

16 Apr 1992

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AUTOMATED SEEBECK MEASUREMENTS APPLIED TO CONDUCTING CERAMICS

J. S. Shapiro
Physics

ABSTRACT

The Seebeck coefficient (also known as thermopower) is important in the characterization of conducting ceramics because it is very sensitive to the electronic structure. An apparatus was built during the Fall of 1990 and Spring of 1991 which was designed to measure the Seebeck coefficient in small high-resistivity samples in the temperature range from 80 K to 450 K. A reproducible thermocouple-to-sample electrical and thermal contact technique was found to be important to data accuracy but difficult to achieve. The goals of this project were to improve the thermocouple block design to give better thermal and electrical contact with the sample and to make statistically significant and accurate measurements on several sets of samples.

INTRODUCTION

If a conducting sample is placed in a thermal gradient, a voltage across the sample equal to the temperature difference multiplied by the Seebeck coefficient, is produced. The Seebeck coefficient is accordingly defined to be:

$$S = \lim_{\Delta T \rightarrow 0} \frac{\Delta V}{\Delta T} \quad (1)$$

The Seebeck coefficient represents the transport entropy per unit charge carrier. In certain types of ceramics known as hopping conductors (so named because the charges hop from site to site) the Seebeck coefficient represents the charge carrier concentration as given by Heikes' formula [1].

$$S = \frac{k}{q} \ln \left[\frac{1-c}{c} \right] \quad (2)$$

where k is Boltzmann's constant; q is the charge carrier; and c is the fractional charge density.

The Seebeck coefficient is measured by applying various thermal gradients across the sample and then dynamically measuring several δT , δV pairs, as shown in Figure 1. The slope of the linear best fit for this data is the Seebeck coefficient at the average temperature.

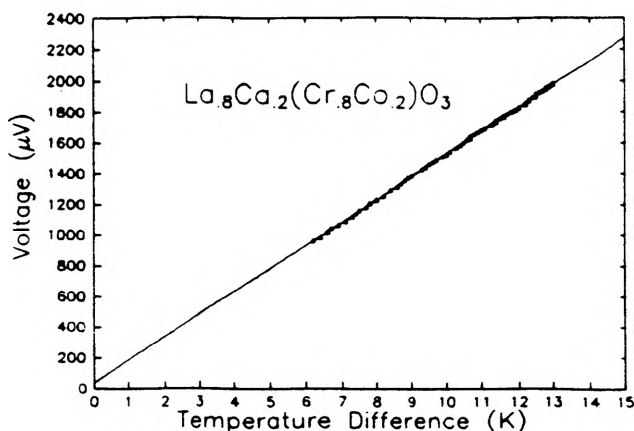


Figure 1 δV vs δT

Previous Work.

An apparatus was built during the Fall of 1990 and the spring of 1991 which was designed to measure high impedance samples from 450 K to 80 K. The use of thin, wide samples of high resistivity materials provides the smallest electrical impedance of the sample. Such a sample would also have a small thermal impedance and generate a small δT . The $\text{La}_{0.9}\text{Sr}_{0.1}(\text{Mn},\text{Cr})\text{O}_3$ series was measured. When the sample-remounted-reproducibility of the $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ data was tested a variety of Seebeck coefficients were recorded. The trends were the same for the different sample remounts but the maximum Seebeck values were scaled. This indicates a problem with the thermal impedance between the sample and the thermocouple blocks, which will be discussed later.

EXPERIMENTAL SETUP

An IBM PC is used to control all the instruments through an Hewlett-Packard Interface Bus (HPIB) card. The PC also has an IBM Data Acquisition and Control Adapter (DACA) which is used to control the sample heater. All the software is written in QuickBasic and is usually run interpreted (non-compiled) to facilitate changes and or corrections.

An HP 3497A Data Acquisition/Control Adapter (with HPIB) with a room temperature compensation thermocouple board is used to measure the temperature at the ends of the sample. The copper leg of the T-type thermocouple (Special-Limit-of-Error grade) is used as the voltage lead.

