

## THERMODYNAMIC PARAMETERS OF LITHIUM DEUTERIDE IN PRESSURE RANGE 5–1000 GIGAPASCALS

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**Summary.** The results of numerical experiments on shock-wave loading of lithium deuteride using the thermodynamic equilibrium model of TEC (thermodynamic equilibrium components) are presented. The developed model allows us to describe thermodynamic parameters of lithium deuteride of different porosity, in a wide range of pressures using model relations, the experimental and theoretical data for lithium deuteride. Comparison of calculated results with experimental data confirms the validity and acceptable accuracy of the used model equations.

### 1 INTRODUCTION

It is well known that compounds of lithium with hydrogen are of interest as applied as fundamental points of view. Compounds of lithium isotopes with hydrogen isotopes possess some unique properties and are used as an important element in various structures. There are many works devoted to the study of thermophysical properties of these compounds, in which a huge part is occupied by investigations at high shock and static pressures [1–8]. Thermodynamic equilibrium model TEC (thermodynamic equilibrium components) was considered in works [9–12] in relation to some materials. This model allows us to describe the thermodynamic parameters of the samples under shock wave loading in wide range of pressures, including those for mixtures whose components may experience polymorphic phase transition.

The purpose of this article is to adapt this model to shock wave loading of mixtures comprising lithium deuteride LiD. The parameters of the equation of state, which is developed for this model, can be used for calculations of thermodynamic parameters as for the pure LiD, as for mixtures and alloys comprising LiD in its composition, as at relatively low pressures and temperatures as at in high pressures, temperatures and densities, the condition in which can be judged only by theoretical models. Comparison of model TEC calculations with experimental data and calculations by other models, which confirms the validity and acceptable accuracy of used model relations. In this work, as an example, we show the capabilities of the modeling of mixture of LiD with lithium Li. These simulation results allow one to accurately describe the thermodynamic parameters of the compounds consisting of complex components in its composition.

**2010 Mathematics Subject Classification:** 74A15, 74J40, 76L05, 80A10, 82D32.

**Key words and phrases:** equation of state, lithium deuteride, shock wave, high pressure, thermodynamic equilibrium.

## 2 MODEL TEC

In order to calculate thermodynamic parameters of porous mixtures under dynamic loadings, the model of shock-wave loading with allowance for gas in the pores is used [9–13]. The model is based on the assumption of thermodynamic equilibrium of all the components of a material under shock-wave loading. The choice of the equation of state (EOS) of matter is very important when building any model, for example see work [14]. The most complete review of modern approaches to choice of EOS for condensed media is given in [15]. In order to describe the behavior of condensed phases, the equations of state of Mie–Grüneisen type are used. The equations that determine the state of the condensed component are written as follows:

$$P(\rho, T) = P_C(\rho) + P_T(\rho, T), \quad E(\rho, T) = E_C(\rho) + E_T(T), \quad (1)$$

$$P_T(\rho, T) = \Gamma \rho E_T(T), \quad E_T(T) = c_V(T - T_0). \quad (2)$$

Here  $P_C$ ,  $E_C$ ,  $P_T$ , and  $E_T$  are the potential and thermal components of pressure and specific energy, respectively;  $c_V$  is the specific heat capacity;  $T_0$  is the initial temperature; and the function  $\Gamma = P_TV/E_T$  that determines the contribution of the thermal component depends explicitly only on the temperature  $\Gamma(T)$  in the model [9–11]. Cold pressure component  $P_C$  is described by Tait-type equation. Therefore, the thermal and caloric forms of the equation of state for a condensed component with current density  $\rho$  and initial density  $\rho_0$  are as follows:

$$P(\rho, T) = A \left[ (\rho/\rho_0)^k - 1 \right] + \Gamma \rho c_V(T - T_0), \quad (3)$$

$$E(\rho, T) = A/\rho_0 \left[ 1/(k-1) (\rho/\rho_0)^{k-1} + \rho_0/\rho - k/(k-1) \right] + E_T. \quad (4)$$

