Anomalous Nernst and Seebeck effects in NiCo$_2$O$_4$ films

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We investigated both the Seebeck and anomalous Nernst effects in NiCo$_2$O$_4$(001) epitaxial films with a preferential magnetization direction normal to the film plane. Since the thermoelectric signals were extremely small, we custom-built a measurement system to detect the weak voltage signals. To suppress spurious voltage signals originating from the electrical contacts in the measurement circuit, we employed the following measures. We reduced the number of electrical contacts between the output of a commercial cryostat with a superconducting magnet and the nano-voltmeters. We employed silver soldering while making the electrical contacts to reduce the thermal electromotive force voltages at the remaining contacts. By adopting these measures, we have succeeded in detecting thermoelectric voltages as small as 5 nV. The observed thermoelectric efficiency of NiCo$_2$O$_4$ is quite small compared to conventional ferromagnetic metals.

Key words: NiCo$_2$O$_4$, Anomalous Nernst effect, Perpendicular magnetic anisotropy

1 Introduction

In the recent past, different types of energy conversion technologies have been studied due to the increasing need for alternative and sustainable energy sources $^{1,2}$). Among the energy conversion technologies, the thermoelectric device has received much attention as it enables the direct conversion of waste heat energy into electrical energy $^{3,4})$. Moreover, thermoelectricity is interesting from the perspective of condensed matter physics because it depends on the electrical and thermal transport phenomena, which are intrinsically related to the electronic state of materials. Particularly in magnetic materials, the temperature gradient can be converted into electrical voltage through thermomagnetic phenomena, such as the anomalous Nernst effect (ANE) and the spin Seebeck effect $^{5,6)}$. Another transport phenomenon as a counterpart of ANE is known anomalous Hall effect (AHE). Both the AHE and ANE reflect well the electronic state of materials, they have contributions from the extrinsic and intrinsic mechanisms $^{7,8)}$. However, since the electric field generated by ANE is smaller than AHE one’s, it hinders to investigate the relation between thermal and electrical transport in various materials. Therefore, for understanding the electronic state of materials by ANE, a measurement system that can detect the weak thermoelectric voltage desired.

The ANE is defined as the generation of an electric field ($E_{ANE}$) along the direction of the outer product of the magnetization ($M$) and the temperature gradient ($\nabla T$). Thus, it is experimentally observed as an anomalous transverse voltage $^{9)}$. For example, in the case of $\nabla T$ and $M$ parallel to $x$- and $z$-axis respectively, $E_{ANE}$ appears along the $y$-axis direction. In other words, ANE in a magnetic material with perpendicular magnetic anisotropy (PMA) could generate a large thermoelectric voltage by expanding the area in the vertical direction from the temperature gradient. Therefore, PMA can be a crucial factor for generating large ANE voltage $^{3,10)}$.

Oxide-based thermoelectric materials have many advantages such as the following: they are non-toxic and non-polluting; they can be synthesized in the air and do not need inert conditions or vacuum; they are stable even at high temperatures. These advantages make oxide thermoelectric materials a potential candidate for practical applications at elevated temperatures. As a candidate oxide thermoelectric material with PMA, we focused on NiCo$_2$O$_4$(NCO). NCO has an inverse spinel-type structure ($Fd\bar{3}m$) and is a conductive ferrimagnet with a high transition temperature ($T_C \approx$ 400 K) $^{11)}$. Further, some previous studies reported that NCO has mixed-valence cations and can be expressed by a general formula, Co$_{2+x}$[Co$_{2-x}$Ni$_{2-x}$Ni$_x$]Ni$_{8-x}$O$_{12}$ ($0 < x < 1$), where tetrahedral ($T_d$) site is occupied by high spin Co$^{2+}$ ($d^7$, $S = 3/2$) and Co$^{3+}$ ($d^6$, $S = 3/2$), octahedral ($O_h$) site is occupied by low spin Ni$^{2+}$ ($d^8$, $S = 1$), Ni$^{3+}$ ($d^7$, $S = 1/2$), and diamagnetic low spin Co$^{3+}$ ($d^6$, $S = 0$). The saturation magnetic moment is 2 $\mu_B$/f.u. irrespective of $x$. It has been reported that in the presence of such a large number of states in the system, a large thermoelectric signal can be generated via an increase in entropy $^{12,13)}$. In addition, NCO film grown on the MgAl$_2$O$_4$(MAO) substrate exhibits strong PMA $^{14,15)}$, which is approxi-mately 0.3 MJ/m$^3$ at room temperature for a $-0.3\%$ epitaxial strain. A recent theoretical investigation showed that Co at the $T_d$ site is responsible for PMA $^{16)}$.

