COMPLETE THERMODYNAMIC EQUATIONS OF STATE OF METALS (SOLID PHASE)

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Complete thermodynamic equations of state of solids are constructed either on a phenomenological basis [1], or on the basis of model representations at the atomic level [2]. The first way necessitates a thorough preliminary experimental study of the thermodynamic properties of the material as a basis for establishing a system of partial differential equations. In the second case a valid model leads not only to explicit functional relations between thermodynamic quantities over a broad range of values of the parameters, but also makes it possible to relate the macroscopic characteristics of the material to its atomic characteristics and to discover the mechanism of the phenomena under consideration. Since a model without parameters is generally impossible, it is sufficient to use the experimental values of a few easily measured quantities to determine the adjustable parameters. Thus, various forms of Mie–Gruneisen equations of state are obtained depending on the specific assumptions about the structure of the material, the strength of the interatomic binding, and the nature of the motion of the microparticles which constitute the material. Using the quasi-harmonic approximation of solid-state theory and the Debye model of thermal vibrations, we derive a caloric equation of state which enables us to develop a complete thermodynamic description for a number of metals.

We derive an expression for the internal energy as a function of the internal variables by using the quasi-harmonic approximation of solid state theory and the Debye model of thermal vibrations, assuming that the effect of the thermal excitation of the electrons of a metal is negligibly small in comparison with the lattice part.

For high temperatures we have [3]

$$E = E_c + 3NkT\left(1 + \frac{1}{20}y^2 - \frac{1}{1680}y^4 + \ldots\right); \tag{1}$$

$$q = \frac{S}{3Nk} = \frac{4}{3} - \ln y + \frac{1}{40}y^2 - \frac{1}{2240}y^4 + \ldots, \tag{2}$$

where $y = \Theta/T$; E_c and Θ, cold energy and the characteristic temperature, which depend only on the volume strain; T, temperature; k, Boltzmann constant; N, number of particles. The expansions in Eqs. (1) and (2) converge rapidly for most metals beginning at room temperatures, i.e., temperatures at which shock experiments are generally performed. This enables us to limit ourselves to quadratic terms in these expansions. Eliminating the temperature from (1) and (2) we obtain

$$E = E_c + 3Nk\Theta\varphi(q), \quad \varphi(q) = e^{q-4/3}\left(1 + \frac{1}{40}e^{2(4/3-q)}\right). \tag{3}$$

It is convenient to transform Eq. (3) to a form which explicitly separates the energy of isentropic compression E_i with the entropy S_0, corresponding to the initial conditions (ordinarily $T_0 \simeq 300$°K, $p = 0$) from the entropy energy E_S

$$E = E_i + E_S, \quad E_S = 3NkT_0\frac{\Theta}{\Theta_0}\frac{\varphi(q) - \varphi(q_0)}{\varphi'(q_0)} \tag{4}$$

where the prime denotes differentiation with respect to q.

Equation (4) is valid at room temperatures and above. A similar expression can be derived for $T \ll \Theta_0$; in this case $\varphi(q) \sim q^{4/3}$. We were not able to construct an explicit expression for the internal energy as a function of the entropy for intermediate temperatures. Henceforth we consider only high temperatures.

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TABLE 1

Material	$C_{11}^{(2)}$	$C_{12}^{(2)}$	$-C_{111}^{(3)}$	$-C_{112}^{(3)}$	$-C_{123}^{(3)}$	$\frac{3NkT_0}{V_0}$	γ_0	$-\Gamma_{11}^{(2)}$	$-\Gamma_{12}^{(2)}$
	kbar								
Cu	2002	1055	22 580	6320	1030	10,5	2,01	2,2	4,2
Al	1113	610	13 290	2450	480	7,6	2,18	0,5	2,5
Pb	529	361	5 760	2190	560	4,1	2,41	2,7	4,7

It is clear from the form of Eq. (3) that the entropy and strain do not enter the internal energy in equivalent ways. The dependence of E on S does not involve the properties of the particular material. Hence it follows directly that the specific heat C_V depends only on the entropy

$$C_V = \frac{\partial E/\partial S}{\partial^2 E/\partial S^2} \simeq 3Nk\left(1 - \frac{1}{20}e^{2(4/3-q)}\right).$$

To make the dependence of E on the strain more specific it is expedient to consider separately stresses of moderate intensity and stresses produced behind strong shock fronts.

