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EQUATION OF STATE OF COPPER*

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RESUMEN

The equation of state for the noble metals recently proposed by Koehler and Duvall is explored for the case of copper. The adjustment of the parameters is fully discussed, and results are presented of the volume dependence of some thermodynamical functions in the pressure range from 100 to 1200 kbar. These results are in very good agreement with the available experimental data. The coefficient which appears in the exponential assumed for the closed shell repulsive term is found to be 13.38, and is in reasonable agreement with the values obtained by similar fittings at low pressures and low temperatures.

1. INTRODUCTION

This is the second of a series of papers devoted to the exploration of the

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exploration of the validity of the equation of state for the noble metals recently proposed by Koehler and Duvall[1]. In the first paper[2], this equation was successfully used for silver,and it is the purpose of the present paper to show that the Koehler and Duvall equation is also adequate for the thermodynamical description of copper in the high pressure range; we found however that the constants reported by Koehler and Duvall[1] do not fit the McQueen and Marsh data for copper[3], there are errors up to the 30% in the 1Mbar pressure range, and for this reason we decided to make a new determination of the constants. The theoretical results are found to be in good agreement with the experimental data on the shock wave compression of copper up to 1200 kbar reported by McQueen and Marsh[3]. Since the treatment is quite similar to that of silver, we omit in the present paper most of the equations which are given in full detail in the paper on silver[2] (to be refered to in what follows as I).

2. ADJUSTMENT OF THE PARAMETERS

The equation proposed by Koehler and Duvall[1] is

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

where W is the energy per atom, that is, the cohesive energy plus the ionization energy, V_o is the atomic volume at zero pressure zero temperature, and V is the atomic volume under pressure. A, B, C, H and a are five arbitrary constants to be chosen using the experimental information on those quantities which are directly connected with the energy, such as the pressure along the 0° K isotherm (cold isotherm) given by

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

and the bulk modulus defined by

$$B_K = -V\partial P_K/\partial V \tag{3}$$

Since the energy per atom and the bulk modulus seem to be strongly dependent on changes in the values of the parameters, we decided to include them in the fitting, together with three points on the cold isotherm. The experimental information used is shown in table I.

V/V_0	1.000	0.8353	0.7555
W (kcal/mol)	−259.3786		
B (k bar)	1440.0		
P_K (k bar)	0	400	800

Table I. Experimental data used to fit the parameters (see references 3 and 4)

To solve the system of five inhomogeneous equations for the five arbitrary parameters, we took advantage of the fact that the system is linear in A, B, C, and H, so that we used the Gauss' elimination method[5] to express these quantities as functions of the remaining parameter a; the substitution of the expressions so obtained in the energy equation (1) leads to a trascendental equation relating the energy per atom to the parameter a, and this equation was solved numerically.

As expected, $W(V_0)$ was found to be strongly sensitive to changes in the value of the parameter a. Fig. 1 shows a plot of $W(V_0)/V_0$ vs a; a change in a from 13.00 to 13.95 reduces $-W(V_0)/V_0$ from 2000 to 1000kbar. The value $a = 13.38$ was finally chosen, and this gives −81.2 kcal/mol for the cohesive energy.

Table II shows the values reported by several authors for the coefficient in the exponent of the repulsive term. The value 13.38 obtained in this paper is