In this study, we designed a measurement system to detect the weak thermoelectric voltage signal and investigated the thermoelectric properties of NCO. This manuscript is organized as follows. Sample preparation and design of the measurement setup are explained in Section 2. We present experimental results and discussion in Section 3 and summarize the work in the final section.
2 Experiment

2.1 Sample preparation

Epitaxial NCO thin films with a thickness of 50 nm were grown by reactive radio frequency magnetron sputtering technique (ES-250MB: Eiko Engineering Co., Ltd.)[17-19]. We used a 2-inch alloy target with the ideal composition of Ni:Co= 1 : 2. Before growing the film, a single crystal MAO substrate was ultrasonically degreased using acetone, ethanol, and deionized water for 5 min at each step. The growth conditions of NCO thin films were as follows: Ar and O₂ flow rates were set to 10 and 2.5 sccm, respectively; the process temperature was 300°C, and the working pressure was 1.3 Pa. Thereafter, we annealed the NCO films at 300°C for 30 min under an oxygen pressure of 0.2 Pa[20]. The film structure was characterized by reflection high-energy electron diffraction (RHEED), X-ray reflectivity (XRR, by Rigaku Smart Lab, using Co Kα1 radiation), and X-ray diffraction (XRD). Magnetic hysteresis (MH) loops were measured by a vibrating sample magnetometer (VSM) option of the Physical Property Measurement System (PPMS) from Quantum Design.

2.2 Measurement setup

To perform the thermoelectric measurements, we designed and built a sample holder, as illustrated in FIG. 1. Figure 1 shows schematic illustrations of the sample holder. The sample was bridged on the top of two Cu plates (5 × 13 × 1 mm² and 5 × 13 × 3 mm³). The one Cu plate was directly placed on the sample holder (P102/3A, Quantum Design), where the temperature was measured using the PPMS system. The another Cu plate was placed on the sample holder through Bakelite (5 × 13 × 2 mm³) for thermal insulation. Moreover, a chip resistor (R = 330 Ω, TE Connectivity, 3522330RFT) acting as a heater was attached to this side to raise the temperature. Here, the electrodes on the back of the chip resistor were removed by polishing. Input electric power was supplied to the chip resistor using a source meter (Keithley2400). To monitor the actual temperature difference between the Cu plates, we fabricated a type-E thermocouple from chromel (TFCH-003) and constantan (TFCC-003), supplied by Omega Engineering Inc. The thermal contact between the thermocouple and each Cu plate was made using GE7031 varnish via a small piece of thin paper. The thermal electro motive force (TEMF) of the thermocouple was measured by a voltmeter (Keithley196) and converted into the temperature difference (ΔT) using the reference table[21]. In the designed holder, the distance between the two Cu plates is ℓ = 4 mm. Therefore, the temperature gradient is expressed as VT ≈ ΔT/ℓ. The typical width of the sample is w = 3 mm. Note that we have confirmed the error between the actual temperature difference of the two Cu plates and the output of the thermocouple is less than 5%.

Next, the film was patterned by the photolithography technique, and Cr and Au were sputtered as the electrodes. Four electrodes were deposited on the top of the films for thermoelectric measurement as illustrated in Fig.1. Two electrodes placed along the thermal gradient are for measuring the Seebeck signal (Vₛ), and the other two are for measuring the ANE signal (Vₐ). Here, a point contact electrode was fabricated to prevent a decrease in TEMF[22]. The sample was cut into a rectangular shape (5 × 10 mm²) to place it on the sample holder and was glued by GE7031 varnish. We used aluminum wires for making connections between electric pads and the sample puck. One side of the sample was heated, and VT was induced along the long side of the rectangle. The voltage induced along the long side (Vₛ) was measured as a Seebeck voltage using Channel 2 of Keithley 2182, and the voltage induced across the long side (Vₐ) was measured as a Nernst signal using Channel 1 of Keithley 2182. For ANE measurements, a magnetic field perpendicular to the sample plane was applied. Further, to reduce the number of electrical contacts, we fabricated a signal cable to directly connect above measurement instruments and output connectors of PPMS. In the sample holder and the cable, we used silver soldering at all electrical contact points to reduce contact voltages.

![Fig. 1 Structure of the sample holder and configuration for measuring thermoelectric properties.](image-url)
~ 0.3% due to the lattice mismatch. These results are consistent with the previous studies 14–16, 20, 23).

3.2 Thermoelectric properties

First, we show the effect of reducing the number of electrical connections on the measurement system. We tested two different ways of connecting the 14-pins LEMO connector (FGG.3B.314.CLAD92) of the interface of the cryostat of PPMS to the nanovolt-meters; (1) the interface was wired to the nanovolt-meters as explained in Section 2 (direct connection), (2) the interface was directly connected to the instruments using the home-built cable as shown in Fig. 2 (c) and (d). Figure 2 (a) shows the time dependence of the measured signals \( V_{xy} \) for \( \Delta T = 0 \).

