BaI-BaII phase boundary and the maximum on the melting curve of BaI at high pressures

Yu. A. Boguslavskiĭ, F. F. Voronov, M. A. Il'ina, and O. V. Stal'gorova

Institute of High Pressure Physics, USSR Academy of Sciences
(Submitted 7 July 1978)
Zh. Eksp. Teor. Fiz. 77, 946–951 (September 1979)

The slope of BaI–BaII phase boundary is calculated from the results of ultrasonic investigations of the elastic properties of solids under pressure, with barium as the example. This boundary is experimentally determined from the jumps of the resistivity of barium in the temperature interval 100–350 K and in the pressure range 50–62 kbar. The calculated and experimentally obtained slopes of the BaI–BaII phase boundary are negative and their values are in good agreement (-27 ± 10 and -30 ± 10 deg/kbar). An expression for the melting temperature of solids at high pressures in terms of the elastic-wave propagation velocity is obtained on the basis of the Lindemann criterion and the theory of finite deformations. It is shown that in the case of barium the onset of the maximum is due to anomalies in the behavior of the rate of propagation of the shear waves under pressure. The singularities of the BaI phase boundaries are attributed to the onset, at high pressures, of the soft shear acoustic modes *TA* 1 and *TA* 2 in the phonon spectrum of barium.

PACS numbers: 64.70.Dv, 62.30. + d, 62.50. + p

Polymorphism in the melting of barium at high pressures has been the subject of many investigations, carried out by various methods, in a wide range of pressures and temperatures. The results are used to construct and discuss the phase diagram of barium.[1–5]

Barium under pressure undergoes at 293 K a bcc–hcp structural phase transition, designated BaI–BaII. The pressure at which this transition takes place was determined in a number of studies[6–8] and amounts, according to Ref. 8, to 56.8 ± 0.7 kbar. This point is used as the reference in the calibration of high-pressure chambers, so that the question of the slope (dT/dp) of the phase boundary of the BaI–BaII transition is important. However, the published data are contradictory and disagree not only quantitatively but also qualitatively. Thus, measurements by the method of differential-thermal analysis (DTA) yielded positive values of the slppe, $dT/dp = 22.0$ deg/kbar (Ref. 5) and $dT/dp = 58.8$ deg/kbar (Ref. 3), while measurements in apparatus of the cylinder–piston type[7] and using a piston manometer[9] yield an almost vertical BaI–BaII boundary, while in Ref. 10 the method of resistivity jumps yielded a negative value $dT/dp = -35.0$ deg/kbar (estimated from the figure, see below).

An interesting feature of the phase diagram of barium is the presence of a maximum on the melting point at pressures near 14 kbar and at a temperature 770 °C.[4,5]

In our investigations of the elastic properties of barium, we obtained the first information on the change of the low-frequency branch of the phonon spectrum of barium at pressures up to 70 kbar and at a temperature 293 K.[11] The observed decrease of the propagation velocities of the shear waves at pressures higher than 30 kbar points to the onset of soft acoustic modes TA1 and TA2 long ahead of the phase transition.

It is of interest in principle to consider the phase diagram of barium by starting from the singularities of the phonon spectrum of barium at high pressures and by resorting to additional experimental research.

THE Ba I-Ba II PHASE BOUNDARY

We now calculate the slope of the BaI–BaII phase boundary at the phase-transition point $p = 56.8$ kbar, $T = 293$ K. We write down the thermodynamic potential of a solid in the Debye approximation[12]

$$\Phi=\Phi_0(p)+N\nu T[3\ln(1-e^{-\Theta/T})-D(\Theta/T)]$$

(the notation here is the same as in Ref. 12). From the thermodynamic potential we obtain the value of the entropy per atom:

$$S=-[3\ln(1-e^{-\Theta/T})-4D(\Theta/T)].$$

This expression enables us to calculate the entropy S_1 for BaI and the entropy S_2 for BaII at the phase-transition pressure. Using the values given in Ref. 11 for the Debye temperatures at $p = 56.8$ kbar and 293 K : $\Theta_1 = 128.4 \pm 1.3$ K for the bcc phase and $\Theta_2 = 115.0 \pm 2.3$ K for the hcp phase, we obtain respectively $S_1 = 6.49 \pm 0.03$ and $S_2 = 6.82 \pm 0.04$. We determine the slope of the phase boundary from the Clausius–Clapeyron equation, using a volume jump[5,13] $\Delta V/V_0 = (1.9 \pm 0.2)\%$:

$$\frac{dT}{dp}=\frac{V_2-V_1}{k(S_2-S_1)}=-27\pm10\,\frac{\text{deg}}{\text{kbar}},$$

where V_1 and V_2 are the volumes per atom in BaI and BaII, respectively. It follows therefore that the phase transition is accompanied by absorption of heat. The obtained value -27 ± 10 deg/kbar agrees with the data of Ref. 10 and disagrees with the rssults obtained by the DTA method in Refs. 3 and 5.

The BaI–BaII phase boundary was investigated by us experimentally in the temperature interval 100–350 K and at pressures 50–62 kbar from the jumps of the electric resistivity of barium with changing pressure or temperature. These measurements were made for barium for the first time ever. The measurements were performed on 99.6% barium wires with diameter 0.3 mm and length 5–8 cm, placed in silver chloride and in a catlinite container in accordance with the procedure described previously.[14] The chamber was calibrated at room temperature using the jumps of the resistivity of Bi, Tl, and Ba, and the transition pressures were taken to be 25.4, 39.4, and 56.8 kbar in accordance with Ref. 8. The measurement results are marked on the barium phase diagram plotted in accordance with the published data,[1,3,5,10] and reduced to a pressure scale in accordance with Ref. 8. It should be noted that our values of p and those from Ref. 10, which are marked on the phase diagram, were obtained while the pressure was increased along the isotherms, while the values of T were obtained with increasing temperature along the isobars.

The obtained values of p and T for the BaI–BaII transition yield the estimate $dT/dp = -30 \pm 10$ deg/kbar and lie on the common line drawn through the results of Ref. 10. Thus, the value of dT/dp obtained by us in experiment is also negative and agrees well with calculation based on ultrasonic measurements.

We note that the determination of the slope of the phase boundaries from ultrasonic data using the Debye model is possible only for a number of solids with simple crystal lattices in the absence of strong anisotropy of the elastic properties. The transition between the phases must be reversible.

MAXIMUM ON THE MELTING CURVE OF Ba I

To determine the dependence of the melting temperature on the pressure we start from the vibrational theories of melting, and accordingly assume the Lindemann criterion to be valid. The Lindemann criterion and the Debye model were used earlier to predict the melting curves of solids (see, e.g., Ref. 15). In those papers, however, the Debye temperature under pressure was estimated from the dependences of the volume and of the bulk elastic modulus on the pressure, without allowance for the singularities of the shear characteristics of the solids, using therefore only a rough approximation.

We obtain an expression for the melting temperature in terms of the propagation velocity of the elastic waves, using the theory of finite deformations, without using the Debye model of a solid. It is known that the probability of the change of the total free energy of a solid due to fluctuations at constant temperature and at a constant total volume of the body is

$$W \sim \exp(-\Delta F/T). \tag{1}$$

In our experiment the change of the total free energy of an isotropic body, in the case of fluctuations under conditions of the hydrostatic compression, is

$$\Delta F = \int (F - \bar{F})\, dV = \frac{1}{2}(1+2\eta)^2 \int (\lambda e_{ii}^2 + 2\mu e_{ik}^2)\, dV,$$

where F is the free energy per unit volume of the undeformed body, $e_{ij} = 1/2(\partial u_i/\partial x_j + \partial u_j/\partial x_i)$ are the components of the fluctuation deformation tensor, x_i is the coordinate that characterizes the initial deformed state, u_i are the components of the vector of the fluctuation displacement from the initial deformed state at the given instant, η is the final deformation in Lagrange variables under hydrostatic compression, and $\lambda(\eta)$ and $\mu(\eta)$ are Lamê coefficients, which are functions of the final deformation.

