left(\frac{r_o}{r}\right)^m \right\} \tag{8}$$

which contains four arbitrary parameters D, r_o, m, n. The Born-Bradburn equation of state, which follows from this interatomic potential, may be expressed in the form

$$P = A \xi (1 + \xi)^{\frac{m+3}{n-m}} + T \psi(\xi) \tag{9}$$

in which ψ is a known function of ξ, and this is defined by

$$1 + \xi = \left(\frac{V}{V_o}\right)^{-\frac{n-m}{3}} = v^{-\frac{n-m}{3}} \tag{10}$$

V_o is as usual the volume at zero pressure zero temperature, and is one of the arbi-

47

trary constants, the other arbitrary constants are A, n and m. V and T are the volume and temperature at pressure P, respectively.

The adjustment of the parameters may be done in many different ways. Furth[13] adjusted the parameters to fit the zero-pressure values of compressibility thermal expansion and their derivaties, and also the cohesive energy. Furth's values are in reasonable agreement with the low-pressure data reported by Bridgman[14], but if one uses the same parameters in the shock-wave range. the agrement is far from good. Duvall and Zwolinski[15] reported the comparison of two calculated points for aluminum and two for copper with the high-pressure data of Walsh and Christian[16], with differences of the order of 20%, and we got a similar results for silver.

In an attempt to improve the results for silver, the parameters A, m and n were adjusted to fit the cold isotherm reported by McQueen and Marsh[4] in the pressure range from 100 to 1300 kilobars. The best fit was obtained with $m = 3.5$, $n = 7$; one gets then excellent agreement in the cold isotherm, (see Fig. 1), but a zero pressure catastrophe, 40% error in the Grüneisen ratio and 100% error in the cohesive energy.
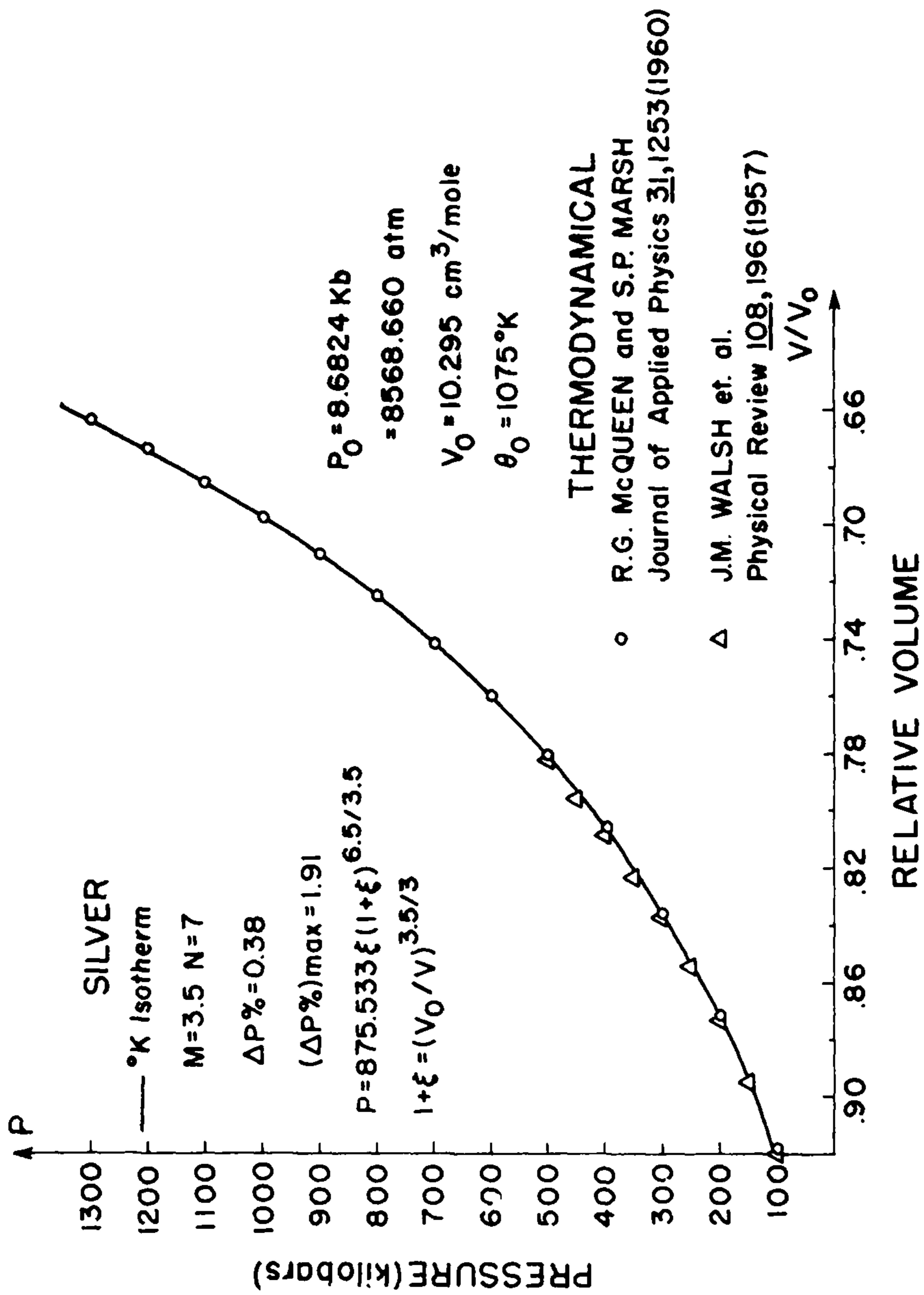
Another trial was carried out by inverting the previous procedure, m and n were adjusted to fit the cohesive energy and Grüneisen ratio, and then A was adjusted to fit the cold isotherm as well as possible. With the values $m = 4.5$, $n = 8$ the results are improved, but there are errors up to the 10% in pressure in the IMbar region.