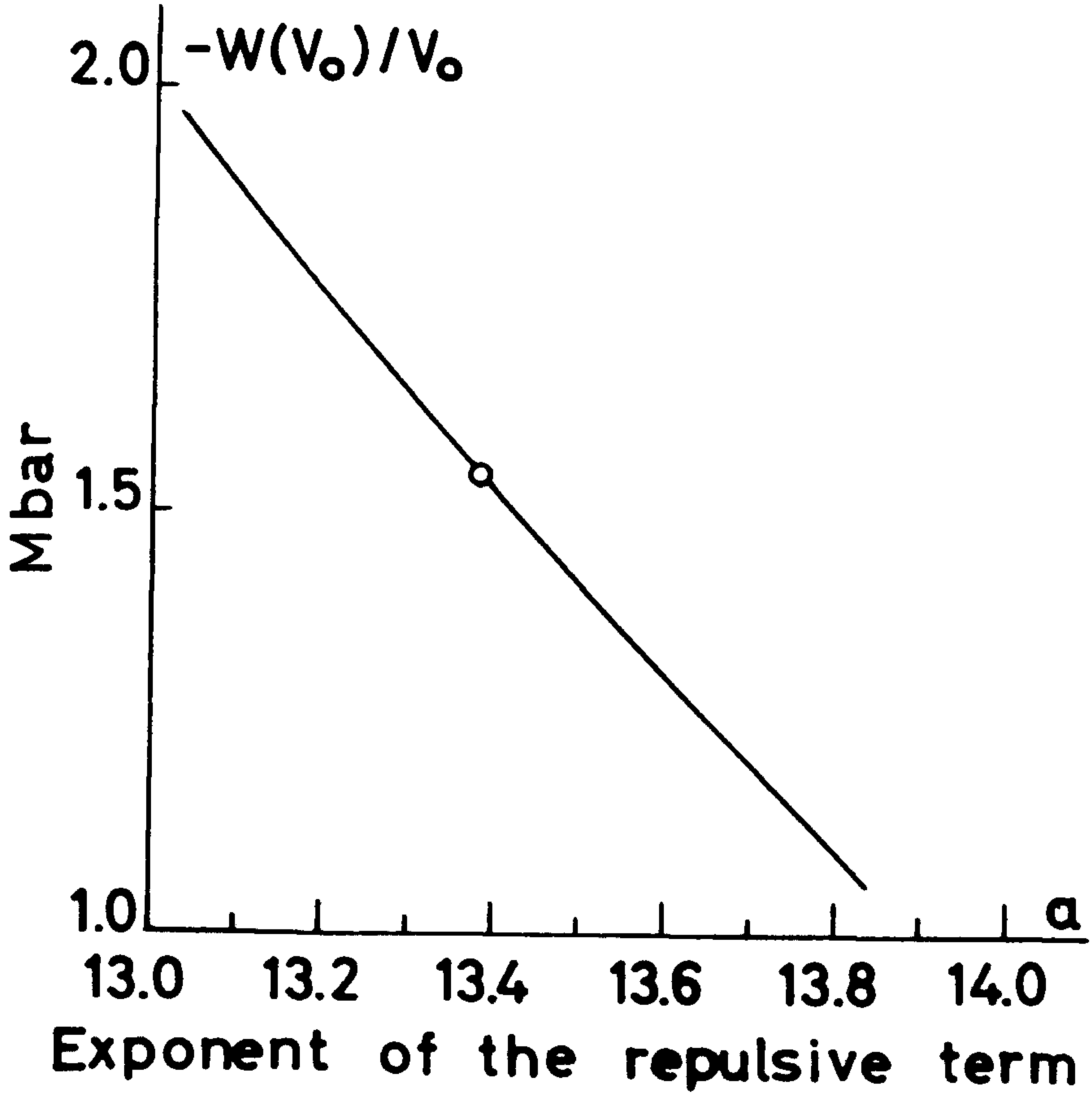

Fig. 1. Dependence of the zero pressure 0°K energy per atom on the exponent of the repulsive term

in good agreement with the value 16.0 reported by Daniels and Smith[6] from their experiments on the derivatives of the elastic constants of the noble metals in the low pressure range (0 – 10 kbar), but it is too low as compared with the value 24.2 reported by Neighbours and Alers[7] from their determinations of the elastic constants of the noble metals. Dienes[8] reports the value 12.75, and Huntington[9] obtains 14.9 but brackets the value between 13.9 and 17.2. Zener[10] uses the value 13.5 and this is the one in best agreement with the value obtained in the present paper. The lowest value, 10.06, is reported by Koehler and Duvall[1]. In general, the value 13.38 obtained in this paper is in good agreement with other determinations of this parameter, excepting the one reported by Neighbours and Alers[7].

	Author	Reference
16.0	Daniels and Smith	6
24.2	Neighbours and Alers	7
12.75	Dienes	8
14.9	Huntington	7
13.5	Zener	10
10.06	Koehler and Duvall	1
13.38	This paper	

Table II. Values reported by several authors for the coefficient in the exponent of the repulsive term.

The value 13.38 obtained for a is higher than the values reported by Koehler and Duvall[1], 10.06 for *Cu* and 10.00 for *Ag*; this difference is probably due to the fact that Koehler and Duvall used only energy and pressure to fit the constants, whereas we included also the compressibility. Daniels and Smith[6] report the values 16.0 for *Cu*, and 17.1 for *Ag*, which are very different from the values reported by

Neighbours and Alers[7] (24.2 for Cu, and 34.4 for Ag); it is very difficult to compare these values with the one obtained in this paper, because of the different methods used to obtain the parameters. It would be desirable to have one single value of this parameter for all the noble metals, and leave only four arbitrary parameters in the Koehler and Duvall equation, but one is then faced with the problem of the selection of this value from the set of reported values[1,6-10] covering a range from 10 to 80.

Once the value of a is known, the other parameters may be easily obtained. The calculations were carried out in the system of atomic units introduced by Hartree[11], and the results are shown in table III in the more usual (kbar) units.

