Thermoelectric response as a tool to observe electrocaloric effect in a thin conducting ferroelectric SnSe flake

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We experimentally investigate thermoelectric response of a 100 nm thick SnSe single crystal flake under the current-induced dc electric field. Thermoelectric response appears as a second-harmonic transverse voltage $V_{xy}^{2\omega}$, which reflects temperature gradient across the sample due to the Joule heating by harmonic ac excitation current $I_{ac}$. In addition to strongly non-monotonous dependence $V_{xy}^{2\omega}$, we observe that dc field direction controls the sign of the temperature gradient in the SnSe flake. We provide arguments, that electrocaloric effect is the mostly probable reason for the results obtained. Thus, our experiment can be understood as demonstration of the possibility to induce electrocaloric effect by in-plane electric field in conducting ferroelectric crystals and to detect it by thermoelectric response.

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INTRODUCTION

Recent interest to conductors with broken inversion symmetry is connected not only with topological materials [1], but also with conducting ferromagnetic and ferroelectric crystals. For ferromagnetic conductors with spin-orbit coupling, current-induced spin polarization leads to spin-orbit torques [2], which opens a new field in spintronics. In ferroelectrics, current-induced electric field opens a way to control ferroelectric polarization in polar crystals. The latter effect can be expected for mono- or di- chalcogenides of transitional metals like WTe$_2$, SnS, SnSe, etc. [3, 4], or for monolayer-based artificial structures [5, 6].

One of the sophisticated phenomena in ferromagnetic or ferroelectric systems is the caloric effect, which is also important for applications. For example, it can be useful in development of new refrigeration technologies and materials [7, 8], and cooling/heating environmentally friendly devices [9] or renewable energy sources [10, 11]. Magnetocaloric and electrocaloric effects occur due to the entropy difference between (ferromagnetically or ferroelectrically) ordered or disordered states, which can be controlled by applying or removing of the external magnetic or electric fields, respectively [8, 12]. For the electrocaloric effect, this difference leads to the temperature variation if the ferroelectric polarization changes at stable entropy experimental environments [13, 14]. Recent experimental investigations are performed for insulating ferroelectric crystals [8] or thin films [12, 14, 15], which are placed between two metallic capacitor plates. Electrocaloric effect is controlled by external out-of-plane electric field in this case. In addition to general fundamental problems [11, 13], applied research is mostly intended to improve the caloric effect in lead-free insulating materials [8, 10].

On the other hand, electrocaloric effect should principally be observable in ferroelectric conductors. Ferroelectric polarization is also sensitive to current-induced electric field in conducting structures, which is impossible for ferroelectric insulators. Even for small absolute values of the effect, corresponding temperature gradients should be detectable by in-situ thermoelectric response measurements [16–20]. Among different materials, layered SnSe single crystals can be convenient for these investigations: thin SnSe flakes (300 nm and below) are characterized by the in-plane ferroelectric polarization [21], which opens a way to control ferroelectric polarization in conducting SnSe flakes.

Here, we experimentally investigate thermoelectric response of a 100 nm thick SnSe single crystal flake under the current-induced dc electric field. Thermoelectric response appears as a second-harmonic transverse voltage $V_{xy}^{2\omega}$, which reflects temperature gradient across the sample due to the Joule heating by harmonic ac excitation current $I_{ac}$. In addition to strongly non-monotonous dependence $V_{xy}^{2\omega}$, we observe that dc field direction controls the sign of the temperature gradient in the SnSe flake. We provide arguments, that electrocaloric effect is the mostly probable reason for the results obtained. Thus, our experiment can be understood as demonstration of the possibility to induce electrocaloric effect by in-plane electric field in conducting ferroelectric crystals and to detect it by thermoelectric response.

SAMPLES AND TECHNIQUES

SnSe compound was synthesized by reaction of selenium vapors with the melt of high-purity tin in evacuated silica ampoules. The SnSe layered single crystal was grown by vertical zone melting in silica crucibles under argon pressure. The structure of single crystal is verified by X-ray diffraction methods. The initial SnSe is characterized the layered structure with orthorhombic crystal...
Resistance of the investigated samples varies from 1 kOhm to 20 kOhm, an actual value depends mostly on the overlap area between SnSe flake and Au leads in Fig. 1.