At this stage we gave up the assumption that the parameter in eq. (9) is a constant independence of volume. If one starts from the $0°K$ energy function in the form

$$W(\xi) = - A(\xi) \, F(\xi) \tag{11}$$

the cold isotherm contains an additional term in the volume derivative of A:

$$P_C = A \frac{dF}{d(V/V_0)} + F \frac{dA}{d(V/V_0)} \tag{12}$$

SILVER

—— °K Isotherm

M=3.5 N=7

ΔP%=0.38

(ΔP%)max=1.91

$P = 875.533 \xi (1+\xi)^{6.5/3.5}$

$1+\xi = (V_0/V)^{3.5/3}$

$P_0 = 8.6824$ Kb

$= 8568.660$ atm

$V_0 = 10.295$ cm^3/mole

$\theta_0 = 1075°$K

THERMODYNAMICAL

o R.G. McQUEEN and S.P. MARSH
   Journal of Applied Physics 31,1253(1960)

△ J.M. WALSH et. al.
   Physical Review 108,196(1957)

V/V$_0$

RELATIVE VOLUME

PRESSURE (kilobars)

P

where

$$F(\xi) = \frac{3(n \cdot m)}{m\,n} (1 + \xi)^{\frac{m}{n \cdot m}} [1 - \frac{m}{n - m} \xi] \tag{13}$$

With the values $m = 4.5$, $n = 8$ and the set of (P_C, V) zero temperature state of silver reported by McQueen and Marsh[4], eq. (12) gives a first-order linear differential equation for A, with the inhomogeneous term given in tabular form. This differential equation was solved numerically by the Runge-Kutta method[17] to obtain A an its volume derivative, also in tabular form, and an analytical curve was fitted by the standard procedures to this set of points[18]; values of the volume derivative of A were first fitted to the curve

$$\frac{dA}{dv} = 1.526 + 267.500(1 - v) + 8.684 (1 - v)^{11.387} \times 10^7 - 1.526\, e^{55.599[1 \cdot v]} \tag{14}$$

and the equation for $A(V)$ was obtained by integration. These equations fit very well the points obtained by numerical methods (See Fig. 2).

The results are very interesting because and additional term appears in the expresions for the cold isotherm and for the lattice energy, and this term includes an exponential of the type used by Koehler and Duvall[8] to fit the shock-wave data for the noble metals. Although the value 55.599 of the exponent is too high compared with the value of 10 reports by Koehler and Duvall, the procedure look quite promising. Calculations carried out for silver give excellent agreement with the cold isotherm, (see Fig. 3), and very good results for the zero-pressure Grüneisen ratio ($\Gamma_S = 2.626$) and bulk modulus ($B_0 = 1129.677$ Kbor), as well as the volume dependence of the cohesive energy and compressibility.