A/V_o	+ 2578.778562
B/V_o	− 4011.119920
C/V_o	+ 94.387543
H/V_o	+ 36.888928

Table III. Values in kbar of the coefficients in the Koehler and Duvall energy equation, obtained with $a = 13.38$

There is a physical difficulty with the value obtained for the parameter B, because it is very large and negative (minus 29 eV per atom at the equilibrium volume), and it represents the Fermi energy of the valence electrons. The only explanation we have for this result is that if one assumes the existence of a set of constants, the good constants, free from physical difficulties, the constants we have just obtained are only linear combinations of the good constants, and this may account for the wrong sign and order of magnitude. To be more explicit, let R stand for the column vector

$$\underline{R} = [\,A, B, C, H\,] \qquad (4)$$

this vector was then obtained as a solution of the equation

$$\underline{\alpha}\,\underline{R} = \underline{Q} \tag{5}$$

where $\underline{Q}$ is the four component column vector

$$\underline{Q} = [B_o, P_o, P_1, P_2] \tag{6}$$

representing the experimental data chosen for the fit, and $\underline{\alpha}$ is a 4 x 4 matrix whose elements depend on the choice of $\underline{Q}$, because they are functions of V/V_o.

Suppose now that the good set of constants $\underline{R}'$ is obtained as solution of the equation

$$\underline{\alpha}'\,\underline{R}' = \underline{Q}' \tag{7}$$

where $\underline{Q}'$ and $\underline{\alpha}'$ are in general different from $\underline{Q}$ and $\underline{\alpha}$, and contain the experimental data appropriate to obtain the good physical solution $\underline{R}'$. It is always possible to find a diagonal matrix $\underline{\delta}$ such that

$$\underline{Q} = \underline{\delta}\,\underline{Q}' \tag{8}$$

and so, one obtains

$$\underline{R} = \underline{\alpha}^{-1}\,\underline{\delta}\,\underline{\alpha}'\,\underline{R}' \tag{9}$$

showing that the parameters A, B, C, and H may be obtained as linear combinations of the good set. Although the problem of the determination of the good set of constants is open, the constants reported in this paper may be used for the thermodynamical description of the high pressure states of copper, as will be shown in the next sections.

3. THE 0°K ISOTHERM, BULK MODULUS, AND ENERGY

With the values of the parameters obtained in the previous section, the volumetric dependence of some thermodynamical functions may be easily computed.

The pressure P_K along the cold isotherm is given by equation (2) (or equation I.3 to I.7). The results are shown in Fig. 2 in the range from 0 to 1.2 Mbar; the circles show the results obtained by McQueen and Marsh[3] reducing their shock wave data to 0°K by means of the Mie-Grüneisen[12] equation The agreement with these data is very good, the average percentage deviation is of 0.4% with a maximum of 1% in the lower part of the curve.

Figure 3 shows the volumetric dependence of the bulk modulus* (eqs. I.4 to I.9); the agreement with the values obtained by numerical differentiation of the McQueen and Marsh's data[3], shown with circles, is quite good.

In Fig. 4, the results obtained for the cohesive energy using the Koehler and Duvall energy equation are shown; the circles show the results reported by Benedek[13] using the Mie-Gruneisen[12] equation. The agreement with Benedek's results is good, deviations being of the order of 3%.

4. GRUNEISEN RATIO AND HUGONIOTS

The volume dependence of the Grüneisen ratio is usually calculated either using the Slater[14] formula (eqs. I.10, 12, 13) or the Dugdale-MacDonald[15] formula (eqs. I.11, 13, 14). Figure 5 shows the results obtained in both cases; curve I is for the Slater formula, and curve II for Dugdale-MacDonald's. At zero pressure, the calculated values are 2.19 for Slater formula, and 1.86 for Dugdale-MacDonald's; these values are in reasonable agreement with those reported by Rice, McQueen and Marsh[16], 2.04 and 1.96 respectively.

The previous results for the Grüneisen ratio may now be used to obtain the volume dependence of the Hugoniot, by solving for the Hugoniot pressure P_H the Mie-Gruneisen equation (I.15) with $V_{oH}/V_o = 1.0101$, $\Theta = 315$ °K, and $E_o = 1136.74$ cal/mol. The results are shown in Fig. 6 using the Slater formula for the Gruneisen

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*Equation (9) in ref. 2 is in error, the factor $(V_o/V)^{1/3}$ should read $(V/V_o)^{1/3}$.