The ideal gas equation of state is taken for a gas. The conditions of dynamic compatibility at the wave front are written, namely, the conditions of conservation of the mass flux for each component of the material and the conditions of conservation of momentum and energy fluxes for the media considered as a whole. The obtained equations, together with the equations of state of each component, are sufficient to find dependences  $P(U)$  or  $D(U)$  ( $P$ ,  $U$ , and  $D$  are the pressure, mass velocity, and wave velocity, respectively;  $A$ ,  $k$  the coefficients in the equations of state of condensed component). These dependences can be treated as a shock adiabat of a multicomponent material. The following expression can be obtained for a material with  $n$  condensed components ( $\mu_{i0}$  is the volume fraction of  $i$ -th condensed component):

$$P = \frac{\sum_{i=1}^n \mu_{i0}/(\sigma_i) A_i \left[ \left( h_i - \frac{k_i+1}{k_i-1} \right) \sigma_i^{k_i} + \frac{2k_i \sigma_i}{k_i-1} - h_i - 1 \right]}{\sum_{i=1}^n \frac{\mu_{i0}}{\sigma_i} h_i + \frac{h_g}{\sigma_g} (1 - \sum_{i=1}^n \mu_{i0}) - 1}. \quad (5)$$

Here  $h_i = 2/\Gamma_i + 1$ ,  $i = 1, \dots, n$ ;  $h_g = 2/(\gamma - 1) + 1$ ;  $\sigma_i = \rho_i/\rho_{i0}$ ,  $\sigma_g = \rho_g/\rho_{g0}$  are the compression ratios of the corresponding component,  $\mu_{i0}$  is the volume fraction,  $\rho_{i0}$ ,  $\rho_i$  are the density of the  $i$ -th phase of the substance ahead of the shock wave front and behind it, respectively ( $i = 1, \dots, n$ , and  $g$ );  $\gamma = 1.41$  (ratio of specific heats). By adding to equation (5)  $n$  relationships following from the equations of state of  $n + 1$  components and expressing the equality in the temperatures of all the components, we finally have  $n + 1$  equations for  $n + 2$  unknowns  $P$ ,  $\sigma_i$  ( $i = 1, \dots, n$  and  $g$ ), which allow us to construct the shock adiabat of the material. In the case of calculation of the behavior of a solid material, we assume that  $\sum_{i=1}^n \mu_{i0} = 1$ . The analysis of the experimental data of solid and porous materials resulted in the empirical dependence of Grüneisen coefficient on temperature in the following form:

$$\Gamma(T) = \left[ (\Gamma(T_0) - \Gamma(T_\infty))^{-1} + C(T - T_0) \right]^{-1} + \Gamma(T_\infty). \quad (6)$$

Coefficient  $C$ , which allows describing the experimental points upon moderate compression, is determined by intermediate value  $\Gamma(T_*)$  at temperature  $T = T_*$ , as follows:

$$C = \left[ (\Gamma(T_*) - \Gamma(T_\infty))^{-1} - (\Gamma(T_0) - \Gamma(T_\infty))^{-1} \right]^{-1} / (T_* - T_0). \quad (7)$$

Asymptotic value  $\Gamma_\infty$  corresponds to the maximum temperatures.

It should be noted that the possibility of calculation of the behavior of the mixture model of TEC allowed to describe the phase transition of materials under shock wave loading [12]. The material is considered in this area as a mixture of the low-pressure phase and high-pressure phase. Models in which one of the phases was changed in the shock wave were used in the calculations [16, 17] for samples of graphite.

### 3 MODELING RESULTS

The simulation results for the thermodynamic parameters of LiD with average density  $\rho_0 = 0.891 \text{ g/cm}^3$  and the data obtained by experiments [6, 18] are shown in figure 1 in the variables pressure  $P$  versus compression ratio  $\sigma$  for solid samples  $m = 1$  (porosity  $m$  is ratio of density of solid substance to the density of sample). The limit value of the pressure is 600 GPa. The calculations for the solid and porous samples with  $m = 1.061$  are shown in figure 2. The truthful description of the available data is obtained. Because of the large uncertainty of the points of phase transition in lithium deuteride, the equation of state is developed in the single-phase approximation.

Calculation of thermodynamic parameters for lithium-6 deuteride  ${}^6\text{LiD}$  was performed to determine the reliability of the description of thermodynamic parameters at higher pressures. The results of the simulation and the data [18, 19] are shown in figure 3.