The voltage across the sample is measured with a Keithley 197 Microvolt DMM. The meter has $1\mu\text{V}$ resolution and an input impedance of $>1\text{G}\Omega$. The voltage measurement error is below 1% when the sample impedance is less than $10\text{M}\Omega$.

The temperature of the Janis SuperTran 2 cryostat head is controlled to within 0.1K using a Lakeshore Cryotronics Model DRC 81C Temperature Controller. The cryostat can reach

temperatures from 100K to 450K. The cryostat chamber is operated under a rough vacuum for thermal insulation.

The sample holder consists of two blocks of aluminum with embedded thermocouples. Because the thermocouple is not in direct contact with the sample it is possible that the measured temperature difference is larger than that of the sample. However, because the blocks are made of aluminum, which has a thermal conductivity of $2.86 \text{ W cm}^{-1} \text{ K}^{-1}$ [2] (70% as conductive as silver), and the thermocouples are mounted close to the surface of the blocks, the temperature of the thermocouples is very close to that at the surface of the aluminum block.

There have been three different sample holders built. The first was used from October, 1990 through January, 1991. It used a single alignment rod and small isothermal blocks. The second design was used from February to October, 1991. This design used two alignment rods to facilitate sample mounting. The isothermal blocks were still relatively small and thin. The third design was used from October, 1991 to present. This design uses four alignment rods which make sample mounting very easy. The isothermal blocks on this design are both much larger and thicker than previous designs. The third sample holder is shown in Figure 2.

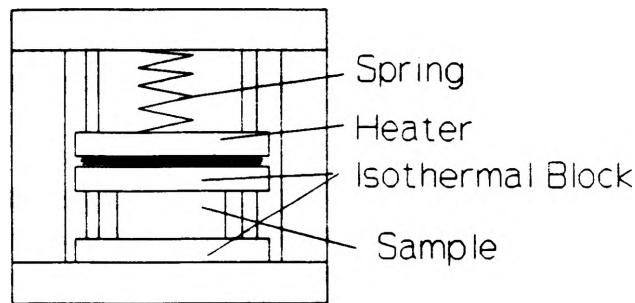


Figure 2 Sample Holder

Measurement Method

The measurements on this apparatus are taken while the temperature is decreasing. This means that the cryostat starts at the highest setpoint and decreases by some user defined amount until it reaches the lowest setpoint. If a setpoint is below room temperature an operator must turn on the flow of liquid nitrogen. When the lowest setpoint is reached the computer resets the setpoint to room temperature and the operator must then turn off the liquid nitrogen.

As the sample temperature approaches a setpoint the computer turns on the sample heater to create a range of temperature differences across the sample. The computer repeatedly reads the voltage and temperature difference across the sample. It fits these data with a straight line and saves the slope as the Seebeck coefficient at the average temperature of the data set. This process is repeated for each setpoint.

Error in the Measurements

A sample geometry which has a large area and small thickness is chosen to reduce the overall sample impedance for high resistivity samples. The problem with this geometry is that the temperature difference across the sample is less accurately known. Because the thermocouples are inside the isothermal block, and if the junction between the isothermal block and the sample has a high thermal impedance, then the temperature across the sample will be smaller than the measured temperature difference. This results in a Seebeck coefficient which is lower than the actual Seebeck coefficient.

By knowing the thermal impedances of the materials involved in Figure 2, the actual Seebeck coefficient can be shown to be:

$$S_g = S_m + \frac{2R_b(S_m - S_b) + 2R_j(S_m - S_j)}{R_g} \quad (3)$$

where the subscripts s, m, b, and j correspond to: sample, measured, (isothermal) blocks, and junction. R is the thermal impedance. The isothermal block term is included because the thermocouple is not at the surface of the block. Generally this term would be very small given the low thermal resistivity of aluminum. If the junctions and the isothermal blocks have a very low thermal impedance compared to the sample then the measured Seebeck coefficient approaches the actual value.