The treatment of the propagation of stress waves of moderate intensity in a material is closely related to the tensor character of the equations of state. Ordinarily, equations of state following from the generalized Hooke's law are employed for these purposes. Thermal effects are neglected.

Using Eq. (4) for the internal energy we derive complete thermodynamic equations of state in tensor form. We introduce the distortion tensor Λ to characterize the change in the radius vector **a** as a result of a uniform strain in the laboratory Cartesian coordinate system $\mathbf{a} = (1+\Lambda)\,\mathbf{a}_0$. The components of the finite strain tensor ε are expressed in terms of Λ in the form

$$\varepsilon = (1/2)(\Lambda + \Lambda^* + \Lambda^*\Lambda),$$

where the asterisk denotes transposed matrices. We expand E in a series in ε for the initial state

$$\frac{E-E_0}{V_0} = \frac{1}{2}C^{(2)}_{ikmn}\varepsilon_{ik}\varepsilon_{mn} + \frac{1}{6}C^{(3)}_{ikmnrs}\varepsilon_{ik}\varepsilon_{mn}\varepsilon_{rs} + \frac{3NkT_0}{V_0}\left(1 - \Gamma^{(1)}_{ik}\varepsilon_{ik} - \frac{1}{2}\Gamma^{(2)}_{ikmn}\varepsilon_{ik}\varepsilon_{mn}\right)\frac{\varphi(q)-\varphi(q_0)}{\varphi'(q_0)}, \tag{5}$$

where $C^{(2)}_{ikmn}$ and $C^{(3)}_{ikmnrs}$, the components of the second and third order adiabatic elastic moduli tensors, are the corresponding derivatives of E_i with respect to ε; $\Gamma^{(1)}_{ik}$ and $\Gamma^{(2)}_{ikmn}$ are the components of the first and second Gruneisen coefficient tensors.

Taking account of the small contribution of the entropy term in comparison with the isentropic part in the range of strains under consideration, we can limit ourselves to quadratic terms in ε.

The components of the stress X_{ik} as functions of the distortion tensor Λ

$$X_{ik} = \frac{1}{V}\left[(1+\Lambda)_{i\mu}\frac{\partial E}{\partial \varepsilon_{\mu\nu}}(1+\Lambda^*)_{\nu k}\right], \tag{6}$$

the temperature

$$T = T_0\left(1 - \Gamma^{(1)}_{ik}\varepsilon_{ik} - \frac{1}{2}\Gamma^{(2)}_{ikmn}\varepsilon_{ik}\varepsilon_{mn}\right)\frac{\varphi'(q)}{\varphi'(q_0)}$$

and other thermodynamic quantities can be derived from (5) in the usual way.

The fourth rank tensor $C^{(2)}$ for an isotropic material is characterized by the two Lamé coefficients; λ and μ; the third order elastic moduli tensor $C^{(3)}$ is reduced to three Murnaghan coefficients: l, m, and n. In the Voigt notation $\lambda = C^{(2)}_{12}$, $\mu = (C^{(2)}_{11} - C^{(2)}_{12})/2$, $l = C^{(3)}_{112}/2$, $m = (C^{(3)}_{111} - C^{(3)}_{112})/4$, $n = (C^{(3)}_{111} + 2C^{(3)}_{123} - 3C^{(3)}_{112})/2$. The $\Gamma^{(1)}$ tensor is transformed into a spherical tensor with a component γ_0 (the thermodynamic Gruneisen coefficient) and the quantities $\Gamma^{(2)}_{ikmn}$ are determined from the temperature dependence of the second-order elastic moduli

$$\Gamma^{(2)}_{ikmn} = -\gamma_0\left(\frac{1}{\alpha B}\frac{\partial C^{(2)}_{ikmn}}{\partial T} + \frac{\partial C^{(2)}_{ikmn}}{\partial p} - \delta_{ik}\delta_{mn} + \delta_{im}\delta_{kn} + \delta_{in}\delta_{km}\right),$$

where α is the volume coefficient of expansion, B is the bulk modulus, and the derivatives of $C^{(2)}$ with respect to the pressure p are expressed in terms of the components of the tensor $C^{(3)}$.

