

pressures could definitely provide information on the validity of this assumption. In fact, our resistance melting curves are quite similar to those of Stager and Drickamer⁶ and our data thus lend evidence to the fact that Ba may be liquid at room temperature above 144 kb.

The measurements were made using a tetrahedral anvil device described previously.^{7,8} The pyrophyllite sample tetrahedrons contained a graphite heater with stainless steel current leads, inside of which was placed a cylinder of pyrophyllite, boron nitride, or AgCl containing both the Ba sample and a chromel-alumel thermocouple. The Ba samples were extruded from commercial stock with a purity of 99+%. Copper or platinum wires were tied around the ends of the 380- to 750- μ Ba samples to provide resistance measurement leads. No correction was made for the effect of pressure on the emf of the chromel-alumel thermocouples. The thermocouple was positioned about 0.5 mm from the center of the Ba wire and was electrically insulated from it by the pyrophyllite, boron nitride, or AgCl. Temperatures are thought to be accurate to $\pm 1.5\%$. Pressure calibration was made in the usual way^{7,8} with Bi and Tl as well as Ba wires being placed in each of the sample cell configurations used. The pressure values are believed to be accurate to $\pm 2.5\%$ and no pressure correction due to the elevated temperature is assumed. All data were automatically recorded to facilitate analysis.

The data obtained on melting and on the BaI-BaII transition are shown in Fig. 1. The experimental points shown were taken directly from resistance-temperature curves (isobars) or resistance-pressure

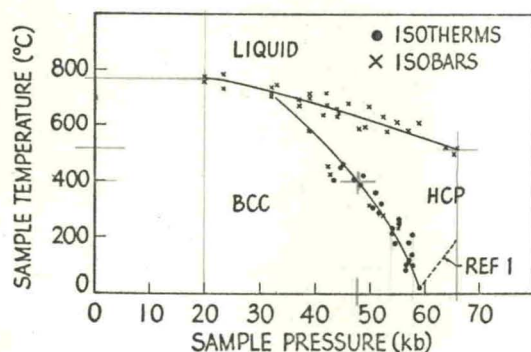


Fig. 1. Phase diagram of barium as determined by high-pressure, high-temperature resistance measurements. The dashed line is the data of Jayaraman and others obtained from differential thermal analysis.

curves (isotherms) and the solid lines represent what we consider to be the best fit to the experimental points. The scatter in the data is thought to be caused by the pressure uncertainty. No data are shown below 20 kb because of equipment limitations at high temperatures in this pressure range. Our melting curve data agree quite closely with those of Jayaraman and others,² but the BaI-BaII transition line obtained in the present work has a pronounced negative slope in contrast with the positive slope found by differential thermal analysis (see Fig. 1). Repeated attempts failed to show any resistance discontinuities corresponding to the positive sloping phase line reported, and it seems unlikely that the transition would not show up as a resistance discontinuity at elevated temperatures. The transitions indicated by resistance measurements were sharper at high temperatures and were much less sluggish than the room temperature BaI-BaII transition. The triple point observed in the present work is found to occur at about 35 kb, 700°C, approximately where the fusion curve of Jayaraman and others² shows a slight break in slope. Recent high-pressure x-ray studies by Barnett, Bennion, and Hall⁹ indicate that the Ba bcc structure changes to hcp structure at 59 kb, *i. e.*, at the BaI-BaII transition. No evidence of the 17-kb resistance transition reported by Bridgman³ was observed in the present work.

If, indeed, our negative sloping curve is the BaI-BaII transition line, then an important conclusion is that the fusion curve determined above about 35 kb is that of BaII. The fusion curve has a negative slope that continues to the highest pressures achievable in our apparatus and if extrapolated to higher pressures would cross the room-temperature line in the vicinity of 140 kb. It is thus quite possible that the resistance transition near 144 kb and 25°C corresponds to melting.

Resistance vs temperature curves for the various phases of Ba are shown in Fig. 2. The transitions corresponding to melting and the BaI-BaII transformation are indicated. The melting transition shows a definite subcooling and sluggishness on decreasing the temperature as was observed also by Stager and Drickamer⁶ in their resistance-temperature curve at 440 kb. The BaI and BaII phases show definite metallic behavior, each having a positive temperature coefficient of resistance. Our measurements of the resistance of the liquid phase are very rough, but indicate a very small positive temperature coefficient of resistance for the liquid. The similarity between the resistance