

Seebeck coefficient measurements of lithium isotopes <sup>☆</sup>V. Surla <sup>a,b,\*</sup>, M. Tung <sup>a</sup>, W. Xu <sup>a</sup>, D. Andruczyk <sup>a</sup>, M. Neumann <sup>a</sup>, D.N. Ruzic <sup>a</sup>, D. Mansfield <sup>b</sup><sup>a</sup> Center for Plasma–Material Interactions, Department of Nuclear, Plasma and Radiological Engineering, University of Illinois at Urbana Champaign, Urbana, IL 61801, USA<sup>b</sup> Princeton Plasma Physics Laboratory, Princeton, NJ 08543, USA

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## ABSTRACT

Lithium, owing to its many advantages, is of immense interest to the fusion community for its use as plasma facing component (PFC) material. Various experiments are under progress in the Center for Plasma Material Interactions (CPMI) at the University of Illinois at Urbana Champaign (UIUC) aimed at understanding the plasma–lithium interactions. In one such experiment called Solid/Liquid Lithium Divertor Experiment (SLiDE), it was recently observed that the flow of liquid lithium in the presence of magnetic fields is dominated by thermoelectric Magnetohydrodynamic (TEMHD) effects. To describe these results accurately, a knowledge of the thermoelectric properties of lithium is essential. For this purpose, an apparatus to measure the Seebeck coefficient of lithium was developed. Using this apparatus, the Seebeck coefficient of lithium as a function of temperature has been obtained. The Seebeck coefficient of lithium-7 is found to gradually increase from 11  $\mu\text{V}/\text{K}$  to 25  $\mu\text{V}/\text{K}$ , as the temperature is raised from 25 °C to 240 °C. These measurements are in good agreement with Kendall's thermoelectric measurements on natural Li. Furthermore, using the same apparatus, the thermoelectric curve of lithium-6 is obtained and for the first time are reported in this paper.

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## 1. Introduction

Lithium is a low Z-material which offers several benefits for plasma performance; for example low recycling, high edge temperatures, improved plasma confinement, and the suppression of ELMs. Hence there is growing world-wide interest in the use of lithium as a wall or divertor target material. Further, liquid lithium is potentially even more beneficial [1] as it could minimize problems due to wall erosion and could be effectively used for power handling. The schemes involving the future use of liquid lithium as a plasma facing material generally rely on successful initial wetting of porous backing material with liquid lithium. The center for plasma material interactions has been actively involved in lithium research [2] and in this regard, the practical problems of lithium wetting and flow properties have been the subject of laboratory experiments which have demonstrated the importance of thermoelectric effects in the Solid/Liquid Lithium Divertor Experiment (SLiDE) facility [3]. To enhance understanding of the lithium swirling flow observed in SLiDE, determining the thermoelectric properties of lithium is essential. For this purpose, an apparatus to measure the Seebeck coefficient of lithium was developed and is presented here.

The thermoelectric effect, also known as the Seebeck effect, is the principle upon which a thermocouple works. Briefly, when two junctions of dissimilar metals are placed at different temperatures, a voltage is generated and this is called Seebeck effect. To quantify the Seebeck effect of different materials, the Seebeck coefficient is generally used which is defined as the thermoelectric voltage developed per unit temperature difference. The Seebeck coefficient ( $S$ ), which is also referred as thermoelectric power, is thus given by

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

The Seebeck coefficient of materials is known to vary with temperatures. Thermoelectric power curves, a plot of Seebeck coefficient as a function of temperature, are important in order to determine the variation of Seebeck coefficient as the material undergoes phase changes. These are relevant in a fusion reactor where the thermoelectric currents generated due to phase changes could have adverse effects on liquid metal PFCs, like material ejection resulting from  $\mathbf{J} \times \mathbf{B}$  thermoelectric forces. Hence in this study, the Seebeck coefficient of lithium as a function of temperature is investigated.