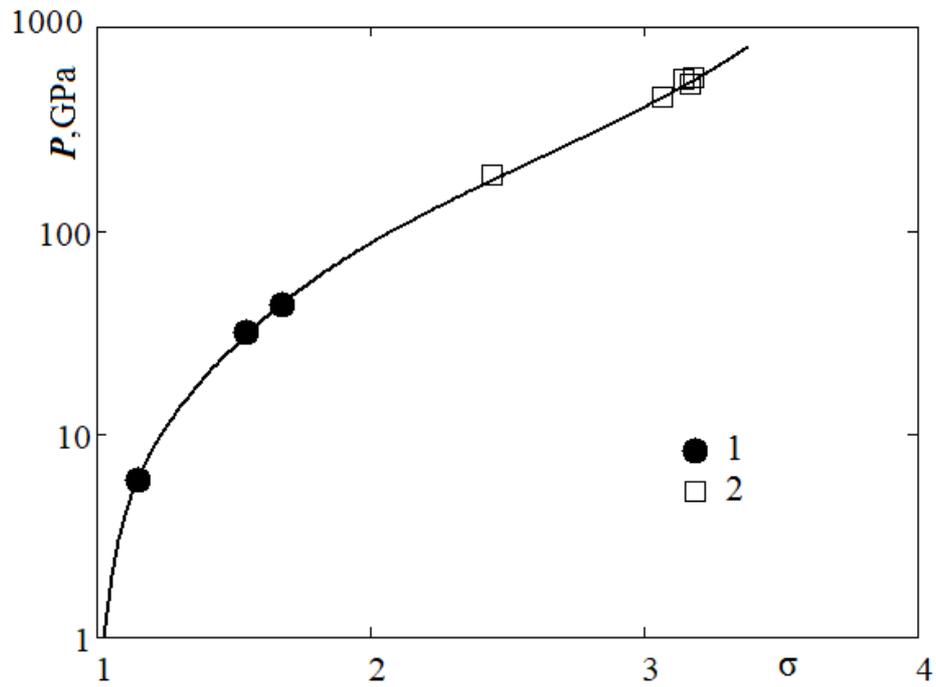


Figure 1. The shock adiabat of LiD. Solid line is from the calculation with the model TEC. Dark circles 1 are from paper [18]; open squares 2 are from paper [6].

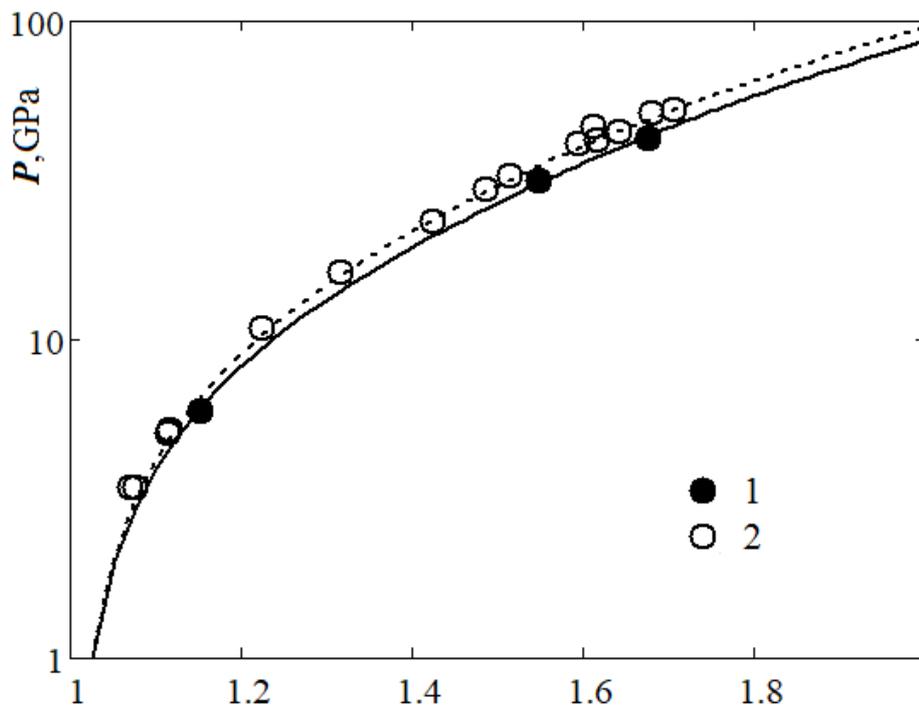


Figure 2. The shock adiabat of LiD. Solid line is from the calculation with the model TEC. Dark circles 1— $m = 1$ ; open circles 2— $m = 1.061$ ; all markers are from paper [18].

