Equation of State of Silver*

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The closed-shell repulsive potential for noble metals proposed by Koehler and Duvall is used to obtain the volume dependence of the 0°K isotherm, bulk modulus, and Grüneisen ratio for silver. The results are found to be in very good agreement with some recent data on the shock wave compression of silver.

1. INTRODUCTION

IN a recent paper, Koehler and Duvall[1] proposed a closed-shell repulsive potential for the noble metals and noted the importance of this interaction potential for calculations concerning imperfections. It is the purpose of this paper to see to what extent the values of some thermodynamical properties calculated using the Koehler and Duvall potential reproduce the values obtained from the experimental data on the shock wave compression of silver up to 1300 kbar reported by McQueen and Marsh.[2]

The interatomic potential proposed by Koehler and Duvall[1] is of the form

$$W(V)=A\left(\frac{V_0}{V}\right)+B\left(\frac{V_0}{V}\right)^{2/3}-C\left(\frac{V_0}{V}\right)^{1/3}+He^{a[1-(V/V_0)^{1/3}]}, \quad (1)$$

where W is the energy per atom, V_0 is the atomic volume at zero pressure, and V is the atomic volume under pressure. A, B, C, H, and a are arbitrary constants. The first three terms in this potential are of the form used by Bardeen[3] to fit the static compressibility data for alkali metals, while the last term is used to describe the closed-shell repulsive potential.[4] The values of the five constants in this potential were adjusted to fit the following data: $W(V_0)$, the energy per atom at zero pressure 0°K temperature; $P_K(V_0)$, the initial pressure on the 0°K isotherm; three points at pressures 150, 350, and 500 kbar along the 0°K isotherm.

TABLE I. Values of the constants in the Koehler and Duvall interatomic potential for silver, All except a are in units of 10^{-12} erg per atom.

Yield stress	A	B	C	H	a
$\sigma_0=0$	−2.8256	0.0613	16.6623	2.5017	10.00
$\sigma_0=7$	−4.3543	7.2170	21.6293	1.8417	11.00

Two different sets of values of the constants were reported by Koehler and Duvall,[5] one assuming zero yield stress ($\sigma_0=0$), and the other assuming a constant yield stress ($\sigma_0=7$ kbar) independent of pressure. The values of the constants in each case are listed in Table I; A, B, C, and H are given in 10^{-12} erg per atom; a is dimensionless.

2. THE 0°K ISOTHERM AND BULK MODULUS

The volume dependence of the pressure P_K along the isotherm is given by

$$P_K=-\partial W/\partial V, \quad (2)$$

and may be conveniently expressed in the form

$$P_K=P_1+P_2-P_3+P_4, \quad (3)$$

where

$$P_1=(A/V_0)(V_0/V)^2, \quad (4)$$

$$P_2=\tfrac{2}{3}(B/V_0)(V_0/V)^{5/3}, \quad (5)$$

$$P_3=\tfrac{1}{3}(C/V_0)(V_0/V)^{4/3}, \quad (6)$$

$$P_4=(Ha/3V_0)(V_0/V)^{2/3}\exp\{a[1-(V/V_0)^{1/3}]\}. \quad (7)$$

The constants have now units of pressure, and are given in Table II in kbar.

TABLE II. Values in kbar of the constants in the expression for the 0°K isotherm.

Yield stress	A/V_0	$2B/3V_0$	$C/3V_0$	$Ha/3V_0$
$\sigma_0=0$	−167.7282	2.4258	329.6925	495.0046
$\sigma_0=7$	−258.4721	285.6016	427.9732	400.8531

In both cases, with and without yield stress, the main contribution to P_K is given by the closed-shell repulsive term P_4. Without yield stress, the contribution due to the Fermi energy term P_2 is almost negligible except at low pressures; it goes from 1% at 300 kbar to 0.3% at 1300 kbar. The theoretical curves are shown in Fig. 1; the points marked are those reported by McQueen and Marsh[2] correcting their shock wave data to 0°K by the use of the Mie-Grüneisen equation of state.[6] The agreement with McQueen and

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[1] J. S. Koehler and G. E. Duvall (to be published).

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

[3] J. Bardeen, J. Chem. Phys. **6**, 367 (1938); **6**, 372 (1938).

[4] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 265.

[5] J. S. Koehler and G. E. Duvall (to be published).

[6] G. Mie, Ann. Physik **11**, 657 (1903); E. Grüneisen, *ibid.* **26**, 393 (1908). See also G. Leibfried, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, p. 104.