Further, it has been demonstrated experimentally that anomalously large differences exist in the physical properties of liquid lithium-7 (<sup>7</sup>Li) and liquid lithium-6 (<sup>6</sup>Li). In particular, the viscosity of <sup>6</sup>Li has been measure to be significantly lower that of <sup>7</sup>Li – far lower than could be expected classically based on the ratio of their respective masses [4]. Similarly, the measured particle self-diffusivity of <sup>6</sup>Li in a <sup>6</sup>Li liquid matrix is larger than for <sup>7</sup>Li in a <sup>7</sup>Li liquid

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matrix – larger than classically expected value on the basis of their respective masses [5]. A quantum mechanical explanation for these anomalous differences has been offered by Omini [6]. These observed differences in physical parameters between lithium isotopes and the importance of thermoelectric effects to the wettings and flow properties of liquid lithium have motivated the measurement of the thermoelectric powers of  $^6\text{Li}$  and  $^7\text{Li}$  in this present work.

The details of the experimental setup and measurement approach are given in Section 2. The results of Seebeck coefficient measurements of natural lithium ( $^7\text{Li}$ ) and lithium-6 ( $^6\text{Li}$ ) are presented in Section 3 and finally, conclusions are given in Section 4.

## 2. Experimental setup

The key components of the experimental setup are the extruding system and the Seebeck coefficient measurement setup. The extrusion apparatus, described in Section 2.1, was used to produce lithium wires and, the measurement apparatus, described in Section 2.2, was used to measure the thermoelectric power of metals as a function of temperature.

### 2.1. Extrusion apparatus

In order to make reliable measurements of thermoelectric power, it was necessary that clean, and reproducible samples are prepared for each run. In addition, the metal of choice in the current study being lithium, special attention is needed due to its high chemical reactivity. For this purpose, a wire extruding die made of stainless steel was used to obtain thin lithium wires. The extrusion apparatus consisted of a cylindrical block to hold the lithium metal, a piston or ram that moved in the cylinder, and finally a die with a hole through which the metal could be pushed out. The components of the extruding apparatus are shown in Fig. 1a. As pressure was applied on the piston, it pushed lithium out of the die forming a wire as seen in Fig. 1b. The dies are available in various hole diameters, and were chosen based on the diameter of the wire required for the experiment. In this work, lithium wires of 1/16" dia. ( $\text{\O}1.5875\text{ mm}$ ) were extruded in mineral oil. Mineral oil is inert to lithium and so prevented lithium from reacting with air or moisture. Once the lithium wire was obtained, it was cut into several sections of appropriate lengths and placed in quartz tubes for storage. As a note on lithium's condition in oil, it was observed that the lithium slowly turned black in color, in a few days, indicating the high reactivity of lithium even in inert conditions. However, the lithium wires that were inserted in the quartz tube stayed clean and shiny for longer periods of up to a month, which is why all the lithium wires were placed in quartz tube for storage. In all experimental runs, lithium wires of approximately 75 mm were used for the measurements. It is known that the Seebeck coefficient

is independent of the length of the material and the length of 75 mm is chosen only for convenience.