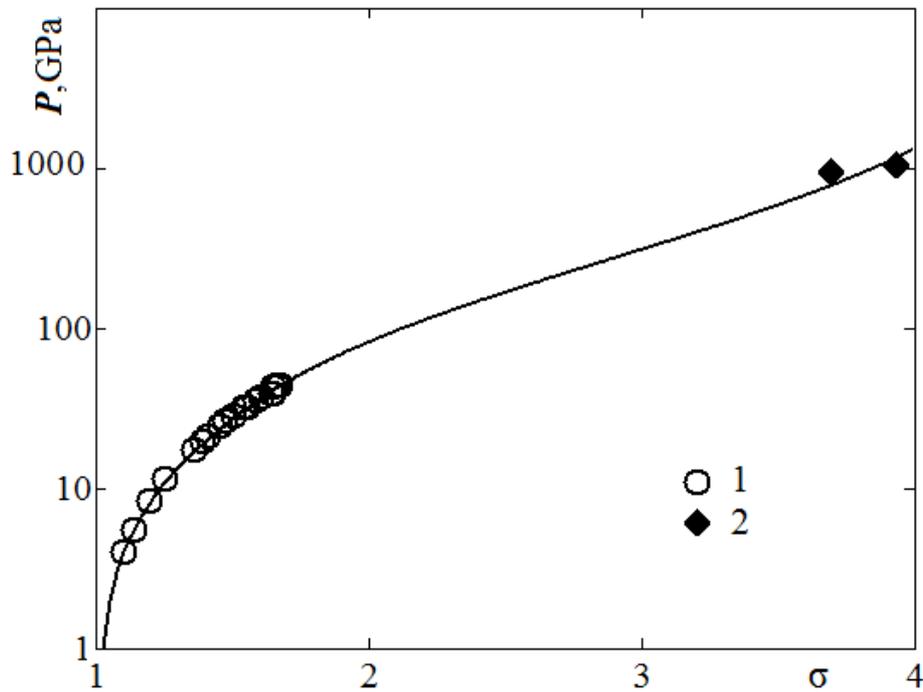


Figure 3. The shock adiabat of  ${}^6\text{LiD}$ . Solid line is from the calculation with the model TEC. Open circles 1 are from paper [18]; dark diamonds 2 are from paper [19].

The calculation results are in a good agreement with the data over whole investigated region to pressure of 1000 GPa. The calculations and data obtained by experiments for porous  ${}^6\text{LiD}$  samples with porosity 1.045, 1.081, 1.02 are shown in figure 4.

We need to know only mixture composition for the description of thermodynamic parameters of dynamic loading of mixture by model TEC. The component parameters are taken the same as in the description of pure substances. On the basis of subsequent calculations it was possible to obtain the conclusion that the parameters defined for LiD allow to describe data both for pure materials and for solid and porous mixtures with the accuracy of experiment. The calculations for mixtures of  ${}^6\text{LiD}$  with Li were performed. The parameters for pure lithium were determined provisionally. The simulation results for Li  $\rho_0 = 0.534 \text{ g/cm}^3$  is shown in figure 5. Thermodynamic parameters for the mixture  ${}^6\text{LiD}$ –Li with volume fraction 50 vol % of  ${}^6\text{LiD}$  to 50 vol % of Li respectively are described in figure 6. The model calculations and experimental data for components of mixtures are shown there for comparison.

The good correspondence of the calculated results with data obtained in experiments for pure materials LiD,  ${}^6\text{LiD}$  and Li is shown. The deviation of the calculations from the data obtained on the basis of experiments for  ${}^6\text{LiD}$  with  $m$  more than 1.2 probably due, in part, to the possible existence of polymorphic phase transition.