We represent the vector of the fluctuation displacement of a small section in the form of a Fourier series

$$\mathbf{u} = \sum_n \mathbf{u}_n e^{i\mathbf{n}\mathbf{x}},$$

with the vector $\mathbf{n}$ assuming both positive and negative values; since $\mathbf{u}_n$ is real, the condition $\mathbf{u}_{-n} = \mathbf{u}_n^*$ is satisfied. The expansion contains terms with not very large vectors ($|\mathbf{n}| \leqslant 1/d$, where d is the linear dimension of the displaced section).

We find next that ΔF is of the form

$$\Delta F = \frac{1}{2}(1+2\eta)^2 V \Sigma u_{in} u_{ln}^* \varphi_{il}(n_1, n_2, n_3),$$

where

$$\varphi_{il} = (\lambda+\mu) n_i n_l + \mu \delta_{il} n^2.$$

For the mean squared fluctuations of the Fourier components of the displacement vector we have, taking (1) into account,

$$\langle u_{in} u_{ln} \rangle = \frac{T}{V(1+2\eta)^2} \varphi_{il}^{-1}, \tag{2}$$

where φ_{il}^{-1} are the components of the tensor inverse to the tensor φ_{il}. The mean values $\langle u_i u_l \rangle$ are obtained by changing over in (2) in the usual manner from summation over $\mathbf{n}$ to integration with respect to n:

$$\langle u_i u_k \rangle = 0 \quad \text{at} \quad i \neq k,$$

$$\langle u_i^2 \rangle = \frac{T}{(1+2\eta)^2} \left[\frac{2}{\mu} + \frac{1}{\lambda + 2\mu} \right] \frac{1}{d}.$$

We use next the Lindemann melting criterion $\langle u_i^2 \rangle / d^2 = \text{const}$ and change over, with the aid of the method of finite deformations,[16] from the Lamê coefficients to the velocities of longitudinal and transverse ultrasonic waves under pressure:

$$\rho v_l^2 = -p + (1+2\eta)^{1/2}(\lambda + 2\mu), \quad \rho v_t^2 = -p + (1+2\eta)^{1/2}\mu.$$

As a result we obtain ultimately

$$T_{\text{melt}}(p) = T_0 \frac{\rho_0}{\rho} \left(\frac{2}{v_{t0}^2} + \frac{1}{v_{l0}^2} \right) \left(\frac{2}{v_t^2 + p/\rho} + \frac{1}{v_l^2 + p/\rho} \right)^{-1}. \tag{3}$$

This expression differs from the formula that can be obtained for the melting temperature by starting from the Lindemann criterion and the Debye model of a solid:

$$T_{\text{melt}}(p) = T_0 \frac{\Theta^2 \rho_0^{2/3}}{\Theta_0^2 \rho^{2/3}} = T_0 \left(\frac{v_{l0}^{-3} + 2v_{t0}^{-3}}{v_l^{-3} + 2v_t^{-3}} \right)^{2/3}. \tag{4}$$

The subscript 0 in (3) and (4) corresponds to $p = 0$, while the remaining quantities pertain to the melting curve.

Since there are no data on the density and propagation velocities of the elastic waves in barium at high tem-

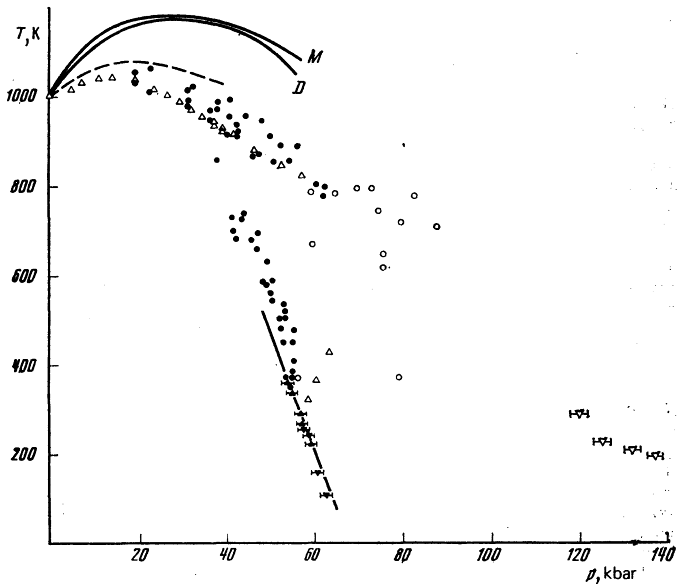

FIG. 1. Phase diagram of barium (●, △, ○, and ▽—from Refs. 10, 5, 3, and 1, respectively. ▲ and ▼—our measurements along the isotherms and isobars, respectively; solid and dashed curves—results of calculation, *M*—by the finite deformation method, *D*—by the Debye-model method.