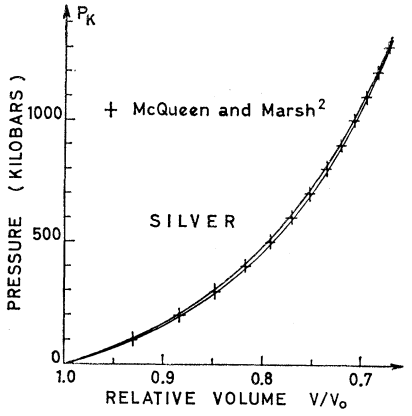

FIG. 1. 0°K isotherms. The upper curve is for zero yield stress, and the lower for a constant 7-kbar yield stress.

Marsh data is very good in both cases, though it is perhaps slightly better without yield stress.

The volume dependence of the 0°K bulk modulus may be obtained from the definition

$$B_K=-V\partial P_K/\partial V, \tag{8}$$

using the expression (3) for the 0°K isotherm, and is given by

$$B_K=2P_1+(5/3)P_2-\tfrac{4}{3}P_3+[\tfrac{2}{3}+(a/3)(V_0/V)^{1/3}]P_4. \tag{9}$$

As in the previous case, the main contribution is due to the closed-shell repulsive term, and without yield stress the contribution from the Fermi energy term is almost negligible even at low pressures, since it is always less than 0.3%. The theoretical curves are shown in Fig. 2, together with some points obtained from the reduced values of McQueen and Marsh[2]; the agreement with these data is very good, but it is perhaps slightly better for the case with yield stress. At zero pressure the values obtained are 1209.0 kbar without yield stress, and 1125.4 kbar with yield stress;

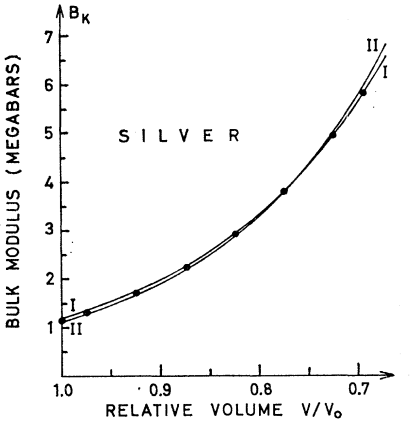

FIG. 2. 0°K bulk modulus without yield stress (I) and with a constant 7-kbar yield stress (II). Points marked by circles were obtained by numerical differentiation of the data of McQueen and Marsh (see reference 2).

these values may be compared with the experimental value 1096.7 kbar obtained by an extrapolation[1] to 0°K zero pressure of the data reported by Neighbours and Alers,[7] and one finds an error of 10.2% for the case without yield stress and 2.8% for the case with yield stress.

Assuming a constant yield stress of 7 kbar, one gets also a better agreement than without yield stress, with some reported experimental values for the contribution to B_K due to the Fermi energy. The calculated values are 4.0 kbar without yield stress, and 475.9 kbar with yield stress, whereas Neighbours and Alers[7] report 462 kbar, and de Launay[8] 473 kbar.

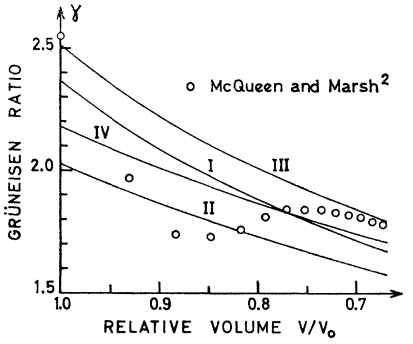

FIG. 3. Grüneisen ratio as a function of volume. Curves I and II are for zero yield stress using the Slater (I) and Dugdale-MacDonald (II) formulas. Curves III and IV are for a constant 7-kbar yield stress using the Slater (III) and Dugdale-MacDonald (IV) formulas.

3. GRÜNEISEN RATIO AND HUGONIOTS

The volume dependence of the Grüneisen ratio is usually calculated either using the Slater formula,[9]

$$\gamma_S=\frac{2}{3}+\frac{1}{2}\frac{V\,d^2P_K/dV^2}{dP_K/dV}, \tag{10}$$

or the Dugdale-MacDonald formula,[10]

$$\gamma_D=\frac{1}{3}+\frac{1}{2}\frac{V\,d^2(P_KV^{2/3})/dV^2}{d(P_KV^{2/3})/dV}. \tag{11}$$

Using the expression (3) for P_K, one gets with the Slater formula

$$\gamma_S=\frac{1}{3}+\frac{1}{B_K}\left\{P_5+\left[-\frac{1}{9}+\frac{a^2}{18}\left(\frac{V}{V_0}\right)^{2/3}\right]P_4\right\}\equiv\frac{1}{3}+\frac{P_6}{B_K}, \tag{12}$$

where

$$P_5=P_1+(5/9)P_2-(2/9)P_3. \tag{13}$$

[7] J. R. Neighbours and G. A. Alers, Phys. Rev. **111**, 707 (1958).
[8] J. de Launay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 220.
[9] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), Chap. 13.
[10] J. S. Dugdale and D. K. C. MacDonald, Phys. Rev. **89**, 832 (1953).