### 2.2. Apparatus for Seebeck coefficient measurements

Fig. 2 shows a schematic of the apparatus used for the Seebeck measurements. The extruded lithium wires were placed inside of a 75 mm long quartz tube (3 mm inner dia.) and put in a mineral oil container. The entire experimental apparatus is inside the mineral oil providing an inert atmosphere for lithium to stay clean. First, the extruded solid wire of lithium ( $\text{\O}1.5875\text{ mm}$ ) is inserted into the 3 mm I.D. quartz tube filling the entire length of the quartz tube. The stainless steel shim stock pieces are then placed at the ends of the quartz tube in order to prevent the escape of lithium during melting, from the ends of the quartz tube and serve as "stoppers" against the flow of liquid lithium. In addition, the shim stock also assists in holding the thermocouple wires in place. Thermocouple wires are inserted at each end of the shim stock just making enough contact with the solid lithium wire. However, it is when the lithium is melted that one can achieve good contact of the thermocouple with the lithium wire. To achieve this, the mineral oil in the pan is heated with the help of a heating plate until the lithium melts inside the quartz tube. This can be seen visually and also from the temperature measured by the thermocouples when the value is greater than the melting point of lithium. At this point, the heater is turned off. When lithium melts, it is made to shrink and conform to the shape of the tube by pushing the shim stock at both ends against the lithium. Also, the contact of each of the thermocouples is established with lithium during its molten phase. This is achieved by pushing the thermocouple wires on both ends carefully into molten lithium and letting the lithium solidify slowly. The leads going from each of the thermocouple wires to the multimeter assist in establishing the contact of thermocouples on both ends with lithium. Once the contact is registered on the multimeter, the thermocouples are clamped and their position is fixed. It is these clamps and the shim stocks that help the thermocouple stay in place and attach to the lithium during the entire course of the experimental measurements. The photograph of the experimental setup is added for clarity.

Any apparatus to measure Seebeck coefficient should have the ability to induce a temperature gradient across the material and measure the voltage generated across it. Thus, the experimental setup included an external heater coil (with  $\sim 1\text{ A}$  of current) wrapped around the quartz tube to produce a temperature gradient along the lithium wire. A variac was used to vary the current passing through the heater coil and thus controlled the temperature gradient produced. To measure the temperature gradient, two K-type thermocouples (1 mm diameter) with stainless sheaths were inserted into each end of the lithium wire. Typically, a gradi-

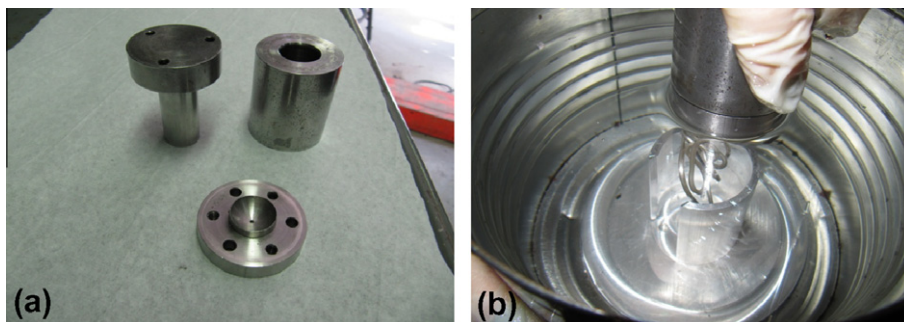


Fig. 1. Photograph of the extrusion apparatus used to produce lithium wires. The key parts of the extrusion apparatus are shown in (a) which consists of a piston like ram, a cylindrical bore, and a wire-making die to produce lithium wires as shown in (b).

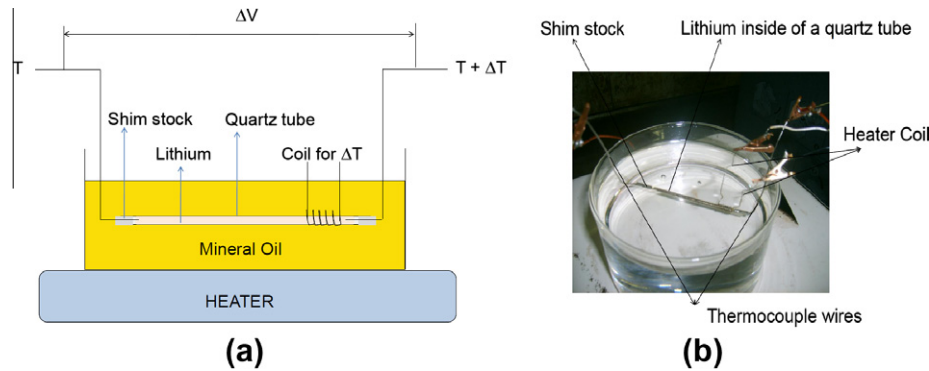


Fig. 2. (a) Schematic of the measurement apparatus used for Seebeck coefficient measurements and (b) photograph of the experimental setup.