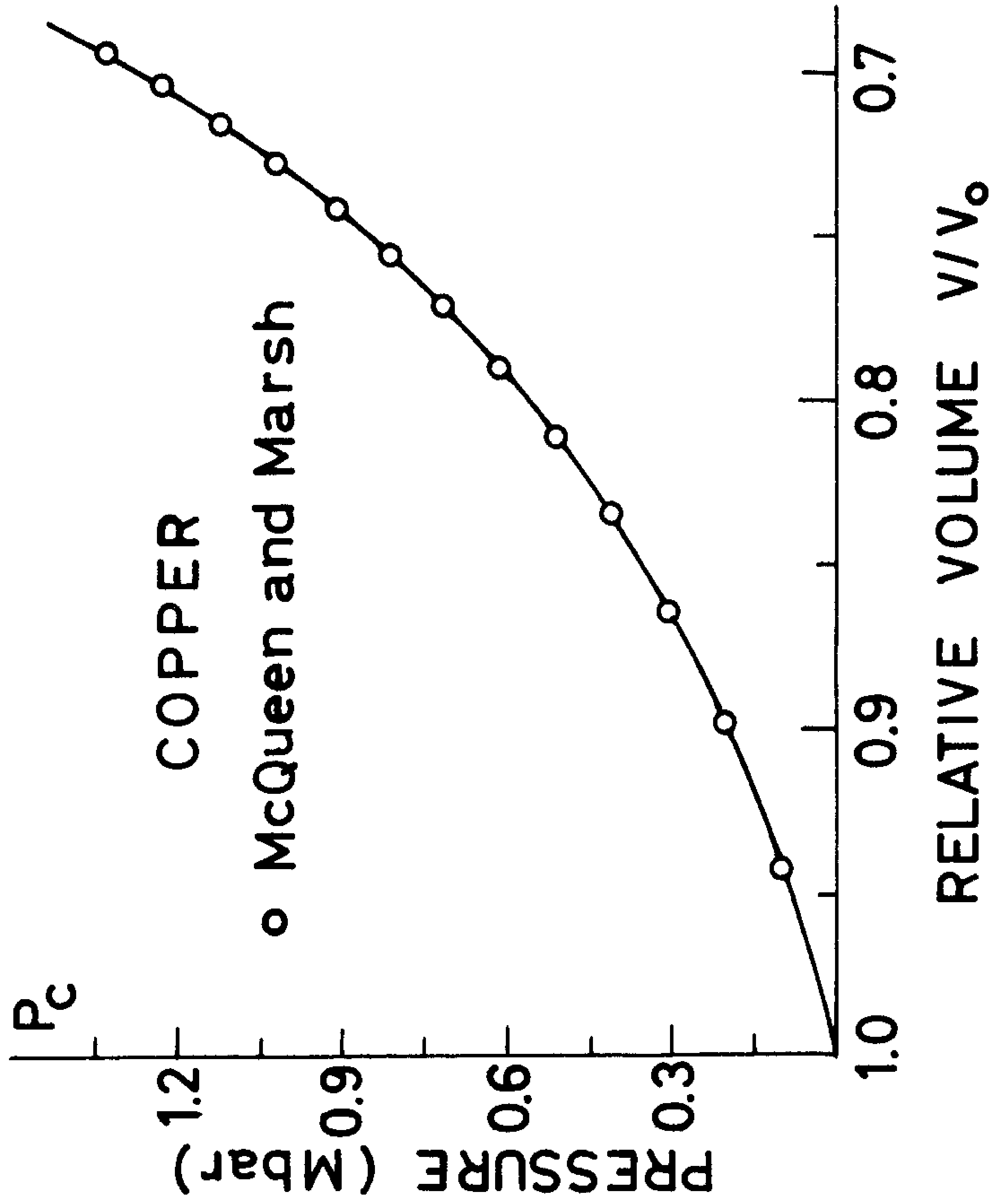

Fig. 2. Cold (0°K) isotherm

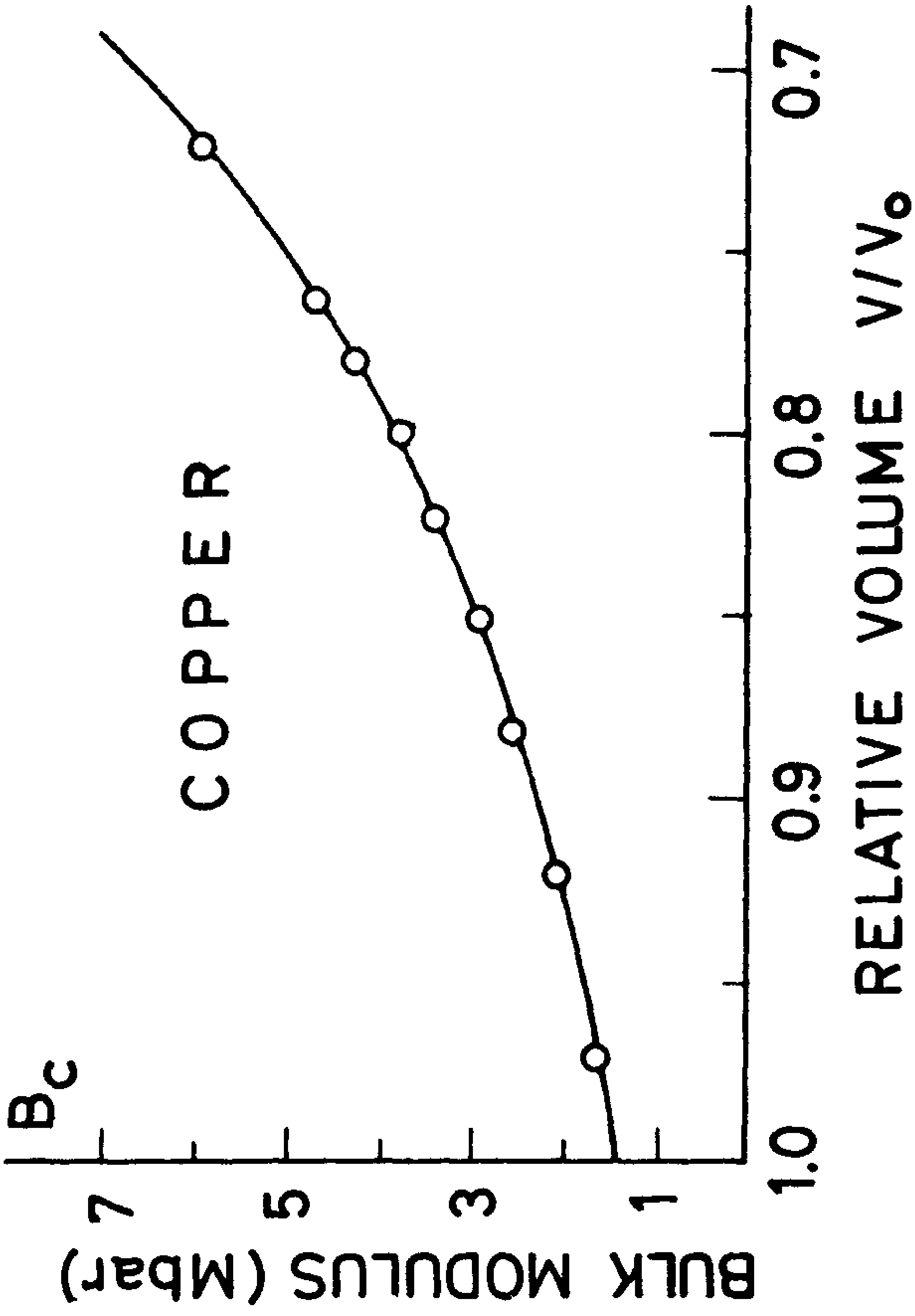

Fig. 3. 0°K bulk modulus
Points marked by circles were obtained by numerical differentiation of the data of McQueen and Marsh (see reference 3)