There are practically no reliable values of the Murnaghan coefficients in the literature. Therefore, we determine them, and for generality the Lamé coefficients also, by using the Voigt–Hill–Reuss scheme [4] to relate the elastic moduli of an isotropic polycrystal to the known values for a single crystal.

The coefficients in Eq. (5) determined in this way are listed in Table 1 for three metals.

TABLE 2

p, kbar $T_0=300$ °K	Cu		Al		Pb	
	G, kbar	ν	G, kbar	ν	G, kbar	ν
−10	457	0,345	233	0,357	70	0,407
0	473	0,345	251	0,354	84	0,406
20	503	0,346	284	0,351	102	0,407
40	530	0,348	311	0,350	113	0,411
60	553	0,349	334	0,350	121	0,415
80	575	0,351	355	0,350	125	0,420
100	594	0,352	372	0,351	127	0,424

Table 2 lists the calculated values of the effective shear modulus G and Poisson's ratio ν for isothermal compression up to a pressure of 100 kbar. The shear modulus increases by ≈50%, but ν varies much more slowly with pressure. For copper and lead ν increases monotonically by 2 and 4.5% respectively. For aluminum ν first decreases, and then above ~50 kbar it begins to increase. The decrease of ν with pressure for aluminum and its increase for copper and lead are in good agreement with the estimate of $\partial\nu/\partial p$ made in [5].

A comparison of the equations of state following from the generalized Hooke's law and from Eq. (6) showed that beginning with a strain of 2–3% there is an appreciable discrepancy in the results. For example, for a volume strain of 5% the difference in pressure is ~20%.

Analysis of the calculated temperature dependences of the coefficient of thermal expansion, the specific heat C_p, and the quantities considered above, showed that the equations of state (6) correctly describe the behavior of a material for pressures up to 100 kbar and temperatures from ~200°K to the melting point.

These equations of state can be used to construct models of elastoplastic media to solve specific problems of the mechanics of a continuous medium, in particular problems related to the repeated plastic deformation of a material, leading to a substantial increase in entropy.

To analyze the state of material attainable behind strong shock fronts and accompanying phenomena such as heating and isentropic unloading it is sufficient in a number of cases to consider volume strains only. Taking account of the appreciable increase in entropy in shock loading, it is reasonable in this case to retain only the first term in $\varphi(q)$, which corresponds to a constant specific heat $C_V = 3Nk$.

The basic relations in this approximation have the form

$$E = E_i + 3NkT_0 \frac{\Theta}{\Theta_0}(e^{q-q_0} - 1); \tag{7}$$

$$p = p_i + \frac{3NkT_0}{V}\gamma\frac{\Theta}{\Theta_0}(e^{q-q_0} - 1), \quad T = T_0\frac{\Theta}{\Theta_0}e^{q-q_0}, \tag{8}$$

where the Gruneisen coefficient γ is related to Θ by the equation

$$\Theta = \Theta_0 \exp\left(\int\limits_V^{V_0} \frac{\gamma}{V}\,dV\right). \tag{9}$$

Unknown functions E_i and γ enter Eqs. (7)–(9). An analysis of numerous calculations of the Gruneisen coefficient shows that $\gamma(V)/V$ can be assumed approximately constant and equal to γ_0/V_0. Then $\Theta = \Theta_0 \exp(\gamma_0(1-x))$, $x = V/V_0$. Any interpolation expression which can represent the cold compression energy E_c can be used to specialize the dependence of the energy of isentropic compression E_i on volume. Certain considerations show that for pressures in the megabar region, when the shell structure of the atoms has still not been disturbed [6], this dependence must be exponential

$$E_i = \frac{9}{2}V_0\frac{B_i^0}{\beta^2}[\exp(2\beta(1 - x^{1/3})) - 2\exp(\beta(1 - x^{1/3}))]. \tag{10}$$

This potential is widely used in the literature to analyze bulk properties of a material, and calculations show that it is a good approximation. The parameters in (10) are determined from the condition that the shock adiabat and the isentrope p_i have contact of the second order. If a linear relation $D = a + bu$ is used between the shock front velocity and the mass velocity, we have

$$B_i^0 = \rho_0 a^2, \quad \beta = 2(2b - 1), \tag{11}$$

where ρ_0 is the density.

