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SHOCK ADIABATS AND ZERO ISOTHERMS OF SEVEN METALS AT HIGH PRESSURES

L. V. AL'TSHULER, A. A. BAKANOVA, and R. F. TRUNIN

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Shock compression of seven metals to 9×10^6 atm was investigated experimentally. The density was found to increase 1.94—2.01 times in copper, iron, and nickel, 2.21—2.36 in zinc and cadmium, and 2.58—2.66 in tin and lead. A transition was effected from the shock adiabats to zero isotherms for the metals investigated. The shock compression temperatures are calculated. For the upper experimental points on the adiabats they are equal to $(15-35) \times 10^3$ degrees for slightly compressible metals and $(50-70) \times 10^3$ degrees for zinc, tin, cadmium and lead. Extrapolated formulas are given for the zero isotherms.

INTRODUCTION

THE application of strong shock waves in high pressure physics has made it possible to make pressures equal to millions of atmospheres and compression temperatures in the material of several tens of thousands of degrees an object of scientific experiment. In researches published earlier,[1-3] the peak pressures achieved amounted to $\sim 5 \times 10^6$ atm. Under these conditions the metals, in spite of the high temperature of the shock compression, have increased their density by a factor of 1.7—2.2.

There is particular interest in the experimental recording of shock adiabats in the region of still higher densities, pressures and temperatures for the theory of solids, astronomy, and for a series of other related disciplines.

No less important is the problem of finding the compression curves of metals at the temperature of absolute zero—the zero isotherms. The behavior of metals behind the shock front is determined by the interaction of electrons and ions at zero temperature, by thermal vibrations of the lattice, and by thermal excitation of the degenerate or partially degenerate electron gas. The zero isotherms are obtained from the results of dynamic experiments by subtracting the thermal component from the total shock pressure or, in other words, by resolving the pressure into thermal and "cold" components.

At relatively small degrees of shock compression, the "cold" components of the pressure and energy play a dominant role, which allows us to limit ourselves, in the development of the parameters of the zero isotherms, to the Debye approximation in the estimate of the thermal contribution of the lattice, not taking the thermal excitation of the electrons into consideration.

The role of the temperature increases with increase in the amplitude of the shock waves. Thus, at shock compression pressures of 4×10^6 atm, the thermal pressures for copper and lead amount to ~ 30 per cent of the total pressure, and the heat fraction in the general internal energy balance to about 70 per cent.[3] The correct estimate of the thermal component under these conditions requires an account of the thermal excitation of the electron gas.

Upon further increase in the amplitude of the shock waves, it becomes necessary to introduce temperature corrections to the value of the thermal capacity and of the Grüneisen coefficients of the lattice, brought about by anharmonic thermal vibrations.

In the experimental part of the report, the shock adiabats are described for seven metals (Fe, Ni, Cu, Zn, Cd, Sn, Pb) up to pressures of 9×10^6 atm. The transition to the zero isotherms of simple and transition metals is considered in the next two sections. The final section is devoted to the extrapolation of the zero isotherms in the region of pressures and densities that can be reliably considered by quantum-statistical methods.

1. SHOCK ADIABATS

The experimentally measured parameters of the shock waves are their wave velocities (D) and mass velocities of the material behind the shock front (U). With the aid of the conservation laws, these quantities determine the pressure $P = \rho_0 DU$ and the degree of compression $\sigma = D/(D-U)$.

The measurements of the shock compressibility

Table I

Series No.	Shock wave parameters											
	Zinc				Cadmium				Tin			
	D, km/sec	U, km/sec	$P \cdot 10^{-10}$, dyn/cm^2	ρ/ρ_0	D, km/sec	U, km/sec	$P \cdot 10^{-10}$, $\frac{\text{dyn}}{\text{cm}^2}$	ρ/ρ_0	D, km/sec	U, km/sec	$P \cdot 10^{-10}$, $\frac{\text{dyn}}{\text{cm}^2}$	ρ/ρ_0
I	4.70	1.04	35,0	1.280	4.10	1,02	36,0	1,330	4,20	1.08	33.0	1.350
II	6,85	2.41	117.9	1.543	6.32	2.31	126.1	1.576	6.36	2.46	113.9	1.631
III	9.90	4.54	320.9	1.847	9.14	4.36	344.3	1.912	9.02	4.65	305.3	2.064

Series No.	Shock wave parameters in the screens	
	D^s, km/sec	U^s, km/sec
I	5.30	0,95
II	7,53	2.24
III	10.67	4,26

Table II

Series No.	Striker material	Velocity of striker, km/sec	D, km/sec	U, km/sec	P×10^{-10}, dyn/cm^2	ρ/ρ_0	D, km/sec	U, km/sec	P×10^{-10}, dyn/cm^2	ρ/ρ_0
			Zinc				Cadmium			
I	Al	5.60	6,30	2,12	95.4	1.507	5.88	1.99	101.0	1.512
II	Fe	5.60	7,92	2,98	168.5	1,604	7.16	2.88	178.8	1,674
III	Fe	9,10	10.39	4.85	359,6	1,877	9,55	4,67	385,0	1.958
			Tin				Nickel			
I	Al	5.60	5.99	2,15	93.8	1.560	7.28	1,72	111,6	1.311
II	Fe	5.60	7,22	3,06	160,8	1.735	8.72	2,63	203,3	1,432
III	Fe	9,10	9,50	4.97	343,7	2.097	11,20	4.35	431,9	1,634

of the metals under consideration (except nickel) reported previously[1,2] lie in the range from 400×10^3 to $(4—5) \times 10^6$ atm. For iron, copper, and lead the course of the shock adiabats was more accurately established in [3]. The experiments set forth in the indicated work are in satisfactory agreement with the results recently reported by McQueen and Marsh[4] on the shock compression of 19 metals, taken in the pressure range from 1×10^6 to 1.9×10^6 atm.