With the Dugdale-MacDonald formula, the Grüneisen ratio is given by

$$\gamma_D=(\tfrac{1}{9}P_K+P_6)/(B_K-\tfrac{2}{3}P_K). \quad (14)$$

The theoretical curves calculated using equations (12) and (14) are shown in Fig. 3. Curves I and II correspond to zero yield stress, and III and IV to a constant yield stress of 7 kbar. The points marked by circles are the values reported by McQueen and Marsh[2]; the best agreement with the initial zero pressure value used by these authors ($\gamma=2.55$) is given by the Slater formula assuming a constant yield stress ($\gamma=2.51$). The Dugdale-MacDonald formula, also assuming a constant yield stress, gives the best agreement ($\gamma=2.18$) with the values obtained from the linear relationship between shock and free surface velocities[2,11] ($\gamma=2.17$).

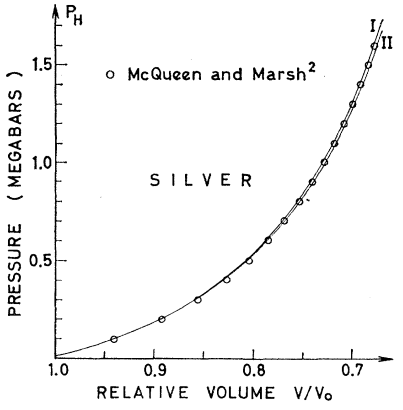

FIG. 4. Hugoniot curves for zero yield stress. Curve I was obtained using the Slater formula for the Grüneisen ratio, and curve II, using the Dugdale-MacDonald formula.

These calculated values of the Grüneisen ratio may now be used to obtain the volume dependence of the Hugoniot, by solving for the Hugoniot pressure P_H the integrated form[11,12] of the Mie-Grüneisen equation:

$$P_H\left[\frac{V}{V_0}-\frac{\gamma}{2}\frac{V_{0H}-V}{V_0}\right]=\frac{V}{V_0}P_K+\gamma\frac{E_0}{V_0}+\frac{\gamma}{V_0}\int_{V_0}^{V}P_K dV, \quad (15)$$

in which V_{0H} is the volume for $P_H=0$, and E_0 is the initial energy at the foot of the Hugoniot; the former was taken from McQueen and Marsh[2] data $V_{0H}/V_0=1.0131$ and the latter was obtained integrating a Debye specific-heat curve from $T=0°K$ to $T=293°K$ using $\Theta=215°K$ as Debye temperature[8] with the result $E_0=0.09077\times10^{-12}$ erg per atom.

The Hugoniots obtained following the previously outlined procedure [using Eq. (3) for P_K], are shown in Fig. 4 for zero yield stress, and in Fig. 5 for a constant yield stress of 7 kbar. In both figures the upper curve corresponds to the use of the Slater formula for the Grüneisen ratio, and the lower curve to the use of Dugdale-MacDonald formula. The agreement of the four curves with the experimental data of McQueen and Marsh[2] is very good, but it seems to be better for the case of 7-kbar yield stress using the Dugdale-MacDonald formula for γ. It is not surprising that these almost coincident Hugoniot curves might be obtained using so different values of the Grüneisen ratio (see Fig. 3); this merely reflects the fact already noted by Dugdale and MacDonald[10] and by Koehler and Duvall[1] that the relation between P_H and P_K through the Mie-Grüneisen equation is not very sensitive to errors in the Grüneisen ratio.

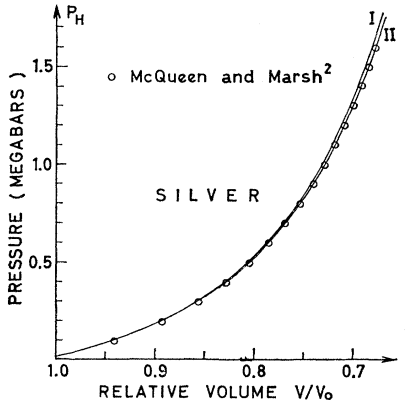

FIG. 5. Hugoniot curves for a constant 7-kbar yield stress. Curve I was obtained using the Slater formula for the Grüneisen ratio, and curve II, using the Dugdale-MacDonald formula.