A thermal paste is applied to both sides of the sample to minimize the thermal impedance of the junctions. However, if a different amount of thermal paste is applied, or a different thermal paste is used in successive runs, then the junction thermal impedance will be different and this will cause different measured Seebeck coefficients. Because there is no method in which the Seebeck coefficient can be artificially amplified, the highest value is the closest to the actual Seebeck coefficient. This can be seen in Figure 3 (note: the data in Figure 3 was taken using the second sample holder design.)

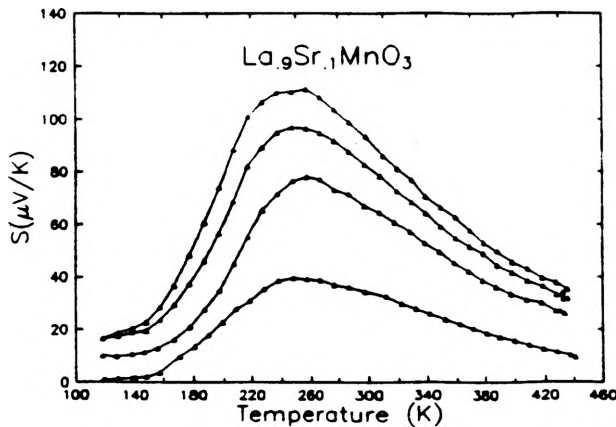


Figure 3 The Seebeck coefficient is scaled when the sample is removed and remounted

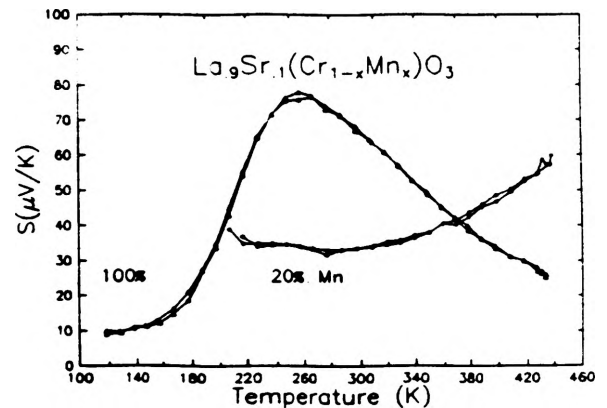


Figure 4 When the sample is not remounted the reproducibility is excellent

Although it would be possible to correct for the thermal impedance of the materials and junction, it would be much better to minimize such impedances. One way to lessen this is to use larger isothermal blocks (as with the third sample holder design). Another is by putting a silver paint on the samples. This greatly aids the electrical contact and, because of the polymeric binder in the paste, the paste can conform better to the isothermal block if it was not smooth. Using this method the remount-reproducibility is greatly improved ($\pm 15\mu\text{V/K}$). One thing to note is that the reproducibility when the sample is not removed is excellent ($\pm 2\mu\text{V/K}$) as shown in Figure 4.

EXPERIMENTAL RESULTS

Calibration

The apparatus was calibrated against two metals: chrome and cobalt. Even though these samples are not high impedance, the Seebeck coefficient in each is relatively small and therefore can test the limits of the apparatus. The cobalt sample (99.999%) was essentially ideal. It was a right cylinder about 1-1.5 cm long with a diameter of about 0.4 cm. The chrome sample (>99%) was much less ideal; it was 1.5 cm long, 0.5 cm at the maximum radius and shaped like a teardrop. The data in Figure 5 shows the effect of this geometry (and thus thermal impedance) on the Seebeck coefficient.