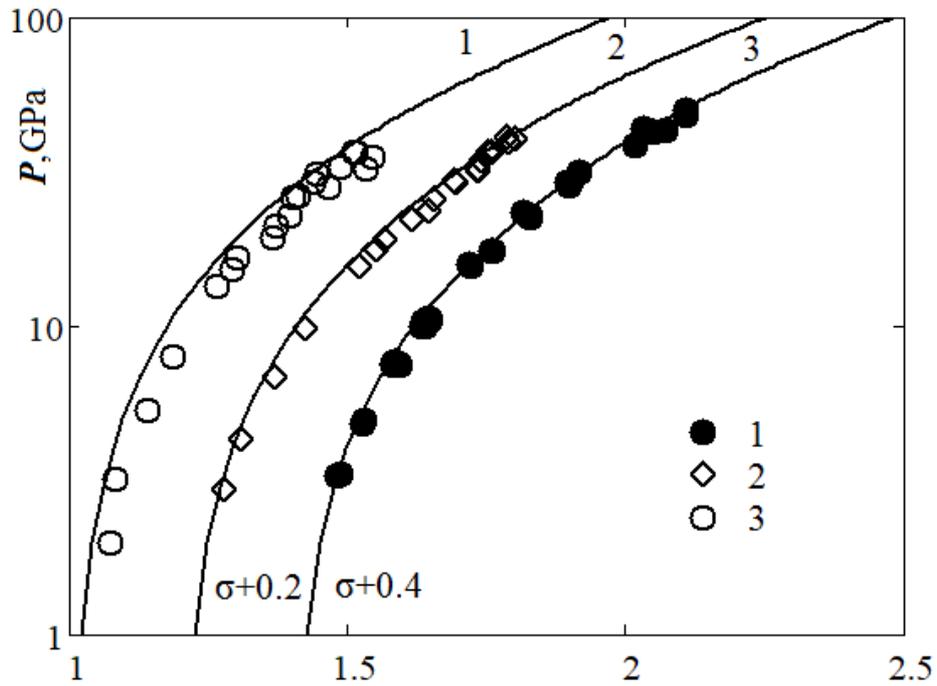


Figure 4. The shock adiabat of  ${}^6\text{LiD}$ . Solid line is from the calculation with the model TEC. The experimental data dark circles 1  $m = 1.045$ , diamonds 2  $m = 1.081$  and open circles 3  $m = 1.2$  are from paper [18].

