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ABSTRACT

A method for thermally shocking a metal under pressure is described. This method appears to yield thermodynamic values of the phase boundaries. For purposes of calibration the following fixed points have been obtained: Bismuth, 81 ± 4 kbars; Tin, 99 ± 4; and Iron, 118 ± 6 kbars.

INTRODUCTION

It is well known that when a phase transformation occurs under pressure, the pressure at which the transition is observed under compression is higher than the thermodynamic pressure for the phase boundary between the two phases. This was discussed at great length by Bridgman, who referred to the region between the pressures at which the transformation occurred on compression and decompression as the region of indifference.[1] He chose as the transition pressure a point midway between the compression and decompression values. More recently, Kennedy and coworkers have obtained thermodynamic pressures by shearing the sample, a technique which decreases the difference between the two experimental transition pressures to a negligibly small quantity and thereby obtains thermodynamic values of the transition pressure.[2] The reluctance of one phase to transform to the second is apparently a time effect. A sample can be compressed to a pressure greater than the known thermodynamic transition pressure, but less than the pressure at which the transition occurs on isothermal compression, and no detectable change is observed for hours.

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(1) P. W. Bridgman, "The Physics of High Pressure", London, G. Bell & Sons, 1958.

(2) G. C. Kennedy and P. N. La Mori, "The Progress in Very High Pressure Research", p. 304, John Wiley, New York (1961).

In dynamic shock experiments, where the maximum pressure is available for only a few microseconds, phase transitions are observed to occur in a period of time less than the duration of the shock. This suggests that the temperature of the sample plays an important role in the transformation between the phases. The method that we suggest is to momentarily increase the temperature of the sample so that a partial transformation will occur. The Bridgman anvil, with a metal wire sample in a silverchloride medium, is an ideal system for raising the temperature of the sample for short periods of time. The method to be described, thermal shocking of the sample, has been applied to the high pressure transition of bismuth, iron, and tin. It is suggested that values obtained in this manner be used as high pressure calibration points, as well as having thermodynamic value.

METHOD

A phase transformation may be slow and overdriven to a greater or lesser extent for several reasons. First, the process may have a high activation energy; if so, an elevated temperature will facilitate the transformation. Second, the free energy difference between the two phases may be very small over a large pressure region. In either case the region of indifference will be large, and an increase of the temperature to a high value would facilitate the transition. In studying a transformation, the ideal situation would be one in which the two different phases would be formed in direct contact at the temperature of interest. Then, if one phase grew at the expense of the other, it could be said with reasonable certainty that this was the thermodynamically stable phase at that temperature. This is the basis of the work that follows; the method of obtaining the two coexisting phases is described.

It is evident that in order for this technique to be applicable, dT/dP must be negative. Heating must transform some of the material to the higher pressure phase. If the slope of this phase boundary were positive, it would be necessary to perform these experiments under decompression, an unreliable procedure at best. Alternatively, a method would have to be found that could cool the sample alone in a few milliseconds. The latter does not appear to be feasible at the present time.

In a metal, it is easy to heat the sample in a short period of time by sending through a high amperage pulse. The samples used are of the order of 10^{-4} moles; consequently a high current pulse is sufficient to raise the temperature of the sample as much as 1500°C. This temperature may be fixed by the fact that it is possible to melt iron (actually the entire sample is not melted, but breakage occurs at the thinnest spot of the wire). Even though the heat leak from the sample is great, if the duration of the pulse is sufficiently short, the surrounding silver chloride is not appreciably heated, and the sample returns to the ambient temperature in about ten milliseconds after the cessation of electrical heating. If the silver chloride is heated, then a time as long as a minute is required for the return to room temperature. Either of the above times is short compared to the duration of the study of the effect of the energy pulse. The above can be nicely illustrated with a material such as silver which has no known phase transition or with a material such as tin as long as the pressure is far from the transition pressure. If a silver wire 0.003 inches in diameter and about one inch long is pulsed with 6 volts for about ten milliseconds, the resistance returns to its initial value in less than 0.1 minute. The recorder is of no value in showing the change of resistance with time and it is necessary to use an oscilloscope to follow the resistance of the sample.