ent of 6–8 °C was maintained during the entire experimental run. To measure the Seebeck voltage, electrical leads were attached to each thermocouple sheath and connected to the voltage measuring circuit shown in Fig. 3. The voltages generated were typically in the  $\mu\text{V}/\text{K}$  range hence requiring amplification. This is achieved by the use of LJTick-In Amp (LJT1A purchased from labjack) signal-conditioning module which provided two instrumentation amplifiers designed for low-level thermocouple signals. Each amplifier module converted the differential thermocouple inputs to a single-ended output. All voltage outputs were then sent to data acquisition using a U6 labjack device. A custom written Labview program records those values and provided a direct computer display of the Seebeck coefficient at a given temperature. Seebeck coefficient measurements were taken every 5 °C from 25 °C to 240 °C. At each temperature, several contemporaneous Seebeck values were recorded in order to determine the error in the measurement.

During the course of the measurements it was observed that the resulting Seebeck values were sensitive to the placement of the heater coil. The coil position corresponding to the position at which a maximum gradient was recorded on the  $\Delta T$  measurement is referred as the “center” coil position. By moving the coil position to either side of this position decreases  $\Delta T$ , and the thermoelectric curves were affected. In this work, the position corresponding to

–1.5875 mm from the “center” coil position is referred as the coil position being “left” and +1.5875 mm from the “center” coil position is referred as the coil position being “right”. The measurements were made by positioning the coil at all the three (left, center, and right) positions in order to determine the effect of coil position on the Seebeck coefficient measurements made.

### 3. Results and discussion

The Seebeck coefficient of a material is defined in Eq. (1) and represents the magnitude of the thermoelectric voltage generated when a temperature gradient is induced across that material. It should, however, be noted that the Seebeck coefficient cannot be measured using a single material. To illustrate this, consider a lithium wire that is hotter on one end and colder on the other end and if one were to measure the voltage difference generated across the lithium wire, using connecting wires which are also of lithium. In this scenario, the net emf measured will be zero, because the same temperature difference exists on the connecting wires as well. Thus, Seebeck coefficient measurements are always obtained with reference to a standard material, for example, like platinum. The

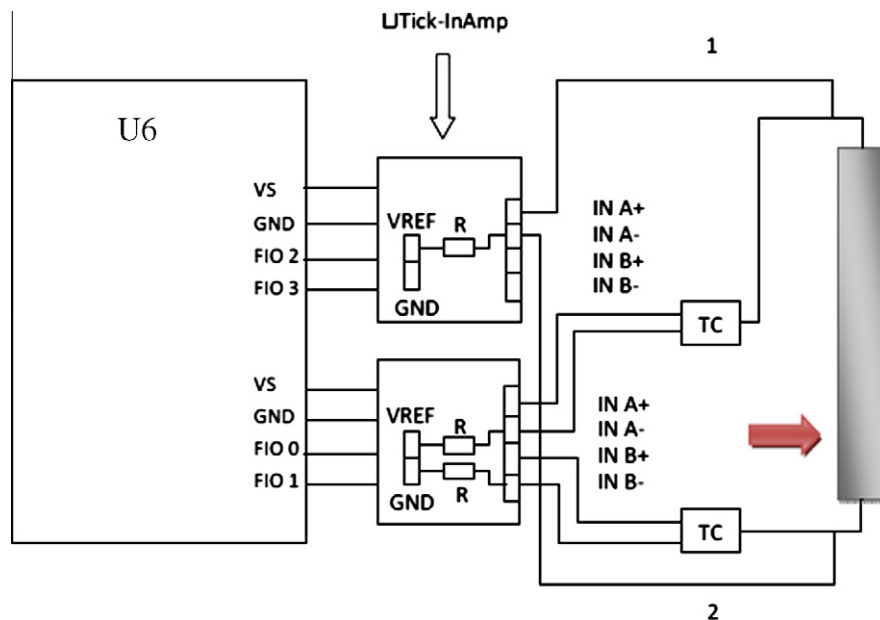


Fig. 3. Circuit diagram of the electrical connections of thermocouples (TC) and connecting wires 1 and 2 for measuring the voltage generated due to Seebeck effect. LJTick-In Amp provides the amplification of voltage signals before sending to data acquisition using Labjack U6.