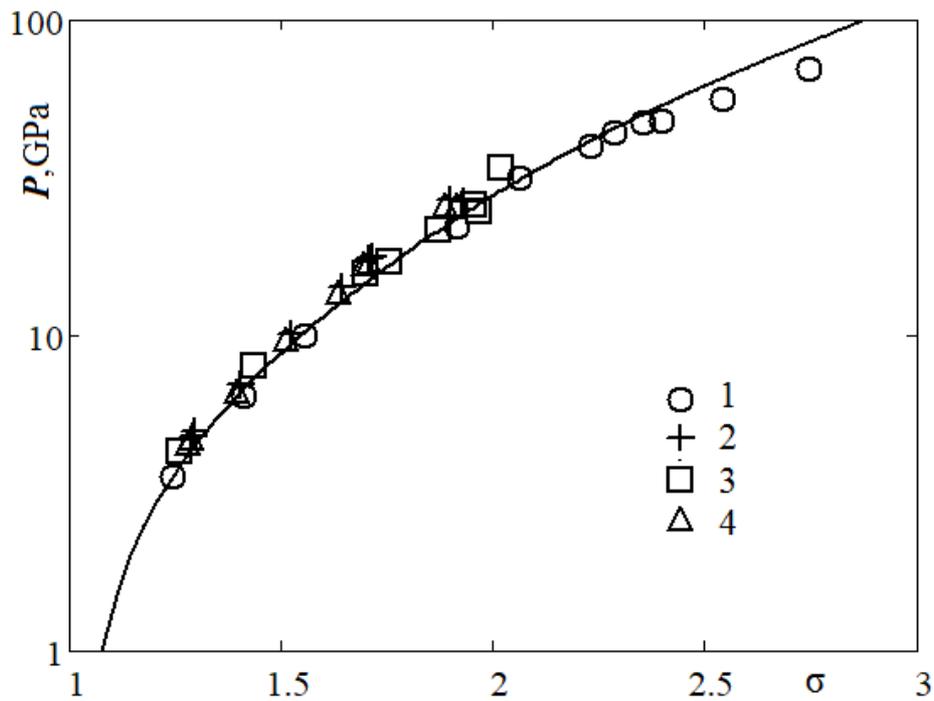


Figure 5. The shock adiabat of lithium. Open circles are from paper [20]; crosses are from paper [21]; open squares are from paper [22]; open triangles are from paper [18].

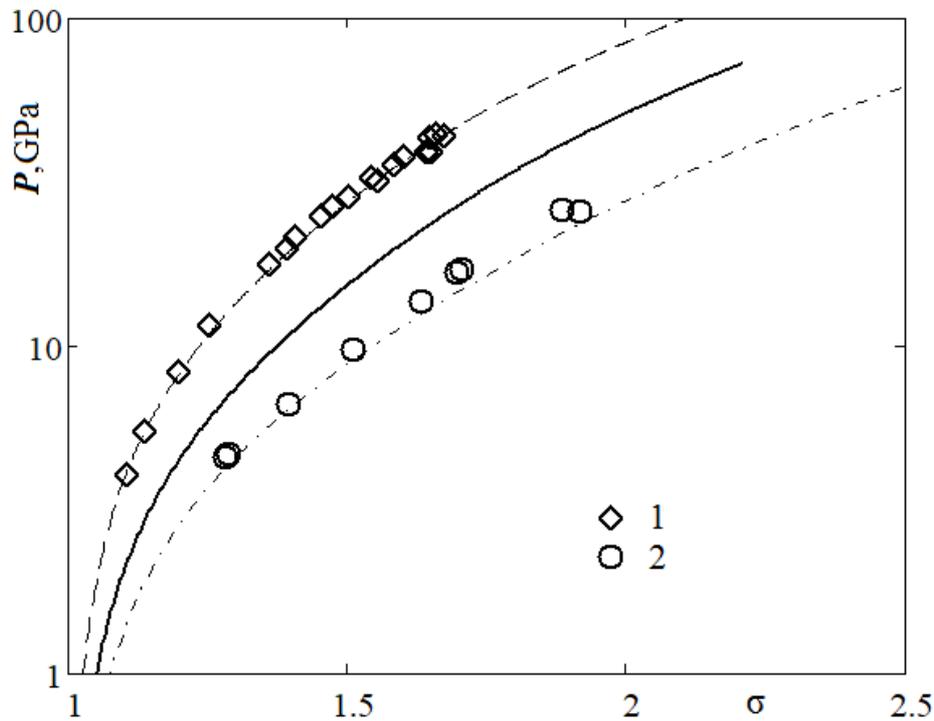


Figure 6. The shock adiabats for the mixture  ${}^6\text{LiD-Li}$ . Solid line is from the calculation for mixture; dotted line—for  ${}^6\text{LiD}$ ; touch dotted line—for Li. Open diamonds 1 and open circles 2 are from paper [18].

In the presence of experimental data that allow to accurately determine the region of phase transition, the model TEC can be used and in this case, similarly to [23, 24].

#### 4 CONCLUSIONS

The EOS of Mie–Grüneisen type together with the condition of thermodynamic equilibrium of the mixture components gives a closed system of equations that defines the properties under dynamic loading, taking into account the interaction between the components. The selected model parameters allowed to reliably describe the thermodynamic properties of the pure LiD,  ${}^6\text{LiD}$ , Li and mixtures on their basis. As a result, in order to describe the behavior of a mixture under dynamic loadings, it is necessary to know only the volume fractions of its components. It is recommended to use this model both in the range of comparatively moderate pressures and temperatures available for experimental investigations and in the range of high pressures, temperatures, and densities where the states can be currently estimated only theoretically.

**Acknowledgments:** The paper is based on the proceedings of the XXXIII International Conference on Equations of State for Matter, which was held in Elbrus and Tegenekli settlements, in the Kabardino-Balkar Republic of the Russian Federation, from March 1 to 6, 2018.

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