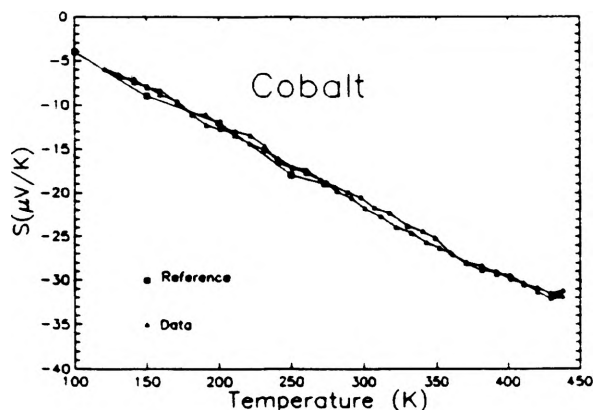


Figure 5 Cobalt Calibration

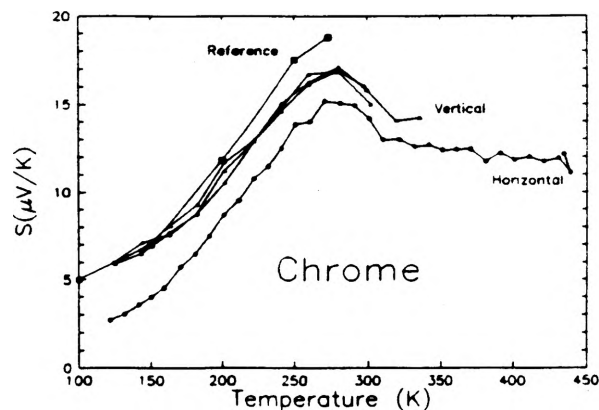


Figure 6 Chrome Calibration



The data from this series is shown in Figure 7. The most interesting sample in this series was $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$. The Seebeck coefficient falls from a high value at high temperatures to a lower value with a hump in it at the lower temperatures.

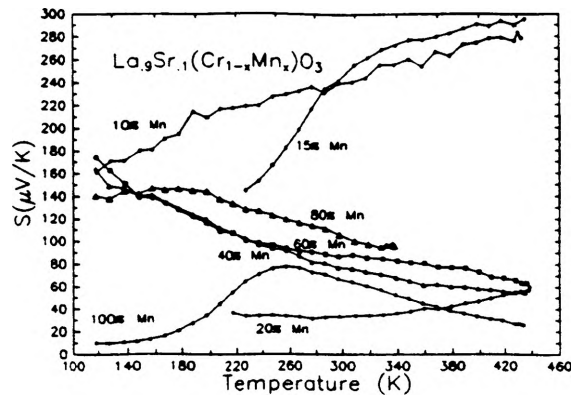


Figure 7

LaCr_{1-x}Co_xO₃

The data from this series is shown in Figure 8. This data is very interesting, especially those samples with $x > 60\%$. Scott Sehlin, a graduate physics student, was measuring the 100% Co sample from 1500 K to 300 K, where the value of the Seebeck coefficient is flat, but at around 400 K the value for the Seebeck coefficient dropped off very quickly (this is often the sign of a run which is no longer good) and he believed the data to be invalid below 450 K. When the sample was placed in this apparatus it was shown that the Seebeck coefficient did drop off very quickly and crossed zero. The 100% Co sample was then remeasured in his apparatus from 600 to 300 K and the agreement between the two apparatus is excellent ($\pm 5\mu\text{V/K}$). Figure 9 shows two of the samples from this series.