Seebeck coefficient between two dissimilar metals A and B is given by

$$S_{AB} = S_A - S_B \quad (2)$$

where,  $S_{AB}$  denotes the absolute Seebeck coefficient of material A with respect to material B,  $S_A$  is the absolute Seebeck coefficient of A (with respect to Pt) and  $S_B$  is the absolute Seebeck coefficient of B (with respect to Pt). In this work, Seebeck coefficient measurements of lithium isotopes were made with respect to stainless steel (represented by  $S_{Li-SS}$ ). Thus, in order to obtain the absolute Seebeck coefficient of Li, Eq. (2) can be used which is represented as:

$$S_{Li-SS} = S_{Li} - S_{SS} \quad (3)$$

where  $S_{Li}$  and  $S_{SS}$  denote the absolute Seebeck coefficient values of lithium and stainless steel respectively. The raw measurements made using the experimental apparatus describe above yields  $S_{Li-SS}$ . The absolute Seebeck coefficient values of stainless steel as a function of temperature ( $T$  in Kelvin) are taken from Ref. [7]:

$$S_{SS} = 2.5269 - 0.0143 * (T) + 0.000008 * (T)^2$$

Using the raw measurements and the above Seebeck coefficient values of stainless steel, the absolute Seebeck coefficient of lithium were calculated using Eq. (3).

### 3.1. Natural lithium ( ${}^7\text{Li}$ )

Natural lithium consists of ~92.5%  ${}^7\text{Li}$  and 7.5%  ${}^6\text{Li}$  but as  ${}^7\text{Li}$  constitutes the majority composition, natural lithium and  ${}^7\text{Li}$  are used interchangeably in this work. Fig. 4 shows the raw data obtained for the Seebeck coefficient of natural lithium as a function of temperature. This represents the thermoelectric curve of  ${}^7\text{Li}$  with respect to stainless steel ( $S_{Li-SS}$ ). A sudden jump can be seen in the Seebeck values around 180 °C, which is indicative of phase change, here, lithium transforming from solid to liquid. Thus, thermoelectric curves may also be used to determine the melting point of lithium. The thermoelectric curves obtained at three different coil positions are also shown in Fig. 4. As can be seen from Fig. 4, at higher temperatures, there is more variation in the Seebeck coefficient measurements as the coil position is changed. To obtain the absolute thermoelectric curve of  ${}^7\text{Li}$ , Eq. (3) is used in combination with the Seebeck coefficient values of Stainless steel taken from Ref. [7], which is plotted in Fig. 5. This conversion allows comparisons to be made with the absolute Seebeck coefficient values reported in the literature. Fig. 5 also shows a comparison plot

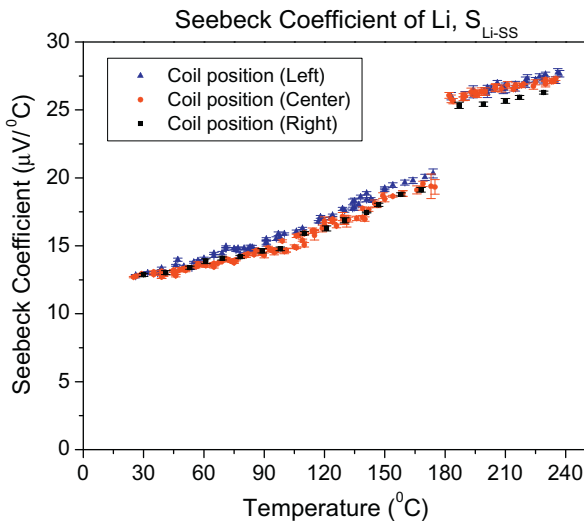


Fig. 4. Thermoelectric curve of natural lithium ( ${}^7\text{Li}$ ) with respect to stainless steel (SS). The raw data obtained at three different coil positions are shown here.