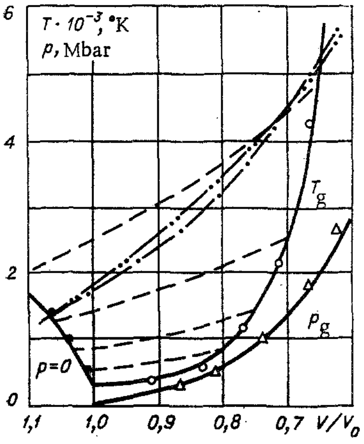

Fig. 1

TABLE 3

	Parameters	Cu	Al	Pb	Mo	W	U
I	p, Mbar	2,05	1,0	0,47	2,8	3,44	1,16
	T, °K	5370	3500	2500	7000	9350	3800
	V/V_0	0,648	0,645	0,700	0,657	0,650	0,700
	u, km/sec	2,8	3,55	1,1	3,1	2,5	1,36
II	p, Mbar	1,5	0,65	0,25	2,25	2,85	0,9
	u, km/sec	2,3	2,65	0,75	2,7	2,2	1,15
	T_{mp}, °K, $p=0$	1356	933	600	2898	3659	1406
	$T_{\text{mp}}(V_0)$, °K	1705	1136	692	3214	4123	1571

Equations (7)-(11) represent a completely determined system of functions which can be used to calculate and analyze the properties of a material at high hydrodynamic pressures and high temperatures. Using these equations we calculated shock adiabats, bulk sound speeds, the temperature behind shock fronts, residual temperatures, and a number of other thermomechanical properties of a material. The most significant quantity in the sense of interpolation properties of the expression chosen for the internal energy is the speed of sound, since it characterizes the slope of the shock adiabat. For all the metals considered (Cu, Al, Pb, Mo, W, U) the discrepancy between our calculations and the experimental values in [7] and the dependence of the speed of sound on pressure calculated in [8] did not exceed a few percent up to compressions $x \approx 0.65$.

The solid curves of Fig. 1 are the calculated shock adiabats for copper in T–V and p–V variables. The points plotted are experimental values of p_g and calculated values of T_g from [7]. They are in good agreement with our calculations. The dashed curves represent unloading isentropes from the shock adiabat to zero pressure. The isobar $p=0$ is on the left-hand side of Fig. 1. The plotted points are calculated from the temperature dependence of the coefficient of thermal expansion. Similar results hold for other metals also.

It follows from the results presented above that Eqs. (7)-(11) are suitable for investigating the behavior of metals under large dynamic loads. Equations (8) make it possible to reduce the Lindemann melting criterion relating the melting point to the characteristic temperature Θ to the form [2]

$$T_{\text{mp}}(V) = T_{\text{mp}}(V_0)\left(\frac{\Theta}{\Theta_0}\right)^2\left(\frac{V}{V_0}\right)^{2/3} = T_{\text{mp}}(V_0)\, x^{2/3}\, e^{2\gamma_0(1-x)}, \tag{12}$$

where $T_{\text{mp}}(V_0)$ is the melting point at constant volume V_0. Its values calculated from Eqs. (8) and the experimental melting point at zero pressure are shown in Table 3. It can be seen from (12) that within the framework of the approximations chosen, the melting point is determined by the volume of the material only.

The dot–dash curve in Fig. 1 is the melting curve (12). The general character of its behavior agrees with the experimental fact that the entropy increases on melting (the melting curve intersects the unloading isentropes). There is a range of states on the shock adiabat where the material behind the shock front is solid but melts in the unloading wave. The values listed in part I of Table 3 are the critical pressures, temperatures, volumes, and mass velocities starting from which melting is possible in a shock wave, and the values in part II are the pressures and mass velocities of a shock wave beginning from which partial melting of the unloaded material may occur. The values in part II are considerably smaller than the corresponding values in part I.

