I-II Transition

Pressurization Procedure	$P_{I\text{-}II}$, K-atm	$P_{II\text{-}I}$, K-atm	$\Delta P_{I\text{-}II}$, K-atm
500-atm increments	24.23 (24.10-24.50)	23.29 (22.90-23.50)	0.94 (0.60-1.20)
250-atm increments	24.25 (24.20-24.30)	23.20 (23.00-23.50)	1.05 (0.75-1.30)
100-atm increments	24.20 (24.05-24.30)	23.49 (23.40 23.70)	0.71 (0.55-0.90)
Uninterrupted at 50 atm per min.	24.31 (24.25-24.35)	23.20 (23.15-23.40)	1.11 (0.95-1.20)

II-III Transition

Pressurization Procedure	$P_{II\text{-}III}$, K-atm	$P_{III\text{-}II}$, K-atm	$\Delta P_{II\text{-}III}$, K-atm
500-atm increments	25.55 (25.50-25.60)	24.84 (24.70-25.10)	0.71 (0.50-0.80)
250-atm increments	25.65 (25.60-25.70)	24.98 (24.95-25.00)	0.67 (0.65-0.70)
100-atm increments	25.70 25.70	25.15 (24.95-25.30)	0.55 (0.40-0.75
Uninterrupted at 50 atm per min	25.75 25.75	25.13 (25.10-25.15)	0.62 (0.60-0.65)

the first cycle in case of recycling) in the specific category and the double values, in parentheses, the data spread. Although the differences are relatively small, it can be seen that the magnitude of the hysteresis in the I-II transitions tends to increase with increasing pressurization rates, which most probably is due to nonequilibrium conditions resulting in "over-driving" of the transitions.

Recycling several times through either of the transitions seems to have little, if any, effect on the magnitude of the hysteresis. For example, passing through the I-II transitions three times does not result in any consistent change in the hysteresis. Recycling four times through the II-III transition resulted in a reduction from 750 to 500 atm.

It is of concern whether the observed hysteresis is, in fact, a real phenomenon associated with these transitions or simply a function of the experiment. From the standpoint of the experiment, the two possible causes of observed hysteresis are substantial nonequilibrium associated with too rapid a pressurization rate and/or natural hysteresis in the manganin-coil pressure transducer.

Considering the first possibility, using 100-atm increments with a 5-min stabilization period there was usually a substantial period of elapsed time at the transition pressure before the transformation initiated. This is clearly shown in Fig. 3 which is a typical plot of relative resistance vs time as obtained from the continuous oscillographic recording of voltage change for simultaneously pressurized single and polycrystalline samples. Time = 0 on the abscissa corresponds to the time at which the transition pressure was reached. In any given experiment, the transitions normally did not initiate simultaneously in both samples. However,

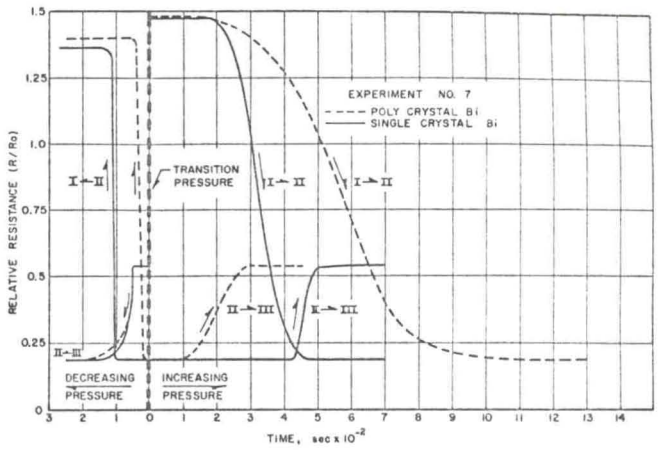

Fig. 3—Typical relative resistance vs time curves for I-II and II-III transitions.

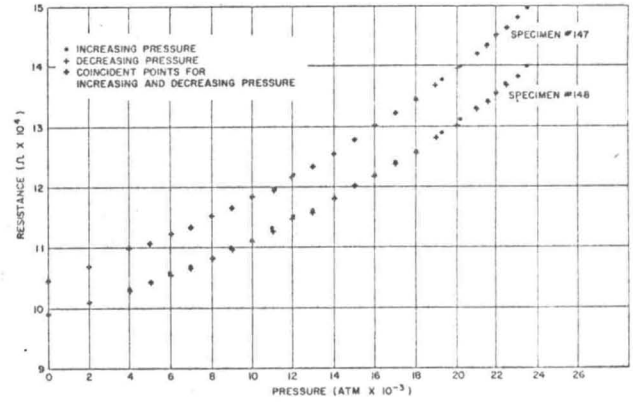

Fig. 4—Resistance vs pressure for single crystals.

considering the curve for the single crystal shown in Fig. 3 as an example, approximately 3 min elapsed before the I-II transition initiated and 7 min before the initiation of the II-III. For decreasing pressure, the elapsed time was approximately 1 and 2 min, respectively, for the III-II and II-I. Apparently, then, using 100-atm increments with a stabilization period is close enough to equilibrium conditions so that the hysteresis is not attributable to "overdriving" of the transitions. Using the larger pressure increments, the transitions often occurred during the increase or decrease of pressure, resulting in little or no elapsed time at the transition pressure and short durations of transformations. In these instances, there is a greater tendency to "overdrive" the transitions, resulting in an increase in the magnitude of the hysteresis.

That the observed hysteresis is not due to the manganin-coil transducer is based on the following two considerations. First, any hysteresis occurring in the pressure measurement would vanish at the peak pressure and be a maximum at the midpressure range. However, the hysteresis in the transition was observed even when the applied pressure just exceeded the transition pressure by a few hundred atmospheres, and also in the case of the partial I-II transformation. Second, as a further check, two bismuth single crystals were pres-