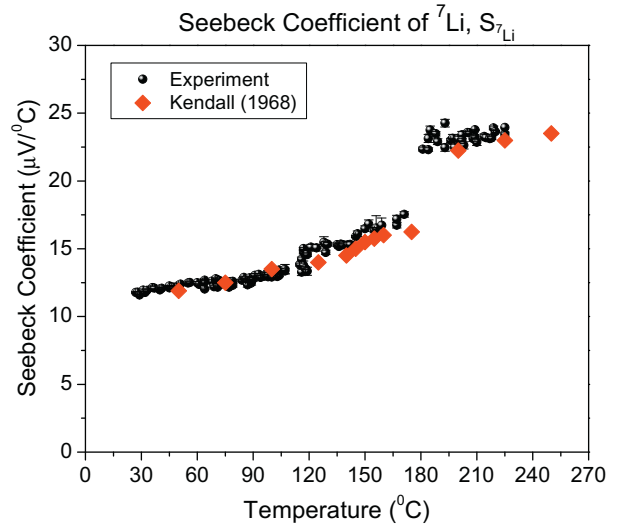


Fig. 5. Comparison of absolute thermoelectric curves of natural lithium,  ${}^7\text{Li}$ , obtained in the current setup with that of Kendall's measurement. The "solid circles" represent the current experimental points and "diamonds" represent Kendall's measurements showing a good agreement.

where the thermoelectric curve of natural lithium obtained by Kendall [8] in 1968 is also plotted on the same graph. As can be seen, there is a very good agreement between both the measurements, which validates the current measurement approach.

### 3.2. Lithium-6 ( ${}^6\text{Li}$ )

Once the measurement apparatus was validated for natural lithium measurements, the same apparatus was used to obtain the thermoelectric curve of  ${}^6\text{Li}$ . Fig. 6 shows the absolute Seebeck coefficient measurements of lithium-6 as a function of temperature. For comparison, current experimental measurements of natural lithium ( ${}^7\text{Li}$ ) are also plotted in Fig. 6. It can be seen from Fig. 6 that within the accuracy of the experimental measurement, there is no significant evidence to differentiate Seebeck coefficient measurements of  ${}^7\text{Li}$  and  ${}^6\text{Li}$ . Thus it is safe to conclude that the isotopic differences have no effect on Seebeck coefficient measurements of lithium. In addition, from the thermoelectric curves of  ${}^7\text{Li}$  and  ${}^6\text{Li}$ , it can be seen that the melting point also stays the

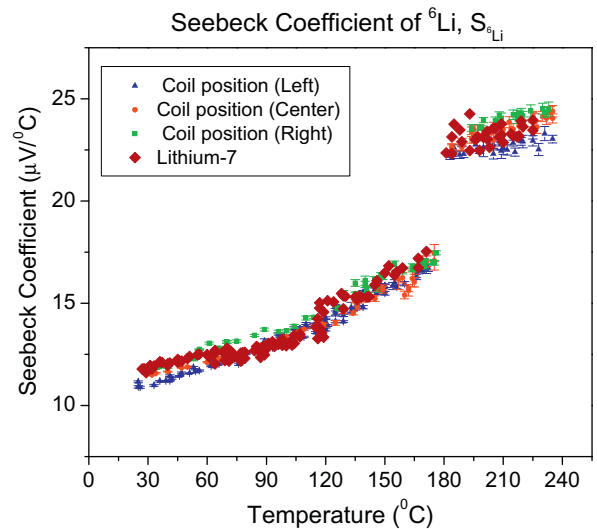


Fig. 6. Absolute Seebeck coefficient of lithium-6 ( ${}^6\text{Li}$ ) as a function of temperature. The measurements at three different coil positions are shown here. A comparison with Kendall's measurement of natural lithium is also shown here.