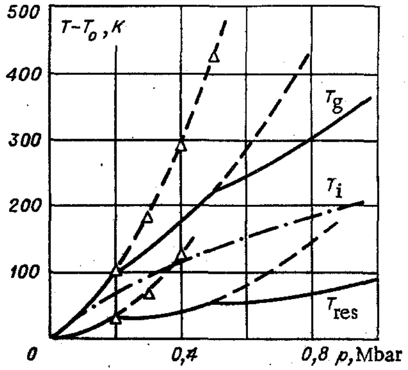

Fig. 2

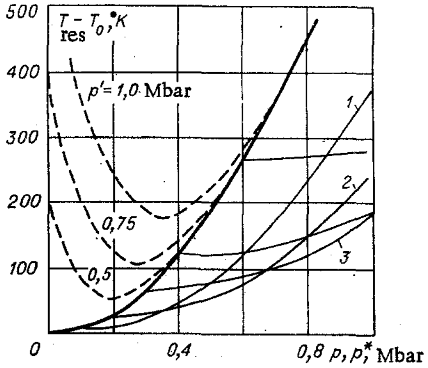

Fig. 3

TABLE 4

p′, Mbar	Cu			W		
	$T-T_0$, °K	p*, Mbar	$T-T_0$, °K	$T-T_0$, °K	p*, Mbar	$T-T_0$, °K
1,00	650	0,35	175	485	0,42	125
0,75	400	0,25	105	260	0,32	65
0,50	190	0,17	50	100	0,21	24

The dot–dot–dash curve in Fig. 1 is the melting curve from [9] where it was calculated for copper, aluminum, and lead. There is good agreement between (12) and the corresponding relation from [9] for copper and aluminum. For lead the melting curve from [9] is appreciably lower. This appears to result from the fact that our calculations do not take account of the electron component, which plays an appreciable role in lead according to estimates in the literature.

Figure 2 for copper shows the dependence of the temperature along the shock adiabat T_g and the residual temperature T_{res} on the pressure behind a shock front for a three-stage loading. The pressures of 200 kbar behind the first shock front and 500 kbar behind the second were chosen arbitrarily. The dashed curves indicate the behavior of the relations when there are no repeated loadings. The points plotted were calculated in [8], and T_i is the temperature of the material in an isentropic compression.

It is clear from Fig. 2 that multistage loading has an appreciable effect on the T−p diagram. As the number of loading stages is increased the slope of the T_g(p) curve decreases, while the residual temperature remains practically constant over a wide range of pressures. This behavior of shock adiabats indicates that isentropic (really quasiisentropic) compression can be achieved by a small number of successive loadings.

In Fig. 3 the solid curves for copper show the dependence of the residual temperature on the pressure p behind the secondary shock front as a function of the pressure p* in the primary wave. The open curves show the dependence of the residual temperature on p* for a fixed pressure behind the secondary wave front. It can be seen from Fig. 3 that there is a certain pressure in the primary wave which ensures the minimum residual temperature after isentropic unloading from the secondary adiabat with a given pressure. The optimum value of p* is 30–40% of the pressure in the secondary wave, and the residual temperature is approximately a factor of four lower than with a single loading up to the same pressure. Table 4 shows the corresponding values for copper and tungsten. The first column gives the pressure p′ on the shock adiabat; the second and fifth columns give the residual temperatures after a single loading to a pressure p′; the third and sixth columns give the optimum pressure p* in the first wave; the fourth and seventh columns give the minimum residual temperatures which can be obtained in two-stage loading to the pressure p′.

The proposed equations of state, based on the representation of the internal energy as the sum of the isentropic compression energy and the entropy energy, are superior to existing equations in permitting a simpler treatment of isentropic processes, which is particularly important in the analysis of unloading processes. By introducing the characteristic temperature into the entropy part the melting curve can be directly related to the equation of state of the material in terms of the Lindemann melting criterion. In contrast with [1] the proposed melting criterion (12) correctly describes the behavior of the entropy during melting, and is considerably more convenient in practical use than [9].

The results obtained can be used directly to develop models of continuous media and to analyze the behavior of a material in a dynamic action.