For zinc, cadmium, and tin the results of three series of experiments, described previously,[2] are given in Table I. These are corrected by account of the adiabat of iron given in [3]. The data of the first series of experiments for very low pressures were the same as in [2]. For the experiments of series II, the parameters of the shock wave in the calibration (iron) specimens were again computed from the precise D – U relation in iron and the experimental wave velocity in iron specimens, which is equal to 7.53 km/sec.[2] For the experiments of series III, the states of the passing wave (before reflection from the screen-specimen boundary), relative to the median plane of the samples, were determined from the velocity W (8.64 km/sec) of motion of the striker at the middle of the measurement base of the wave velocities. As a consequence of the damping of the shock wave in the screen and in the specimen, and of the heating of the striker which takes place in this series of experiments, a value of U = 4.26 km/sec was taken for the mass velocity, just as in [3], i.e., smaller than W/2 by 1.5 per cent. The parameters of the shock waves in the metals studied (listed in Table I) were found as usual[2] by graphic construction on pressure-velocity diagrams.

The data from the new measurements of the shock compressibility of the same metals and nickel, made with the measuring apparatus used previously[3] and in the same pressure range, are shown in Table II.

Much higher densities and pressures close to 10×10^6 atm* were achieved (see Table III) in the deceleration of the iron striker which was smoothly driven by the explosion products to a velocity of 14.68 km/sec. In the acceleration process, the temperature of the striker did not

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*The first measurements of the shock compressibility of iron for the indicated pressures were made in 1951 by K. K. Krupnikov and M. I. Brazhnik by a scheme suggested by one of the authors of the present paper (L.A.). The conditions of the experiments led to a strong heating of the striker, which made it difficult to interpret the results that were obtained.

Table III

	Metal						
	Fe	Ni	Cu	Zn	Cd	Sn	Pb
D, km/sec	15.10	14.60	14,20	14,19	12.99	12,98	11.36
U, km/sec	7,34	7.09	7.15	7.78	7.49	7.96	7.00
$P \cdot 10^{-10}$ dyn/cm²	870,0	918,0	907,0	786,0	841.0	752,0	915,0
ρ/ρ_0	1,947	1,944	2,014	2.214	2.362	2.585	2.666

become much higher than several hundred degrees Celsius. The base line of the wave velocities in these experiments was 4 mm, the thickness of the iron screens covering the specimen—2 mm. In each experiment, the recording of the time intervals was carried out by four electron double beam oscilloscopes OK-21. The motion of the beams was modulated by a reference generator with a frequency up to 20 Mc. The velocity of the steel striker was determined in 12 experiments with a probable error of ± 1.5 per cent. The values of the wave velocities obtained by averaging 6—8 separate experiments were found with an error of ± 1 per cent. The resultant inaccuracy in the determination of the degree of compression in the front of the shock waves ($\sigma = \rho/\rho_0$)

$$\Delta\sigma = \sigma(\sigma - 1)\sqrt{(\Delta U/U)^2 + (\Delta D/D)^2}$$

increases with increase in σ. $\Delta\sigma$ is equal to ± 0,035 for iron, copper and nickel, ± 0.05 for zinc, and ± 0.07 for tin, cadmium and lead.

The experimental results are shown in Figs. 1 and 2. For nickel, iron, copper, and zinc the lines passing through the experimental points are slightly curved; for lead, cadmium, and tin the D – U relations are approximated by two straight lines of different slope, with a transition region between them at U ~ 2.5—3.5 km/sec. The experimental points obtained by Walsh[5] and by McQueen and Marsh[4] are also plotted in the figure. For some metals, as has already been pointed out, the agreement between the Soviet and western experiments is entirely satisfactory. However, in the mean, the mass velocities of McQueen (for one and the same D) exceed the mass velocities obtained by the present authors by about 2 per cent. One of the reasons for the divergence can lie in the different methods of finding the mass velocities.

As has already been pointed out,[2] to calculate all the parameters in the investigated specimens, it is necessary to know the dynamic adiabat of the screen which covers the specimens, the values of D^S and U^S in it, and D in the specimens. In our experiments, U^S was found by the deceleration method from the velocity W of a body that strikes against the screen and is made of the same material as the screen.[1] Under these conditions, it follows rigorously that W = 2U. On the other hand, in special experiments, McQueen and Marsh[4] measured not the velocity of the striker but the rate of expansion of the screen after the emergence of the shock wave on its free surface. The resolution of $W^{\exp} = U^S + U^{\exp.S}$ into the sought velocity U^S and the velocity $U^{\exp.S}$ acquired in the isentropic expansion depends on the form of the equation of state of the screen material in the little studied region $\rho < \rho_0$. This can bring about a certain error in the value of U^S and conse-

