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① Phase change or polymorphism

② Barium

ELECTRICAL RESISTANCE OF BARIUM AT ELEVATED PRESSURE AND TEMPERATURE

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Experimental results on the melting and polymorphism of barium at elevated temperature and pressure were first reported in 1963, the measurements being made by differential thermal analysis[1]. We report here data on the electrical resistance of barium wire samples at pressures to 67 kilobars (kb) and temperatures to 800°C. Bridgman has published data on room temperature resistance discontinuities in barium at 17 and 59 kb[2,3], and more recently, Balchan and Drickamer[4] found a sharp discontinuity in resistance near 144 kb. Since it has been tentatively assumed that the room temperature transition at 144 kb corresponds to melting[1,5], it was felt that a study of the resistance upon melting at lower 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 Drickamer[5] and our data thus lend evidence to the fact that barium may be liquid at room temperature above 144 kb.

The measurements were made using a tetrahedral anvil device described previously[6,7]. 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 barium sample and a chromel-alumel thermocouple. The barium samples were extruded from commercial stock with a purity of 99+%. Copper or platinum wires were tied around the ends of the .015 to .030" barium 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 .020" from the center of the barium 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[6,7] with bismuth and thallium as well as barium wires being placed in each of the sample cell configurations used. The pressure values are believed to be accurate to $\pm 2.5\%$ assuming no pressure correction due to the elevated temperature. 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 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 that of Jayaraman, et. al[1], 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. 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 observed resistively in the present work 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, et. al.[1] shows a slight break in slope. Recent high pressure x-ray studies by Barnett, Bennion and Hall[8] indicate that the barium body-centered cubic structure changes to hexagonal-close packed structure at 59 kb, i.e., at the BaI-BaII transition. It should be noted that no evidence of the 17 kb resistance transition reported by Bridgman[2] was observed in the present work.

If, indeed, our negative sloping curve is the BaI-BaII transition line, then an important conclusion of the present work is that the fusion curve determined above about 35 kb is that of BaII. The fusion curve has a negative slope which 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 barium are shown in Fig. 2. The transitions corresponding to melting and the BaI-BaII transformation are indicated. It is seen that the melting transition shows a definite subcooling and sluggishness on decreasing the temperature as was observed also by Stager and Drickamer[5] 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 melting curves observed at low pressures in the present work and those obtained at higher pressures[5] lend support to the tentative conclusion that the 144 kb transition at 25°C is indicative of melting. Positive identification of this phase as liquid, however, can be made only after high pressure x-ray measurements are carried out. If barium is liquid above 140 kb at low temperatures, the technological implications would be significant since true hydrostatic measurements would be possible in the very high pressure range at reasonable temperatures.

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REFERENCES

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1. A. Jayaraman, W. Klement, Jr. and G. C. Kennedy, Phys. Rev. Lett. 10, 387 (1963).

2. P. W. Bridgman, Proc. Am. Acad. Arts Sci. 72, 157 (1938).

3. P. W. Bridgman, Proc. Am. Acad. Arts Sci. 81, 165 (1952). The pressures are given in terms of the revised pressure scale.

