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Abstract

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ON THE QUESTION OF THE TRUE VALUE OF THE PRESSURE OF THE POLYMORPHIC TRANSFORMATION IN IRON

As is known, at one time all researchers engaged in studying various phenomena under high pressure used the high-pressure scale proposed by Bridgman. The reference points on this scale were the abrupt changes in electrical resistance under pressure of bismuth, thallium, cesium, and barium. Subsequently Kennedy and LaMori ([1]) introduced corrections into this scale, using a free-piston manometer operating up to $\sim$ 40 kbar. The new scale, called the Kennedy-LaMori scale, gives values reduced by $\sim$ 30% for pressures above 25 kbar. Later the correctness of the Kennedy-LaMori scale was confirmed in a paper by one of the authors of the present article with co-workers ([2]), which reported the development of a free-piston manometer up to 100 kbar. Balchan and Drickamer ([3]) attempted to establish reference points in the portion of the scale from 100 to 500-600 kbar. As reference points they took the abrupt increase in resistance with pressure of iron, barium (the second jump), lead, and rubidium, as well as the maxima on the curves of the dependence of the resistance of calcium and rubidium on pressure. The pressures of the reference points were determined from Bridgman' s extrapolation data for measurements of the resistance of lead, platinum, and indium up to 30,000 kg/cm^2 to higher pressures. Balchan and Drickamer themselves point out that the calibration method used may be subject to criticism because of possible errors caused by the long extrapolation.

In this connection, it seems important to us to refine (and perhaps revise) the pressure values of a number of generally accepted reference points. In the present work we were interested in establishing the true value of the reference point for iron.

As indicated above, Balchan and Drickamer ([3]) studied, at room temperature, the dependence of the electrical resistance of iron on pressure. As can be seen from Fig. 1, the resistance of iron, with increasing pressure, first decreases, then rises rapidly, passes through a maximum, and again decreases. The polymorphic transformation, which is accompanied by an increase in resistance, is spread over a pressure interval of $\sim$ 50 kbar. In this region coexistence of the old and

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

new phases is observed, which was discovered by Jamieson and Lawson ([4]) in carrying out X-ray structural studies under pressure.

The onset of the sharp increase in the resistance of iron at a pressure of 133 kbar is proposed by Balchan and Drickamer as a reference point for calibrating pressure apparatus. The pressure value 133 kbar, determined with an accuracy of ±1.5%, agrees well, in the opinion of Balchan and Drickamer, with the transition pressure value obtained in the study of iron by the shock-wave method ([5,6]) (131 kbar), and agrees poorly with the data of Strong ([1]), Claussen ([1]), Kaufman, Leyenaar and Harvey ([1]), Hilliard ([7]), and Kennedy and Newton ([7]), obtained at static pressures not exceeding 80 kbar. Strong studied the dependence of the temperature of the polymorphic transformation of the α-phase into the γ-phase on pressure. Tempe-

the transformation temperature was recorded from the change in resistance of the specimen. The same dependence was studied by Claussen using a differential method for measuring thermal conductivity, by Kaufman, Leyenaar, and Harvey, and also by Hilliard—by the metallographic method; by Kennedy and Newton—by the method of differential thermal analysis.

The data obtained under static pressures fit well the calculated curve obtained by Kaufman from thermodynamic relations (see curve 5 in Fig. 2).

Fig. 1. Dependence of the relative resistance of iron on pressure (data of Balchan and Drickamer)

Fig. 2. Effect of hydrostatic pressure on the $(\alpha - \gamma)$-transformation in iron. 1 —boundary between the α- and γ-phases, obtained during cooling and heating by the method of differential thermal conductivity (Claussen); 2 —$\alpha \rightarrow \gamma$ transformation, metallographic method (Kaufman, Leyenaar, and Harvey); 3 —$\gamma \rightarrow \alpha$ transformation, metallographic method (Hilliard), 4 —$\alpha \rightarrow \gamma$ transformation, method of differential thermal analysis (Kennedy, Newton); 5 —Kaufman' s calculated curve. Data from (7)

According to this curve, the transition of the α-phase to the γ-phase at room temperature should be observed near 165 kbar. In discussing Strong' s work, Kaufman pointed out that, according to Benedick' s data, in experiments with shock waves the substance is heated (at 130 kbar by approximately 200°), and this is in agreement with the calculated values $P - T_0^{\alpha \rightarrow \gamma}$ (T_0 is the absolute temperature of the transition of the α-phase to the γ-phase at pressure P).

We also studied the pressure dependence of the electrical resistance of iron at room temperature. The investigations were carried out for the purpose of calibrating a three-stage apparatus (8) with respect to pressure. It was intended to use, as a reference point, the onset of the polymorphic transformation at 133

Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

kbar. The result proved to be somewhat unexpected. The onset of a sharp increase in the resistance of iron was observed by us at a higher pressure than that indicated by Balchan and Drickamer. Figure 3 presents standard curves of the dependence of the electrical resistance of iron (I) and lead (II) on press load. The onset of the sharp increase in resistance was observed at 548 tons for lead and 483 tons for iron. We determined the value of the pressure at the onset of the polymorphic transformation in iron using a calibration curve obtained from the reference points of bismuth (Bi_{I-II} 24.5 kbar, $Bi_{VI-VIII}$ 88 kbar) and lead (Pb_{I-II} 161 kbar) (Fig. 4). It is 152.5 ± 2.5 kbar.

One of the possible reasons for the difference between our data and those of Balchan and Drickamer may have been that our investigations were carried out in a substantial volume (~ 0.25 cm^3), whereas in their work the pressure was produced in a thin film. Our specimens were made of carbonyl iron, additionally purified by remelting in vacuum. Purity $\geq 99.99\%$. Carbon content $\leq 0.002\%$. The degree of purity of Drickamer and Balchan' s specimens is not indicated.

Fig. 3. Dependence of the electrical resistance of iron (*I*) and lead (*II*) on the press load

Fig. 4. Pressure calibration curve of the three-stage apparatus

The values we obtained for the pressure of the polymorphic transition in iron are closer to Kaufman' s calculated data. A certain discrepancy (10–15 kbar) can be explained by the assumptions that were made in the calculations. In particular, it was assumed *a priori* that at high pressures the compressibilities of the α- and γ-phases are the same.

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Note: Figure translations are in progress. See original paper for figures.