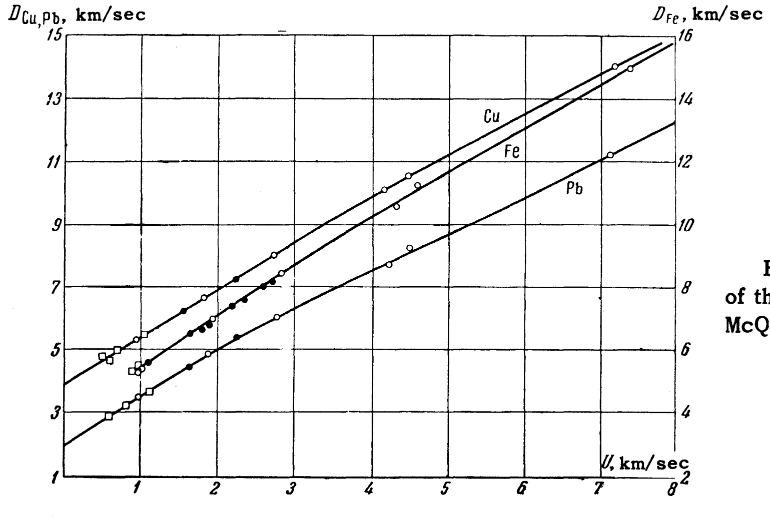

FIG. 1. D–U diagrams for copper, iron, and lead: ○ – data of the authors, □ – results of Walsh et al [5], ● – data of McQueen and Marsh.[4]

Table IV

U, km/sec	D, km/sec						
	Ni	Cu	Fe	Zn	Cd	Sn	Pb
0	4.62	3.92	—	3.05	2.40	2.45	1.91
0.5	5.38	4.68	—	3.83	3.26	3.26	2.75
1.0	6.14	5.44	5.38	4.62	4.12	4.08	3.56
1.5	6.90	6.22	6.30	5.40	4.99	4.89	4.33
2.0	7.66	6.96	7.15	6.18	5.82	5.68	5.07
2.5	8.42	7.70	7.96	6.97	6.58	6.41	5.76
3.0	9.18	8.45	8.76	7.74	7.31	7.09	6.43
3.5	9.92	9.19	9.54	8.48	8.00	7.71	7.05
4.0	10.61	9.93	10.33	9.18	8.68	8.31	7.65
4.5	11.27	10.64	11.10	9.88	9.32	8.90	8.25
5.0	11.91	11.31	11.82	10.55	9.96	9.49	8.85
5.5	12.55	11.99	12.52	11.20	10.56	10.09	9.45
6.0	13.19	12.67	13.22	11.86	11.18	10.68	10.04
6.5	13.84	13.34	13.92	12.52	11.79	11.26	10.64
7.0	14.48	14.00	14.62	13.17	12.40	11.86	11.24
7.5	15.12	14.68	15.32	13.82	13.01	12.44	11.84
8.0	—	—	—	14.47	—	13.04	—

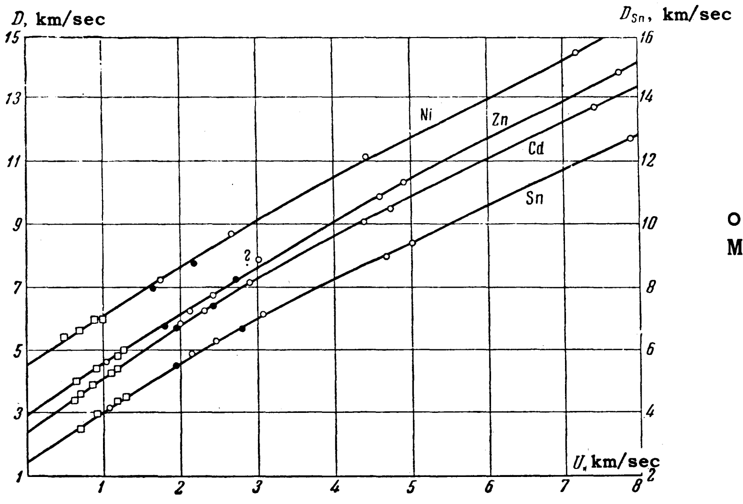

FIG. 2. D–U diagrams for nickel, zinc, cadmium and tin: ○ – data of authors, □ – results of Walsh et al [5], ● – data of McQueen and Marsh.[4]

quently in the mass velocities of the investigated specimens. Another possible reason for the divergence lies in the errors of our experimental determination of the striker velocities, or of the rate of expansion of the screens in the experiments of McQueen and Marsh.

The experimental data of the authors and of McQueen and Marsh were given equal weights in plotting Figs. 1 and 2. The numerical connection between the wave and mass velocities for the metals studied is listed in Table IV. The relative location of the points of the dynamic adiabats is demonstrated on the graphs of Figs. 3–6 in the coordinates pressure-relative compression. The possible errors in the positions of the upper experimental points are pointed out. The largest pressures ~ 9.2×10^6 atm were achieved in the experiments with nickel. The maximum degree of compression (2.58–2.66 times) was achieved in tin and lead.