5. SOME RESULTS ON NaCl

Recent data on the shock-wave compression of sodium chloride[5] have been

SILVER

$V_o \dfrac{dA}{dV}$ (kbar)

$V_o \dfrac{dA}{dV}$ (kbar)

A (kbar)

RELATIVE VOLUME V/V_o
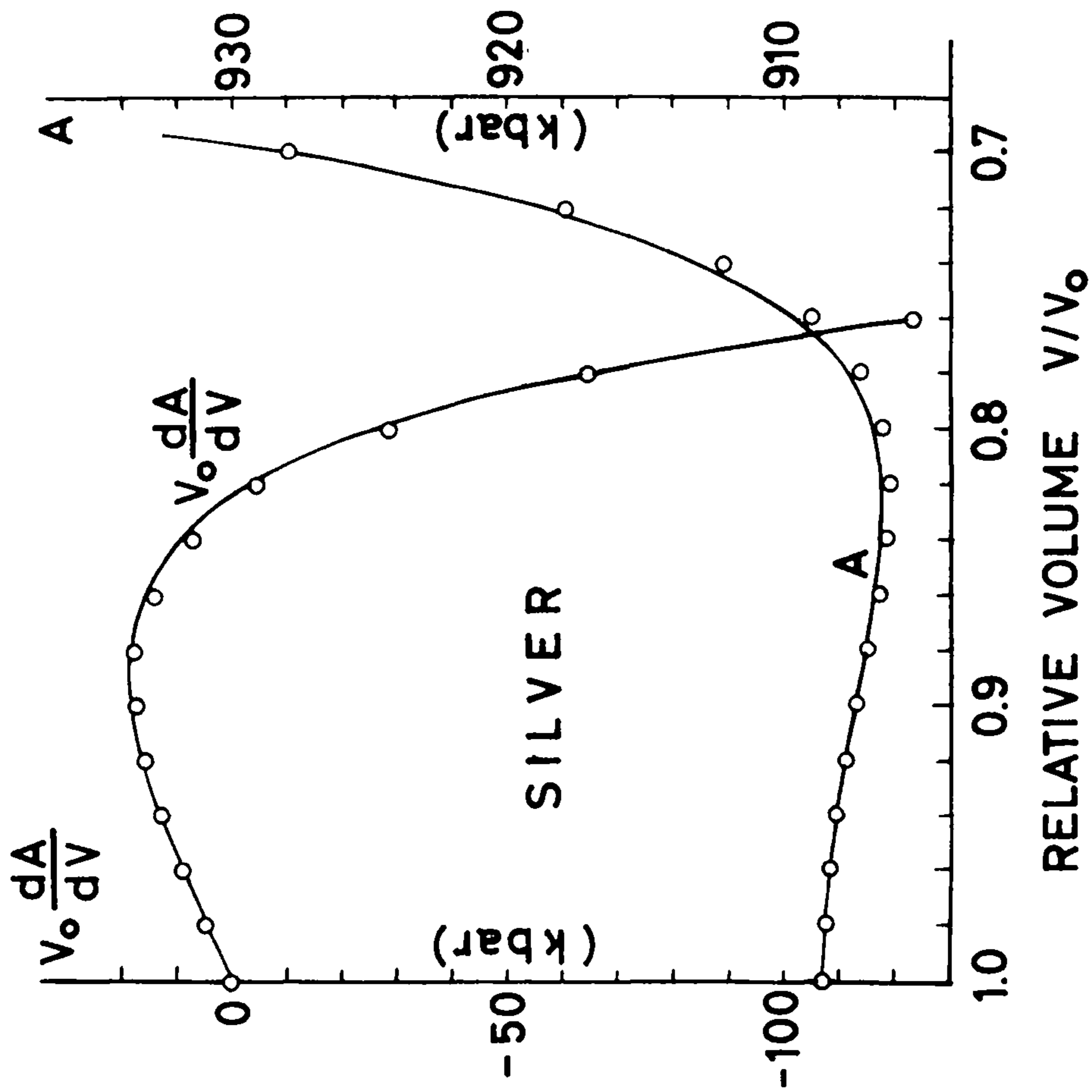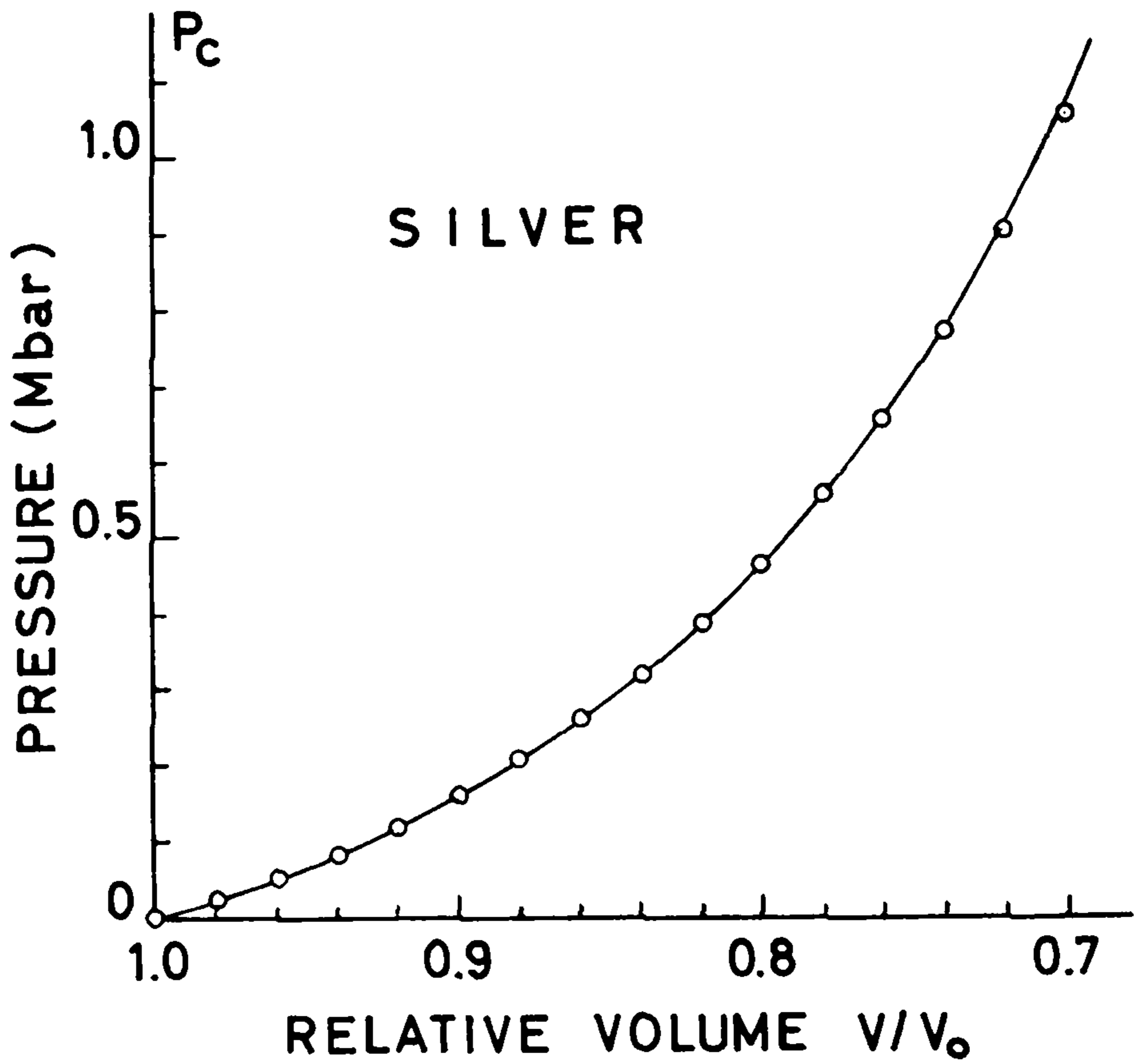
used to examine the validity of some of the expressiones proposed for the lattice energy.