The geometry of the system is too complex to compute the sample temperature behavior as the energy is electrically generated in the wire. An analysis of a simple and idealized system indicates that the heat leakage from the sample becomes appreciable in a microsecond. That this is so can be shown by the fact that a 0.010 second, 1 volt pulse through a silver sample should melt the entire sample if there were no heat leak. Experimentally it is found that a pulse of about 10 volts is necessary to melt a part of the sample. What has been repeatedly observed is that for a pulse of duration up to 0.060 second, the temperature of the system, as determined by the resistance of the sample, returns to the ambient temperature in less than 1 minute, provided the pressure is far from a transition pressure. The total heat generated is small compared to the heat capacity of the surroundings and the heat leak is large; consequently the short pulse of energy used in these experiments does not appear to have a long-term effect on the temperature of the system.

The experimental procedure is as follows: 0.003 inch diameter wires are bent into circular arcs and mounted in Bridgman anvils. The method of resistance determination has been previously described.[3] The present

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(3) P. W. Montgomery, H. Stromberg, G. H. Jura, and G. Jura, in "High Pressure Measurements", p. 1, A. A. Giardini and E. C. Lloyd, eds. Butterworths, Washington, 1963.

addition and the circuit as used is illustrated in Figure 1. Twelve Volt auto storage batteries, connected in parallel, are so arranged that by setting a selector switch current may be drawn from one to six cells; the available voltage varies from 2 to 12 volts in 2 volt increments. The leads from the battery and from the constant current supply go through a switching and gating unit. Pressing a switch in the gate box shunts current from the constant current supply through a dummy load of 1 ohm, and at the same time the power from the battery is sent through the sample. The length of time which the battery heats the sample is continuously variable from about 3 to 60 milliseconds. After the preset time of the power pulse, the switching is reversed; the battery power is turned off, and the constant current is again sent through the sample. Several preliminary experiments are needed to determine the optimum conditions to be used. Obviously, the voltage and duration of the heating pulse must have values such that the sample is heated to a sufficiently high temperature, but not so high as to melt the sample. A sufficiently high temperature is one in which the two phases coexist. In determining the transition pressure, the resistance-pressure relation is found in the usual fashion. For example if bismuth is the metal under consideration, an isotherm is made to about 60 kbars. At this pressure a 2 volt pulse of 8 millisecond duration is used. The resistance of the sample may be decreased between the extrapolated value of the next phase and the value of the present phase. The resistance is followed on the recorder as a function of time. If the resistance should return to its initial value, as it would in bismuth, the pressure is increased by 5 kbars, the resistance noted, and the sample is pulsed again. If the resistance returns to its initial value a further pressure increment is made. This procedure is repeated until the resistance decreases to its value in the high pressure phase. In the case of bismuth, the resistance-pressure relation is followed during decompression; if the transition pressure is the same on compression and decompression, the run is discarded as this would indicate that too large an energy pulse was applied, driving the entire sample irreversibly into the high pressure phase. In general, if the pulse strength is such that the entire sample is not transformed to the high pressure form, this difficulty is not encountered.

Tin exhibited the sharpest transitions; iron is not as simple as bismuth, but there can be little doubt that a reasonably reproducible value is obtained. The particular problems encountered with each materials will be discussed in the paragraph devoted to that metal.