2. ZERO ISOTHERMS OF COPPER, ZINC, CADMIUM, TIN, AND LEAD

For a description of the properties of the nontransition metals at high temperatures of shock compression, the equation of state of Mie-Grüneisen was supplemented, just as in [3], by terms which take into account the thermal excitation of electrons.* We shall now write down the expressions for the pressure and internal energy in the following form, neglecting temporarily the effect of the anharmonicity:

$$P = P_c(v) + \frac{\gamma_l(v)\cdot 3RT}{Av} D\left(\frac{\Theta}{T}\right) + \frac{\gamma_e \beta(v)}{2v} T^2, \qquad (1)$$

$$E = E_c(v) + \frac{3RT}{A} D\left(\frac{\Theta}{T}\right) + \frac{\beta(v)}{2} T^2. \qquad (1a)$$

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*The form of the electron terms used here and in [3] was proposed and established by S. B. Kormer.

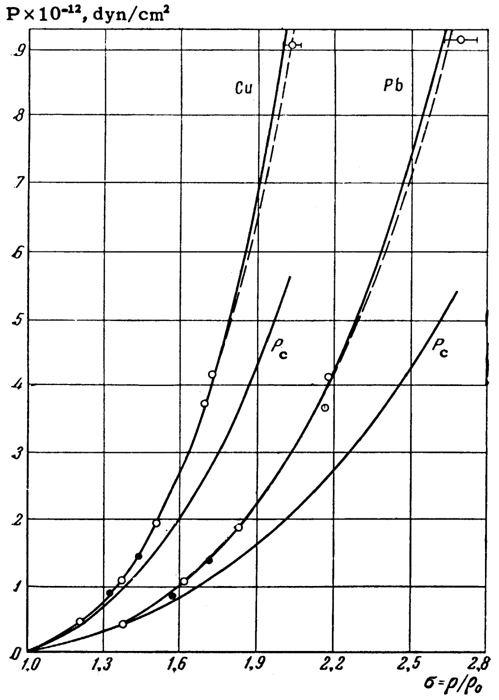

FIG. 3. Shock adiabats and zero isotherms of copper and lead: o – data of authors, ● – results of McQueen and March.[4] The results of a calculation with accurate values of E and P are shown by the dashed lines (see below, Table VI.)

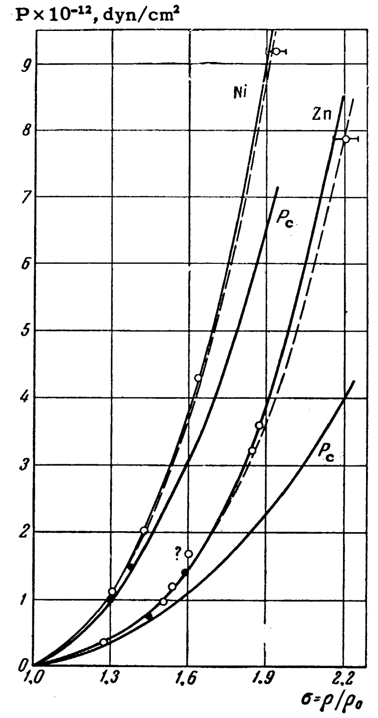

FIG. 5. Shock adiabats and zero isotherms of nickel and zinc. Notation the same as in Fig. 3.

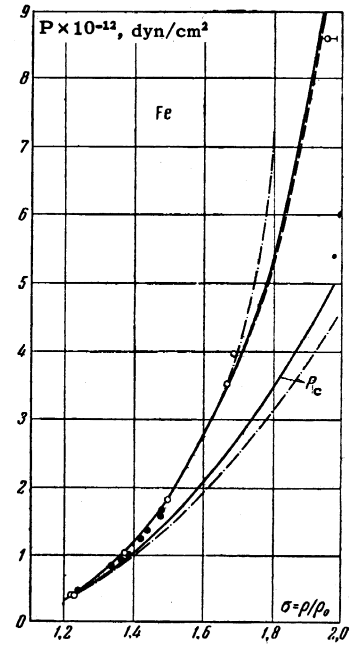

FIG. 6. Shock adiabat and zero isotherm of iron. The dashed lines denote $P_H(\sigma)$ and $P_c(\sigma)$ according to V. S. Zharkov and V. A. Kalinin.[11] The rest of the notation is the same as in Fig. 3.

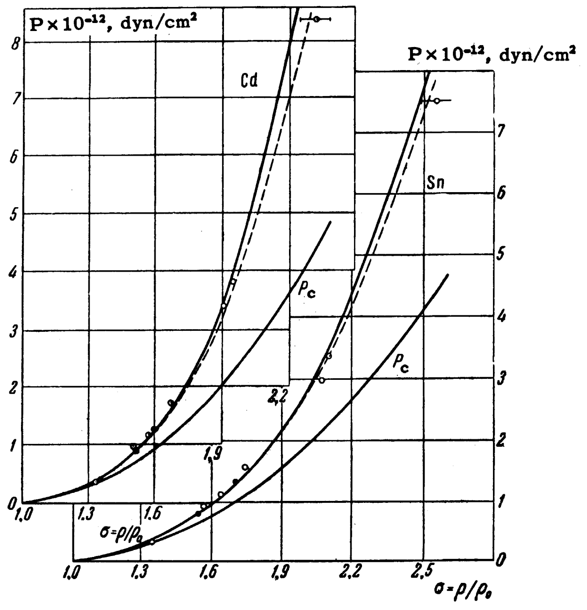

FIG. 4. Shock adiabats and zero isotherms of cadmium and tin. Notation the same as in Fig. 3.