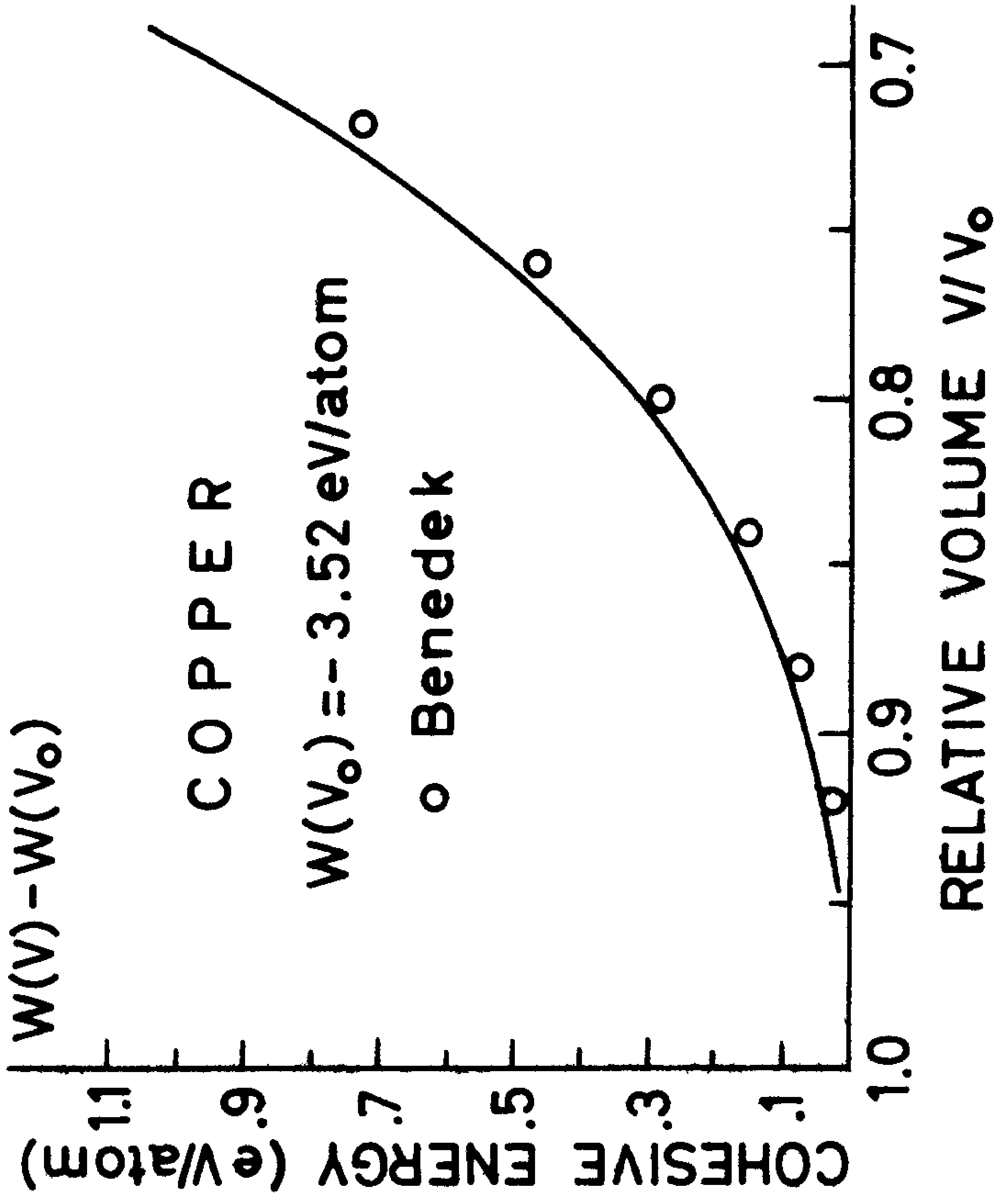

Fig. 4. Volume dependence of the cohesive energy

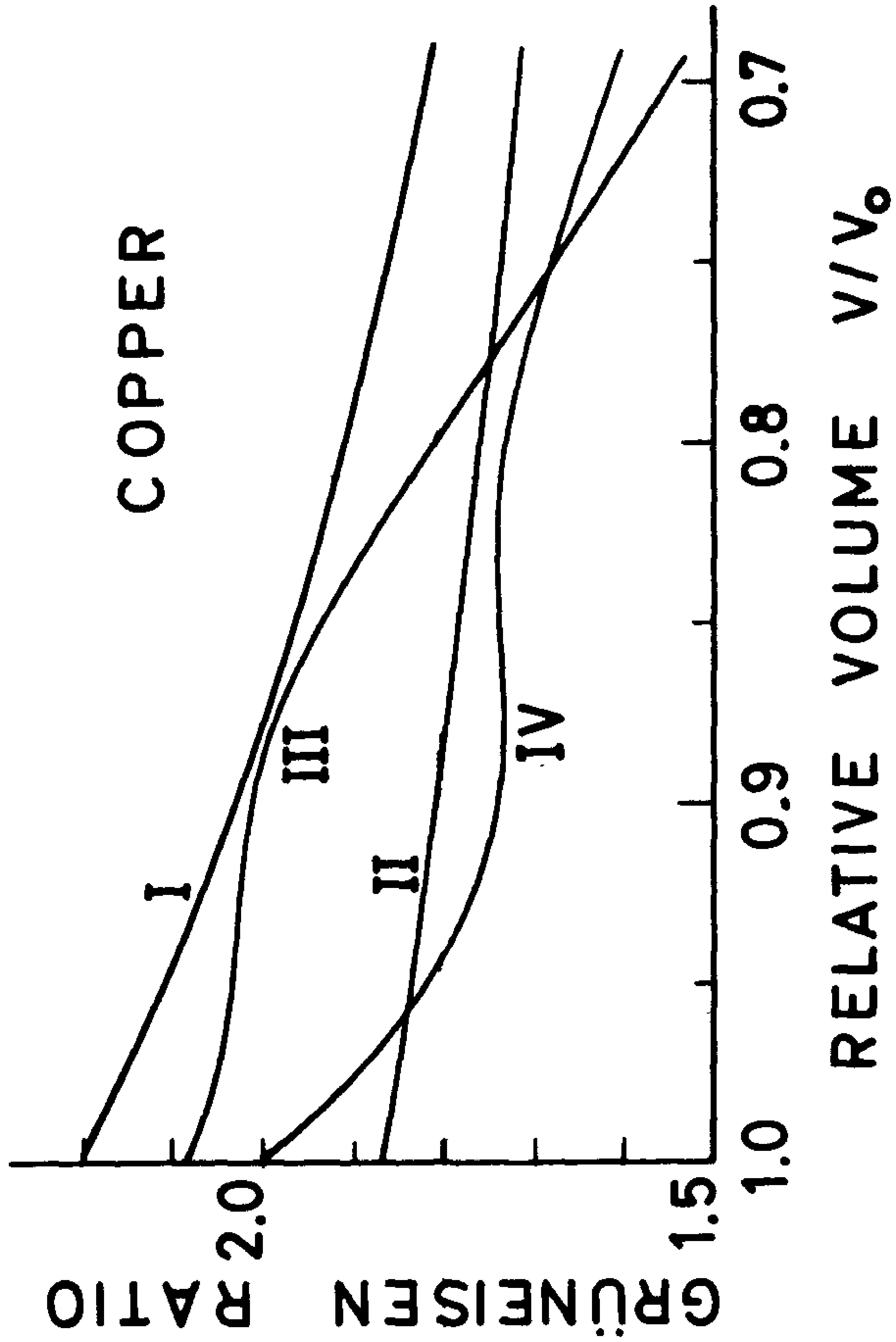

Fig. 5 Grüneisen ratio as a function of volume. Curve I was obtained using the Slater formula; curve II using the Dugdale MacDonald formula; III was obtained from the known 0°K isotherm, and an analytical fit for the Hugoniot; IV is the one reported by McQeen and Marsh (see reference 3).