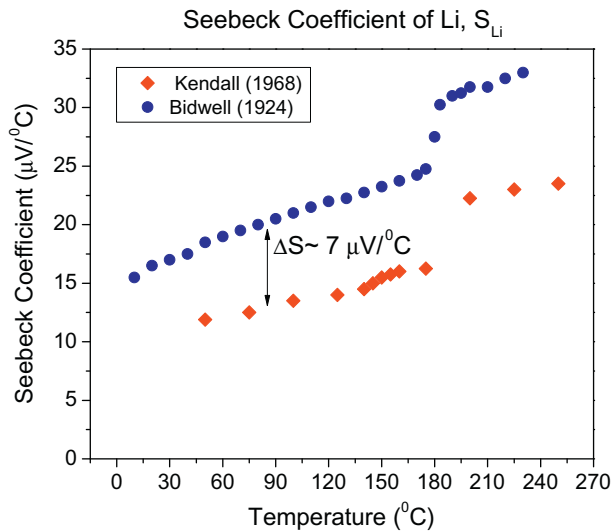


Fig. 7. Comparison of Bidwell's measurements ("circles") with Kendall's measurements ("diamonds"). There is a difference of  $\sim 7 \mu\text{V}/^\circ\text{C}$  in the reported values.

same. This indicates that the isotopes of Li can be mixed without affecting the melting point.

### 3.3. Seebeck coefficient measurements of natural lithium by Bidwell in 1924 [9]

Finally, we bring to the notice of the readers a discrepancy in the reported values of Seebeck coefficient of lithium. Bidwell [9] reported the first measurements of thermoelectric properties of lithium and commented that "the work on lithium was by far the most satisfactory as regards reproducibility on different runs and with different specimens". However, if one compares Bidwell's data to Kendall's data there is inconsistency in the values. From Fig. 7, it can be seen that over the investigated temperature range, Bidwell's measurements differ from Kendall's measurements by a magnitude of, approximately,  $\sim 7 \mu\text{V}/^\circ\text{C}$ . This discrepancy could be due to the position of the heater coil in Bidwell's experimental setup as it was clearly observed from our previous measurements (although not reported here) that the heater coil position could lead to such higher values. Indeed, it is one of the reasons why careful investigation of the Seebeck coefficient as a function of heater coil position was performed in the present study by defining an absolute reference position of heater coil.

## 4. Conclusions

An apparatus for measuring Seebeck coefficient of lithium is described here. This apparatus is useful for measuring thermoelectric

power of lithium and similar metals in the temperature range of 20–240 °C. Specifically, in this study, the difference in the thermoelectric properties of lithium isotopes is investigated. First, the Seebeck coefficient measurements of  $^7\text{Li}$  are made and compared against available measurements in the literature and find that they are in good agreement over the temperature range investigated. This verified the accuracy of the experimental apparatus that was then used to measure the thermoelectric properties of  $^6\text{Li}$ . For the first time, the Seebeck coefficient measurements of  $^6\text{Li}$  as a function of temperature are measured and reported here. Within the experimental error, it was found that there is no statistical significant difference of the Seebeck Coefficient between the two isotopes of Li. From the thermo electric curves, it is found that the melting point of Li isotopes also remains the same. This indicates that the isotopes of Li can be mixed or dissolved without affecting the melting point. Considering that both isotopes have the same thermoelectric behavior,  $^6\text{Li}$  might still be advantageous as a PFC material because of its lower density and lower viscosity. Especially, it might be beneficial to investigate the effect of segregations processes in binary alloys to form protective coatings as described by Krauss and Gruen [10] for  $^6\text{Li}$ -Metal alloys (Li-W or Li-Mo alloy) wherein the surface can be covered by a dominant layer of  $^6\text{Li}$ . The usefulness of  $^6\text{Li}$  to effectively remove the heat flux making use of thermoelectric Magnetohydrodynamic effects in SLiDE facility will be investigated in the future.

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