Here P is the pressure, v the specific volume, T the absolute temperature, E the specific internal energy, $E_c(v)$ the energy of the metal at T = 0; $P_c(v) = -dE_c(v)/dv$ is the pressure at T = 0, A is the atomic weight, R the gas constant, $D(\Theta/T)$ the Debye function, $\gamma_l(v)$ the Grüneisen coefficient for the lattice, γ_e the Grüneisen coefficient for the electrons, $\beta = \beta_0 (v/v_{0k})^{\gamma_e}$ is the electronic heat capacity coefficient, v_{0k} is the specific volume at T = 0° K, P = 0.

The right sides of (1) and (1a) contain, in addition to known quantities, two parameters β_0 and γ_e in the electron terms and two unknown functions of the volume: $\gamma_l(v)$ and $P_c(v)$.

The values of β_0 are found from precise measurements of the thermal conductivity at low temperatures. As concerns the electron coefficient of Grüneisen, it is about 0.5 in the quantum-statistical analysis.[6]

The relation of McDonald and Dugdale

$$\gamma_l(v) = -\frac{1}{3} - \frac{v}{2}\frac{d^2(P_c v^{2/3})/dv^2}{d(P_c v^{2/3})/dv}, \qquad (2)$$

which connects the Grüneisen coefficient of the lattice with the "cold" compression curve $P_c(v)$, leaves one unknown function $P_c(v)$ in the system (1). This function can be determined by substitution in Eq. (1) of the parameters of the Hugoniot adiabats —the pressure P_H, the specific volume v_H and the specific energy

$$E_H = \tfrac{1}{2}P_H(v_0 - v_H) + 3RT_0 D(\Theta/T_0) + \tfrac{1}{2}\beta_0 T_0^2 + E_c(v_0). \qquad (3)$$

($T_0 \sim 300°K$ is the temperature of the specimens in the initial state, v_0 is the volume at $P = 0$, $T = T_0$).

A similar method, which requires the numerical solution of equations of the form (1), was applied in a number of researches.[3-5] As was shown by Kormer and others,[8] this method does not lead to unique values of γ_l for small compressions, and does not give analytic expressions for $P_c(v)$ that are suitable for extrapolation.

Another way of obtaining the equations of state from the results of dynamic experiments was based on the furnishing of $P_c(v)$ in analytic form. This contains a certain number of free parameters, selected according to the experimental data. Experimental data on Al, Cu, and Pb were treated in this fashion by Kormer, Urlina, and Popov[8] and are shown in [3].

The new treatment gives a result for $P_c(v)$ which is identical with that of [3]. Here, we represent the zero isotherms in the form

$$P_c(\delta) = Q'\delta^{2/3}\exp(-q\delta^{-1/3}) - Q\delta^{4/3}, \qquad \delta = v_{0k}/v, \qquad (4)$$

which contains three free parameters Q', Q, and q. By eliminating Q', and using the condition $P_c(1) = 0$, we get the following simple expressions for the pressure and the energy:

$$P_c(\delta) = Q\,[\delta^{2/3}\exp\{q(1-\delta^{-1/3})\} - \delta^{4/3}], \qquad (5)$$

$$E_c(\delta) = (3Q/\rho_{0k})\,[q^{-1}\exp\{q(1-\delta^{-1/3})\} - \delta^{1/3}] \qquad (5a)$$

with two unknown constants Q and q.

For ionic compounds, the first terms in (5) are determined by the repulsive potential of the ions, and the second by the Coulomb attraction. For metals, the positive term in (5) expresses approximately the sum of the repulsive forces (kinetic pressure of the electrons, interaction of closed shells of ions, etc.), and the negative the attractive forces (Coulomb and exchange forces, etc.). Expressions of the form (5) were used earlier for description of the equations of state of rock salt[9,10] and iron.[9,11]

On the basis of (5) and (2), the Grüneisen coefficient for the lattice

$$\gamma_l(\delta) = \frac{1}{6}\frac{q^2\delta^{-4/3}\exp\{q(1-\delta^{-1/3})\} - 6}{\delta^{-1}q\exp\{q(1-\delta^{-1/3})\} - 2} \qquad (6)$$

depends on the single parameter q. For $\delta = 1$ ($v = v_{0k}$) we have

$$\gamma_l = (q^2 - 6)/6(q-2). \qquad (6a)$$

In order to estimate the unknown parameters, the system (1) was solved [after substitution of E, P_c, E_c, and γ_l from (3), (5) and (6)] for P_H with different values of Q and q. The chosen combinations of these quantities were best approximated by the experimental adiabats on their lower parts from zero to 4×10^6 atm.

The parameters $\rho_0 = 1/v_0$, $\rho_{0k} = 1/v_{0k}$, q, Q, γ_e, and β_0 are given for five simple metals and nickel (see the next section) in Table V, together with the computed and experimental values of $\gamma_l(v_0)$ and the isothermal bulk moduli $K = -dP/d\ln v$[12] for $v = v_0$ and $T = T_0$. The zero isotherms and the shock adiabats under consideration are drawn as functions of $\sigma = v_0/v$ as solid lines in Figs. 3—6. For Cu and Pb, the course of the zero isotherms virtually coincides with the curves obtained in [3].

As the tables and graphs show, a great divergence takes place between calculation and experiment for strongly compressible metals. A notable difference in the experimental modulus of volume compression and the Grüneisen coefficient is observed in lead for $\rho = \rho_0$ and $T = T_0$. The computed adiabats of cadmium and tin (for a pressure of the order of 350×10^3 atm) are higher than the experimental points (by ~ 8—10 per cent, i.e., by 30×10^3 atm), and for ~ 1.6×10^6 atm by somewhat less (by ~ 5 per cent, i.e., by 80×10^3 atm).