Equation (15) may be also used to obtain the volume dependence of the Grüneisen ratio knowing the Hugoniot and the 0°K isotherm. Figure 6 shows the curves for γ obtained using Eq. (3) with and without

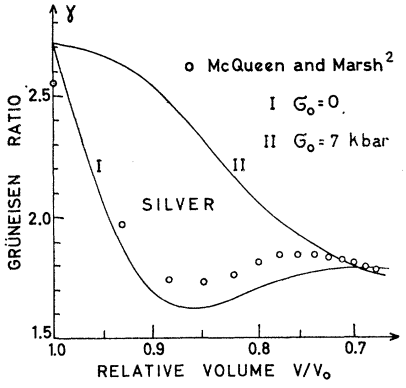

FIG. 6. Grüneisen ratio as a function of volume obtained from the known 0°K isotherm and an analytical fit for the Hugoniot. Curve I is for zero yield stress, and curve II for a constant 7-kbar yield stress.

[11] M. H. Rice, R. G. McQueen, and J. M. Walsh, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 1.

[12] L. V. Al'tshuler, L. V. Kuleshova, and M. N. Pavlovski, Soviet Phys.—JETP **12**, 10 (1961).

yield stress for the 0°K isotherm, and an equation of the type[13,11,2]

$$P_H=C_0^2(V_0-V)/[V_0-S_0(V_0-V)]^2 \qquad (16)$$

for the volume dependence of the Hugoniot pressure. The values of the parameters in this equation were taken from McQueen and Marsh[2]: $C_0=0.3243$ cm/μsec, $S_0=1.586$; the better agreement with these authors' data is obtained assuming zero yield stress, but the initial value for γ, 2.71, is too high.

4. CONCLUSION

The results obtained using the closed-shell repulsive potential proposed by Koehler and Duvall are in very good agreement with the experimental data on the shock wave compression of silver. Though the assumption of zero yield stress gives a slightly better agreement with the experimental data, the introduction of a nonzero yield stress presents some points of interest, such as the stressed influence of the Fermi energy term, and further exploration of this possibility would perhaps be worthwhile.

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[13] L. V. Al'tshuler, K. K. Krupnikov, and M. I. Brazhnik, Soviet Phys.—JETP **7**, 614 (1958); L. V. Al'tshuler, K. K. Krupnikov, B. N. Ledenev, V. L. Shuchikhin, and M. I. Brazhnik, *ibid.* **7**, 606 (1958).

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Diffusion of Single Vacancies and Divacancies in Quenched Gold*

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An effective diffusion coefficient D_{eff}, and an effective energy of migration E_m are derived which describe the combined diffusion of single vacancies and divacancies which are in thermal equilibrium. D_{eff} is the appropriate diffusion "constant" to be used in Fick's law, if one wishes to describe the flow of voids, and expresses the fact that each vacancy during its random walk spends part of its lifetime as a single vacancy and part of its lifetime as a divacancy. E_m can be expressed in terms of E_m^1 and E_m^2 (the energies of migration of a single vacancy and a divacancy, respectively), and is concentration- and temperature-dependent. Its minimum is $E_m^2-B_2$, where B_2 is the binding energy of a divacancy. From analysis of measurements of E_m on Au specimens quenched from above 800°C, one finds that $E_m^2-B_2\sim 0.56$ eV, or more directly that $E_m^1+B_2-E_m^2=0.26\pm 0.03$ eV. The same value for this latter parameter was derived from another independent experiment, namely from the critical concentration of vacancies for which clustering will just occur.

The binding energy of a divacancy in Au was observed to be: $B_2=0.10\pm 0.03$ eV, and its energy of migration: $E_m^2=0.66\pm 0.06$ eV. B_2 was obtained from an analysis of the decrease in resistivity observed during the transient process in which single vacancies and divacancies come into equilibrium with one another. In addition it was found that the resistivity of a divacancy is $(4.6\pm 3)\%$ less than that of two well-separated single vacancies.

I. INTRODUCTION

GOLD was quenched from high temperatures and annealed in the vicinity of room temperature by Bauerle and Koehler.[1] Specimens quenched from 700°C annealed by a first-order annealing process. The energy of migration was 0.82 eV and about 10^6 jumps were required to reach the sinks. The quenched in lattice vacancies anneal out at existing dislocations.

They observed a much lower energy of migration during annealing if the specimens were quenched from 800°C or above. For a specimen quenched from 800°C, $E_m=0.66\pm 0.03$ eV; after a 925°C quench $E_m=0.63\pm 0.06$ eV; and after a 1000°C quench $E_m=0.60\pm 0.04$ eV. Koehler, Seitz, and Bauerle[2] attributed this to the presence of divacancies which are in thermal equilibrium with single vacancies. They defined an effective diffusion constant which we shall elaborate in this paper in detail, experimentally and theoretically.

Koehler, Seitz, and Bauerle[2] made a first attempt to

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[1] J. E. Bauerle and J. S. Koehler, Phys. Rev. **107**, 1493 (1957).

[2] J. S. Koehler, F. Seitz, and J. E. Bauerle, Phys. Rev. **107**, 1499 (1957).