An automatic technique for the measurement of thermoelectric power at high pressures

T G RAMESH*, A S RESHAMWALA* and M T SRIVATSA†
National Aeronautical Laboratory, Bangalore 560017

MS received 30 August 1974

Abstract. We describe an automatic technique for direct recording of the thermoelectric power of metals either as a function of temperature or pressure. This technique facilitates the process of measurement especially when one has to scan a wide temperature and pressure range. Typical experimental recordings of the γ-α electronic phase transition in cerium are also presented.

Keywords. Thermopower; cerium; high pressure.

1. Introduction

The measurement of thermoelectric power of metals and alloys has gained considerable importance in recent years (see for example Barnard 1972, Huebner 1972). A unique feature of this property is its dependence on the energy derivative of the mean free path. Some pressure-induced phenomena like the γ-α phase transition in cerium and the freezing of liquid mercury have been studied recently (Ramesh et al 1974, Reshamwala and Ramesh 1974) using thermoelectric power as a probe. These studies have further demonstrated the usefulness of thermoelectric power not only as a tool in the investigations on the phase transitions in metals, but have also provided new information on their electronic structure.

The measurement of thermoelectric power of a substance at high pressures is time consuming especially when one has to scan a wide pressure and temperature range. This is because of the fact that in the manual mode of measurement of the thermoelectric voltages, one has to wait till the steady state condition is reached in the set up. Berglund and Bairisto (1957), Caskey et al (1969) and Freeman and Bass (1970) have described different circuits for the automatic recording of thermoelectric power. For reasons to be discussed later, the circuit developed by Berglund and Bairisto (1967) cannot be used in the study of metals and alloys and moreover it is not possible to plot directly the thermoelectric power. The other two techniques are not suitable for studies at high pressures.

The object of this paper is to present an automatic recording system developed by us for the rapid measurement of the thermopower as a function of either the

* Materials Science Division.
† Instrumentation Division.
mean temperature when the pressure over the sample is held constant or the pressure at a specified mean temperature. This system is considerably simpler than the previous ones (Caskey et al 1969, Freeman and Bass 1970) and compares well with the other two techniques in the accuracy of measurement. Some typical recordings on the $\gamma$-$\alpha$ phase transition in cerium are presented to demonstrate the performance of the system.

2. Thermopower measurement

Figure 1 presents a schematic diagram of the differential method of measuring the thermopower of a specimen. The relative thermopower of the specimen(s) with respect to the material a (one of the thermo couple wires) is given by

$$Q_{s_{a}}(T) = Q_{s} - Q_{a} = \lim_{\Delta T \to 0} \frac{\Delta V_{13}}{\Delta T}$$ (1)

where $\Delta V_{13}$ is the open circuit voltage between the terminals 1 and 3 through the sample and $\Delta T$ is the temperature difference between two points along the sample length. Similarly the relative thermopower with respect to the material b (which forms the other thermocouple probe) is given by

$$Q_{s_{b}}(T) = Q_{s} - Q_{b} = \lim_{\Delta T \to 0} \frac{\Delta V_{24}}{\Delta T}$$ (2)

In these expressions $Q_{s}$ and $Q_{a}$ represent the absolute thermopowers of the materials forming the thermocouple. $Q_{a}$, the quantity of main interest, represents the absolute thermopower of the specimen. The temperature difference $\Delta T$ is given by the relation

$$\Delta T = \frac{\Delta V_{13} - \Delta V_{24}}{Q_{s} - Q_{b}}$$ (3)

Combining eqs (1) and (3), we have,

$$Q_{s}(T) = Q_{s}(T) + \left[\frac{\Delta V_{13}}{\Delta V_{13} - \Delta V_{24}}\right](Q_{a} - Q_{b})T$$ (4)
Equation (4) forms the basis for the automatic recording system for thermopower measurement.

3. Automatic recording system

Berglund and Beairsto (1967) have described a technique for thermopower measurement of semiconductor specimens. The circuit described by these authors essentially plots \( \frac{1}{2} (\Delta V_{13} + \Delta V_{24}) \) versus \( \Delta V_{24} - \Delta V_{13} \) on an X-Y recorder. If \( M \) is the slope of this plot, then the relative thermopower \( Q_s \) can be calculated using the relation

\[
Q_s(T) = (M + \frac{1}{2}) (Q_s - Q_0) T
\]

It is to be noted that using this circuit one cannot directly plot the relative thermopower. Moreover this method has an inherent limitation in that to obtain just one value of the thermopower at some temperature, we need to take a record of \( \frac{1}{2} (\Delta V_{13} + \Delta V_{24}) \) vs \( \Delta V_{24} - \Delta V_{13} \). Further this method cannot be directly applied to the study of metals for the following reason. For a semiconductor specimen \( Q_s \ll Q_s \) or \( Q_0 \), so that the voltages \( \Delta V_{13} \) and \( \Delta V_{24} \) have the same polarity and their average value can be measured conveniently using a dc microvoltmeter. On the other hand, for metals, the thermopower of the specimen will be generally of the same order of magnitude as that of the thermocouple probes and \( \Delta V_{13} \) and \( \Delta V_{24} \) could have opposite polarities. This makes it particularly difficult to measure their average value accurately.