For thermoelectric measurements we use four-point lock-in technique with second harmonic detection [18–20]. Thermal gradient is created by ac current \( I_{ac}\cos(\omega t) \) applied between two Au-SnSe heating contacts C1 and C4, see Fig. 1 which we refer as \( z \) axis. Thermal gradient appears due to the Joule heating of the sample \( \nabla T \sim (I_{ac})^2 \cos(2\omega t) \), it is perpendicular to the current line in Fig. 1. For this reason, we detect thermoelectric response as the second-harmonic transverse (i.e. along \( y \) axis) voltage \( V_{xy}^{2\omega} \) between contacts C2 and C6. To obtain \( V_{xy}^{2\omega} \) dependence on the in-plane electric field, we additionally apply high dc current \( I_{dc} \) between the same heating contacts in Fig. 1. We wish to note, that longitudinal (along \( x \)) dc current can not directly contribute to the transverse (along \( y \)) \( V_{xy}^{2\omega} \) second-harmonic ac response.

Amplitude and frequency of \( I_{ac} \) is verified to have the correct Ohmic behavior of the longitudinal first harmonic \( V_{xx}^{1\omega} \) component. In particular, \( I_{ac} \) is below 10 \( \mu A \) at the frequency of 1.7 kHz. \( I_{dc} \) is swept within \( \pm 1 mA \) range, which corresponds to \( 10^7 A/m^2 \) current density for our dimensions, and to in-plane electric field \( 10^7 V/m \) for 1 kOhm sample resistance. All measurements are performed at room temperature.

**Experimental Results**

Fig. 2 shows typical examples of four-point longitudinal (along \( x \)) \( V_{xx}^{1\omega}, V_{xx}^{2\omega} \) and transverse \( V_{xy}^{1\omega}, V_{xy}^{2\omega} \) voltage components in dependence on the ac current amplitude \( I_{ac} \). The first harmonic longitudinal voltage \( V_{xx}^{1\omega} \) component demonstrates standard Ohmic behavior \( V_{xx}^{1\omega} = RI_{ac} \) with four-point sample resistance \( R = 1.2 \) kOhm, see Fig. 2(a). The first harmonic transverse voltage \( V_{xy}^{1\omega} \) is much smaller, it seems to appear due to the contacts mismatch. Ohmic behavior is also confirmed by nearly zero second-harmonic longitudinal \( V_{xy}^{2\omega} \) component in Fig. 2(b). In contrast, there is significant transverse second-harmonic voltage \( V_{xy}^{2\omega} \) in Fig. 2(b). \( V_{xy}^{2\omega} \) is clearly non-linear and follows to \( (I_{ac})^2 \) law, as depicted in the inset to Fig. 2(b). This behavior well corresponds to thermoelectric origin of \( V_{xy}^{2\omega} \sim \nabla T \), where the temperature gradient \( \nabla T \) is defined by Joule heating of the sample \( \nabla T \sim (I_{ac})^2 \cos(2\omega t) \). One can estimate maximum temperature difference \( \Delta T \approx 0.5 K \) between contacts C6 and C2 for the known [21] SnSe thermoelectric coefficient 520\( \mu V/K \).

Our main result is the dependence of the thermoelectric response \( V_{xy}^{2\omega} \) on the dc bias current \( I_{dc} \), which is applied between the same contacts C1 and C4 as the ac current component. The experimental \( V_{xy}^{2\omega}(I_{dc}) \) curve...
The first harmonic longitudinal voltage $V_{xx}^{1\omega}$ component in dependence on the ac current $I_{ac}$ amplitude. It demonstrates standard Ohmic behavior $V_{xx}^{1\omega} \sim I_{ac}$ with corresponding four-point sample resistance value $R \approx 1.2 \, \text{kOhm}$. The first harmonic transverse voltage $V_{xy}^{1\omega}$ is much smaller, it seems to appear due to the contacts mismatch. (b) Longitudinal $V_{xx}^{2\omega}$ and transverse $V_{xy}^{2\omega}$ voltage components in dependence on the ac current $I_{ac}$ amplitude. $V_{xy}^{2\omega}$ is about zero, as it should be expected for the linear Ohmic $V_{xx}^{1\omega}(I_{dc})$ curve. In contrast, there is significant transverse second-harmonic voltage $V_{xy}^{2\omega}$, which is non-linear and follows to $(I_{dc})^2$ law, as it is shown in the inset. This behavior well corresponds to thermoelectric origin of $V_{xy}^{2\omega} \sim \nabla T$.

consists of two $\sim 1/I_{dc}$ branches with sharp switching between them around zero bias, see Fig. 3 (a). Surprisingly, there is inversion of the thermoelectric response sign with the direction of $I_{dc}$: $V_{xy}^{2\omega}$ is negative for $I_{dc} < 0$, while it is positive for positive current values.