4. A. S. Balchan and H. G. Drickamer, Rev. Sci. Instr. 32, 308 (1961).

5. R. A. Stager and H. G. Drickamer, Phys. Rev. 131, 2524 (1963).

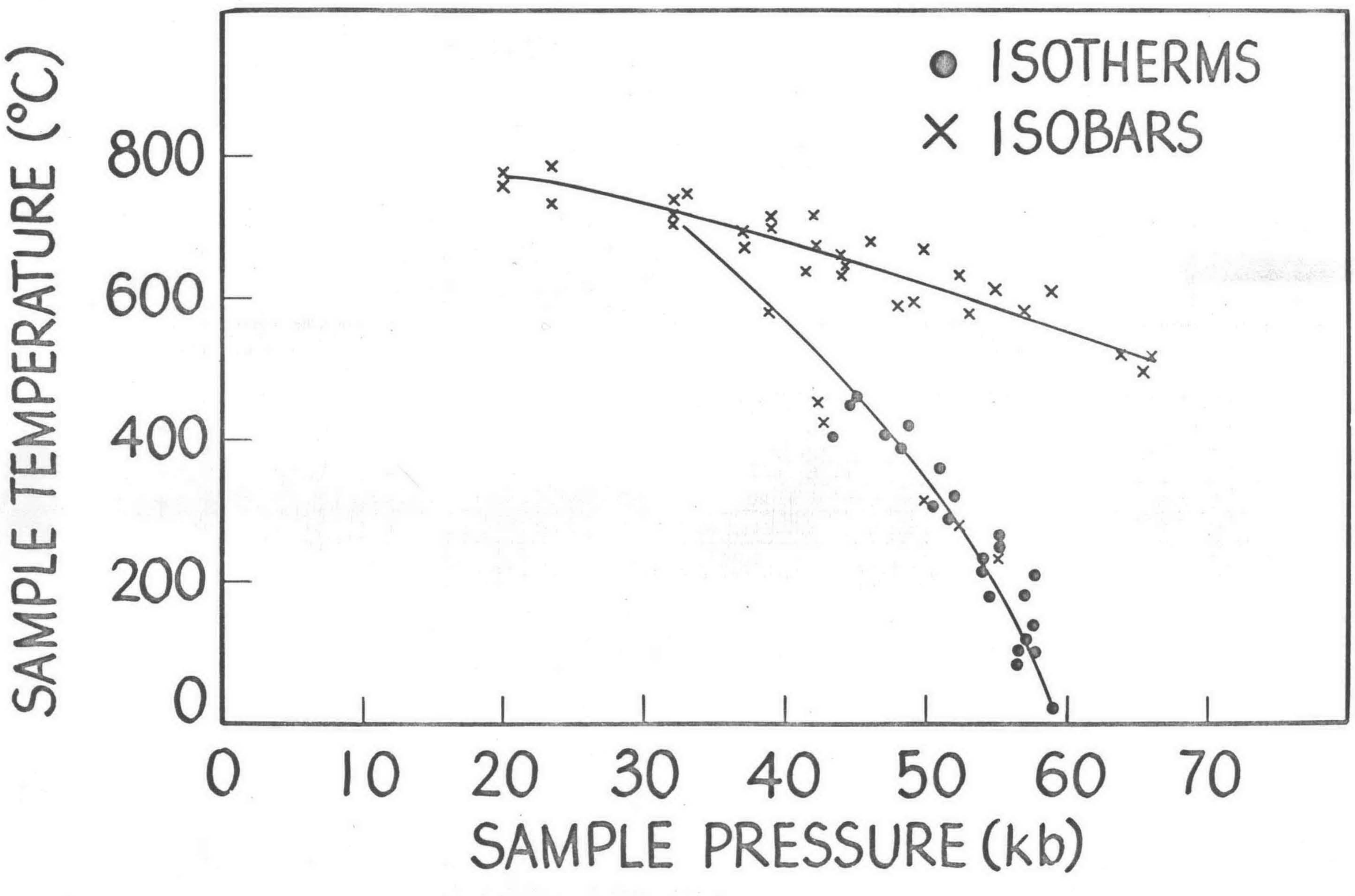
6. B. C. Deaton and R. B. Graf, Rev. Sci. Instr. 34, 45 (1963).