The precision of a transformation found in this manner is not as great as when the sample is isothermally compressed in the usual fashion. In the usual experiment, if the transformation starts while the sample is being compressed, the compression can be immediately stopped and the pressure noted. In our technique all that is known is that at some pressure P the material is in one phase, and that after an increment of pressure is added, the material is in another phase. We have assumed that the transition pressure is given by the arithmetic mean between these two pressures. The pressure scale we have used as a reference is that given in an earlier paper.[3]

RESULTS

Bismuth: The bismuth used in these experiments had a supposed purity of 99.999% and was supplied by the American Smelting and Refining Company, South Plainfield, New Jersey. It was drawn to wire 0.003 inches in diameter. The samples were bent into circular arcs of 0.2 inch diameter and had resistances of about 2 ohms. Three different geometries were used. It was found that the transition pressure was 81 ± 4 kbars. This is to be compared to the 88 kbars obtained with experiments performed in the usual fashion. Either of these values could be used as a calibration for pressure in this region.

Tin: The tin metal was obtained from A. D. MacKay, New York, New York, and was 99.9% pure. The metal was extruded to wire 0.003 inches in diameter and the measurements were made as for bismuth. The present value for the transition is 99 ± 4 kbars.

Iron: Iron wire, 0.003 inches in diameter and 99.9% pure was obtained from United Mineral and Chemical Company, New York, New York. The work on iron is not as simple or as clearly cut as with the other metal discussed in this paper. This situation might be expected from the isothermal work that has been done. Our personal experience with iron in the past has been that the transition to the hexagonal phase would start at any pressure above 160 kbars and that it might take as much as 80 kbars for the transition to run. This extreme sluggishness could be caused by a small difference in the free energy of the two phases over a wide region of pressure. This argument is supported by the fact that the energy difference between α-iron and β-iron is small. One would not expect a large difference between the β and γ phases; therefore, it seems reasonable that the difference between α-iron and γ-iron would be small. Since our samples are under almost hydrostatic conditions, there is essentially no stress gradient in the sample to aid in the nucleation. Once a pressure of about 80 kbars was reached, there apparently was always a certain amount of sample that transformed to the hexagonal phase.

The criterion that was used here was that if the resistance decayed with time, then the pressure was below the true transition pressure. It was not feasible to wait for the resistance of the sample to stabilize before going to the next pressure increment as the resistance would decrease for periods longer than one hour. The transition pressure was taken to be that at which no decay occurred in a period of minutes. A total of 21 determinations were made with the voltage of the heating pulse varying from 6 to 12 volts. No dependence on the voltage of the pulse was found. The resistance of the samples was about 0.2 ohms. The value found for the iron transition is 118 ± 6 kbars. This is lower than the 130 kbars reported by Drickamer[7] and the 131 kbars derived from dynamic shock experiments.[8]

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(7) H. G. Drickamer and A. S. Balchan, in "Modern Very High Pressure Techniques", p. 25, Butterworths, London, 1962.

(8) D. Bancroft, E. L. Peterson, and S. Minshall, J. Appl. Phys., 27, 291 (1956).

CONCLUSION

In the three metals studied, there was no indication that the high pressure phase was quenched into the system at a low pressure when tin and bismuth were studied. In the case of iron, a certain amount of the higher pressure phase was present at all pressures. We did not take the time to determine whether or not the sample would decay completely back to the α phase. The rate at which the γ phase decayed was so slow that it was not practical to wait the estimated days from the initial rates for the sample to return to the α form. The fact that part of the sample was in two different phases did not seem to interfere with the determination of the pressure at which the entire sample went and remained γ.

The pressure scale used in determining these points are based on the scale determined by us at an earlier time.[3] If this scale should be in error, enough information is available so that the presently proposed values can be easily corrected. Lastly, if the pressure observed is not the thermodynamic transition pressure, it can be definitely stated that the quoted pressure is too low. The technique is such that if an error is made, it is to make the transition pressure too low. However, at the present time, we believe that these pressures are correct within the error that is quoted.

ACKNOWLEDGMENT

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ILLUSTRATIONS

Fig. 1. Block diagram of the apparatus used in the thermal shock experiments.