Significant divergences between calculation and experiment are observed in the upper parts of the shock adiabats for the highest temperatures of the shock compression, requiring a consideration of the anharmonicity of the thermal vibrations. For an estimate of the temperature corrections,* the "free volume" approximation was used.[13] In this approximation, an interaction of the atom with its nearest neighbors is considered which is symmetric over the sphere. In an elementary consid-

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*These calculations were completed by V. N. Zubarev at the request of the authors.

Table V

	ρ_0, g/cm^3	ρ_{0k}, g/cm^3	β_0, $\frac{\text{ergs}}{\text{g-deg}^2}$	γ_e	q	$Q\cdot 10^{-10}$, dyn/cm^2	$K(v_0)\cdot 10^{-10}$, $\frac{\text{g}}{\text{cm-sec}^2}$ experiment [12]	$K(v_0)\cdot 10^{-10}$, $\frac{\text{g}}{\text{cm-sec}^2}$ calculation	$\gamma_l(v_0)$ expt.	$\gamma_l(v_0)$ calc.
Ni	8.87	8.94	1240	0.5	11.0	65.00	186,91	189.16	2.18	2,14
Cu	8.93	9.02	110	0.5	10.5	50.00	136,98	136.98	2.06	2.06
Zn	7.14	7,28	100	0.5	10.5	26.46	59,07	70.09	2.11	2.08
Cd	8,64	8,82	55	0.5	11.1	20.04	44.44	55.98	2.22	2,19
Sn	7.28	7.41	140	0.5	9.1	26.30	52.38	58.51	2,01	1.83
Pb	11.35	11.62	144	0.5	9.6	24.23	41.41	55.85	2.64	1.93

eration, under the assumption that the neighboring atoms are fixed in their equilibrium positions, the statistical configuration integral has the form

$$z^{A/N} \approx e^{-nU(a)/2} \int_0^{a/2} \exp\left[-\frac{n}{2}\frac{\overline{U(r,a)}-U(a)}{KT}\right] r^2\,dr. \quad (7)$$

Here n is the number of nearest neighbors, U(a) is the potential energy of the pair interaction of atoms separated by a distance a(v) from one another ($a^3 = \sqrt{2}\,Av/N$, N is Avogadro's number), and $\overline{U(r,a)}$ is the energy of the pair interaction of an atom with a displacement r, averaged over all directions. The potential of the pair interaction is found from the relation

$$nU(a)/2 = E_c(a)A/N.$$

According to Lennard-Jones and Devonshire,[13] approximate account of the motion of neighbors leads to a replacement of the coefficient 0.5 in the exponential of the integrand by unity. Comparison with the results of some exact calculations by the Monte Carlo method, however, suggests the advisability of keeping the fractional coefficient at 0.5.

We now write down the thermal energy of the lattice and its thermal pressure for the region of high temperatures in the form

$$E_{T_l} = \bar{C}_v(T)\,T/A, \qquad P_{T_l} = \bar{\gamma}(v,T)\,\bar{C}_v T/Av.$$

Here $\bar{C}_V$ is the average molar heat capacity of the lattice in the temperature range from zero to T; $\bar{\gamma}(v,T) = \gamma(v,0) - \Delta\gamma(v,T)$ is the mean Grüneisen coefficient in the same range of temperatures. The results of a calculation of $\bar{C}_V$ and $\Delta\gamma$ are given in Fig. 7 as a function of the dimensionless temperature $\Theta = RT\rho_{0k}/3QA$. The dynamic adiabats, computed from precise values of E_{T_l} and P_{T_l}, are shown by dashed lines in Figs. 3—6. Their coordinates, together with the temperature of the shock compression, are shown in Table VI.

As expected, account of the temperature dependence of C_V and γ_l shifts the computed adiabats of the metals to the right, bringing them closer to the experimental points. As a result, we can declare the agreement between calculation and experiment to be satisfactory over the entire range of shock pressures studied experimentally, both for slightly and strongly compressible metals.

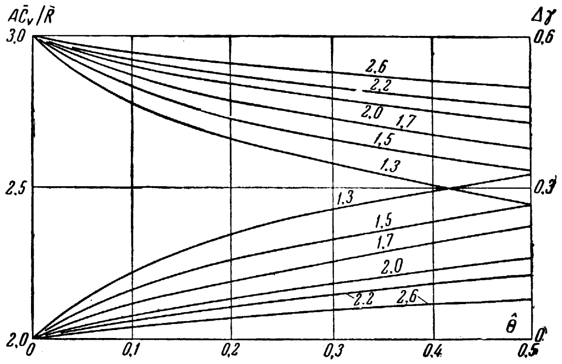

FIG. 7. Change in the mean heat capacity (upper curves) and the Grüneisen coefficient (lower curves) with temperature: the numbers on the curves are the values of ρ/ρ_0.

Inasmuch as the difference between the obtained adiabats and the experimental results does not exceed the limits of experimental scatter, it is impossible to draw definite conclusions on the nonmonotonic or irregular change of the parameters of the equation of state. Clarification of this problem is a matter for further experiments. In the first place, it is desirable, from this point of view, to study in detail the sections of the adiabats of lead, tin and cadmium in the pressure range from 1.5×10^6 to 3.0×10^6 atm, i.e., in the region where a change takes place in the slope of the lines of the D – U diagram for these metals.