We wish to note, that the dc current contribution to Joule heating $\sim (I_{dc})^2$ is not sensitive to the current direction. Also, longitudinal dc bias $I_{dc}$ can not be electrically detected in the transverse ac second-harmonic response $V_{xy}^{2\omega}$. On the other hand, the odd antisymmetric second-harmonic $V_{xx}^{2\omega}(I_{dc})$ curve is in sharp contrast to usual symmetric resistance behavior, which is shown as first-harmonic longitudinal $V_{xx}^{1\omega}$ in the upper inset to Fig. 3 (a). The first-harmonic transverse voltage $V_{xy}^{1\omega}$ is small, it qualitatively reproduces the $V_{xx}^{1\omega}$ behavior, as one could expect for small contact mismatch, see the lower inset to Fig. 3 (a).

We check, that $V_{xy}^{2\omega}$ still reflects the sample thermoelectric response at any finite $I_{dc}$. Fig. 3 (b) shows $V_{xy}^{2\omega} \sim (I_{dc})^2$ dependence for several fixed $I_{dc}$ values, the curves differ only by proportionality coefficient, which depends on the sign and value of $I_{dc}$ as $\sim 1/I_{dc}$. Thus, the direction of $I_{dc}$ indeed affects the direction of the temperature gradient $\nabla T \sim V_{xy}^{2\omega}$, which can not be due to the dc current contribution to Joule heating $\sim (I_{dc})^2$.

The antisymmetric behavior of $V_{xy}^{2\omega}(I_{dc})$ is independent of the particular choice of contacts or any specific direction within SnSe flake. Fig. 4 (a) shows qualitatively similar $V_{xy}^{2\omega} \sim 1/I_{dc}$ dependence for the exchanged current and voltage probes in comparison to Fig. 1. In this case both current components $I_{dc}$ and $I_{ac}$ are applied in $y$ direction between contacts C2 and C6, while transverse $V_{xy}^{2\omega}$ is measured along $x$ between contacts C1 and C4, just opposite to the configuration in Fig. 1. Thus, the antisymmetric behavior of $V_{xy}^{2\omega}(I_{dc})$ is not connected with any specific sample inhomogeneity.

These results can be also qualitatively reproduced for the sample with much higher resistance (about 20 kOhm). Fig. 4 (b) shows antisymmetric odd $V_{xx}^{2\omega}(I_{dc})$ dependence, while the $I_{dc}$ range is narrowed in this case. Due to the resistive sample, it is possible to directly apply bias voltage to the heating contacts in Fig. 1. The result is shown in the inset to Fig. 4 (b) as antisymmetric $V_{xy}^{2\omega}(V_{dc})$ curve with two $\sim 1/V_{dc}$ branches, so the sign of the thermoelectric response is determined by the direction...
V \sim 1 \text{dc electric field.}

response is indeed determined by the direction of the in-plane \( \nabla V \) is narrowed in this case. Inset shows behavior of \( \frac{V_{xy}}{V_{dc}} \) for the sample with \( \frac{V_{xy}}{V_{dc}} \) is not connected with any specific direction in the sample. (b) Similar results for the sample with much higher resistance (about 20 kOhm), while the \( I_{dc} \) range is narrowed in this case. Inset shows \( V_{xy}(I_{dc}) \) curve with two \( \sim 1/V_{dc} \) branches if the bias voltage is directly coupled to the heating contacts in Fig. 4. Thus, the sign of the theolectric response is indeed determined by the direction of the in-plane dc electric field.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.png}
\caption{(a) Qualitatively similar \( V_{xy} \sim 1/I_{dc} \) dependence for the exchanged current and voltage probes in Fig. 4. Both current components \( I_{dc} \) and \( I_{ac} \) are applied along \( y \) between contacts C2 and C6, while \( V_{xy}^{ac} \) is measured between contacts C1 and C4 (\( x \) axis). There are additional high-bias crossing points, however, \( \nabla V \) sign inversion around zero bias is similar to the previous configuration. Thus, antisymmetric behavior of \( V_{xy}^{ac}(I_{dc}) \) is not connected with any specific direction in the sample. (b) Similar results for the sample with much higher resistance (about 20 kOhm), while the \( I_{dc} \) range is narrowed in this case. Inset shows \( V_{xy}(I_{dc}) \) curve with two \( \sim 1/V_{dc} \) branches if the bias voltage is directly applied to the heating contacts in Fig. 4. Thus, the sign of the theolectric response is indeed determined by the direction of the in-plane dc electric field.

\section*{DISCUSSION}

As a result, we demonstrate that the transverse second-harmonic ac voltage response \( V_{xy}^{ac} \) indeed reflects temperature gradient \( \nabla T \) at any \( I_{dc} \) value. To our surprise, \( \nabla T \) obeys \( \sim 1/I_{dc} \) dependence with inversion of the \( \nabla T \) sign with the direction of \( I_{dc} \).