Figure 1 shows the circuitry developed by us for plotting directly \( Q_s \) versus the mean temperature \( T \) at a given pressure. The low thermal noise chopper (Guildline Instruments, Model 9745) which is motor driven essentially consists of two double-pole double-throw switches. The chopping frequency is approximately 29 cycles/sec. The chopper connections for one of the DPDT’s are made in such a way that the thermocouple voltages across the terminals 1 and 3, and 2 and 4 are connected to the input of the lock-in amplifier (Princeton Applied Research Model HR-8) on alternate half cycles. The reference signal required for ‘locking-in’ purpose is derived by making a small attachment to the motor shaft that drives the chopper. The attachment essentially serves as a switch for a dc voltage source and the output wave form has the same frequency as the signal. Since the motor speed is identical to the chopping frequency, the reference signal derived in this way will always be coherent with respect to the actual voltage signal irrespective of the variations in the motor speed. The wave form of the input signal to the lock-in amplifier approximates quite well to a symmetric square wave superposed on a dc level. The dc level can be suppressed through an isolation transformer. It is clear that the r.m.s. value of the square wave is equal to \( \frac{1}{2} (\Delta V_{13} - \Delta V_{24}) \). Since this quantity is proportional to \( \Delta T \) [see eq. (3)], the lock-in amplifier serves to measure this quantity accurately. The other DPDT switch in the chopper selects the voltages \( V_{12} \) and \( V_{24} \) on alternate half cycles and are connected to the input terminals of a dc microvoltmeter (Keithley Vibrating Capacitor Electrometer, Model 640). Since any dc meter measures the average value, the dc microvoltmeter essentially measures \( \frac{1}{2} (V_{12} + V_{24}) \), a quantity corresponding to the mean temperature \( T \) of the specimen. The output of the dc microvoltmeter forms the X-input of an X-Y recorder (Mosley, Model 2D).
It is clear from eq. (4) that a measurement of $\Delta V_{13}$ accurately, apart from $\Delta T$, will suffice to determine the relative thermopower of the specimen with respect to the material 'a'. Since $\Delta V_{13}$ will in general be a low level signal, a dc nanovolt amplifier (Keithley Instruments, Model 140) is used to measure this quantity accurately. The gain of the nanovolt amplifier being high, the output of the amplifier will be of the order of a few volts. The use of an analogue divider (Burr Brown, Model 4094/15C) for dividing the output voltage from the dc nanovolt amplifier by that from the lock-in amplifier yields precisely the main quantity of interest, viz., $\Delta V_{13}/(\Delta V_{13} - \Delta V_{24})$, apart from a scale factor. The output of the analog divider forms the Y-input of the X-Y recorder.

The use of chromel-alumel thermocouple along with this system has many advantages. The relative thermopower of chromel-alumel, i.e., $Q_a - Q_b$ is approximately $40\mu V/°C$ and nearly independent of temperature (in the range 0-150 °C) so that this term in eq. (5) can also be absorbed into the scale factor. Further the effect of pressure on chromel-alumel thermocouple is small (Bundy 1961) with the result that the scale factor turns out to be more or less independent of temperature and pressure. However, for more accurate analysis, the recorded data can always be corrected for, to include the effects of temperature and pressure on chromel-alumel thermocouple. It is also possible to subtract a certain voltage corresponding to $Q_a$ on the Y-axis of the X-Y recorder such that the Y-axis yields directly the absolute thermopower of the specimen.

The main source of error in this technique is from the analog divider. The error introduced in the division operation is of the order of 1%. The overall error in the set up would be of the order of 3 to 4%. It was found essential that all the chopper connections should be adjusted for ‘break-before-make’ mode of operation in order that the various voltage signals are not loaded. This results in the lock-in amplifier being open-circuited twice during each cycle. However this transient is twice the frequency of the voltage signals so that it is rejected by the lock-in amplifier completely.

![Figure 2. Record of the relative thermoelectric power of cerium versus temperature at 5 kbar pressure.](image-url)
4. Performance of the automatic recording system

In order to demonstrate the performance of the automatic technique, we present here some typical data obtained on cerium. The teflon cell technique for thermopower measurement at high pressures has been described earlier (Reshamwala and Ramesh 1974). The experimental conditions in a high pressure set up generally require collection of thermopower data as a function of temperature at a given pressure and repeat the measurements at the desired pressures. Although one is finally interested in obtaining the various isotherms depicting the thermopower variation with pressure, these data cannot be obtained directly using a single thermopower cell. This is in view of the limitation that the thermopower cells do not stand many pressure cycles. The isobaric mode of measurement has many advantages in that all the data required for constructing the different isotherms can be collected using a single thermopower cell.

Figure 2 presents an actual record of the thermoelectric power of cerium relative to chromel as a function of the mean temperature $T$, when the pressure inside the thermopower cell is maintained at 5 kbar pressure. In this record every inch along the $Y$-axis corresponds to about $2\mu V/°C$.

Figure 3 shows a record of the relative thermopower of cerium with pressure when the sample is at a mean temperature of approximately 30° C. The pressure axis is monitored using a pressure transducer. The sharp increase in the relative thermoelectric power near 7.5 kbar pressure corresponds to the isostructural $\gamma-a$
phase transformation in cerium. The implications of the thermoelectric behaviour of cerium with pressure with regard to the 4f–5d electronic transition have been discussed earlier (Ramesh et al 1974).

5. Conclusions

An automatic technique for measurement of thermopower as a function of temperature (or pressure at a specified temperature) has been described. Some typical records on the thermoelectric behaviour of cerium are presented.

Acknowledgements

We thank S R Rajagopalan for making available to us the low thermal noise chopper and other electronic instruments. Thanks are also due to A V Ramani, K G Gopinathan and T Pratapan for useful suggestions.

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