The temperatures of shock compression at 9×10^6 atm are very high, amounting to 35×10^3 deg for copper and $(50—70) \times 10^3$ deg for strongly compressible metals. Under these conditions, the fraction of the thermal energy in the overall internal energy balance amounts to 70 per cent for copper and 78 per cent for lead. The contribution of the electrons to the thermal energy of the metals is quite appreciable. For copper, tin and lead, it is equal to 28, 56 and 68 per cent, respectively. The thermal pressures, including the thermal

Table VI

Metal	Parameter*	$P \times 10^{-10}$, dyn/cm^2								
		100	200	300	400	500	600	700	800	900
Ni	σ	1,292	1,433	1,543	1,624	1,696	1,761	1.818	1.869	1.915
	T_H	1,00	2,78	4.57	6.34	8.05	9,74	11.34	12.89	14.38
Cu	σ	1,352	1,516	1.624	1.713	1,789	1,853	1,910	1.962	2.006
	T_H	1,71	4.86	8.79	13,11	17,61	22,11	26,60	30.93	35.31
Zn	σ	1,513	1.696	1,829	1.938	2.021	2,092	2,156	2,213	
	T_H	3,32	9.00	15.39	21.78	28.18	34.60	40.85	46,70	
Cd	σ	1,544	1,741	1,874	1,977	2,066	2,142	2,213	2,274	2.329
	T_H	5,03	13,57	22,46	31,29	39.84	48,15	56,51	64,65	71.95
Sn	σ	1,610	1,857	2,032	2,168	2,282	2,382	2,469	2,548	
	T_H	5.62	13,97	22,17	29.83	37,10	43.90	50,53	56.62	
Pb	σ	1,609	1.854	2.023	2,162	2,279	2,372	2,458	2.538	2,608
	T_H	6.00	13,42	20,15	26.58	32.60	38,19	43,50	48,66	53.67
Fe	σ	1,354	1.508	1,612	1,696	1,763	1,816	1,862	1.900	1.934
	T_H	2.05	4,55	7,42	10,29	13.15	16.01	18,89	21.59	24.18

*Values of T_H are given in 10^3 deg.

pressure of the electrons, also play a large role at 9×10^6 atm (from 25 to 50 per cent).

3. TRANSITION METALS

High densities of the energy levels close to the Fermi surface are characteristic of transition metals with unfilled d shells. So also, as a consequence, is the anomalously large electron heat capacity. For a correct description of the thermal properties of the electrons in the region of strong degeneracy, it is necessary to know the dependence of the electron specific heat coefficient on the specific volume. This determines also the electron Grüneisen coefficient $\gamma_e = d \ln \beta / d \ln v$.

The form of the functions $\beta(v)$ and $\gamma_e(v)$ is unknown at the present time. However, it can be asserted from very general considerations that upon increase in the density the difference in the electronic specific heats of transition and simple metals tends to zero as a consequence of the broadening and overlapping of the bands. A similar coincidence of the values of β, which are quite different for normal densities (for nickel and iron β_0 is equal to 1240 and 930, respectively, while for copper and zinc it is 110 and 100), means that the electron Grüneisen coefficients can appreciably exceed the value 0.5 obtained in statistical consideration of the problem for not too high a degree of compression.

We assume that γ_e is constant for the range of densities of iron and nickel studied (up to ≈ 2.0) and, consequently, that $\beta = \beta_0 e^{-\gamma_e}$. For the chosen analytic form of $\beta(\delta)$, the value of γ_e can be estimated from experimental data in this case, however, if the experiments lead to sufficiently high temperatures.

For nickel, the constants of the elastic curve, q and Q, and the locations of the dynamic adiabats were found for three values of γ_e: 0.5, 1.0, and 1.5. The best agreement of calculation and experiment takes place for $\gamma_e = 0.5$.*

In the case of iron, we limit ourselves to the high-pressure phase, which does not intersect with the abscissa axis. We write down the expression for P_c in the form (4) as a function of the independent variable $\sigma = v_0/v$ (and not δ, as earlier). Further, setting the energy $E_c'(v_{0k})$ of the low-pressure phase equal to zero, we represent the energy of the zero isotherm of the second phase in the form

$$E_c''(\sigma) = E_c(\sigma) - E_c'(\sigma_1) + E_1, \tag{8}$$

$$E_c(\sigma) = \frac{3}{\rho_0}\left[Q' q^{-1} \exp\left(-q\sigma^{-1/3}\right) - Q\sigma^{1/3}\right], \tag{8a}$$

where σ_1, E_1 are the relative density and the specific internal energy at the initial point of the curve P_c' of the high pressure phase. Numerically, $\sigma_1 = 1.2$; $E_1 = 29 \times 10^8$.

Zharkov and Kalinin,[11] who applied the equation of the zero isotherm in the form (4), used the experimental data up to pressures of 1×10^6 atm for the determination of the parameters of the equation. The values of the constants selected by

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*For $\gamma_e = 0.8$, the adiabat passes along the left boundary of the range of experimental scatter. With account of the possible inaccuracy in the parameters q and Q, the upper limit is $\gamma_e = 1.0$.