In the case of an indirect connection setup, one can see periodically oscillating \( \approx 1 \) \( \mu V \) of spurious voltage signals, probably because of the change in the temperature in the laboratory due to the air conditioner. In contrast, in the case of the direct connection setup, the periodically varying spurious voltage signal was suppressed, and the standard deviation was approximately 5 nV. This result indicates that thermoelectric voltages generated at the electrical connections of the measurement system could be a serious problem while measuring weak DC voltage signals.

Using the direct connection setup, we investigated the thermoelectric properties of the sample. Figure 3 (b) shows \( \Delta T \) dependence of the Seebeck voltage \( (V_{xy}) \) at 300 K. A single data point represents the average voltage for approximately 5 min after generating a stable \( \Delta T \). The relative Seebeck coefficient \( (S_{xx}) \) between NCO and the Al wire is expressed as,

\[
S_{xx} = \frac{E_{xx}}{\nabla T} = \frac{V_{xx}/\ell}{\Delta T/\ell} = \frac{V_{xx}}{\Delta T}.
\]

Table 1 Temperature dependence of absolute Seebeck coefficient \((S_{xx}^{\text{NCO}})\) and anomalous Nernst coefficient \((S_{xy}^{\text{NCO}})\).

| Temperature (K) | \( S_{xx}^{\text{NCO}} \) (\( \mu V/K \)) | \( S_{xy}^{\text{NCO}} \) (\( \mu V/K \)) |
|----------------|------------------------------------------|----------------------------------------|
| 100            | 2.8                                     | -0.005                                 |
| 200            | 3.6                                     | -0.030                                 |
| 300            | 8.0                                     | -0.035                                 |

Next, we describe the results of the ANE measurement of NCO. Figure 3 (c) shows the time dependence of \( V_{xy} \) from powering up the heater to measurement start. In this measurement, the input power is controlled to be \( \Delta T \approx 10 \) K (\( I \approx 25 \) mA) and 50 times averages are taken per point, which takes about 15 minutes from the beginning to the end. From Fig. 3 (c), while above 200 K, \( V_{xy} \) is stable after elapsing 5 min at least; at 100 K, more than 20 min are needed for the TEMF voltage to become stable. These results may imply that a new path for thermal diffusion appears at low temperatures. Before we start the ANE measurement, we need to wait for a sufficient duration for the \( V_{xy} \) to become stable. \( S_{xy} \) is determined from the experimentally measured voltages as follows:

\[
S_{xy} = \frac{E_{xy}}{\nabla T} = \frac{V_{xy}/w}{\Delta T/\ell},
\]

where \( w = 3 \) mm, \( \ell = 4 \) mm. Figure 3 (d) shows the \( S_{xy}-H \) loop at each temperature. Here, the time dependent background component expected from Fig. 3(a) is smaller than the ANE voltage at each temperatures. In ANE analysis, we extracted only the odd function components, similar to that in the analysis performed for the Hall effect. The shape of the \( S_{xy}-H \) loop is in good agreement with a previously reported VSM measurement result (not shown) 25. Moreover, a larger saturated \( S_{xy} \) appeared at higher temperatures. From Ref.26, the relation between Nernst and Seebeck coefficient can be written as follow,

\[
S_{xy} \approx S_{xx} \tan \theta_H + \rho_{xx} \epsilon_{xy},
\]

where \( \theta_H \) is Hall angle, \( \rho_{xx} \) is longitudinal resistivity, and \( \epsilon_{xy} \) is off-diagonal element of the thermoelectric tensor. In NCO, \( \theta_H \sim -10^{-3} \) and \( \rho_{xx} \sim 10^{-3} \) \( \Omega \cdot \text{cm} \) 14. Therefore, the expected \( S_{xy} \) from \( S_{xx} \) is approximately 0.01 \( \mu V/K \), which is almost same with the experimental results. The little difference may be attributed to the thermoelectric tensor.

4 Conclusion

In this study, we investigated both the Seebeck effect and ANE in NiCo2O4 thin films with PMA. The thermoelectric signals are extremely small that we needed to build a measurement system to detect the weak thermoelectric voltage signals. To suppress the spurious voltage signals originating from the electrical contacts at room temperature of the measurement system, we employed the
following solutions: (i) reduction in the number of electrical contacts by directly connecting the output of a commercial cryostat with a superconducting magnet to the nano-voltmeters, (ii) used silver soldering to make electrical contacts to reduce contact voltages. By adopting the aforementioned measures, we succeeded in detecting thermoelectric voltages as small as 5 nV.

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