peratures and pressures, we estimate the function $T_{melt}(p)$ by using data obtained at room temperature.[11] The *M* and *D* curves in the figure represent estimates of $T_{melt}(p)$ based on formulas (3) and (4), respectively. As seen from the figure, the expected melting curve of barium is approximately obtained, but the maximum lies in the region of 30 kbar, i.e., where the functions $\Theta(p)$ and $v_t(t)$ have maxima at room temperature, corresponding to the relations

$$\frac{dT_{melt}}{dp} \approx 2\Theta\frac{d\Theta}{dp} \approx 2v_t\frac{dv_t}{dp}.$$

As demonstrated above, the BaI–BaII phase transition takes place at lower pressures when the temperature increases ($dT/dp < 0$), meaning we should expect the appearance of soft transverse modes of the phonon spectrum in BaI at lower pressures, i.e., the maxima of $\Theta(p)$ and $v_t(p)$ shift into the region of lower pressures. Allowance for this phenomenon, as well as for the decrease of the elastic characteristic of barium with temperature ($dK_T/dT < 0$, Ref. 17) leads to a satisfactory agreement between the calculated $T_{melt}(p)$ and the experimental data (see the dashed curve in the figure).

Thus, an investigation of the behavior of the sound velocities in solids and the analysis presented in this paper make it possible to determine the singularities of the phase diagram of a solid.

[1]R. A. Stager and H. G. Drickamer, Phys. Rev. **131**, 2524 (1963).
[2]S. Akimoto, T. Jagi, J. Ida, K. Inoue, and J. Sato, High Temp.-High Press. **7**, 287 (1975).
[3]J. P. Bastide and C. Susse, High Temp.-High Press. **2**, 237 (1970).
[4]F. P. Bundy and H. M. Strong, Solid State Phys. **13**, 81 (1963).
[5]A. Jayaraman, W. Klement, and G. C. Kennedy, Phys. Rev. Lett. **10**, 387 (1963).
[6]R. H. Jeffery, J. D. Barnett, H. B. Vanfleet, and H. T. Hall, J. Appl. Phys. **37**, 3172 (1966).
[7]J. C. Haygrarth, I. C. Getting, G. C. Kennedy, J. Appl. Phys. **38**, 4557 (1967).
[8]F. F. Voronov, E. V. Chernysheva, and G. S. Vorotnikov, High Temp.-High Press. **5**, 621 (1973).
[9]L. F. Vereshchagin, E. V. Zubova, and V. A. Stupnikov, Fiz. Met. Metalloved. **43**, 1221 (1977).
[10]B. C. Deaton and D. E. Bowen, Appl. Phys. Lett. **4**, 97 (1964).
[11]F. F. Voronov and O. V. Stal'gorova, Fiz. Tverd. Tela (Leningrad) **20**, 452 (1978) [Sov. Phys. Solid State **20**, 261 (1978)].
[12]L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1964. [Pergamon].
[13]P. W. Bridgman, Proc. Amer. Acad. Arts Sci. **74**, 425 (1942).
[14]M. A. Il'ina and E. S. Itskevich, Fiz. Tverd. Tela (Leningrad) **8**, 2349 (1966) [Sov. Phys. Solid State **8**, 1873 (1967)].
[15]Yu. N. Ryabinin, K. P. Rodionov, and E. S. Alekseev, Zh. Tekh. Fiz. **34**, 1913 (1966) [Sov. Phys. Tech. Phys. **9**, 1477 (1965)].
[16]W. Mason, Physical Acoustics, Vol. 1A Academic, 1964.
[17]P. W. Bridgman, Proc. Amer. Acad. Arts Sci. **62**, 207 (1927).

Translated by J. G. Adashko