Table VII

q	$Q' \times 10^{-14}$, dyn/cm²	$Q \times 10^{-10}$ dyn/cm²	β_0, $\frac{\text{ergs}}{\text{g-deg}^2}$
7.7845	22.68	107.4	1551
8.85	55.54	95.44	930

them are given in the upper row of Table VII. In the equation of state of Zharkov and Kalinin, the magnitude of the electronic Grüneisen coefficients γ_e is unjustifiably large in the density range considered (up to $\sigma = 2.0$), changing from 3.7 to 3.2. Extrapolation of their adiabat in the region $P_H > 5 \times 10^6$ atm contradicts the experimental data (see Fig. 6).

A much better description of the shock adiabat of iron is achieved for $\gamma_e = 1.5$ (see Fig. 6) and a somewhat larger value of q than in [12]. The parameters of the equation of state of iron and the characteristics of the dynamic adiabat are given in the lower rows of Tables VII and VI. The relative positions of the curve $P_c(\sigma)$, obtained in the present work, and the curve $P_c(\sigma)$ from [11] are shown in Fig. 6. The curve $P_c(\sigma)$ from [1] is located close to the corresponding curve in [11]. In both cases, the gentle slope of $P_c(\sigma)$ is explained by the increase in the thermal pressure. In [11], this is associated with large γ_e; in [1], the decrease of γ_l with density was not taken into account.

4. EXTRAPOLATION OF THE ZERO ISOTHERMS

The equations obtained are suitable for a description of the course of the zero isotherms in the range of the experiment and for nearby extrapolation. For iron, nickel, zinc, and copper their application is probably limited to densities less than $2.5\rho_0$. For the remaining metals, $\rho < 3\rho_0$.

For high degrees of compression, the isotherms of absolute zero are taken into account with sufficient reliability by quantum mechanical methods. More accurate and convenient for practical application at the present time are the corrected Thomas-Fermi (TFC) curves computed by Kalitka,[14] which consider both exchange and quantum corrections. In log P vs. $\log(\sigma - 1)$ coordinates, long portions of the TFC curves are straight lines. In P vs. $\sigma - 1$ coordinates, they are parabolic curves of the form $P = B(\sigma - a)^n$. A shift of the vertices of the parabolas to the position $P = b$, $\sigma = a$ makes it possible to obtain a smooth connection of the experimental isotherms P_c in the form (5) with extrapolated curves of the form

$$P_{c,\text{extrap}} = b + B(\sigma - a)^n. \tag{9}$$

Table VIII

Metal	$b \times 10^{-10}$, dyn/cm²	$B \times 10^{-10}$, dyn/cm²	a	n
Ni	5.77	821,180	1.013	2.078
Cu	210.80	840.767	1.364	2.043
Fe	197,07	730.693	1.305	2.042
Zn	112.96	438.112	1.373	2.091
Cd	5,59	196,250	0.917	2.265
Sn	52,04	70.848	0.329	2.420
Pb	50.65	68.559	0.331	2.520

The four desired constants in (9) are found by successive approximations, inasmuch as the introduction of the parameters b and $a \neq 1$ changes the values of B and n somewhat for the new coordinates P, b and σ, a,

The constants of the extrapolated equation are shown for seven metals in Table VIII. For $\sigma = 2.0$, the plotted curves of $P_{c,\text{extrap}}(\sigma)$ and its derivatives coincide with the experimental values. For large σ, the curves of $P_{c,\text{extrap}}$ merge asymptotically with the TFC curves. In the aggregate,

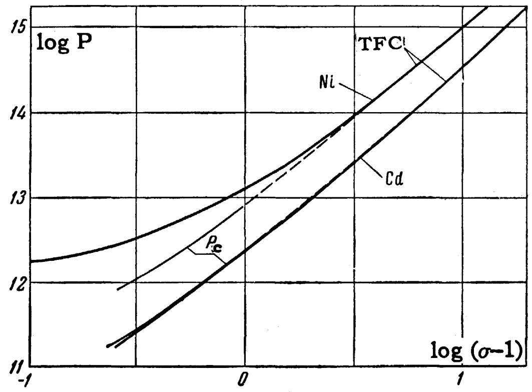

FIG. 8. Extrapolation of the zero isotherms for nickel and cadmium (the values of P are in dyn/cm²). The dashed line is the extrapolation of P_c according to [9].

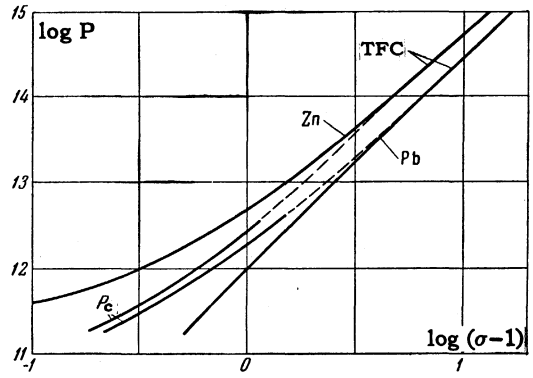

FIG. 9. Extrapolation of the zero isotherms for zinc and lead.

Eqs. (5) and (9) determine the path of the zero isotherms in the range of pressures from zero to $\sim 10^9$ atm. The relative position of the TFC curves (from the work of Kalitkin[15]) and the experimental P_c and $P_{c,\mathrm{extrap}}$ are shown for some metals in Figs. 8, 9.

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