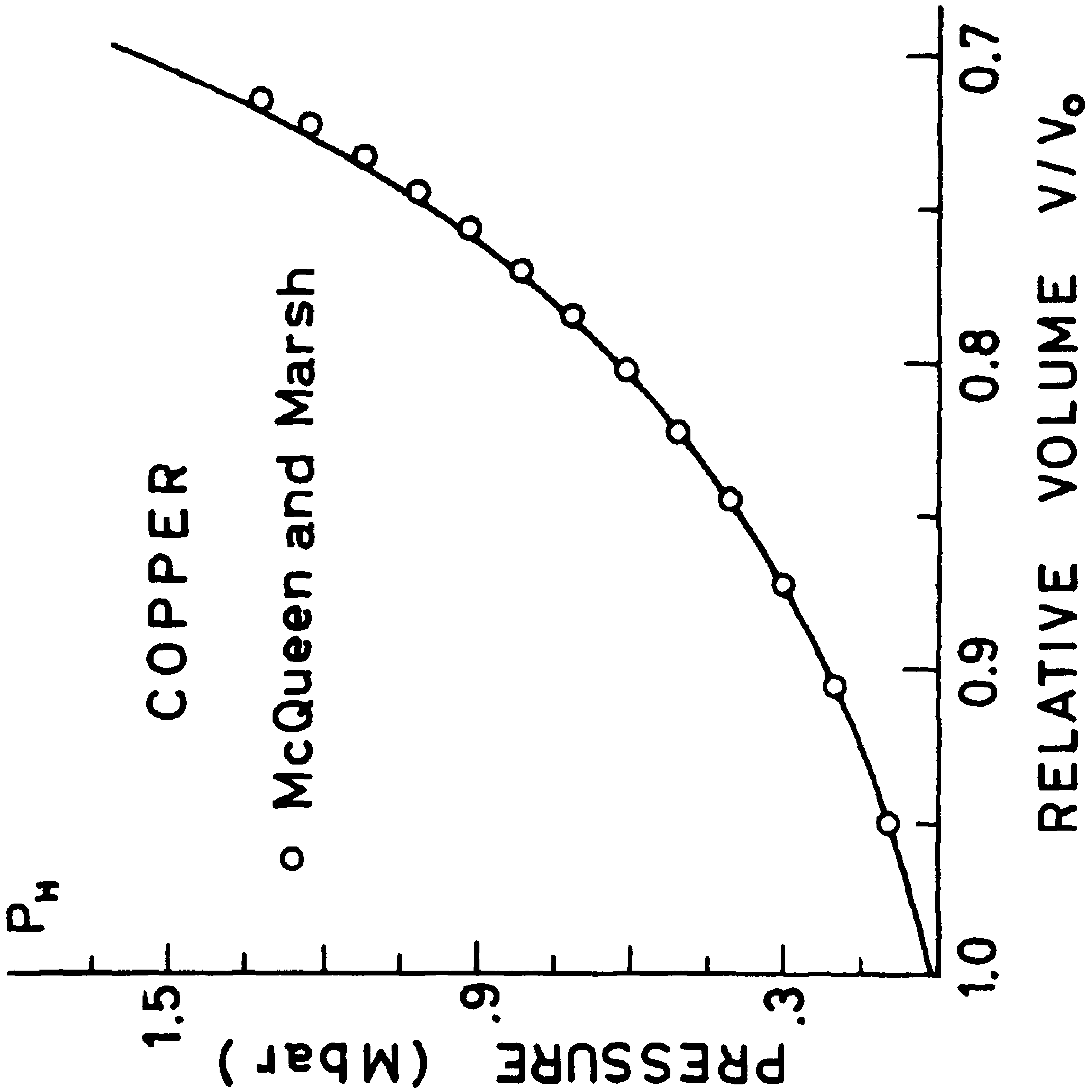

Fig. 6. Hugoniot obtained using the Slater formula for the Grüneisen ratio

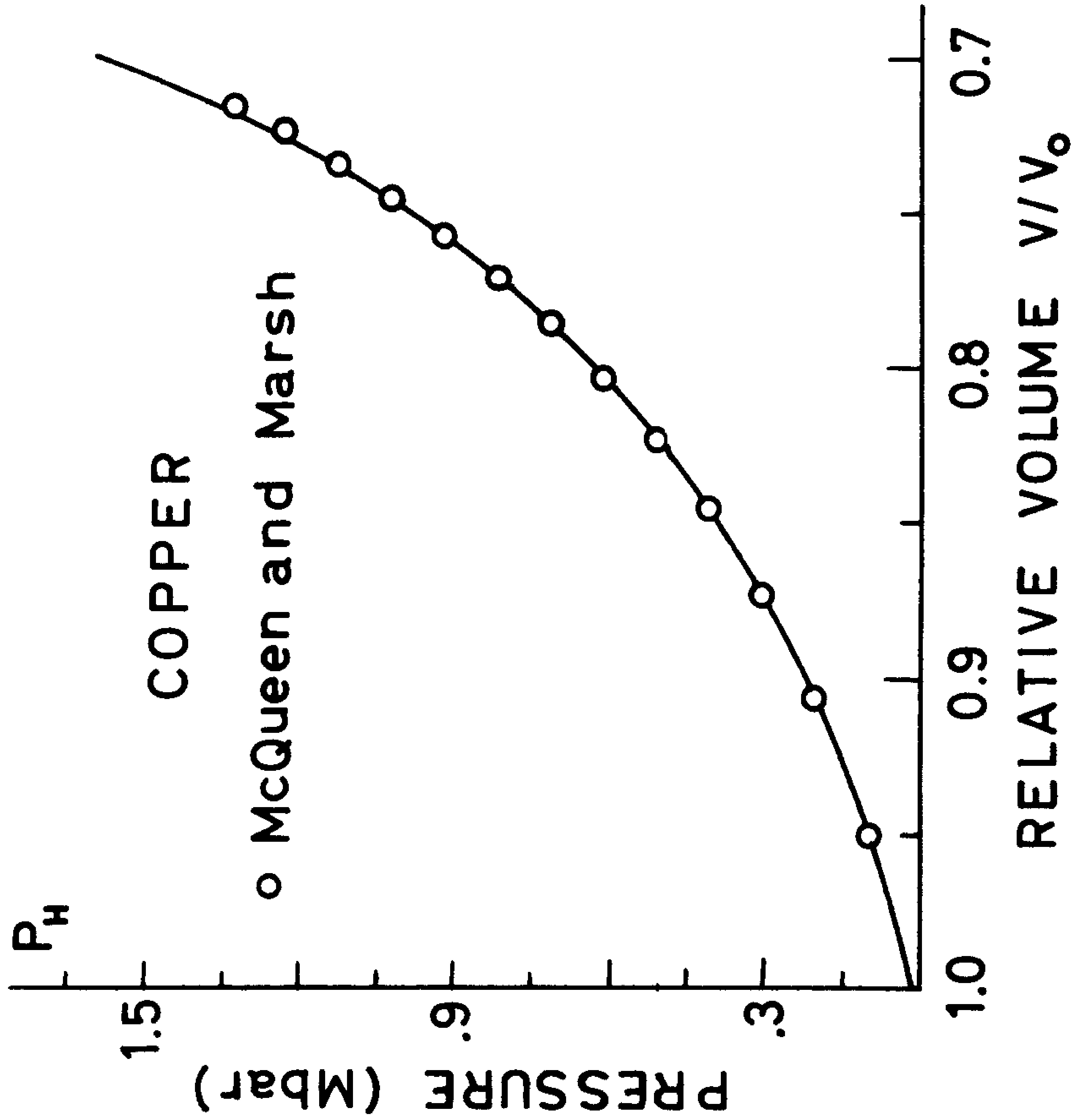

Fig. 7. Hugoniot obtained using the Dugdale-MacDonald formula for the Grüneisen ratio

ratio, and in Fig. 7 using the Dugdale-MacDonald formula. In both cases the agreement is very good compared with McQueen and Marsh's data[3], though it is perhaps a little better using the Dugdale-MacDonald formula; deviations are of the order of 2%.

The Mie-Gruneisen equation may be also used to obtain the Grüneisen ratio if the volume dependence of the Hugoniot and the cold isotherm is already known. Figure 5 curve III shows the values obtained using eq. (2) for the cold isotherm, and a function of the volume fitted to the Hugoniot[3,16,17] (eq. I.16, with C_0 = 0. 0.3243 mm/μsec, S_0 = 1.586). For zero pressure the calculated value is 2.08 in good agreement with other determinations[3,16]. Curve IV in this figure shows the results reported by McQueen and Marsh[3] using the Mie-Gruneisen equation.

These results on the Gruneisen ratio and Hugoniots are quite similar to those of silver[2], the alternative computation methods give very different results for the Gruneisen ratio, but the Hugoniots are almost coincident. This is a consequence of the fact that the relation between P_H and P_K through the Mie-Gruneisen equation is not very sensitive to changes in the Gruneisen ratio[1,2,15]. To make a decision in favour of one of the four curves in Fig. 5, it would be necessary to have more experimental information on the volume dependence of the Gruneisen ratio.

5. CONCLUSION

In conclusion we can say that since the coefficient in the exponent of the repulsive term, the cold isotherm, bulk modulus, cohesive energy, Hugoniot, and zero pressure value of the Gruneisen ratio are in good agreement with the available data, the Koehler and Duvall equation with the values of the parameters reported in this paper is very adequate for the thermodynamical description of high pressure states of copper, at least up to 1200 kbar.

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