7. R. B. Graf and B. C. Deaton, Nature 197, 678 (1963).

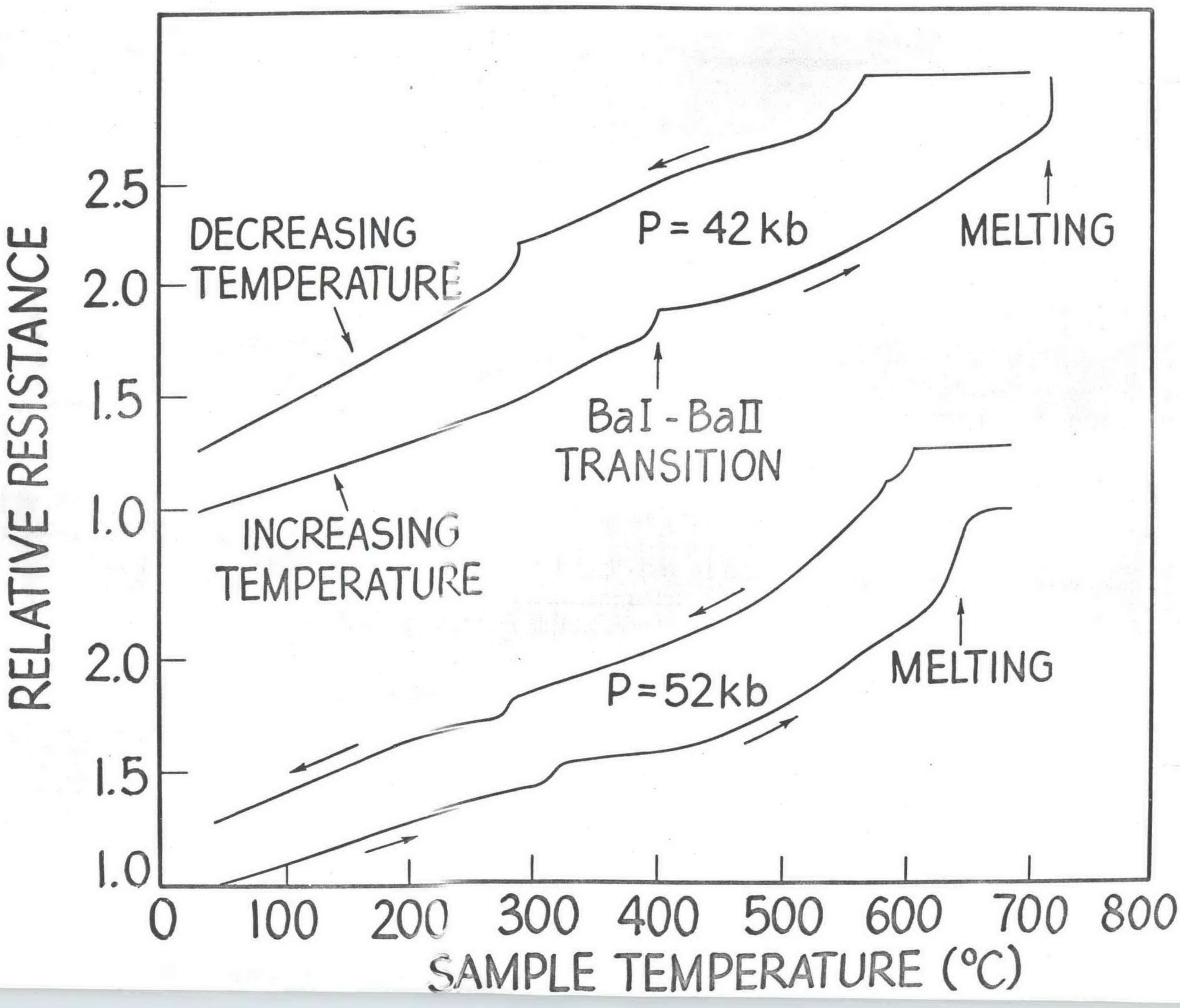
8. J. D. Barnett, R. B. Bennion and H. T. Hall, Science 141, 534 (1963).

FIGURE CAPTIONS

1. Phase diagram of barium as determined by high pressure, high temperature resistance measurements.
2. Resistance vs. temperature curves for the various phases of barium.



ISOTHERMS
ISOBARS
SAMPLE TEMPERATURE (°C)
800
600
400
200
0
0
10
20
30
40
50
60
70
SAMPLE PRESSURE (kb)



RELATIVE RESISTANCE
2.5
2.0
1.5
1.0
2.0
1.5
1.0
DECREASING TEMPERATURE
P = 42 kb
MELTING
BaI - BaII TRANSITION
INCREASING TEMPERATURE
P = 52 kb
MELTING
0
100
200
300
400
500
600
700
800
SAMPLE TEMPERATURE (°C)