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DIFFERENTIAL THERMAL ANALYSIS AT PRESSURES UP TO 100 kbars*

B. R. Churagulov, E. M. Feklichev, Ya. A. Kalashnikov, and L. F. Vereshchagin

Institute of Physics of High Pressures, Academy of Sciences, USSR
Lomonosov Moscow State University
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As is well known, phase transitions of the first kind are accompanied by a change in volume and by thermal effects which are determined from the Clausius-Clayperon equation:

$$dT / dp = T\Delta V / \Delta H.$$

In investigations at high pressures, polymorphic transformations are very often found by the displacement of a piston (from the change in volume ΔV) or by a change in electrical resistance. The method of differential thermal analysis (dta) which enables phase transitions of the first kind to be followed from the thermal effect and also a quantitative determination to be carried out from the magnitude of the thermal effect, started to be used for studying P-T diagrams of various materials at high pressures only in the last ten years, but already it has found fairly wide application in the studies of many investigators both in our country and abroad.

In conditions of hydrostatic pressure up to 34 kg/cm^2 and at temperatures up to 800°, the heat of the polymorphic transitions in metallic cerium and bismuth were determined by the method (dta) and their phase diagrams were studied. Investigations of the melting curves of various metals have also been carried out [1-4]. Ponyatovskii and his coworkers have studied the P-T phase diagrams of the Fe-C system at pressures up to 30 kbars and temperatures up to 1000° K [5], and also the Bi-Sn system at lower temperatures [6].

More recently, Kennedy and his coworkers have carried out several investigations of the phase diagrams of both the metals and the binary compounds of elements of the II-VI and III-V groups up to pressures of 70 kbars and temperatures of 1200°. The method of investigation was described in ref. [7] in which the authors indicated that it was impossible to fix accurately polymorphic transformations of the type solid phase I- solid phase II by the method of dta because it was insufficiently sensitive and therefore these parts of the phase diagrams were investigated by a method of displacing a piston.

In connection with this, we have developed a method of determining polymorphic transformation of the first kind in a solid phase by a dta method up to pressures of 100 kbars at room temperature. The construction which was used in the studies is given in Fig. 1.

The readings of a differential dromel-alumel thermocouple were recorded by a low frequency thermographic recorder (NTR-63) with photographic recording. The weights of the investigated materials were 0.05-0.1 g.

Figure 2, shows the thermograms of bismuth, cerium, barium and silver chloride.

In order to determine the sign of the thermal effects of the polymorphic transformation in the investigated materials, metallic bismuth was placed around the second junction of the differential thermocouple and used as a reference material. It was shown that the transition in metallic bismuth (89 kbars) was endothermic whereas the transitions in metallic barium (59 kbars), silver chloride (88 kbars) and metallic cerium (7 kbars) were exothermic.

The polymorphic transformation for barium (17 kbars) noted by Bridgeman [8] and that for cerium (50-70 k bars) proposed by Lifshits, Genshaft and Markov [9] were not observed.

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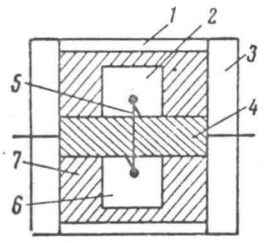

Fig. 1

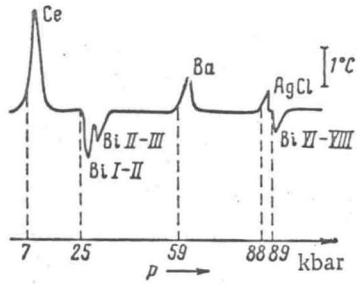

Fig. 2

Fig. 1. Scheme for introducing a differential thermocouple in a high pressure chamber. 1) talc roof; 2) metallic bismuth; 3) talc insulating screen; 4) teflon or talc collar; 5) differential chromel-alumel thermocouple; 6) investigated material; 7) medium for transmitting pressure.

Fig. 2. Combined thermogram for various materials.

The described method may be used successfully not only as a method of calibrating pressure in addition to the electrical resistance method but also for estimating the magnitude of the thermal effect with more or less satisfactory accuracy. It is proposed in the future to estimate quantitatively the magnitudes of the thermal effects of several polymorphic transformation at high pressures.

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