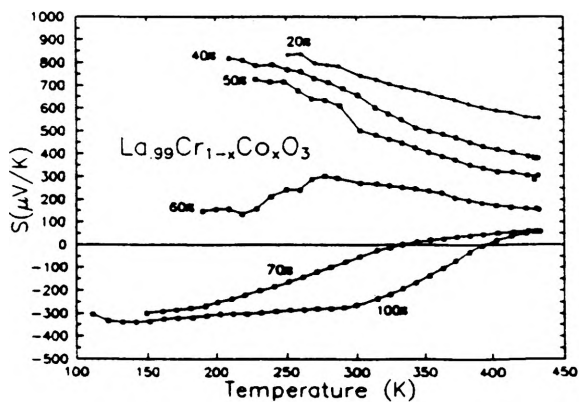


Figure 8

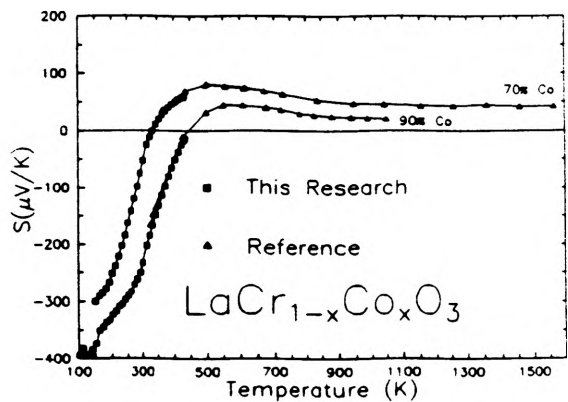


Figure 9



At higher temperatures (> 1000 K) the Seebeck coefficient is more or less flat (small temperature dependence) and between 300-900 K, depending on the sample, the Seebeck coefficient rises to a higher value. In the temperature range covered by this apparatus, the samples with < 40% Co are already flat, while 80% and 100% Co are still rising. One very interesting feature of this data set is the trend of the Seebeck coefficient toward $0 \mu\text{V}/\text{K}$ as T goes to absolute zero. This can be explained if there are a finite number of carriers, perhaps due to defects, as T goes to absolute zero because the entropy in the system goes to zero in a non-degenerate system.

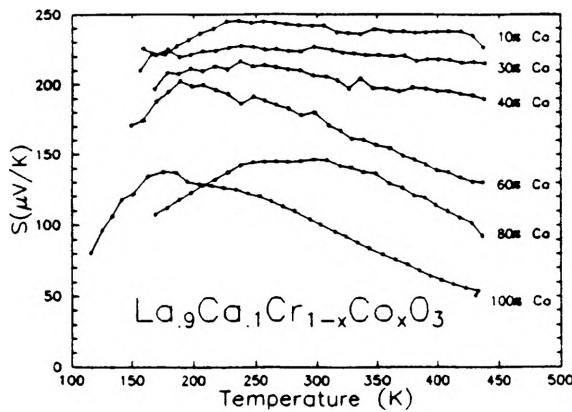


Figure 10

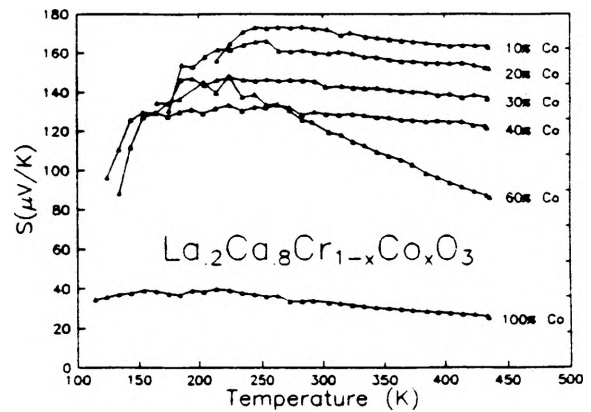
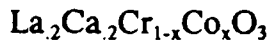


Figure 11



The data from this series is shown in Figure 10. This data is very much like the $\text{La}_9\text{Ca}_1\text{Cr}_{1-x}\text{Co}_x\text{O}_3$ series except that the values are lower.

CONCLUSION

The thermal impedance problems associated with Seebeck coefficient measurements using thin, wide high resistivity samples have been extensively examined. Improved sample holders were designed and built which used silver paste to lower thermal impedances between the sample and the thermocouple block. The ideal thermal geometry is opposite to that required for electrical measurements in high resistivity material and a satisfactory compromise was reached.

Four series of conducting ceramics, with 5-7 samples each, were measured. Good agreement was achieved with other researchers and between the low and high temperature apparatus at UMR.

ACKNOWLEDGEMENTS

I would like to thank Dr. Don Sparlin for his patience and wisdom in advising this project. I would also like to thank Scott Sehlin for providing the $\text{La}_{1-y}\text{Ca}_y\text{Cr}_{1-x}\text{Co}_x\text{O}_3$ samples and Jason Hoerner, a Jackling Institute student, for writing all the graphics routines used.

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