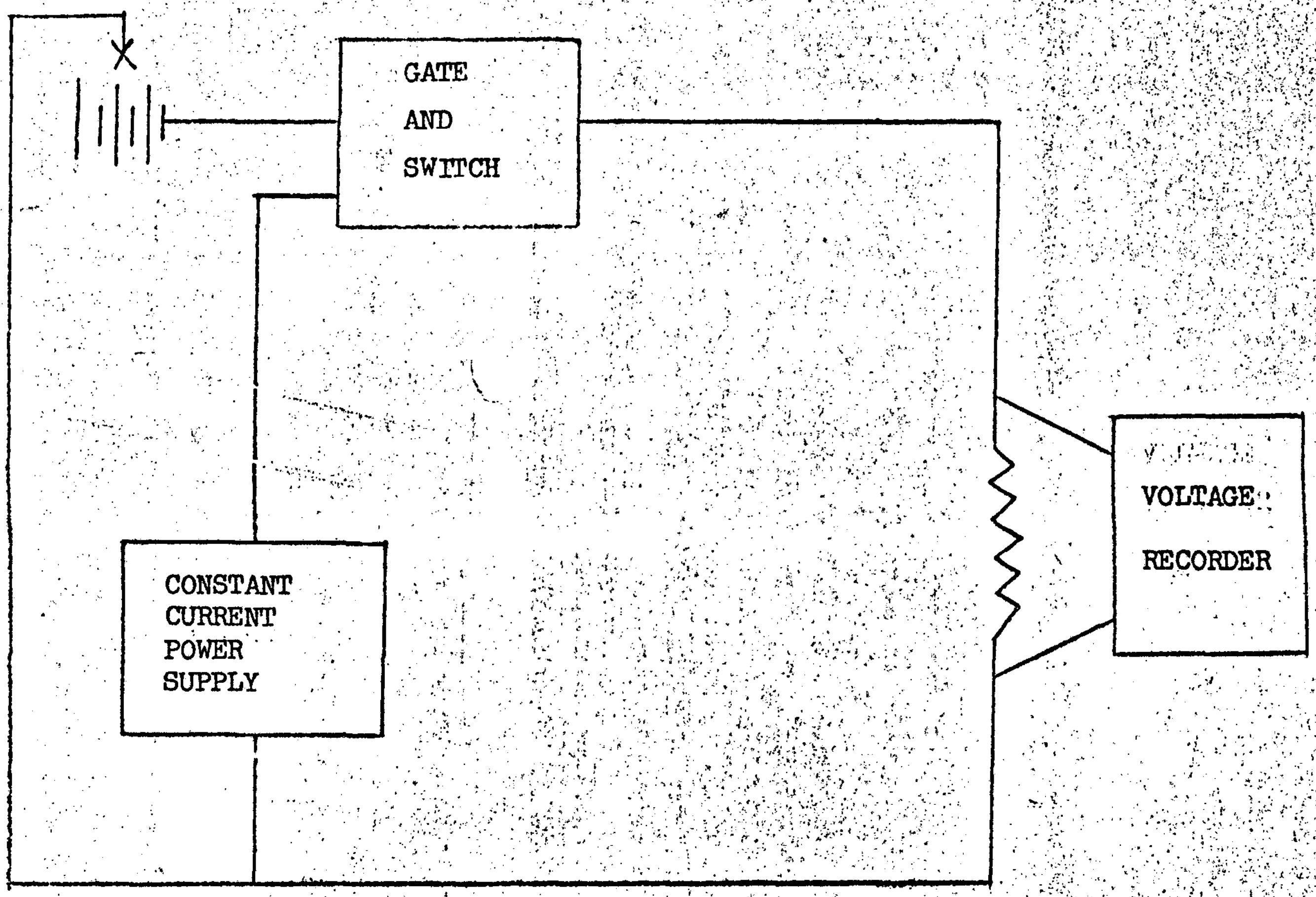
GATE
AND
SWITCH
CONSTANT
CURRENT
POWER
SUPPLY
VOLTAGE
RECORDER

FIGURE 1