First of all, \( \nabla T \) sign inversion cannot be explained by simple geometrical factor. In Fig. 4 (a) temperature gradient \( \nabla T \) is measured between 80 \( \mu \)m spaced contacts C2 and C6, while the distance between heating contacts C1 and C4 is about 40 \( \mu \)m. Since the contact resistance exceeds the bulk SnSe value [22], Joule heating is mostly concentrated in the contact areas. Since two-point resistance strongly depends on the dc bias in the upper inset to Fig. 3 (a), the bias changes relative contribution of the particular contact to the Joule heating. It leads to some variation of \( \nabla T \) direction between C6-C1 and C6-C4 lines in Fig. 4 i.e. within \( \approx \pm 15 \) degrees, so it can not change \( \nabla T \) sign in Fig. 3 and in Fig. 4 (b). In contrast, the curve in Fig. 4 (a) is obtained in the alternative geometry, where voltage probes are situated to both sides from the current line. In this case, \( \nabla T \) sign inversion is possible at high dc biases, which seems to be responsible for the additional high-bias crossing points in Fig. 4 (a). However, \( \nabla T \sim 1/I_{dc} \) dependence around zero bias does not allow geometrical explanation also in this case.

The first power of \( I_{dc} \) indicates that \( \nabla T \) is sensitive to the sign and value of the dc electric field. However, it can not be connected with the Peltier effect, since \( \nabla T \) is proportional to \( \sim 1/I_{dc} \) rather than the expected \( \sim I_{dc} \) dependence for the Peltier effect.

On the other hand, electrocaloric effect should principally be observable in ferroelectric conductors. In contrast to standard ferroelectric insulator films [12, 14, 15], it can be produced by in-plane current-induced electric field in conducting ferroelectric systems.

Recently, three-dimensional WTe2 single crystals were found to demonstrate coexistence of metallic conductivity and ferroelectricity at room temperature [4] due to the strong anisotropy of the non-centrosymmetric crystal structure. The spontaneous polarization of ferroelectric domains was found to be bistable, it can be affected by high external electric field. The possibility to induce polarization current by source-drain field variation has been shown for WTe2 as a direct consequence of ferroelectricity and metallic conductivity coexistence [28]. We have demonstrated qualitatively similar ferroelectric behavior of \( \frac{dV}{dI} \) curves for thin SnSe flakes [23], as it is shortly shown in the present text as small hysteresis for \( V_{xy}^{ac}(I) \) in the upper inset to Fig. 3.

Thin SnSe layers (300 nm and below) are characterized [22], by in-plane spontaneous ferroelectric polarization at room temperature. Ferroelectric domains are much smaller than the contact size in our samples [22]: the domains are about 100 nm, the domain wall region is about 20-50 nm. In this case, any variation of the source-drain bias \( I_{dc} \) affects ferroelectric polarization due to the domain wall shift for varying \( E \sim I_{dc} \) in-plane electric field [23]. It leads to the temperature variation because of the electrocaloric effect [13, 14, 29], so the sign of the temperature \( \delta T \) variation \( \delta T \) is determined by the direction of the electric field \( E \).

More precisely, \( E/T \) ratio is a constant in the conditions of electrocaloric effect. Thus, \( \delta(E/T) \) is zero, which gives \( \delta T = (T/E)\delta E \). In our experiment, we measure only \( T\delta E \) component which is proportional to \( (I_{ac})^2 \) due to the 2\( \omega \) lock-in detection technique, while the in-plane electric field \( E \sim I_{dc} \sim V_{dc} \). It gives exactly \( \nabla T \sim (I_{ac})^2/I_{dc} \) dependence, which we observe in Figs. 3 and 4.

From the \( V_{xy}^{ac} \) values within \( \pm 0.3 \) mV one can estimate [21] maximum temperature variation as \( \Delta T \approx \pm 0.5 \) K. This value well corresponds for the known one (mostly \( 2-5 \) K) in insulating ferroelectric crystals [8] or thin films [12, 14, 15]. Thus, we not only demonstrate possibility to create electrocaloric effect by current-
induced electric field in conducting ferroelectric crystals, but also obtain competitive values of the effect.

CONCLUSION

As a conclusion, we experimentally investigate thermoelectric response of a 100 nm thick SnSe single crystal flake under the current-induced dc electric field. Thermoelectric response appears as a second-harmonic transverse voltage $V_{2\omega}$, which reflects temperature gradient across the sample due to the Joule heating by harmonic ac excitation current $I_{ac}$. In addition to strongly non-monotonous dependence $V_{2\omega}$, we observe that dc field direction controls the sign of the temperature gradient in the SnSe flake. We provide arguments, that electrocaloric effect is the mostly probable reason for the results obtained. Thus, our experiment can be understood as demonstration of the possibility to induce electrocaloric effect by in-plane electric field in conducting ferroelectric crystals and to detect it by thermoelectric response.

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