LITERATURE CITED

1. V. E. Fortov, "Equations of state of condensed media," Prikl. Mekh. Tekh. Fiz., No. 6 (1972).
2. V. N. Zharkov and V. A. Kalinin, Equations of State of Solids at High Pressures and Temperatures [in Russian], Nauka, Moscow (1968).
3. L. A. Girifalco, Statistical Physics of Materials, Wiley (1973).
4. G. R. Barsch, "Relation between third-order elastic constants of single crystals and polycrystals," J. Appl. Phys., 39, No. 8 (1968).
5. J. P. Romain, A. Migault, and J. Jacquesson, "Relation between the Gruneisen ratio and the pressure dependence of Poisson's ratio," J. Phys. Chem. Sol., 37, No. 12 (1976).
6. G. V. Shpatakovskaya, "Shell effects in the equation of state of a cold highly compressed material," in: Numerical Methods of the Mechanics of Continuous Media [in Russian], Vol. 7, VTs SO Akad. Nauk, USSR, Novosibirsk (1976), No. 1.
7. L. V. Al'tshuler, S. V. Kormer, M. I. Brazhnik, L. A. Vladimirov, M. P. Speranskaya, and A. I. Funtikov, "The isentropic compressibility of Al, Cu, Pb, and Fe at high pressures," Zh. Éksp. Teor. Fiz., 38, No. 4 (1960).
8. F. A. Baum, L. P. Orlenko, et al., Physics of Explosions [in Russian], Nauka, Moscow (1975).
9. V. D. Urlin, Melting at Ultra-High Pressures in a Shock Wave, Zh. Éksp. Teor. Fiz., 49, No. 2 (1965).

DETERMINATION OF THE BEHAVIOR OF A STANDARD LINEAR BODY IN A PLASTOMERE OF PLANE-PARALLEL SHEAR

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Consider the behavior of a plastomere containing an easily deformed material, whose local mechanical properties are described by a model of a standard linear body [1-4], represented by three physical quantities: the viscosity η, the instantaneous shear modulus G_0, and the long-term shear modulus μ.

A plastomere, intended for investigating nonflowing materials, is shown schematically in Fig. 1, where 1 is a steel plate rigidly connected to the instrument, 2 is the specimen of thickness l, 3 is the sheared rigid plate, 4 is an indicator rod rigidly attached to the sheared plate, 5 is a retainer for fixing the initial state of the system and for producing the required initial conditions of motion of the plate, 6 is a pulley with a reduced moment of inertia I and external radius R, M_0 is the reduced mass of the sheared plate and the attached rod, P_1 and P_0 are the loads attached to the sheared plate, u(x, t) is the displacement function of an infinitely thin vertical layer of the material investigated in the direction in which the external forces of plane-parallel shear act, x is the axis of coordinates, and t is the time. The load P_0 is connected to the plate with a steel wire. The specimen used has a rigidity much less than the rigidity of the instrument parts [5]. In the initial state the position of the rod is held rigidly by means of the retainer. At the instant of time $t=0$ the upper end of the rod is released from the retainer and the plate begins to move under the action of the resulting load $P=P_1+M_0g-P_0$. Then the connecting mass [5] $M=M_0+(P_1+P_0)/g+I/R^2$, where P_1/g, P_0/g, and I/R^2 are the reduced masses of the loads P_1 and P_0 and of the rotating pulley, and g is the acceleration due to gravity. It is assumed that the force of friction f in the bearings of the pulley is much less than the load P, so that it can be neglected [5]. This system differs considerably from the plastomere used in [5-7]. Its distinguishing features are as follows.

1. Since the shear load is the complex quantity $P=P_1-P_0+M_0g$, and $M=M_0+(P_1+P_0)/g+I/R^2$, for the same values of I, R, and P, one can increase or decrease the value of M over a wide range by varying P_1 and P_0 while keeping P constant. This enables one to investigate materials both when the system is oscillating and under aperiodic conditions.

2. The system enables one to eliminate f by removing the load P_0.

Since the above viscoelastic characteristics of easily deformed materials may depend, in particular, on the temperature T [4] and this may cause deformation of the specimen, the experimental conditions must be

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