Two of the expressions used for the energy[5] contain only an attractive Coulomb term, and a repulsive term following an exponential (eq.15) and an inverse power law (eq. 16) respectively.

$$W = - A \left[\left(\frac{V_0}{V}\right)^{1/3} - \frac{\rho}{r_0} \exp \frac{r_0}{\rho} \left(1 - \frac{V}{V_0}\right) \right] \tag{15}$$

$$W = - A \left[\left(\frac{V_0}{V}\right)^{1/3} - \frac{1}{n} \left(\frac{V_0}{V}\right)^{\frac{n}{3}} \right] \tag{16}$$

In the first case it was found[19] that the same value of the parameters used by Löwdin[20] to fit Bridgman's low-pressure data fit also the data in the 50-800 kilobar range. In the second case the results are not so good, and equation of this type cannot be fitted to the high pressure data unless it is modified in a suitable form[19].

Some work has also been done using the expression proposed by Born and Mayer[21] for the lattice potential in a regular ionic lattice; this involves an empirical repulsive potential between the ion centers and of two constants for each ion. Using for the ionic radio the values reported by Huggins and Mayer[22], and adjusting the other five constants of the equation to fit the data on zero pressure, cohesive energy and bulk modulus, as well as three points on the cold isotherm, one gets for the cold isotherm the expression

$$P_C = A_1 v^{-4/3} + A_2 v^{-3} + A_3 v^{-11/3} + B_1 v^{-2/3} e^{-8.156 \, v^{1/3}} + B_2 v^{-2/3} e^{-11.535 \, v^{1/3}} \tag{17}$$

where the values in Haup (10^{-3} Hartree atomic units of pressure = 294.088 kilobars) obtained for the constants are:

$$A_1 = - 0.3929 \qquad\qquad B_1 = 10.0053 \times 10^4$$

$$A_2 = + 0.6658 \qquad B_2 = 4.2163 \times 10^4$$

$$A_3 = - 0.7004$$

and give excellent agreement with the cold isotherm reported by Al'tshuler and co-workers[5]; the average percentage diviation is 0.6%.

6. CONCLUSION

It is not necessary to emphasise the importance of the equation of state within the framework of thermodynamics, but we should like to remark that the main interest of this work lies probably in the fact that at the root of each equation of state there are usually some assumptions concerning the microscopic behaviour of the solid and so, one can use the macroscopic results on shock-wave compression of solids to test the assumptions and theories used to describe their microscopic behaviour.

ACKNOWLEDGMENTS

REFERENCES

1.- For a general review see for instance: M.H. Rice, R.G. McQueen, and J. M. Walsh, in solid State Physics, edited by F. Seitz and D. Trumbull (Academic Press Inc. New-York, 1958), Vol. 6, p. 1.

2. W.J.M. Rankine, Trans. Royal Society (London), 160, 277 (1870) H. Hugoniot Journal de l'ecole polytechnique, 58, p. 1 (1889).

3.- G. Mie, Ann.Physik 11, 657 (1903); E. Grüneisen, ibid. 26, 393 (1908).

4.- R.G. McQueen and S.P. Marsh, J.Appl.Phys. 31, 1253 (1960).

5.- L.V. Al'tshuler, L.V. Kuleshova, and M.N. Pavlovski, J. Exptl. Theoret.Phys (U.S.S.R.), *39*, 16 (1960). Translation: Soviet Physics, JETP *12*; 10 (1961).

6.- J.C. Slater, Phys.Rev. *57*, 744 (1940); also: Introduction to Chemical Physics (McGraw Hill, 1939)

7.- G.S. Dugdale and D.K.C. MacDonald, Phys.Rev. *89*, 832, (1953).

8.- J.S. Koehler and G.E. Duvall, Bull.Am.Phys.Soc. *6*, 132 (1961).

9.- F.E. Prieto, Phys.Rev. *129*, 37 (1963).

10.- C. Renero and F.E. Prieto, BullAm.Phys.Soc. *8*, 111 (1963).

11).- M. Born, Proc.Camb.Phil.Soc. *39*, 100 (1943).

12.- M. Bradburn, Proc.Camb.PhilSoc. *39*, 113 (1943).

13.- R. Fürth, Proc.Roy.Soc. (London) *83*, 87 (1944); also Proc.Camb.Phil.Soc. *37*, 177 (1941).

14.- P.W. Bridgman, The Physics of High Pressures (G.Bell and Sons Ltd.; London 1952); also Revs.Mod.Phys. *18*, 1 (1946).

15.- G.E. Duvall and B.J. Zwolinski, J. Acoust. Soc.Am., *27*, 1054 (1955).

16.- J.M. Walsh and R.H. Christian, Phys.Rev. *97*, 1544 (1955).

17.- See, for instance, K.S. Kuntz, Numerical Analysis (McGraw Hill 1957).

18.- See, for instance, D.S. Davis, Nomography and empirical equations (Reinhold Pub.Co. 1955).

19.- P. Negrete and F.E. Prieto, BullAm.Phys.Soc. *8*, 111 (1963).

20.- P.O. Löwdin, Thesis. Uppsala University (1948).

21.- M. Born and J.E. Mayer, Z.F. Physik *75*, 1 (1932).

22.- M.L. Huggins and J.E. Mayer, J.Chem.Physics *1*, 643 (1933).